Structure Identification of Nanopowder TiO_2 Synthesized by Coprecipitation Method

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Titanium dioxide, or is a semiconductor material with many advanced applications, such as photocatalysts. Generally, TiO_2 has three primary forms of crystal structure: anatase, brookite, and rutile. Among these types of crystal structures, anatase has good properties in photocatalysts application due to its band gap value (3.20 eV) and stability. Further, there are many methods to synthesize TiO_2, such as sol-gel, hydrothermal method, etc. Still, the copreciptation method has a suitable method because it is easy to produce, high pure product and low cost. However, many parameters control the quality of TiO_2 itself: pH, temperature, time and mechanical process. Especially for the mechanical process, no results were reported about structure identification of TiO_2 at mixing time below 25 hours. In this research, titanium dioxide (TiO_2) powder has been investigated using coprecipitation method and $TiCl_3$ as a raw material. The TiO_2 was synthesized by mixing the time duration at 5, 10, and 25 hours in this method. Analysis using x-ray diffraction shows that all the samples have an anatase phase. Further, Rietveld refinement analysis shows that mixing duration time does not significantly affect the lattice parameters.

Keywords: TiO_2, Anatase, Rietica, Coprecipitation

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I. INTRODUCTION

Titanium dioxide,TiO_2, generally consists of three types of crystal structure: anatase, rutile and brookite. Among these structures, anatase with a band gap of 3.20 eV has good photocatalytic properties compared to other structures [1]. Furthermore, it is imperative to focus on some parameters which include crystal shape, morphology and stability of section while synthesizing TiO_2 powder to be implemented as a photocatalyst [2].

Various technique can be used to synthesize TiO_2 powders, such as sol-gel, combustion method, gas phase and coprecipitation method [2]. Using sol-gel method, Vijayalakshmi became successfully synthesized TiO_2 powder with an anatase section and a crystal length of 7 nm [3]. The benefits of the coprecipitation method are that TiO_2 can be synthesized at low temperatures and efficiently regulate the particle size. The smaller and more homogeneous particle size of the sample is expected in this study [4] for photocatalyst application. One of the resilient parameters is changing the the mixing time [5]. Previous results by others found that mixing time at 25 hours obtained an anatase phase and phase transition from anatase to rutile at 45 hours [5]. Further, rutile phase completely formed from 60 hours to 85 hours [5–7]. Among those mixing times from 25 to 85 hours, no results were reported about the structure identification of TiO_2 powders at mixing time below 25 hours.

In this paper, we report the successful synthesis of TiO_2 nanopowders by using coprecipitation method with $TiCl_3$ as the main precursor by using the variation of mixing time at 5, 10 and 25 hours. The structure analysis of the samples was evaluated by refinement technique using the least-square method.

II. METHOD

The TiO_2 powder was synthesized from titanium trichloride ($TiCl_3$) as a precursor by coprecipitation method [8] [9]. A $TiCl_3$ (Merck) solution with 15% concentration was mixed with deionized water and then stirred for 5 hours. The pH of the combined solution was adjusted at 9 through adding NH_4OH 28.9% solution (Aldrich) and constantly stirred until a white precipitate was acquired. The solution was maintained at room temperature for 24 hours and then filtered and washed using deionized water to cast off the last ammonium. The white TiO_2 precipitate was then calcined for 3 hours at 300°C. The crystal structure of TiO_2 powder was identified by using the powder X-ray diffraction method (CuKα radiation, λ=1.5405 $\mathring{A}$, and $2\theta = 20°$ to 70°). The identical process was repeated with altered mixing duration at 10 and 25 hours.

III. RESULTS AND DISCUSSION

The X-ray diffraction pattern of TiO_2 powder synthesized by the coprecipitation method as a function of mixing time can be seen in Fig. 1. Phase analysis in *Match!* software

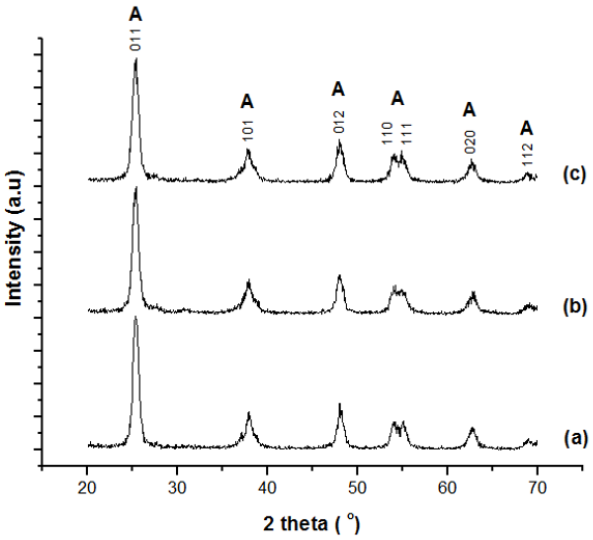

FIG. 1: XRD pattern of TiO_2 powder with mixing time: a) 5 hours, b) 10 hours and c) 25 hours (A = anatase).

shows a diffraction peak at $2\theta = 25.3°$ and no peak at $2\theta = 27°$ giving information that all samples have an anatase phase (ICSD No. 202243).

Synthesis of TiO_2 as a variation of mixing time has also been done by Widaryanti et al. at 25, 45 and 65 hours [5]. The anatase phase was obtained at a mixing time of 25 hours. This could be attributed to the concentration of oxygen vacancies that hinder the converesion of anatase to the rutile phase [10], anatase and rutile phases were obtained with a mixing time of 45 hours. At mixing time of 65 hours, anatase completely transformed into rutile phase [5]. This result indicates that anatase phase occurs when the mixing time is less than 45 hours. Over 45 hours, the anatase transforms into a rutile phase. Determination of crystalline size can be found using *MAUD* software. Based on the software analysis, the crystalline size values of the TiO_2 powders synthesized with varying mixing times of 5, 10 and 25 hours were 11.83 nm, 10.7 nm and 9.6 nm, respectively. It can be seen that the decrease in the crystalline size of the sample because of the amount of mixing time leads to the complete dissolution process from chemical interaction [11]. Determination of the crystalline size of TiO_2 powder using $TiCl_3$ as a precursor was also reported by Molea et al., with a crystalline size value of 13.91 nm [12]. Fig. 2. shows a graph of refinement result of TiO_2 powders using *Rietica*. It can be seen visually that the calculated data (red line) match with the data (black dots) and have a less difference factor (green line) indicating a well quality of refinement process [13]. Table 1 shows the lattice parameter of TiO_2 powder obtained by Rietveld refinement using *Rietica* software. Based on Table 1, the variation of mixing time does not significantly increase the lattice parameters due to the anatase phase's complete formation [14]. Moreover, all the refinement results can be accepted when the value of GoF is less than 4% [15].

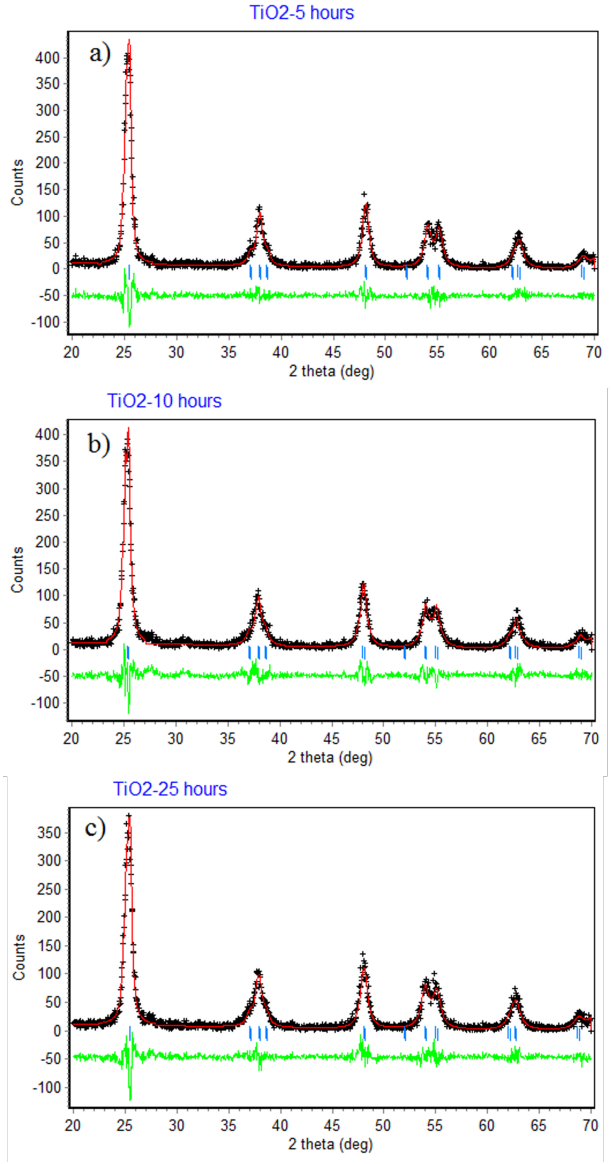

FIG. 2: Refinement pattern of TiO_2 powder with mixing time: a) 5 hours, b) 10 hours and c) 25 hours

IV. CONCLUSION

Based on the results above, it can be concluded that synthesizing titanium dioxide powder by using the coprecipitation method and varying its mixing time at 5, 10, and 25 hours duration will result in an anatase phase starting from 5 to 25 hours with decreasing its crystalline size due to the dissolution process from chemical interaction. Also, for 5 to 25 hours anatase phase forms completely, resulting in no significant change in the lattice parameters of TiO_2.

TABLE I: The lattice parameter of TiO_2 powder as a variation of mixing time duration

Sample	**a=b (nm)**	**c (nm)**	**Gof**
TiO_2 - 5 hours	3.796750±0.000967	9.522018±0.002454	1.2
TiO_2 - 10 hours	3.796793±0.001122	9.514776±0.002857	1.5
TiO_2 - 25 hours	3.798261±0.001152	9.531850±0.002869	1.4

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