

Nanocrystalline Titanium Dioxide Nanotube (TDN) by Hydrothermal Method From Tulungagung Mineral Sand

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Abstract- This research is focused on extraction titanium dioxide nanotubes from Tulungagung mineral sands using the hydrothermal method. Extraction is done by dissolving mineral sand into sulfuric acid solution and vacuums pump to obtain TiO₂ precipitate. Furthermore, TiO₂ precipitate were calcined at 600 ° C for 2 hours. TiO₂ was dissolved in NaOH and stirred for 2 hours. The resulting solution was put into an autoclave and heated at 130° C for 24 hours to form nanotubes structure. The formed titanium dioxide nanotubes are neutralized using HCl and distilled water. TDN was dried using an oven and calcined at 600 ° C for 2 hours. Furthermore SEM, XRD characterization was carried out and analyze with Match! Software and rietveld. The analysis results showed that a single phase anatase TDN with a nanocrystalline size of 43,02 nm was formed based on rietveld analysis. Also the SEM images shows that the diameter of nanotubes are about 15,66-32,33 nm.

Keywords—mineral sands, TiO₂, hydrothermal, TDN

I. INTRODUCTION

Indonesian mineral sands are spread along the coast of Java, especially in the north and south coasts (Mukti, Diantoro, & Fuad, 2016). In general, mineral sand is black and has a smooth texture. The main compounds in mineral sand are the element of Fe and Ti which binds to other elements. Fe and Ti elements will bind to each other to form ilmenite (FeTiO₃), hematite (Fe₂O₃) and magnetite (Fe₃O₄) (Setiawati, Siswanto, & Rochman, 2016). Titanium Dioxide (TiO₂) anatase is extracted from ilmenite that can be used in various fields. Titanium dioxide has many advantages among the others include its low cost, chemically stable and non-toxic (Renuka & Nikhila, 2016). Titanium dioxide is responsive to UV light, pairs of electrons and holes are produced by UV radiation and encourage chemical reactions on the surface of the material (Kijima, 2010). Therefore the characteristics of TiO₂ which are most interesting to examine are the photochemical properties such as high photocatalyst activity (Afshar & Hakamizadeh, 2009). For this reason, TiO₂ has been studied from 1950 to use as a photocatalyst,

solar panel electrodes, gas sensors and so on (Kustiningsih, Slamet, & Purwanto, 2015).

In recent years TiO₂ has been successfully synthesized such as nanowire, nanotube, and nanorod (Jasmeen, 2013). TiO₂ which has tube-sized and nano-sized is called a TiO₂ nanotube (TDN). TDN is interesting to study because it has a large surface area and high photocatalytic ability (Afshar & Hakamizadeh, 2009). Much research has been done to obtain TiO₂ nanotube with a large surface area, such as using the hydrothermal, sol-gel, assisted-template and electrochemical anodic oxidation method (Yadav, 2017). Among those methods, the hydrothermal method is the easiest because the synthesis process is simpler, the structure of nanotubes is more easily formed, does not require large costs and is not harmful to the environment (Setyani & Wibowo, 2017).

Tulungagung has an extensive coastal area with abundant mineral sand. It has the potential to be used as titanium dioxide (TiO₂) extraction material. Tulungagung mineral sand has a high titanium content of 18.8%. Research by Mukti et al. (2016) succeeded in extracting TiO₂ by separating it using magnets 2 times and continued with a dissolution process using H₂SO₄. Based on the previous research, this research will extract TiO₂ from Tulungagung mineral sand using a leaching method with an H₂SO₄ solvent. Then the extracted TiO₂ was dissolved with NaOH and autoclaved to form titanium dioxide nanotubes. The TDN formed was calcined at 600 ° C for 2 hours and characterized by X-Ray Diffraction (XRD).

II. MATERIALS AND METHODS

A. Material

The equipment in this research are a set of glass tools (pyrex), a pipette drops, universal indicator, oven (Mettler), magnetic stirrer (IKA-MAG) and furnace (Barnstead Thermolyne 1400). All chemical reagents used in this research were analytical grade such as mineral sand, distilled water, sulfuric acid (Sigma Aldrich 99%), sodium hydroxide (Merck 99%) and hydrochloric acid (Sigma Aldrich 98%).

B. Experiment

Tulungagung mineral sand is washed with distilled water then dried under the sun. Mineral sand is magnetized so that magnetic and non-magnetic sands can be obtained. Magnetic sand is mashed using mortar and pestle to pass the 200 mesh sieve. Magnetic powders are refit to separate magnetic powders and non-magnetic powders. Furthermore, the magnetic powder was dissolved into H₂SO₄ solution and sterilized at a temperature of 120°C to form a slurry. The slurry obtained is called the pump to separate deposits and filtrate. Then the filtrate is neutralized by adding distilled water and heated to 200° C until a precipitate is formed. The precipitate is washed with distilled water to a neutral pH and dried. The dried sediment is calcined at a temperature of 600°C for 2 hours.

TiO₂ is dissolved in NaOH and stirred for 2 hours. Then the solution is into an autoclave and roasted at 130° C for 24 hours to form the TiO₂ nanotube structure. Then the solution is cooled then neutralized using HCl and distilled water to reach a neutral pH. The neutral solution stands for 1 hour to form a precipitate. The precipitate was dried using an oven and continued with calcination at 600°C for 2 hours. TDN powder formed was characterization by XRD to determine the phase and crystalline size

C. Characterization

The phase identification of TDN samples was conducted with X-ray diffraction (XRD) using a PHILIPS-binary diffractometer equipped with CuK α radiation. The data were collected for scattering angles (2 θ) rangine from 5 to 90° with a step size of 0.02°. Morphology identification was conducted with Scanning electron microscoy (SEM) using a Hitachi S-4800 apparatus.

III. RESULTS AND DISCUSSION

The TiO₂ extraction process can be carried out through pyrometallurgy and hydrometallurgical methods. The extraction process using the hydrometallurgical method is carried out with the help of an acid solution. There are three commonly used methods including the sulfate, chloride, and Becher methods. The sulfate process is known as a process leaching because it is carried out by dissolving mineral sand in a sulfuric acid solution to form titanium sulfate (TiOSO₄). Titanium sulfate will be hydrolyzed which will produce TiO₂.

The result of the leaching process is a slurry. Chemical reactions that occur during the leaching process are as follows:

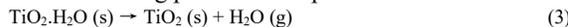


In the reaction, titanium sulfate dissolves in sulfuric acid, whereas FeSO₄ does not dissolve in sulfuric acid. To get the filtrate containing TiO₂, it is necessary to separate the filtrate (TiOSO₄) and sediment (FeSO₄). Then distilled water is added to the filtrate and heated at 200°C. In the process of adding distilled water this chemical reaction occurs as follows:



The above reaction results are TiO₂.H₂O and H₂SO₄. To eliminate sulfuric acid compounds, the ocean must be added with distilled water many times until it reaches a

neutral pH. The H₂O content in TiO₂.H₂O is removed through the heating process. Chemical reactions that occur when the heating process takes place are as follows:



The factors that most influence the success of the leaching process are temperature, reactant concentration, sample particle size and pH of the solution. By determining the right composition of these factors, the leaching process can take place optimally.

Hydrothermal treatment of TiO₂ and acid washing are used to form the nanotubes structure. Hydrothermal treatment causes the crystallinity of the TiO₂ has changed which characterizes the TiO₂ nanotube structure. The acid washing produced the formation of high purity nanotubes due to Na⁺ which is exchanged from the titanate structure to the hydrochloric acid solution. The annealing temperature affects the structure and particle size of the nanotubes. Anatase titanium dioxide nanotube was characterized using X-Ray Diffraction and analyzed with Match! Software. Results of the analysis with Match! shown in figure 1.

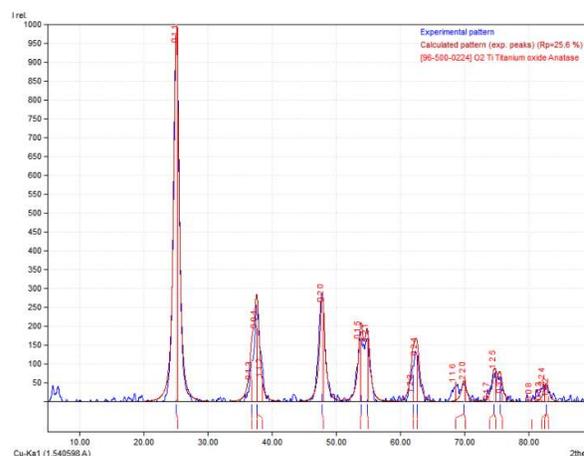


Figure 1. XRD patterns of Titanium Dioxide Nanotube after being analyzed using Match! Software

Figure 1 shows all the peaks corresponding to the reflection from (011), (013), (004), (112), (020), (015), (021), (024), (116), (220), (017), (025), (031), (008), (024), and (112) planes of anatase for TDN. The peak diffractogram of the sample XRD test results are 25,10°, 36,85°, 37,63°, 47,84°, 53,85°, 54,86°, 61,97°, 62,59°, 69,92°, 76,64°, 75,55°, and 82,75°. The highest peak can be seen at a diffraction angle of 25.10° with a crystal orientation (011). The diffractogram shows that the anatase phase has been formed 100% and can be seen from the high relative intensity and suitability of the scattered angle of X-rays produced. Based on Figure 1 above, it appears that the peak of this sample is compatible with the standard spectrum of JCPDS Card No.00-10737. To find out TDN crystalline size, rietveld analysis was used by using rietica software.

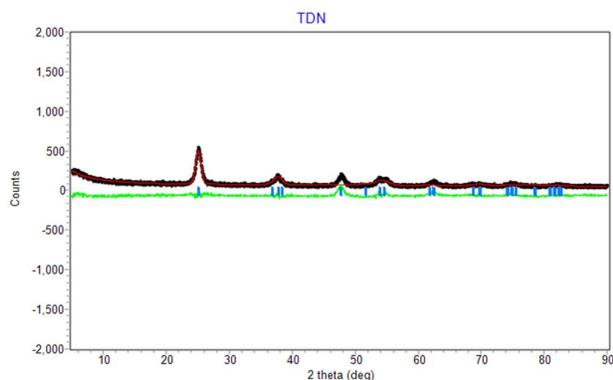


Figure 2. XRD patterns of Titanium Dioxide Nanotube after being analyzed using rietica software

From the analysis with Rietveld software, it can be seen that the crystalline size of the sample is 43,99 nm. This crystalline size shows that the anatase powder has a crystalline size with a nanoscale so that it can be said to be nanocrystalline. In addition to the crystalline size, the lattice parameters of the sample can be seen, $a = b = 3.7845 \text{ \AA}$ and $c = 9.5143 \text{ \AA}$ which indicates that anatase has a tetragonal crystal structure.

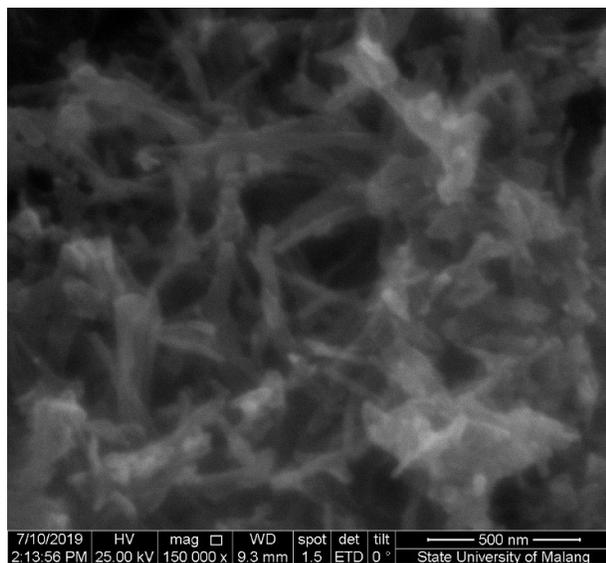


Figure 3. SEM images of Titanium Dioxide Nanotube after NaOH treatment and sulfuric acid washing

The SEM image of the TDN obtained by hydrothermal method is shown in figure 3 with magnification of 150.000 times. The morphology explains its particle has the form of tube with particle size is about 15,66-32,33 nm. TiO_2 which has tube-shape and nano-sized is called a TiO_2 nanotube (TDN) (Afshar & Hakamizadeh, 2009). We can observe

that the uniformity of the structure distribution inside the catalysts is not excellent and there is particle which remained because of the incomplete reaction. As clearly seen in figure 3, numerous fiber like nanotubes grow from nano-size TiO_2 particles.

IV. CONCLUSION

Based on these results, the mineral sand Tulungagung has the main compounds in the form of Fe_2O_3 that can be extracted Titanium dioxide nanotube. Nanocrystalline TDN 100% anatase has been formed at 600°C calcination temperature with a holding time of 2 hours. The phase formed is a single-phase anatase TDN with the crystalline size is 43.99 nm based on rietveld analysis and 16,66-32,33 nm based on SEM results.

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