Characteristics of TiO$_2$ particles prepared by simple solution method using TiCl$_3$ precursor

I M Joni$^{1,2*}$, L Nulhakim$^2$ and C Panatarani$^{1,2}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km 21, Jatinangor 45363, West Java, Indonesia

$^2$Nanotechnology and Graphene Research Centre, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km 21, Jatinangor 45363, West Java, Indonesia

$^*$$^*$imadejoni@phys.unpad.ac.id

Abstract. In this work, TiO$_2$ particle has been prepared by simple solution method using TiCl$_3$ precursor. The XRD analysis confirmed the presence of rutile TiO$_2$ which is indicated by the peaks corresponding to (110), (101), (111), (211) and (002) plane. The crystallite size was about 7.25 nm as obtained by Scherer equation. The SEM image revealed that the rutile TiO$_2$ exhibits agglomeration with spherical morphology. The composition is confirmed by EDS measurement which shows 17.5 at % of titanium and 58.2 at % of oxygen, respectively. Based on SEM result, the size of the primary particle was about 100 nm. The PSA measurement showed that the average particle diameter was about 759 nm with a median d$_{50}$ (<50%) of about 200 nm. These results show that TiO$_2$ sample was nanocrystalline with primary particle diameter of about 100 nm and 759 nm, respectively. The particle diameter was still large probably due to the existence of agglomeration which is acquired by PSA. However, these properties can be used as preliminary information for applications that requires nanocrystalline TiO$_2$ with rutile phase by using simple and low-cost preparation method.

1. Introduction

In the last few years, there has been growing interest in metal oxide particle such as TiO$_2$. A semiconductor is used in wide range of applications such as for lithium-ion batteries, photosensors, photocatalysis, dyes sensitized solar cells, anti-reflective (AR) coatings, electrochromic displays, optical filters, planar waveguides, photovoltaic devices, UV light sensors, biomedical applications, etc. [1-4]. Nanoparticle TiO$_2$ has also been used as a pigment, a thickener and sunscreen in cosmetics and skin care products [5]. Properties and applications of TiO$_2$ are controlled by its morphology, particle size, purity, crystal structure and phase, porosity, surface area, etc. [1, 6]. TiO$_2$ is an n-type wide bandgap semiconductor and has three crystalline phases, i.e. anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) with band gap 3.02 eV (410 nm), 3.20 eV (387 nm) and 2.96 eV (419 nm), respectively [1, 6, 7]. Among these three types, the rutile phase is most stable form while anatase and brookite types are metastable and possible to transform to rutile phase under high temperature of about 750°C [8]. Synthesis of anatase, rutile and brookite of TiO$_2$ particle and thin film from TiCl$_3$ were reported by Leal J L et al. [9], Yu Q et al. [10], Haider A J [11] and Dusan A et al. [4]. The characteristics of TiO$_2$ such as chemical purity and crystalline phase depend on the synthesis method...
The effect of various methods for preparation to obtain different particle size and morphology was reported [13]. The TiO\textsubscript{2} particle can be prepared by several methods such as hydrothermal, solvothermal, microwave assisted method, electrospinning and simple solution method. In the near future, the preparation of TiO\textsubscript{2} using low cost and simple method will be necessary. The preparation of rutile TiO\textsubscript{2} particle using simple solution method still needs to be developed and explored further. Therefore, in this work, the rutile TiO\textsubscript{2} sample will be prepared by using simple solution method. The characteristics of this sample will be analyzed and discussed.

2. Experiments

The preparation of TiO\textsubscript{2} particle was done by simple solution method with TiCl\textsubscript{3} 15% (Merck) as a precursor. 7 ml of TiCl\textsubscript{3} 15% was mixed with 1.5 ml HCl and 9 ml of distilled water, stirred for about 15 minutes. Then the solution was heated at 80°C temperature for about 10 minutes by gently adding 6 ml of concentrated HNO\textsubscript{3}. The process is then continued with mixing and reheating at 80°C followed by washing and drying at about 100°C. Subsequently, the sample was calcined at 200°C for 5 hours.

The structural property of TiO\textsubscript{2} particle was examined by X-ray Diffraction (XRD) Rigaku using Cu-K\textalpha\ (\lambda = 0.15419 nm) radiation source, (X'pert Pro PANalytical) over a 2\theta scan range of 20°-80°. Surface morphology and element composition were studied using Scanning Electron Microscopy (SEM) equipped with energy dispersive X-ray (EDX), FEI-Inspect 550, EDAX Ametek. The diameter of particles was examined by Particle Size Analyzer (PSA) Beckman Coulter LS 13 320, while the purity of particles was examined by XRF (X-ray Fluorescence), Rigaku Nex CG.

3. Results and Discussion

The XRD pattern of sample is shown in figure 1. The peaks corresponding to rutile phase, matches well to JCPDS Card No: 21-1276 as reported by A.J. Haider et al. [11]. The results were also comparable with the other reports of rutile TiO\textsubscript{2} [10]. The position of 2\theta at 27.42°, 36.08°, 41.25°, 54.33° and 63.44° corresponds to Miller indices of (110), (101), (111), (211) and (002) plane, respectively [1]. The peak position of 2\theta and its correlation with Miller indices can be seen in table 1. The crystallite size (D) of sample was calculated using Debye-Scherrer’s equation (1).

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the wavelength of x-ray beam (Cu K\textalpha, with \(\lambda = 0.15418\ nm\)), \(\beta\) (in rad) is the full width at half maximum (FWHM) of the intense peak and \(\theta\) (in rad) is the Braggs angle. The average of crystallite size for this TiO\textsubscript{2} sample was about 7.25 nm. This size was comparable with the result reported by J.H. Leal et al. [9], the crystallite size for rutile phase synthesized from TiCl\textsubscript{3} by simple low-temperature method was examined to be below 10 nm.

| 2 Theta | Miller indices | Phase  |
|---------|---------------|--------|
| 27.42   | 110           | Rutile |
| 36.08   | 200           | Rutile |
| 41.25   | 111           | Rutile |
| 44.20   | 211           | Rutile |
| 56.51   | 220           | Rutile |
| 63.44   | 002           | Rutile |
| 69.11   | 301           | Rutile |
Figure 1. X-ray diffraction patterns of rutile TiO$_2$ particle prepared by simple solution method.

SEM images of TiO$_2$ particle is shown in figure 2. Spherical particles with agglomeration were observed and the diameter of the primary particle was about 100 nm as shown in the inset of figure 2. On the other hand, the elemental analysis was examined by EDX measurement and given in figure 3. The green box in the inset of figure 3 depicts the area of EDX testing. The elemental compositions of sample consist of oxygen and titanium of about 80.5 and 19.5 at%, respectively. The presence of oxygen indicates that the sample is in the form of titanium dioxide.

Figure 2. SEM image of rutile TiO$_2$ particle with two different magnification.

The PSA result showed that the average particle diameter was about 759 nm with d$_{50}$ (<50%) = 200 nm (figure 4). This result indicated that the TiO$_2$ particles occur as agglomerates in suspension and hence a proper dispersing agent is necessary to obtain a well-dispersed suspension of TiO$_2$ nanoparticles.
The purity of sample was about 84 Mass % of TiO₂ as confirmed by XRF measurement and the impurities showed very low Mass percentage. The complete data can be seen in table 2.

Table 2. The percentage (Mass%) of sample composition measured by XRF.

| Component | Mass% |
|-----------|-------|
| TiO₂      | 83.9  |
| K₂O       | 1.1   |
| CaO       | 0.6   |
| SiO₂      | 0.3   |
| Zn        | 0.2   |
| Al₂O₃     | 0.2   |
| S         | 0.1   |
| MgO       | 0.05  |
| P₂O₅      | 0.03  |
| Cu        | 0.004 |
4. Conclusions

TiO$_2$ particle was successfully synthesized by simple solution method using TiCl$_3$ precursor. XRD characterization confirmed that the particle has rutile TiO$_2$ phase. The average crystallite size was about 7.25 nm. SEM measurement revealed that the surface morphology of sample was spherical with agglomeration. The diameter of the primary particle based on SEM image was about 100 nm. While the particle diameter measured by PSA was about 200 nm for $d_{50} (<50\%)$. It is proposed that the TiO$_2$ particle in this work showed nanocrystalline nature (crystallite size $< 10$ nm) with particle diameter $\sim 200$ nm that is most probably due to the existence of agglomeration. In addition, this work described a simple solution method to prepare rutile phase with a relatively small crystallite size (below 10 nm). Since the preparation of TiO$_2$ is using a simple low-cost method, it will be suitable in mass production for industrial applications.

Acknowledgements

The authors would like to acknowledge Academic Leadership Grant, Universitas Padjadjaran, contract no. 855/UN6.3.1/PL/2017 for funding this research work.

References

[1] Dhandayuthapani T, Sivakumar R and Ilangovan R, 2016 Surf. Interf. 4 59
[2] Chen X, Mao S S 2007 Chem. Rev. 107 2891
[3] Hasan M M, Haseeb M A, Saidur R and Masjuki H H 2008 Int. J. Chem. Bio. Eng. 1 92
[4] Dussan A, Bohorquez A, Quiroz H P 2017 Appl. Surf. Sci. 424 111
[5] Verleysen E, De Temmerman P J, van Doren E, Francisco M A D and Mast J 2014 Powd. Tech. 258 180
[6] Wang Y, He Y, Lai Q and Fan M 2014 J. Environ. Sci. 26 2139
[7] Linsebigler A L, Lu G, Yates J T 1995 Chem. Rev. 95 735
[8] Liao Y L, Que W X, Jia Q Y, He Y C, Zhang J and Zhong P 2012 Mater. Chem. 22 7937
[9] Leal J H, Cantu Y, Gonzales D F and Parsons J G 2017 Inorganic Chem.Commun. 84 28
[10] Yu Q, Wang H, Peng Q, Li Y, Liu Z and Li M 2017 J. Hazard. Mater. 335 125
[11] Haider A J, Al-Anbari R H, Kadhim G R and Salame C T 2017 Energy Proc. 119 332
[12] Diebold U 2003 Surf. Sci. Rep. 48 53
[13] Panatarani C, Lenggoro I W and Okuyama K 2003 J. Nanopart. Res. 5 47