A Study on Structure/Phase Transformation of TiO$_2$ nanorods at Various Annealing Temperatures

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Abstract. Synthesis of TiO$_2$ nanorods was conducted through mechanochemical of ball milling at speed of 175 rpm for 5 hours and strong base 12 M NaOH reaction by hydrothermal at 150°C overnight on variation annealing at 400, 500, and 600°C. Material characterization were performed by X-Ray Diffraction (XRD), Transmission Electron Microscope (SEM), and Surface Area Analyzer (SAA). Strong base reaction by hydrothermal showed the presence of anatase, brookite, and rutile phase for annealing up to 400°C. The diffraction pattern of annealing at 500 and 600°C contain peaks of both brookite and rutile phase. Morphology transformation of TiO$_2$ to form nanorods TiO$_2$ was showed by rod-shape from TEM micrographs and increase surface area into 111.9 m$^2$/g.

1. Introduction

Over the past decade, one dimension (1D) nanostructured of metal oxides have attracted much attention due to the advantage of chemical, structural, and physical properties that can be obtained [1]. In particular, TiO$_2$ nano-materials such as nanorods are widely used in solar cells and photocatalytic applications [2-3]. TiO$_2$ is well known has three polymorphs including rutile, anatase, and brookite. Anatase and brookite are metastable and can transform to rutile when they were heated, while rutile is the stable one. Many methods have been developed for the successful synthesis of TiO$_2$ nanorods such as sol gel, template, sputtering, electrochemical, and hydrothermal. Recently, nanorods derived from the alkali treatment of TiO$_2$ nanoparticles by hydrothermal method have attracted interest due to the beneficial method that can be obtained in large surface area and good crystallinity [4].

Effect of thermal treatment in TiO$_2$ and TiO$_2$ nanorods synthesis gives ways to control grain size, morphology, phase composition via experimental parameters such as time and temperatures. According Rath et al. (2009) [5], there are three competition that occur in phase transformation of anatase to rutile titania structure including grain growth of anatase phase, conversion of anatase to rutile, and grain growth of rutile phase, while Hu et al. (2003) [6] showed that phase transformation to rutile can occur from nanosize anatase accompanied brookite phase. This phenomena still has little information in literatures. Therefore, the effect of annealing temperature on the phase tranformation with nanorods morphology were investigated in this work.
2. Experimental

In Anatase-Brookite (A-B) phase nanocrystalline TiO$_2$ was used as precursor to obtain TiO$_2$ nanorods by milling, mechanochemical process. Milling was conducted in ball mill for 5 hours with a ball-to-powder weight ratio of 20:1 at speed of 175 rpm. 1.5 g of as-milled powders were added to 50 mL of 12 M NaOH and the mixture was stirred for a hour at ambient temperature. It then was heated by hydrothermal in Teflon-lined autoclave at 150°C overnight. The white precipitate was filtered and washed with 0.1 HCl until pH neutral continuously. The precipitate was dried in an oven at 105°C. Transformed TiO$_2$ were obtained by annealing of precipitate at 400, 500, 600°C for 2 hours. Phase identification was performed via X-ray diffractometry (XRD) on Bruker D8 Type diffractometer operating at 40kV/35mA using Cu K$_\alpha$ radiation. Particle morphology was observed via electron microscopy (TEM). The volume fraction phase of the samples were calculated from the following equations [7]:

\[ W_A = \frac{k_A A_A}{k_A A_A + k_B A_B + A_R} \times 100\% \quad (1) \]
\[ W_B = \frac{k_B A_B}{k_A A_A + k_B A_B + A_R} \times 100\% \quad (2) \]
\[ W_R = \frac{A_R}{k_A A_A + k_B A_B + A_R} \times 100\% \quad (3) \]

where $W_A$, $W_B$, and $W_R$ represent the weight fractions of the anatase, brookite, and rutile phases, respectively; $A_A$, $A_B$, and $A_R$ are the X-ray integrated intensities of the anatase (1 0 1) peak, brookite (1 2 1) peak, and rutile (1 1 0) peak, respectively; $k_A$ (0.886) and $k_R$ (2.721) are two coefficients. The size of crystallite was calculated by Scherrer equation.

3. Result and discussion

TiO$_2$ nanoparticles by ball milling process that have been formed are used as a precursor in the synthesis of TiO$_2$ nanorods. Synthesis of TiO$_2$ nanorods draws on research Wahyuningsih et al. (2016) [8] by hydrothermal process with development of various annealing temperatures. The various concentrations of alkali NaOH also affect the structure of TiO$_2$ nanorods. In the hydrothermal process with a concentration of 8 M NaOH was not obtained rod structure yet, while at concentrations of 10 and 12 M NaOH obtained structural rods (rods) and the formation of rod structure is more dominant on the concentration of NaOH 12 M [8]. According to Liu et al. (2009) [9], hydrothermal process includes synthesis of TiO$_2$ in alkali solution, turnover proton alkali ion in solution, dried, and washed with acid.

TiO$_2$ undergo hydrolysis when reacted with NaOH 12 M lead to termination of the polymer chain TiO$_2$ (depolymerization). OH is highly reactive of NaOH that attacks bonding Ti-O-Ti. OH replace the damaged O-Ti Ti-OH bonding while loose O-Ti will bind Na$^+$. Neutralized with HCl hydrolysis to the polymerization process again with the release of H$_2$O at the two ends of TiO$_2$ polymers re-formed. The process of re-establishment of TiO$_2$ is called condensation polymers [10].
Figure 1. The scheme of mechanism reaction of TiO$_2$ formation

The structure of TiO$_2$ after polimerization

Figure 2. X-Ray diffractogram pattern of TiO$_2$ by hydrothermal synthesized at annealing temperature of (a) 400, (b) 500, and (c) 600°C. A: anatase, B: brookite, R: rutile.

Figure 2 shows the XRD diffractogram pattern of TiO$_2$ annealed at various temperatures and there are three phase that obtained including anatase, brookite, and rutile (JCPDS No.76-2486, 76-1934, dan 79-1640). For the sample annealed at 400°C, anatase phase at $2\theta = 25.93^\circ$ (d100); brookite phase at $2\theta = 30.69^\circ$ (d211) and $48.13^\circ$ (d321); rutile phase at $2\theta = 35.45^\circ$ (d101) which amorphous peak. When the sample annealed at 500 dan 600°C, there is no diffraction peak of anatase phase, but the sample show diffraction peaks of brookite phase at $2\theta = 30.75^\circ$ (d211) and $48.05^\circ$ (d321); and rutile phase at $2\theta = 27.05^\circ$ (d110), $35.01^\circ$ (d211), $39.57^\circ$ (d111), dan $52.11^\circ$ (d211).

Rhat et al. (2009) [5] explains that the various annealing temperature can affect the structure of TiO$_2$. TiO$_2$ thin layer of titanium isopropoxide precursors undergo a phase transformation of anatase
into rutile at a temperature of 700-800°C and was obtained pure rutile phase at temperatures of 1000°C. The same results occurred on TiO₂ nanotube in which the influence of the annealing able to bring the rutile phase at a temperature of 600°C and an overall transformation into rutile at a temperature of 800°C [11]. In this study, the rutile phase can be formed at annealing temperatures of 400, 500, and 600°C. Although it has not formed of pure rutile phase, this achievement is of great concern that given in this study of phase transformation into rutile. The rutile of TiO₂ can be achieved if the annealing temperature more than 600°C.

Table 1 shows the crystals size of anatase TiO₂ that annealed at 400°C are about 41.25 nm. Brookite phase TiO₂ increased crystal size is comparable with annealing temperature increases, while rutile phase TiO₂ decreased the crystal size is inversely related to the annealing temperature increases. Table 2 indicates that after hydrothermal and various annealing temperature appear new phase i.e. rutile in which the higher the annealing temperature the anatase phase percentage is getting lower while the rutile phase is increasing. This indicates that the closer the relationship between the influence of the annealing temperature increases to changes in the crystal size and the occurrence of phase transformations.

| Annealing temperature (°C) | Phase   | B (°) x 10⁻³(rad) | 2θ (°) | Cos θ | D (nm) |
|---------------------------|---------|-------------------|--------|-------|--------|
| 400                       | Anatase | 0.12              | 3.44   | 24.31 | 0.98   | 41.25  |
|                           | Brookite| 0.28              | 4.85   | 30.40 | 0.96   | 29.62  |
|                           | Rutile  | 0.19              | 3.43   | 35.02 | 0.95   | 42.39  |
| 500                       | Brookite| 0.22              | 3.78   | 30.83 | 0.96   | 38.02  |
|                           | Rutile  | 0.25              | 4.59   | 34.65 | 0.95   | 31.66  |
| 600                       | Brookite| 0.21              | 3.71   | 31.76 | 0.96   | 38.88  |
|                           | Rutile  | 0.28              | 4.84   | 34.50 | 0.95   | 29.98  |

Table 2. Phase percentage of TiO₂ at various annealing temperatures

| Annealing temperature (°C) | Phase percentage (%) |
|---------------------------|-----------------------|
|                           | Anatase   | Brookite | Rutile |
| 400                       | 24.48     | 44.88    | 30.67  |
| 500                       | -         | 57.06    | 42.94  |
| 600                       | -         | 57.06    | 42.94  |

Associated with brookite crystal growth, brookite phase transformation into rutile may occur at the grain boundaries or in the particle brookite. When the core of rutile formed on the inside of the particle brookite, rutile crystals can be increased with increasing annealing temperature. While in this study decreased the crystals size of rutile indicated that rutile core was formed at grain boundaries brookite. An increase in the annealing temperature, brookite crystals grow larger than its size with consequent reduction of the volume fraction of grain boundaries. Because the core of rutile crystals grown at the grain boundaries brookite particles, reducing the volume fraction of grain boundaries at a higher temperature so that it can suppress the growth of rutile crystals. This causes the crystal size of rutile declined against the annealing temperature rise [5,7].
Based on the results of XRD characterization, an increase in the annealing temperature causes phase formed brookite and rutile TiO\textsubscript{2}. Crystal size and percentage calculations showed that the phase of maximum yield generated on TiO\textsubscript{2} annealing temperature of 600°C. Subsequently, TiO\textsubscript{2} that annealed at 600°C was characterized by TEM to confirm that it has formed TiO\textsubscript{2} nanorods. TEM imaging results indicated that it has formed rods (rods) TiO\textsubscript{2} result of hydrothermal treatment with NaOH 12 M and annealing temperature of 600°C with a particle diameter of 8 nm (Figure 24). The existence of brookite are metastable phase transformation into a stable rutile structure facilitates the formation of nanorods with crystal growth upwards to form rods (rods) [12].

![TEM morphology of TiO\textsubscript{2} nanorods by hydrothermal process and annealed at 600°C](image)

**Figure 3.** TEM morphology of TiO\textsubscript{2} nanorods by hydrothermal process and annealed at 600°C

| Table 3. Surface area of TiO\textsubscript{2} by milling process and TiO\textsubscript{2} nanorods |
|-----------------------------------------------|
| TiO\textsubscript{2} | Method | Surface Area (m\textsuperscript{2}/g) |
|----------------------|--------|-------------------------------|
| Milling             | BET    | 7.5                           |
| Nanorods            | BET    | 111.9                         |

The existence of structural engineering TiO\textsubscript{2} nanorods also increases the surface area up to 14 times. TiO\textsubscript{2} surface area is important to the adsorption of compounds dye (dye). The greater surface area of the adsorption also increased the bounding of dye compound to the TiO\textsubscript{2}. The direction of movement of the electrons are regularly when used as a semiconductor. These results are consistent with research conducted by Govindaraj et al. (2014), the structural changes in the form of nanorods were able to improve the characteristics of the surface area of the material [13].

### 4. Conclusion

TiO\textsubscript{2} nanorods were synthesized by hydrothermal method. The structural/phase transformation of TiO\textsubscript{2} nanorods have been investigated. Strong base reaction by hydrothermal showed the presence of anatase, brookite, and rutile phase for annealing up to 400°C. The diffraction pattern of annealing at 500 and 600°C contain peaks of both brookite and rutile phase. Morphology transformation of TiO\textsubscript{2} to form TiO\textsubscript{2} nanorods was showed by rod-shape from TEM micrographs and increase surface area into 111.9 m\textsuperscript{2}/g.

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