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THE EFFECT OF STIRRING TECHNIQUES ON TiO_2 NANOPARTICLE SIZE BY USING A WET CHEMICAL METHOD

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ABSTRACT

THE EFFECT OF STIRRING TECHNIQUES ON TiO_2 NANOPARTICLE SIZE BY USING A WET CHEMICAL METHOD. The TiO_2 nanoparticles were synthesized by a wet chemical method. The influence of stirring on the particle size was investigated. In the first technique, the stirring was done during the process of mixing, while in the second technique the stirring was done after the mixing process is finished. The particle size was characterised using XRD, TEM, and PSA, while the BET surface area used. The first technique, obtained a fairly small grain size of about 12-50 nm, while the second technique obtained particle sizes between 1300-1600 nm.

Keywords: Particle size, Stirring technique, Wet chemical method

ABSTRAK

PENGARUH TEKNIK PENGADUKAN PADA UKURAN NANOPARTIKEL TiO2 DENGAN MENGGUNAKAN METODE KIMIA BASAH. Sintesis nanopartikel TiO_2 dengan metode kimia basah. Telah dilakukan penelitian pengaruh pengadukan pada ukuran partikel. Teknik pertama, pengadukan dilakukan selama proses pencampuran, sedangkan pada teknik kedua pengadukan dilakukan setelah proses pencampuran selesai. Ukuran partikel dikarakterisasi dengan menggunakan *XRD, TEM,* dan *PSA*, sedangkan karakterisasi luas permukaan digunakan *BET*. Pada teknik pertama, diperoleh ukuran partikel yang cukup kecil, yaitu sekitar 12 nm - 50 nm, sedangkan pada teknik kedua diperoleh ukuran partikel antara 1.300 nm - 1.600 nm.

Keywords: Ukuran partikel, Teknik pengadukan, Metode kimia basah

INTRODUCTION

In the last decade, there has been an intensive study of materials with well-doped and non-doped nanostructure TiO_2 [1-13], such as the stability of the structure of TiO_2 whose chemistry, physics, optics [1], the electrical quantities [1-2], and a promising material as a low cost semiconductor [3-5, 9-13].

Materials TiO_2 exist in three mineral forms, namely anatase, rutile, and brookite [15]. This type of anatase has a tetragonal crystal structure, and is used as a photocatalyst under ultraviolet irradiation. The rutile type also has a tetragonal crystal structure and is used as a white pigment in paint, while the brookite-type crystal structure is othorombik [1]. Synthesis of nanostructure TiO_2 can be done through several methods, e.g hydrothermal [3], sol-gel [3, 5, 9,10, 13], nonaqueous (non-sol-gel [2], sputtering thin films [7], and simple colloidal crystal templating [11]. The research on the effects of heat treatment on the particle size and surface area of TiO_2 as a solar cell material has been done, but the effect of stirring time yet many do [14,15].

In this work, we used wet chemical methods for producing powders consisting of anatase TiO_2 nanostructure. In keeping with the level of acidity, we mixed it with ammonium hydroxide. In the mixing process,

we used two stirring techniques. In the first, the solution was still stirred during the mixing process; in the second, the stirring was stopped after the mixing of solutions was finished. The stirring of speed on both techniques was 300 rpm. We would see how the stirring-time influences the technique to measure formed crystals.

EXPERIMENTAL METHOD

The synthesis of titanium oxide TiO_2 powder used MERCK standard materials, namely titanium tetrachloride and pH adjustment using ammonium hydroxide. Titanium tetrachloride was introduced into the reactor at 4 °C, and the stirring was set at a rate of 300 rpm. And then it was added to a solution of aquabidest while it was still being stirred. The level of acidity (pH) was set by using ammonium hydroxide to pH 9. The stirring was done without heating for 4 hours, followed by heating at a temperature of 150 °C until it dried. In the second technique, the stirring was stopped after all the solutions were mixed.

The resulting dry powder was compacted to a diameter of 1.5 cm at a pressure of 3000 psi for 5 minutes, then calcined at a temperature of 500 °C - 700 °C each for 2 hours using a heating furnace. The resulting samples were characterized by XRD (shimadzu 7000), BET (Quantachrome instrument V10.01), TEM (JEOL JEM 1400) and PSA (coulter LS 1000).

RESULTS AND DISCUSSION

The XRD patterns of the nanoparticles with annealing at 500 °C obtained by this method are shown in Figure 1(a). All the peaks in the XRD patterns can be indexed as anatase phases of TiO_2, and has a tetragonal crystalline structure and no existence of the rutile phase. The transition from anatase to rutile phase usually occurs at high temperature over 600 °C [4], and this is shown in the Figure 1(b) where the annealing process is performed at a temperature of 700 °C. Similar results were obtained by David O. Sanlon *et al* [6]. It explains that the temperature between 600 °C -700 °C is a phase transition temperature of anatase to rutile phase. This was confirmed by the results of XRD samples when processed using the second technique and anneal temperature of 800 °C which shows all the rutile phase. See Figure 1 (c). The crystallite size was obtained by Debye-Scherrer's formula, given by Equation (1).

$$D = K\,\lambda\,/(\beta\cos\theta) \quad \text{.....} \quad (1)$$

where:

D = The crystal size
K = Usually taken as 0.89
λ = The wavelength of the X-ray radiation for CuKα λ = 0.15406 nm
β = The line width at half-maximum height [3]

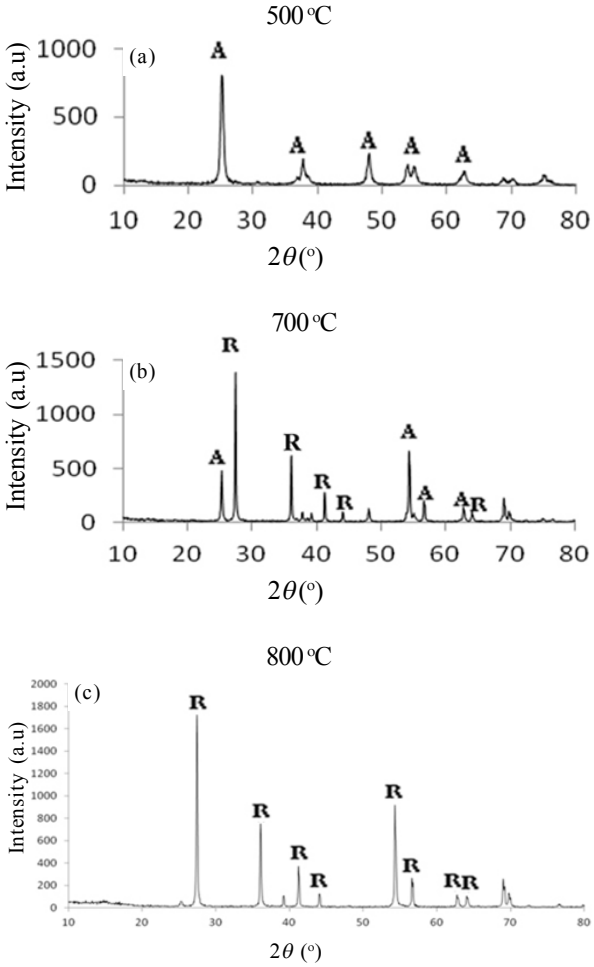

Figure 1. The XRD patterns of TiO_2 (a) with anneal 500 °C, (b) with anneal 700 °C, and (c) The second process uses techniques and anneal at 800 °C.

The crystallite size obtained using this formula is 53 nm. Meanwhile, the average size of the particles produced by the second technique is 1600 nm. The resulting particle size of the second stirring technique is larger than the size of the particles produced in the first stirring technique. This explains the process of diffusion of atoms occur first before stirring, so that the size of the particles formed is greater.

On the other hand, when the mixing process was done after mixing ammonium hydroxide complete, we got particle sizes between 1300 nm-1600 nm. It can be seen from the results of the characterization of particle system analysis, in which the particle size distribution is around that number, see Figure 2.

The addition of the solution of $TiCl_4$ aquabidest stars the phase hydrolysis, namely the reaction as Equation (2).

$$TiCl_{4\,(aq)} + H_2O_{(l)} \rightarrow Ti(OH)_{4\,(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \quad \text{.....} \quad (2)$$

The NH_4OH solution ionize slightly due to a weak alkaline solution.

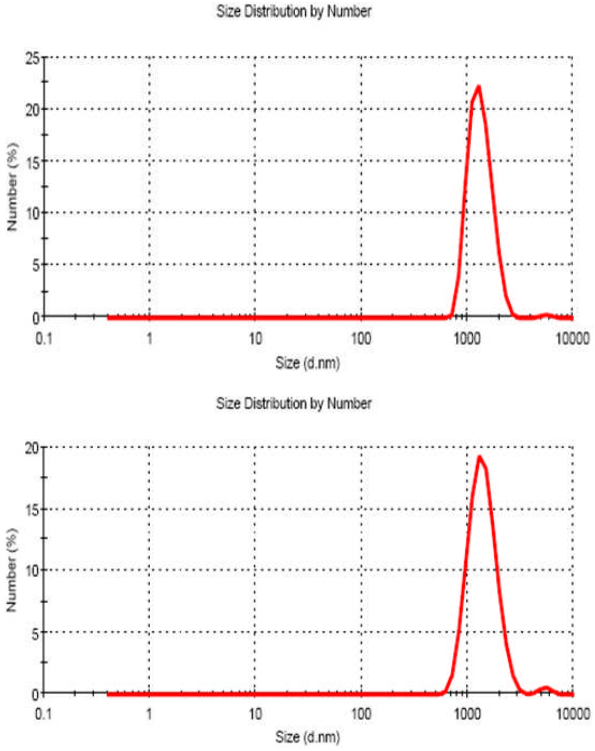

Figure 2. The distribution of particle size with stirring technique after mixing is complet.

$$NH_4OH_{(aq)} \rightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)} \quad \text{..... (3)}$$

This reaction is reversible and the amount of NH_4OH that can be ionized in solution is very slight. The addition of NH_4OH solution give the reaction of Cl^- ions derived from the hydrolysis reaction of $TiCl_4$ with NH_4^+ ions from the ionization reaction NH_4OH, which is formulated as follows Equations (4).

$$NH_4^+{}_{(aq)} + Cl^-_{(aq)} \rightarrow NH_4Cl_{(s)} \quad \text{..... (4)}$$

The NH_4Cl compounds experience that and form the core aggregation. Furthermore, this core is covered by a shell composed of a mixture of TiO_2 and NH_4Cl compounds. The compounds are derived from the condensation reaction of TiO_2, namely :

$$Ti(OH)_{4\,(aq)} \rightarrow TiO_{2\,(s)} + 2\,H_2O_{(l)} \quad \text{..... (5)}$$

The addition of a solution of $TiCl_4/H_2O$ with NH_4OH solution result in hydrolysis and condensation reactions which take place continuously. The hydrolysis reaction leads to the formation of the original nuclei of titanium oxide, while the condensation reaction leads to the formation of the original network system nuclei.

The hydrolysis reaction equilibrium condensation leads to the formation of TiO_2 particles which are likely to produce a rutile phase. The addition of $NH_4OH_{(aq)}$ for neutralization solves the phase equilibrium of hydrolysis and condensation phase. Hydrolysis reaction in this condition increases the formation of anatase phase. The formation of anatase and rutile TiO_2 is determined by hydrolysis and condensation reactions. If the condensation reaction starts before the hydrolysis reaction is completed, then the amorphous and anatase TiO_2 is formed. In addition to the neutral or base conditions, the condensation reaction starts before the hydrolysis reaction is completed, whereas the acidic conditions would improve the hydrolysis reaction and reduce condensation. We argue if the strirring speed increases, the particle size decreases. With increasing stirring speed, the kinetic energy to melt disintegration increases this causes fragmentation of liquid droplets produce smaller particle size. Although we used the same stirring speed, but the first stirring technique has not resulted in agglomeration, so that the particle size obtained is smaller than the size of the particles produced by the second stirring technique.

Based on the characterization results of XRD and PSA on samples produced from mixing the two techniques above, then we just do the TEM measurements on samples generated from the first stirring technique. The results we get through the mixing process is done simultaneously while mixing ammonium hydroxide. Transmission Electron Microscope (TEM) was used to study the morphologies of the sample. Figure 3 presents the TEM morphologies of the synthesized TiO_2. The TEM characterization results, show that the particles have a size between 12 nm-50 nm.

Brunauer Emmett Teller (BET) was the method used to determine the suface area of each sample. An explanation of the physical adsorption of gas molecules on a solid surface is important in the

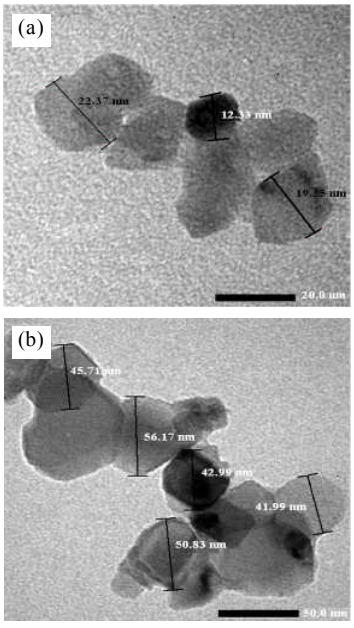

Figure 3. A TEM image of TiO_2 nanoparticle (a). 500 °C and (b) 700 °C.

specified surface area. The results of BET measurements were performed using temperatures of 500 °C and 700 °C and can be seen in Table 1. The surface area of TiO_2 nanoparticles decrease from 57.9 m^2/g to 2.8 m^2/g with increasing annealing temperatures from 500 °C to 700 °C, so that it would cause an increase of crystal size of the TiO_2 nanoparticle from 20 nm to 50 nm.

Table 1. BET results for the TiO_2 photoelectrodes annealed at temperatures 500 °C and 700 °C.

T (°C)	A (m^2/g)	Pore volume (cc/g)	Particle size (nm)
500	57.9	0.02657	20
700	2.8	0.00131	50

Junting *et al* argued that with a higher annealing temperature, the surface area decreases further and the pore volume shows a similar trend, suggesting that densification via grain boundary diffusion in addition to sintering through surface diffusion has occurred [4]. But we obtained somewhat different results. We suspect that the value of pore volume decreases with the increasing annealing temperature. The densification occurs not only through surface diffusion but also through the diffusion of grain boundaries. With increasing temperature and decreasing surface area, it may lead to a decreasing amount of dye adsorbed per unit area of photoelectrode. On the one hand we have to increase the motion of electrons, but this will result in reduced surface area. It is still a challenge to develop higher power efficiency.

CONCLUSION

In the two stirring technique processes used, the resulting TiO_2 nanoparticle size is 20 nm-50 nm for the first technique, in which the mixing is done in conjunction with the mixing. As for the second technique, it obtained a larger nanoparticle size, i.e. 1300 nm-1600 nm. The XRD pattern data indicated clear peaks of anatase phase without those of the rutile phase for the TiO_2 nanoparticles. The anatase phase of TiO_2 nanoparticles were produced with annealing of 500 °C, while the rutile phase appeared with annealing at 700 °C.

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