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The Effect of Polyethylene Glycol (PEG) Concentration on the Characterization of Synthesized Nanoparticles TIO_2 Using the Coopretipitation Method

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Abstract: ***This study aims to determine the effect of the concentration of polyethylene glycol (PEG-6000) on the characteristics of synthesized nanoparticles of TiO2 (Titanium Dioxide). TiO2 nanoparticles have been successfully synthesized using the coopretipitation method of the reaction of TiCl3 compounds with strong bases of NH4OH and PEG-6000 as templets, with variations in the concentration of precursors (TiCl3) and PEG namely 1: 1, 1: 2 and 1: 4. The obtained TiO2 powder was then characterized by X-Ray Diffraction (XRD) to determine the crystal size and the composition of the crystalline phase formed and SEM (Scanning Electron Microscopy) to see the morphology of the surface of TiO2 nanoparticles. The identification results using the Expert High Score Plus application show that TiO2 with 1: 1 concentration variation produces an anatase phase composition of 96.1% and rutile of 3.9% with an average crystal size of 5.82nm. In the 1: 2 concentration variation, the anatase phase composition was 99.7% and the rutile was 0.3% with an average crystal size of 5.01nm. Furthermore, in the variation concentration of 1: 4, the anatase phase composition was 97.1% while the rutile was 2.9% with an average crystal size of 6.5nm. The variation concentration of PEG-6000 affected the characteristics of TiO2 nanoparticles where the number of anatase phases increased whereas the rutile phase decreased in the line with the increasing of PEG-6000 concentration. Meanwhile, the crystal size increased along with the increasing of PEG-6000 concentration, but still PEG-6000 with the suitable concentration was able to increase the Crystal phase and reduce the grain size of TiO2 nanoparticles. This was proven by the variation concentration ratio of 1: 4.***

Keywords: Polyethylene Glycol, Nanoparticles, TiO2 (Titanium Dioxide), Coprecipitation, Grain Size, Crystal Phase

1. Introduction

The development of science and technology at this time, especially in the field of nanotechnology materials is growing rapidly. Nanoparticles has become a very interesting field since the materials which are in nano size usually have particles with chemical or physical properties that are superior to large sized material (bulk). In this case, these properties can be changed through controlling the size of the material, setting the chemical composition, modifying the surface and controlling the interaction between particles (Nurdin., Et al 2015: 1). One type of nanoparticle that has been developed is TiO2 which has many advantages. With these advantages, TiO2 has many benefits including as the solar cells (Taufik, et al, 2015: 16).

In the applications as solar cells, this material is used in new types of solar cells called Dye Sensitized Solar Cells (DSCC). In this type of solar cell, the absorption of photon energy from visible light is carried out by light-sensitive materials (dye) which functions as a sensitizer. With the sensitizer, it is possible to inject/transfer electrons to the TiO2 semiconductor material, which although the photon energy received is smaller than the TiO2 semiconductor band gap (this event is called sensitization). To support this process, the TiO2 semiconductor material must be able to absorb as many dye molecules as possible so that more electrons can be received. For this reason, TiO2 must meet several criteria, including particle size in the nanometer scale, this is necessary because with the particle size in the nanometer scale, the overall particle size becomes larger so that with greater area, it is possible to absorb more dye molecules. In addition, TiO2 particles are also expected to have porous morphology (mesoporus), so that the dye molecule can enter between the pores and can be absorbed throughout the surface of TiO2 particles, as well as the TiO2 crystallinea phase used is also a prerequisite for solar cell applications.

Some of the properties of these TiO2 particles depend on their size, for example when the size of a nanodi particle is below 10nm, it will be superparamagnetic at room temperature so that it can affect the synthesis process. Therefore, how to synthesize uniform nanoparticles is to set the size to be one of the key problems in the scope of synthesis and nanoparticles. One of the substances that can be used to form and control the size and structure of pores is Polyethylene glycol (PEG).

Polyethylene glycol (PEG) is a substance that has the characteristics of being soluble in water, methanol, benzene and dichlorometan. PEG also has a low toxic content. In addition, PEG is also a flexible polymer (Seveny, 2013: 35). In this role, PEG can function as a template, which wraps the particles so that no further aggregates are formed, because PEG attaches to the surface of the particle and covers the positive ions concerned to join and enlarge, so that in the end the particle will be obtained with a uniform spherical shape. However, so that it can work according to its function, PEG is needed with the right molecular length and quantity (Febie et al 2010: 1).

To produce homogeneous and fine grain size nanoparticles, it can be synthesized with several methods of precipitation. One method that can be used is cooprecipitation because this is a method that is quite effective and simple when compared to

the other methods. This method is a part of the wet chemical method, where each material is deposited with a reactant. The results of the deposition are then combined for the expected formation stokhiometrically. This method can also control particle size and the time of relative growth which is shorter and can be carried out in normal environmental conditions.

2. Method

TiO2 nanoparticles were synthesized by the cooprecipitation method. 10 ml of TiCl3 were stirred together with 4.7 ml of distilled water and 0.3 ml of 37% HCl using a magnetic stirrer for 2-3 minutes at 45^0 C. Then 20 ml of 37% HCl was added in a continuous stirring position until the solution was purple runny. Then the solid PEG-6000 was melted by heating at 500C for 15 minutes. The melted PEG-6000 was added to the solution, with variations in the ratio of TiCl3 volume and PEG-6000 volume, 1:1, 1:2, dan 1:4.

The mixing of TiCl3 and PEG-6000 solutions was carried out by continuing to stir using a magnetic stirrer (magnetite stirrer), for 40 minutes. Then 25% NH4OH was added as much as 50 ml in a mixture of TiCl3 while stirring until the solution turned into purple black. The solution was continously added NH_4OH until the solution is white and let stand for 24 hours until it begins to produce sediment. The resulting precipitate, separated from the solution, is then washed using distilled water repeatedly until it is clean of impurities, then filtered. To obtain the nano TiO2 particles, the resulting sediment was dried in an oven at a temperature of about 100^0 C for 2 to 3 hours and was annealed at 400^0 C for 2 hours.

3. Result and Discussion

Data was obtained from X-Ray Diffraction characterization. Furthermore, the Expert High Score Plus software was used to compare the diffraction pattern with the standard patterns contained in the Crystallography Open Database (COD). Data was then used to determine the grain size and crystal phase. The X-ray diffraction pattern for TiO2 samples synthesized by comparison of TiCl3 and PEG can be seen in Figure 3.1

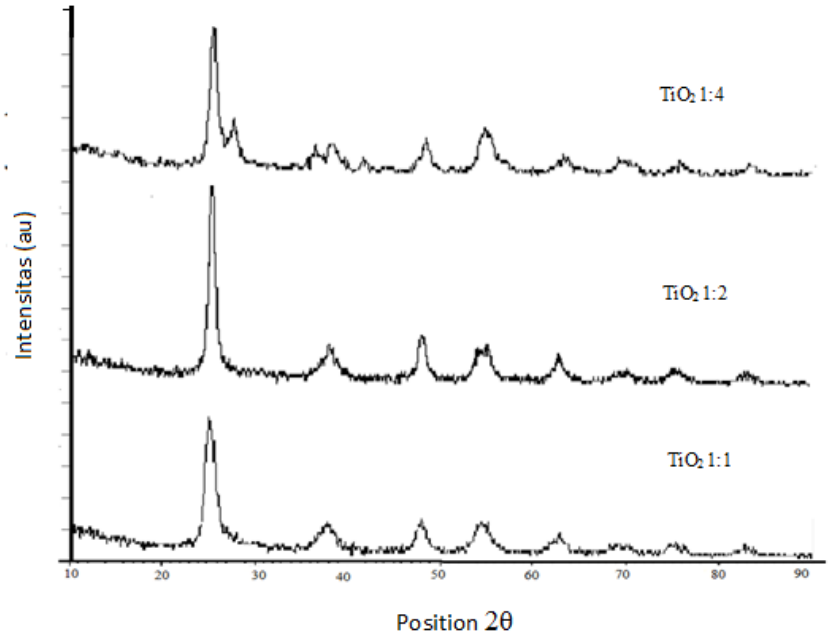

Figure 3.1: The position graph (2θ) of TiO2 intensity

Figure 3.1 shows the results of the diffractogram of TiO2 1: 1, 1: 2 and 1: 4. From the results of these drawings it can be seen the peaks of TiO2 where the peaks of TiO2 are located at 2θ = 25.3668, 38.0735, 48.072, 54.4514,62.86,69.4485,75,459 for TiO2 1: 1 then 2θ = 25.3582, 38.0036, 48.0897, 54.6712, 62.7755 69.7478.75.2951 for TiO2 1: 2 and diffractogram with 2θ = 25.4588, 38.0105.48.159.54.5481,62.9347,69.109,75.5947 for TiO2 1: 4. Of the seven main peaks of each sample is in accordance with the JCPDS anatase structure.

From Figure 3.1, it can be seeen that the highest intensity of each sample is located at an angle of 2θ about 25^0 which indicates the existence of anatase structure which suitable with the miller index of 011. From these data it can be seen that the peak formed with the addition of a 1: 2 PEG concentration appeared to be wider than the sample 1: 1 and 1: 4 which indicates that TiO_2 1:2 has the higher level of crystalitation in comparison with the other two samples. The increase in its intensity is influenced by the concentration of PEG-6000 given to the sample in which PEG-6000 is able to wrap and capture the TiO2 molecules so that a rearrangement process occurs which causes changes in the distance of Ti-O-Ti and O-Ti-O to a shorter distance from the titanium structure.

The data analysis results that are displayed on the practice diagram Figure 1 can be used to calculate the grain size of each sample by using the Debye Scherrer formula. With the value of k is a proportional constant of 0.9 and a wavelength of 0.15406 nm, the results of calculations using the Debye Scherrer equation can be seen in Table 3.1 as follows.

Table 3.1: Results for calculating the average size of TiO2 crystals

Sample	Average grain size (nm)
TiO_2 1:1	5.8
TiO_2 1:2	5.1
TiO_2 1:4	6.5

Based on table 3.1, it can be seen that TiO2 diffraction pattern with the addition of PEG-6000 in 1: 2 concentration variation got the smallest average crystal size (5.1) followed by 1: 1 (5.8), and 1: 4 (6.5). This shows that the increasing in PEG-concentration 6000 added to the sample decreases the size of the TiO2 crystal to a PEG-6000 ratio (1: 2), but an increase in crystal size occurs when the addition of PEG-6000 (1: 4) is produced. The decrease in the size of this crystal was influenced by the concentration of PEG-6000 given in samples where PEG-6000 which has a specific gravity of 1,080 g/cm and has a molecular weight of 6000 g /mol has a large number of molecular chains. This has enabled to coat the entire surface of the particles so as not to give an opportunity for the TiO2 molecules to be in order and to form a further aggregate due to the many molecules of TiO2 that are trapped in the chain. But, still PEG-6000 with the right concentration could reduce the particle size of TiO2, which is evident from the ratio (1: 4). This shows that the homogeneity of the solution affected the grain size of the TiO2 synthesis results.

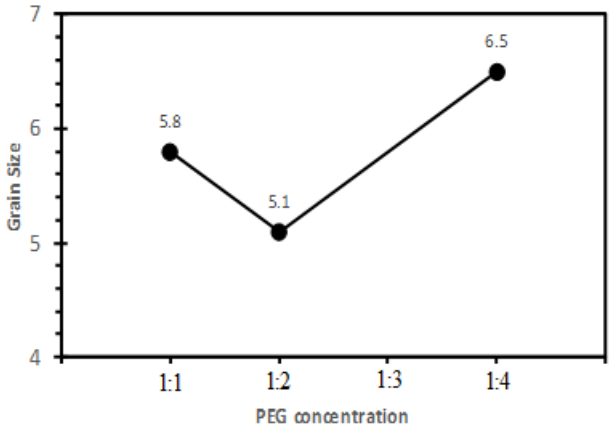

Figure 3.2: The Graph of PEG concentration towards the grain size of TiO_2 crystal

From Figure 3.1, it can be seen that E'xpert High Score Plus software could be used, which utilizes the principle of the Rietveld method, namely non-linear matching of the calculated diffraction pattern curve (model) with a measured diffraction pattern based on crystal structure. The data can be used to determine the crystal phase number of the phase composition TiO2 anatase and rutile as shown in Table 3.2.

Table 3.2: The percentage of phase content in synthesized TiO2 samples

Sample	Anatase hase (%)	Rutile Phase(%)
TiO_2 1:1	96,1	3,9
TiO_2 1:2	99,7	0,3
TiO_2 1:4	97,1	2,9

Figure 3.1 and Table 3.2 shows that these results are in accordance with the expectation that TiO2 anatase could be formed. However, at TiO2 1: 1 and 1: 2, the angular intensity of 2θ in around 25° has decreased and a small peak appeared at $2\theta = 29^0$ which was indicated as the formation of rutile structures. Changes in the structure of the titania from anatase to rutile were caused by variations in the concentration of PEG-6000. PEG-6000 will be substituted into the grid of the crystal structure formation process, resulting in a rearrangement process that causes changes in the distance of Ti-O-Ti and OTi-O to a longer distance from the structure of TiO2. Rutil has a Ti-O-Ti structure with a longer distance compared to anatase.

The effect of these parameters could modify the TiO2 structure. This was evident from Table 3.2 above which indicates the TiO2 crystal phase obtained for all samples with variations in the overall PEG-6000 concentration in the anatase phase, where the largest anatase phase is at 1: 2 compared to 99.7% in follow 1: 4 97.1% and 1: 1 96.1% while the highest rutile is at 3.9% for 1: 1 followed by 2.9% for 1: 4 and the smallest is at 1: 2 ie 0.3%. This shows that PEG-6000 was able to wrap TiO2 particles so that no further aggregates are formed so as to produce a uniform TiO2 with a regular arrangement, but still PEG-6000 with the right concentration ratio is able to influence the TiO2 crystal phase as seen from the TiO2 sample 1: 4 which has decreased anatomic phase and an increase in phaserutyl.

Based on X-ray diffraction characterization data results and analyzes conducted show that there is no PEG-6000 phase in all samples, which indicates that PEG-6000 here only functions as a template or wrapper so that it is able to control particle size but does not react. The relationship of PEG concentration to the percentage of phases formed can be illustrated through the graph in Figure 3.3 below.

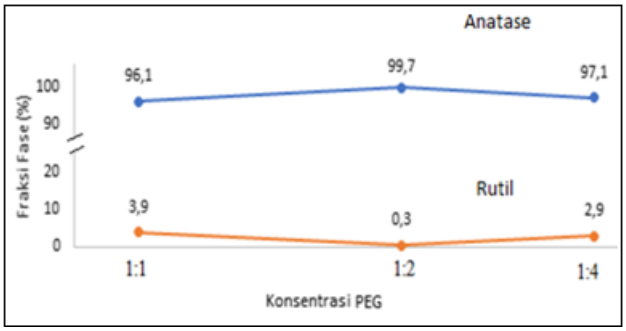

Figure 3.3: Graph of the concentration of PEG towards TiO2 phase

The surface morphology of TiO2 can be known using Scanning Electron Microscopy (SEM) with an enlargement of 50000 times, can be seen in Figure 3.4

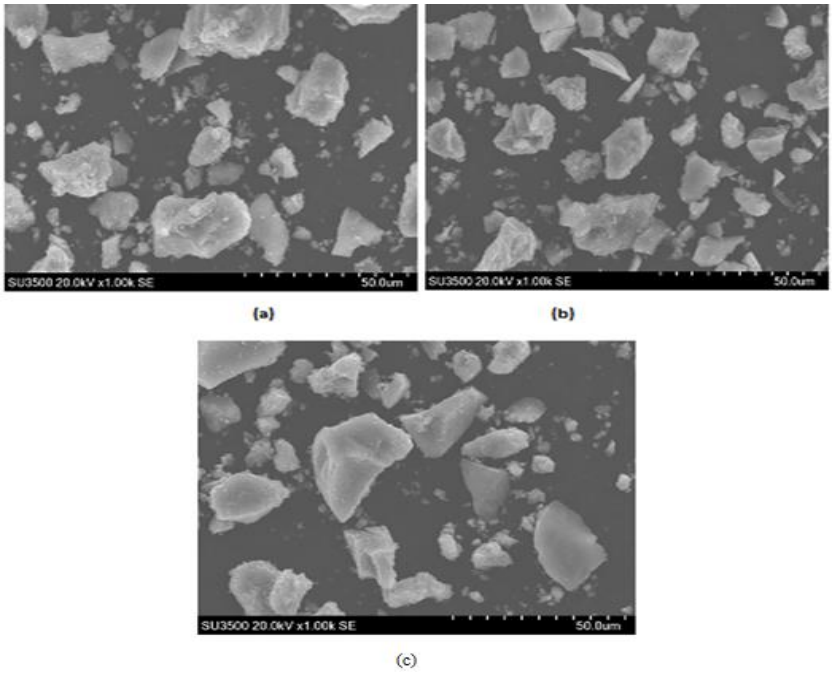

Figure 3.4: The surface morphology of TiO2 synthesized with a concentration ratio of (a) 1: 1, (b) 1: 2 and (c) 1: 4

In Figure 3.4 (a), the particle size distribution of the sample with the addition of PEG 1: 1 looks quite uniform. In this sample, there was a uniform formation of particles but there were still particles that were piled up so that there were many irregular lumps. Whereas in Figure 3.4 (b) TiO2 which was synthesized by comparison of PEG concentrations of 1: 2, uniform sized nanoparticles have been formed. The particle size distribution of the sample with the addition of PEG 1: 2 shows that the particle size is quite small. The addition of PEG 1: 2 also shows a lot of cube-shaped particles, this shows that the TiO2 sample with the addition of PEG 1: 2 can be said to be the optimum point for variations in the concentration of PEG-6000, because it looks uniformity of the particles formed.

The particle morphology for addition of PEG 1: 4 can be seen in Figure 3.4 (c). In the addition of PEG 1: 4, particle formation has occurred but due to variations in PEG concentration variations that are not right to make the particles become irregular, so that the particles were not formed evenly again and looked a lot of lumps that are less regular. This shows that the more particle surface that is coated with PEG, the more it inhibits the growth of particles, so that the particle size decreases because the growth of particles is blocked by the number of PEG chains. Thus it can be stated that the decrease in the size of the crystal is due to the increasing number of TiO2 particles trapped in the PEG chain so that the growth of the crystal is blocked which causes the size of the TiO2 crystal to be smaller. However, due to improper concentration causes low homogeneity occurs in the addition of PEG-6000 (1: 4).

4. Conclusion

Based on the results of research on the effect of the concentration of Polyethylene Glycol (PEG) on the characterization of nano TiO ¬2 particles synthesized using the coopreticipation method, the following conclusions can be drawn. Variations in the concentration of Polyethylene Glycol (PEG) affect the size of the TiO2 nanoparticles synthesized. The variation in the concentration of Polyethylene Glycol (PEG) caused changes in the average crystal size of TiO2 nanoparticles, where in the 1: 1 variation, the average crystal size of TiO2 nanoparticles was 5.8 nm. Meanwhile, in 1: 2 variation, the average crystal size of TiO2 nanoparticles was 5.1nm and in the 1: 4 variation the average crystal size of TiO2 nanoparticles was 6.5 nm. Variation in concentration of Polyethylene Glycol influences the phase composition of TiO2 nanoparticle crystals synthesized. The variation of Polyethylene Glycol composition causes changes in anatase and rutile phases. At a 1: 1 concentration of anatase phase composition of 96.1% and rutile of 3.9%, at a concentration of 1: 2 anatase phase composition of 99.7% and rutile of 0.3% while at a concentration of 1: 4 anatase phase composition by 97.1% and rutile by 2.9%.

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