

## Synthesis of TiO<sub>2</sub> nanorods from titania and titanyl sulfate produced from ilmenite dissolution by hydrothermal method

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**Abstract.** TiO<sub>2</sub> powder has been synthesized through hydrolysis-condensation of titanyl sulfate solution to a starting material of TiO<sub>2</sub> nanorods formation. This processing was conducted by the solid separation of TiO<sub>2</sub> from ilmenite by roasting ilmenite, acidic leaching (hydrolysis), and co-precipitation (condensation). Roasting of ilmenite was carried out by the addition of Na<sub>2</sub>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<sub>2</sub>SO<sub>4</sub> 6 M condition. Separation of Fe impurities of TiO<sub>2</sub> gel from titanyl sulfate (TiOSO<sub>4</sub>) solution was done through complexation using KCNS addition. The characteristic of TiO<sub>2</sub> obtained using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) showed good crystallinity and purity. Further treatment of the TiO<sub>2</sub> is the formation of one-dimensional nano-size (1-D nanorods) through a hydrothermal method under basic condition NaOH 12M solution. TiO<sub>2</sub> nanorods were confirmed by Transmission Electron Microscope (TEM) which indicated that the diameter of TiO<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> is also a material that is inert, harmless and inexpensive, and has good optical characteristics.

The synthesis and characterization of one-dimensional (1-D) nanostructured materials (nanotubes, nanorods, and nanowires) have received considerable attention due to their unique properties and novel applications [4-7]. Much effort has concentrated on the important metal oxide such as TiO<sub>2</sub> and ZnO [4]. Among them, TiO<sub>2</sub> and TiO<sub>2</sub>-derived materials are of importance for utilizing solar energy and

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environmental purification.  $\text{TiO}_2$  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  $\text{TiO}_2$  were synthesized by hyrothermal method under basic condition using  $\text{TiO}_2$  and titanyl sulfate ( $\text{TiOSO}_4$ ) source.

## 2. Experimental Method

Ilmenite was roasted at a temperature of  $800^\circ\text{C}$  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  $90^\circ\text{C}$  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  $\text{H}_2\text{SO}_4$  with concentration variations of 3; 3.5; 4.5; 6; 9 M in a three-neck flask, then was heated at refluxing process under  $90^\circ\text{C}$  for 2 hours. The result obtained was precipitated a few minutes in order to separate the residu of the solution. The resulting filtrate was  $\text{TiOSO}_4$  then characterized using ICP-OES.

About 200 mL of aquades heated to  $60^\circ\text{C}$  then added 0.25 mL 1M KCNS. After it was added a solution of 10 mL  $\text{TiOSO}_4$  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  $100^\circ\text{C}$ . 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  $120^\circ\text{C}$ . The result refluxed then washed using 0.1 M HCl solution and then dried at a temperature of  $60^\circ\text{C}$  for 24 hours. Titania then calcined for 2 hours at of  $400^\circ\text{C}$  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.

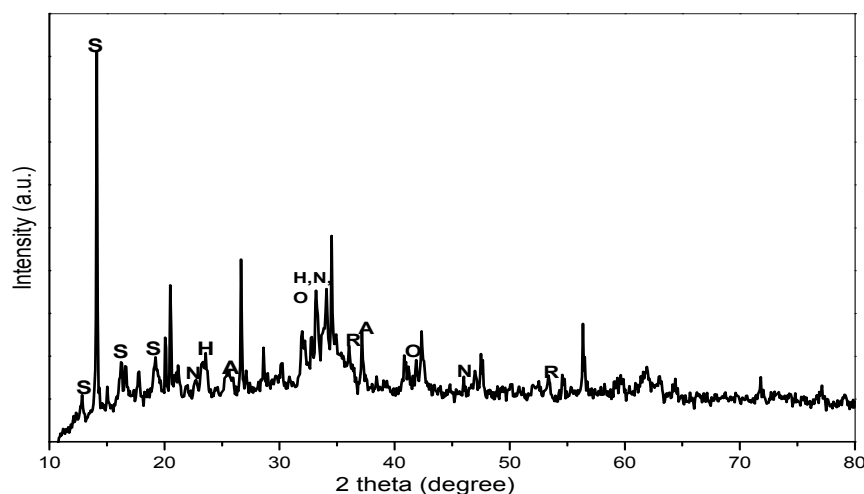
**Table 1.** Chemical composition of ilmenite by XRF (%)

Content	Level (%)	Content	Level (%)
$\text{TiO}_2$	45,35	$\text{Al}_2\text{O}_3$	2,35
$\text{Fe}_2\text{O}_3$	31,48	$\text{SO}_3$	2,24
$\text{Na}_2\text{O}$	3,86	$\text{Cr}_2\text{O}_3$	1,87
$\text{ZrO}_2$	3,57	$\text{MnO}$	1,58
$\text{SiO}_2$	3,29		

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

### *Roasting of Ilmenite*

Roasting of ilmenite was added by  $\text{Na}_2\text{S}$  to simplify the extraction process  $\text{TiO}_2$  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.



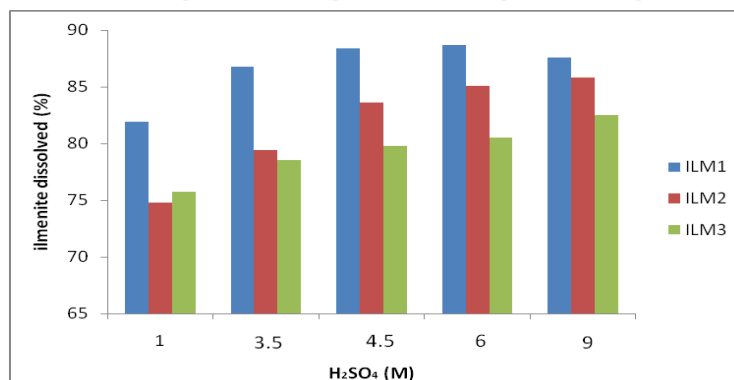
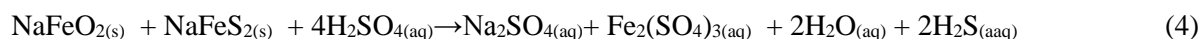
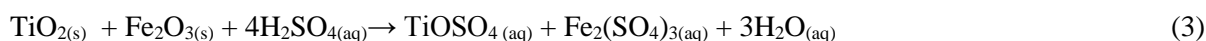
**Figure 1.** Diffractograms roasting ilmenite at 800°C N= Na<sub>2</sub>SO<sub>4</sub> ; S= NaFeS<sub>2</sub> ; O= NaFeO<sub>2</sub> ; H= Fe<sub>2</sub>O<sub>3</sub> ; A= TiO<sub>2</sub> anatase ; R= TiO<sub>2</sub> rutile

Diffractogram (Figure 1) showed the results of the roasting ilmenite decomposed into hematite, TiO<sub>2</sub> anatase, TiO<sub>2</sub> rutile and double salts. Peaks at 23,85° (d<sub>012</sub>); 32,85° (d<sub>104</sub>) characteristic peaks of hematite in accordance with the standard JCPDS No. 88-2359. The peak of the value 25,53° (d<sub>101</sub>) and 37,79° (d<sub>004</sub>) in accordance with the characteristic peaks of anatase TiO<sub>2</sub> standard JCPDS No. 21-1272. Peaks at 36,15° (d<sub>101</sub>); 54,43° (d<sub>211</sub>) showed characteristic peaks of rutile TiO<sub>2</sub> in accordance with the standard JCPDS No. 87-0710.

### Leaching

Leaching of roasted ilmenite product was carried out by H<sub>2</sub>SO<sub>4</sub> at various concentration. In this process, roasted ilmenite dissolved by sulfuric acid, thus obtained titanyl sulfate (TiOSO<sub>4</sub>) and ferrous sulfate (FeSO<sub>4</sub>). 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.



**Figure 2.** Percentage of ilmenite dissolved in H<sub>2</sub>SO<sub>4</sub> 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.

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

No	Concentration of $\text{H}_2\text{SO}_4(\text{M})$	Analysis result of ICP (g / l)		
		Ti	Fe	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

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

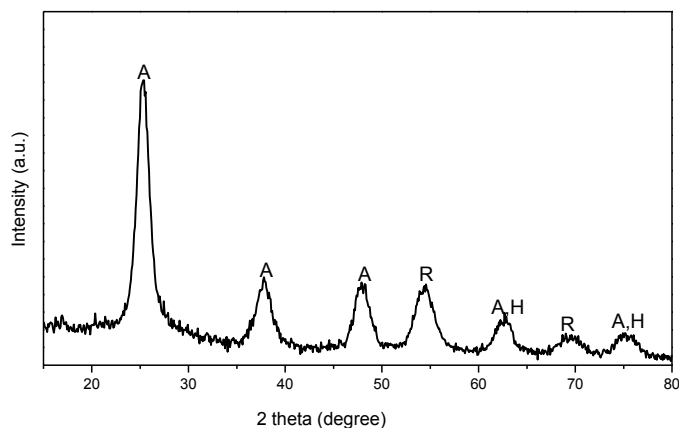
$\text{TiO}_2$  is synthesized from titanyl sulfate ( $\text{TiOSO}_4$ ) with the addition of KCNS. The addition of this KCNS can be separated the iron content with titania to obtain high-purity  $\text{TiO}_2$ . Reactions hydrolysis that happened shown in equations 5 and 6.



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

**Table 3.** Chemical composition of  $\text{TiO}_2$  hydrolysis and complexation

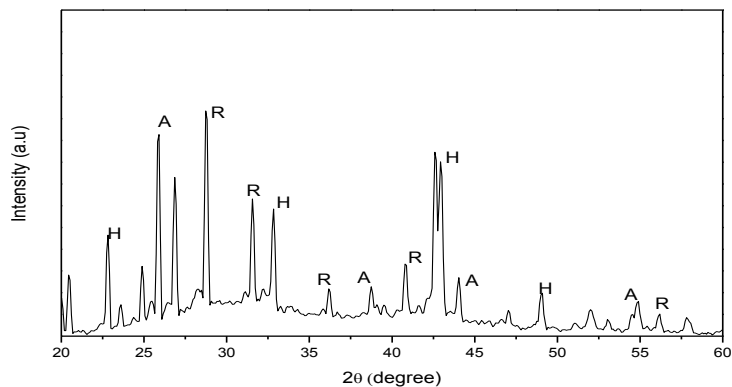
Content	Level (%)
$\text{TiO}_2$	88,03
$\text{SO}_3$	7,94
$\text{Fe}_2\text{O}_3$	2,67
$\text{SnO}_3$	0,49
$\text{P}_2\text{O}_5$	0,35



**Figure 3.** Diffractograms of  $\text{TiO}_2$  hydrolysis and complexation  
H =  $\text{Fe}_2\text{O}_3$ ; A =  $\text{TiO}_2$ anatase; R =  $\text{TiO}_2$ rutile

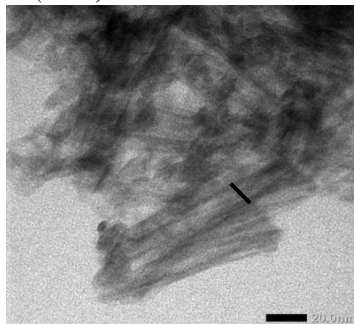
#### *Synthesis of $\text{TiO}_2$ Nanorods*

$\text{TiO}_2$  nanorods preparation was done by mixing  $\text{TiO}_2$  nanoparticles (4.664 nm) and 12 M NaOH for  $\pm$  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 4.** Diffractograms of  $\text{TiO}_2$  nanorods H =  $\text{Fe}_2\text{O}_3$ ; A =  $\text{TiO}_2$  anatase; R =  $\text{TiO}_2$  rutile

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



**Figure 5.** TEM of TiO<sub>2</sub> nanorods

In conclusion, morphology of TiO<sub>2</sub> nanorods from condensation preparation has been formed by hydrolysis and complexation using KCNS, with a hydrothermal process under alkaline conditions. Powder of TiO<sub>2</sub> nanorods has obtained with a diameter of nanorods 7.02 nm.

#### 4. Acknowledgment

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#### 5. References

- [1] Grätzel M, 2001 *Nature* 414 338
- [2] Vasquez R and Molina A, 2008 *Metal* 5 13
- [3] Wunderlich W, Oekermann T, Miao L 2004 *Ceramic Processing Research* 5 343
- [4] Rao CNR and Nath M 2003 *Dalton Trans* 1 1
- [5] Patzke GR, Krumeich F, and Nesper R 2002 *Angew. Chem. Int. Ed.* 41 2446
- [6] Huang M, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R, and Yang P *Science* 292 1897
- [7] Pan ZW, Dai ZR, and Wang ZL 2001 *Science* 292 1947
- [8] Fujishima A, Rao TN and Tryk DA 2000 *J. Photochem. Photobiol. C:Photochem. Rev.* 1 1
- [9] Wahyuningsih S, Ari HR, Edi P, Ariantama D 2014 *Sci.Res.Pub.* 4