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# Phase study of titanium dioxide nanoparticle prepared via sol-gel process

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# Phase study of titanium dioxide nanoparticle prepared via sol-gel process

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**Abstract.** In this study, titanium dioxide nanoparticles have been prepared via sol-gel process using titanium tetraisopropoxide as a precursor with hydrochloric acid as a catalyst, and ethanol with deionized water as solvents. The value of pH used is set to 3, 7 and 8. The sols obtained were dried at 100 $^{o}$C for 1 hr and calcined at 350, 550, and 750 $^{o}$C for 3 hrs to observe the phase transformation of titanium dioxide nanoparticle. The samples were characterized by x-ray diffraction and field emission scanning electron microscope. The morphology analysis is obtained from field emission scanning electron microscope. The phase transformation was investigated by x-ray diffraction. It was found that the pH of the solution affect the agglomeration of titanium dioxide particle. The x-ray diffraction pattern of titanium dioxide shows the anatase phase most abundant at temperature of 350 $^{o}$C. At temperature of 550 $^{o}$C the anatase and rutile phase were present. At temperature of 750 $^{o}$C the rutile phase was the most abundant for pH 3, 7 and 8. It was confirmed that at higher temperature the rutile phase which is the stable phase are mostly present.

Keywords: anatase, nanoparticle, rutile, sol-gel, titanium dioxide.

## 1. Introduction

Titanium dioxide ($TiO_2$) is one of the most current nanomaterials that have been researched a great deal of times due to its unique properties. Titanium dioxide is also referred to as titanium (IV) oxide or titania. Titanium dioxide is categorized as nanoparticle because it is a particle that has one or more dimensions of the order of 100 nm or less [1]. Titanium dioxide which is also a known semiconductor shows unique characteristics, e.g, easy processing control, inexpensive, and non-hazardous. These benefits make titanium dioxide a material of choice in solar cells, chemical sensors for hydrogen gas evolution, as pigments, self-cleaning surfaces and environmental purification applications [2]. The photocatalytic activity of $TiO_2$ is one of its most unique features, and it is mostly determined by properties such as the crystalline phase, crystallite size, and specific surface area [3].

Titanium dioxide is observed to be mainly in the crystalline or amorphous forms in which the crystalline polymorphos, specifically, is anatase, rutile and brookite. The active crystallite phases of titanium dioxide are rutile and anatase [4, 5]. The anatase and rutile phase are tetragonal structure, but brookite phase is an orthorhombic structure [6]. The anatase phase is known to exhibit a higher photocatalytic behavior, while the rutile phase is the most stable phase [7]. The crystalline structure reveals physical properties such band gap which governs their applications and uses [8, 9]. The enlargement of $TiO_2$ surface area employs the use of different methods which includes microemulsion, hydrothermal crystallization and sol–gel by reducing the particle size down to nanoscale [10]. Sol-gel is one of the most successful methods for preparing nano-sized metallic oxide materials and has been mostly applied for the preparation of titanium dioxide nanoparticles. Titanium dioxide nanoparticles prepared via sol-gel method are highly crystalline and have smaller crystallite size compare to the other methods [11]. In this present study, the nano-sized $TiO_2$ was prepared from organometallic precursor-titanium tetraisopropoxide (TTIP). Titanium alkoxide is not hazardous or toxic to the surroundings, and is stable and provides an easy approach in the production of titanium dioxide nanoparticles [12]. In this research, the prepared sample will be characterized by using techniques like X-ray diffraction (XRD) and Field emission scanning electron microscope (FE-SEM). Processing conditions, such as chemical concentration, the pH, calcinations time and temperature have a great influence on the particle size and phase purity of the final powder.

## 2. Materials and methods

Titanium tetraisopropoxide (TTIP, 98+ % solution Acros Organics), Hydrochloric acid (HCl,1.0 M solution, R&M Chemicals), Ethanol ($CH_3CH_2OH$, 95 %, solution, HmbG Chemicals), Deionized water ($H_2O$).

### 2.1 Preparation of Titanium Dioxide Nanoparticle by Sol-Gel Process

Titanium isopropoxide (TTIP) was dissolved in absolute ethanol and stirred for 30 min using magnetic stirrer. In this step, to investigate the effect of pH upon the samples properties, a mixture of deionized water and hydrochloric acid (HCl) was added to the solution dropwise to adjust the pH range. The concentration of acid was 1 M and the Table 1 shows the amount of other materials used. The pH was measured using litmus paper to prepare the different sols at pH 3, 7 and 8. A homogeneous solution was obtained after stirring for 2 hrs at room temperature with a magnetic stirrer. A sol was formed after stirring, and then the sols were aged for 24 hrs to form the gel. In order to obtain the nanoparticle, the gel was dried at 100 $^oC$ for 1hr to evaporate water and organic material. The dried gel was calcined in the LT furnace at 350, 550 and 750 $^oC$ at heating rate of 10 $^oC/min$ and for 3 hrs soaking time to obtain the desired $TiO_2$ nanoparticles.

**Table 1:** The amount of materials.

| Amount of TTIP(ml) | Amount of ethanol (ml) | Amount of $H_2O$ (ml) | Amount of HCl (ml) |
|---|---|---|---|
| 7 | 60 | 2 | 1 |

2.2 Characterization Method
The morphology of the samples was observed by using Field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450). The phase analysis was obtained by utilizing X-ray diffraction (XRD, BRUKER D5 Phaser).

## 3. Result and Discussion
Figure 1 shows the morphology of titanium dioxide at pH 3. The diameter of the particles that was observed was 0.10, 0.22, 0.24, and 0.27 µm. The titanium dioxide particles exhibited irregular morphology due to the agglomeration of the primary particle with an average diameter of 0.22 µm. These particles were classified as fine particles that combined together with a coarse particle in the range between 100 and 2500 nm [13]. The diameter of the particle that was observed from FE-SEM morphology analysis was large because the fine particle easily bond together and formed the coarse particle. According to titanium dioxide manufacturers association (2012), the primary particles are strongly bound together by chemical bonds to form aggregates. These aggregates tend to agglomerate via Van-der Waals attractive forces to form particles in the micron (µm) size range. From the observation at 1KX magnification, the crack was formed after calcination [14]. Due to this problem, the cracks observed after calcination leads to an increase of the crack opening displacement [15].

Figure 2 shows the morphology of titanium dioxide at pH 7. The titanium dioxide powder shows agglomeration with fine powder and irregular shape. The diameter of the particle that was observed by FE-SEM morphology analysis was 0.10, 0.27, 0.31, 0.36, 0.40 and 0.49 µm. The titanium dioxide particles exhibited irregularly morphology due to the agglomeration of an average diameter 0.32 µm. These particles were classified as fine particle because it is between the fine particle ranges [13]. The large crack occurs on the surface of titanium dioxide particle at pH 7 after calcination at 550 $^{o}$C . This crack was clearly seen at 10 KX magnifications.

Figure 3 shows the morphology of titanium dioxide at pH 8. The particle showed the soft agglomerated fine powder with irregular shapes and fused together. The diameter of these particles observed was 0.09, 0.10, 0.14, 0.18, 0.22 and 0.40 µm. These particle sizes were smaller than the particle at pH 3 and 7. These particles were classified as fine particle because the average diameter of titanium dioxide was 0.18 µm is within the range of fine particle size. The fine crack was clearly seen at 1KX magnification. This crack occurs after the calcination process.

Based on the analysis from the Figure 1, 2 and 3, all the samples of titanium dioxide powder from FE-SEM analysis reveals that the crystallites are in micron meter size. These particle sizes are larger than those previously reported. All sample of titanium dioxide particle was classified as a fine particle. The sample of titanium dioxide for pH 3 at temperature 550 $^{o}$C shows higher agglomeration than the sample of titanium dioxide for pH 7 and 8. The particles agglomerates resulting in an increase of particle size as the calcination temperature increases. Consequently, the growth of titanium dioxide nanoparticles is accelerated at higher calcination temperature. The effect of pH also contributes to the changes in particle size. It was observed that the morphology of titanium dioxide greatly depends on pH values. The higher the pH value, the size of the particles becomes smaller and agglomerate.

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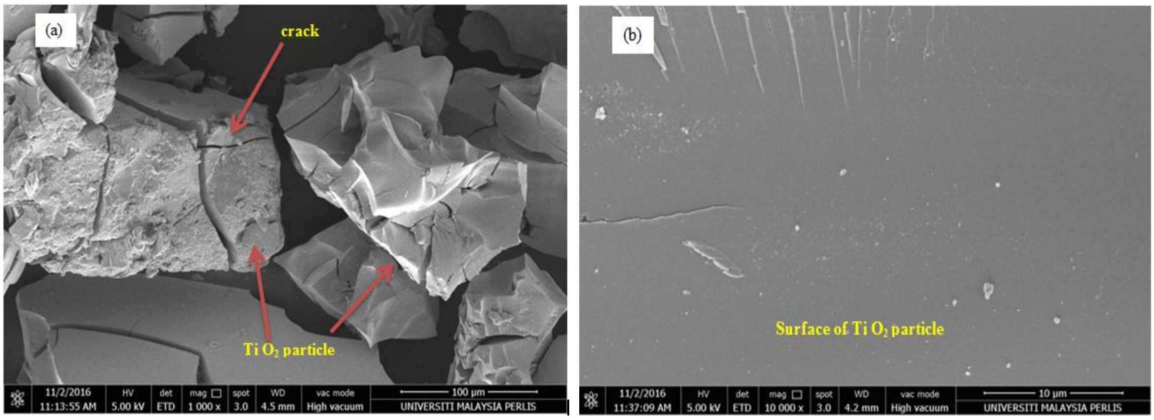


**Figure 1:** FE-SEM morphology of titanium dioxide powder at 550 $^{o}$C for pH 3
(a) 1KX magnification, (b) 10 KX magnification

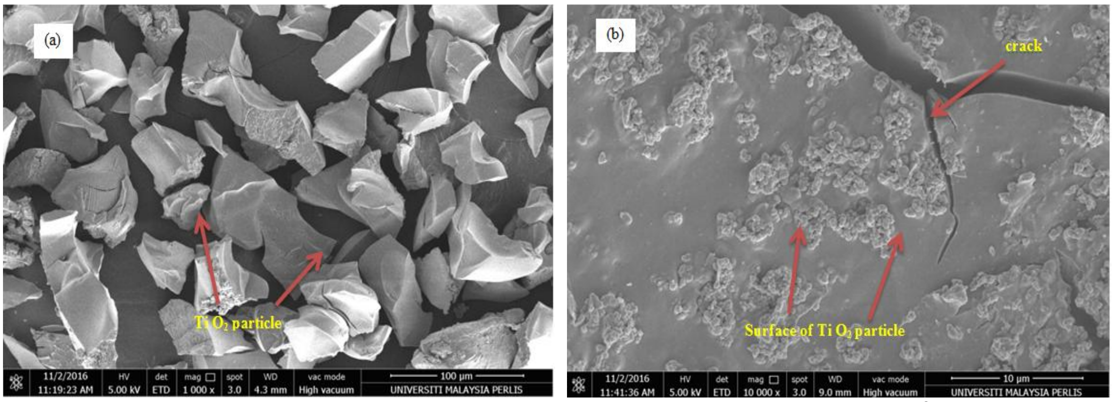


**Figure 2:** FE-SEM morphology of titanium dioxide powder at 550 $^{o}$C for pH 7
(a) 1KX magnification, (b) 10 KX magnification

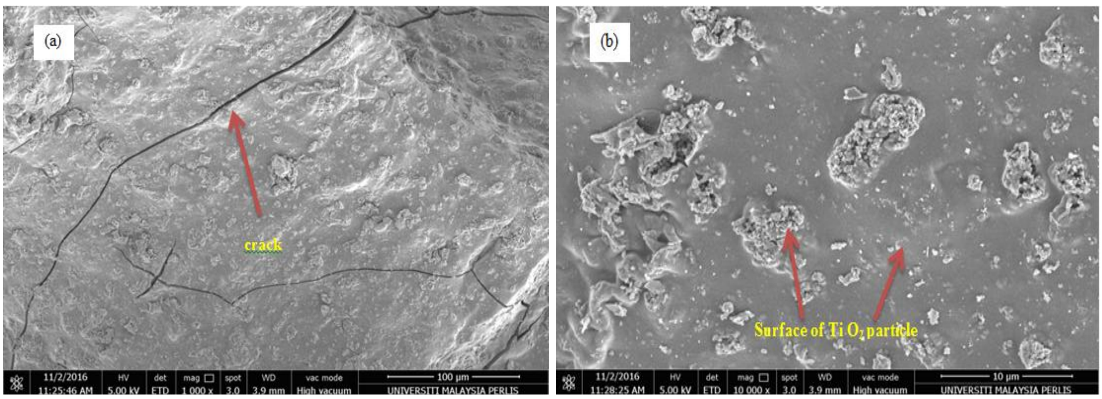


**Figure 3 :** FE-SEM morphology of titanium dioxide powder at 550 $^{o}$C for pH 8
(a) 1KX magnification, (b) 10 KX magnification

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3.1 Phase Analysis

The phase analysis of titanium dioxide nanoparticle was obtained by using X-ray diffraction (XRD). The XRD patterns were recorded in the range $2\theta = 10 - 90^o$ using step size 0.002 $^o$ and scan rate at 5 $^o$/min. Based on the Figure 4, the X-ray diffraction patterns of titanium dioxide particles dried for sample pH 3 shows an amorphous phase but there are some peaks present due to some unintentional contaminations resulting from the preparation of the sols. While, for the sample pH 7 and 8 were largely amorphous as no distinct peak was observed from the XRD pattern.

Figure 5 shows the XRD pattern of titanium dioxide particles calcined at 350 $^o$C for pH 3, 7 and 8. At the pH value of 3, 7 and 8, anatase peaks of $TiO_2$ powder after calcination was obviously obtained. The amorphous phase of titanium dioxide particle dried for pH 3 crystallizes to the anatase phase after calcination at temperature of 350 $^o$C. X-ray diffraction patterns of titanium dioxide particles calcined for pH 3 shows the sharp peak which is anatase peak located at $2\theta$ = 25. 50 $^o$, 38.22 $^o$, 48.30 $^o$, 54.54 $^o$,55.02 $^o$, 63.18 $^o$, 70.14 $^o$, 75.66 $^o$ and 83.10 $^o$ are respond to the (101), (004), (200), (105), (211), (204), (220), (215) and (312) lattice plane of $TiO_2$ at 350 $^o$C. The titanium (Ti) element presence at $2\theta$ = 23. 05$^o$ corresponds to the (101) for all pH. The amorphous phase of titanium dioxide particle dried for pH 7 and 8 crystallizes to the anatase phase after calcination at 350 $^o$C The X-ray diffraction patterns of titanium dioxide particles calcined for pH 8 shows the additional anatase peak located $2\theta$ = 58.32 $^o$ respond to the (222) lattice plane of $TiO_2$ at 350 $^o$C.

Figure 6 shows the XRD pattern of titanium dioxide particles calcined at 550 $^o$C for pH 3, 7 and 8. Definitely phase transformation occurred from anatase phase to thermodynamically more stable rutile phase with increasing calcination temperature [16]. As the temperature is increased to 550 $^o$C, the anatase and rutile peak of $TiO_2$ powder was obtained with decreased intensity. The rutile phase has its peak at $2\theta$ = 27.39 $^o$, 36.15 $^o$ and 41.53 $^o$ which corresponds to (110), (101) and (111) lattice plane of $TiO_2$. The anatase phase retains its peak location with further decrease in intensity.

Figure 7 shows the XRD pattern of titanium dioxide particles calcined at 750 $^o$C for pH 3, 7 and 8. At calcination temperature of 750 $^o$C the rutile phase was noticed as the dominant phase. X-ray diffraction patterns of titanium dioxide particles calcined for pH 3, 7 and 8 shows the rutile peak located at the same location which are at $2\theta$ = 27.70 $^o$, 36.30 $^o$, 39.37 $^o$, 41.53 $^o$, 44.29 $^o$, 54.59 $^o$, 57.04 $^o$, 62.88 $^o$, 62.27 $^o$, 68.18 $^o$, 70.10 $^o$, 76.71 $^o$, 82.70 $^o$, and 84.55 $^o$ are responds to the (110), (101), (004), (111), (210), (105), (220), (204), (204), (400), (220), (215), (312) and (312) lattice plane of $TiO_2$ at 750 $^o$C.

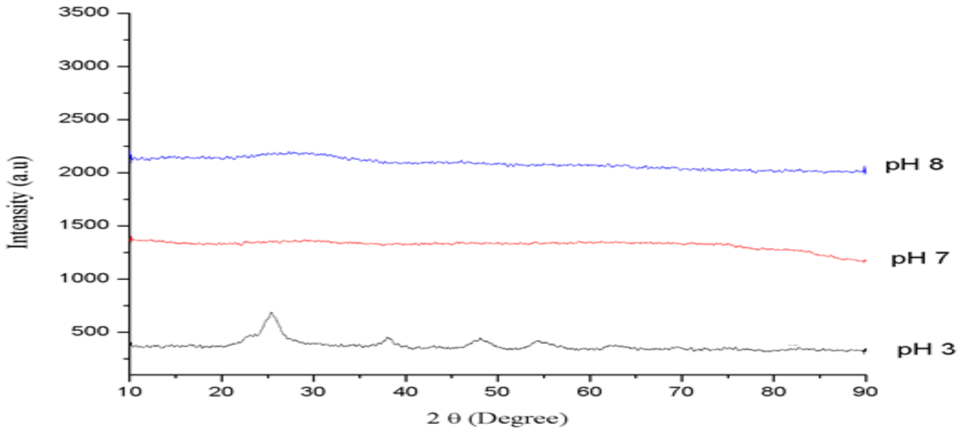


**Figure 4:** XRD pattern of titanium dioxide particles dried at 100 $^{o}$C for pH 3, 7 and 8.

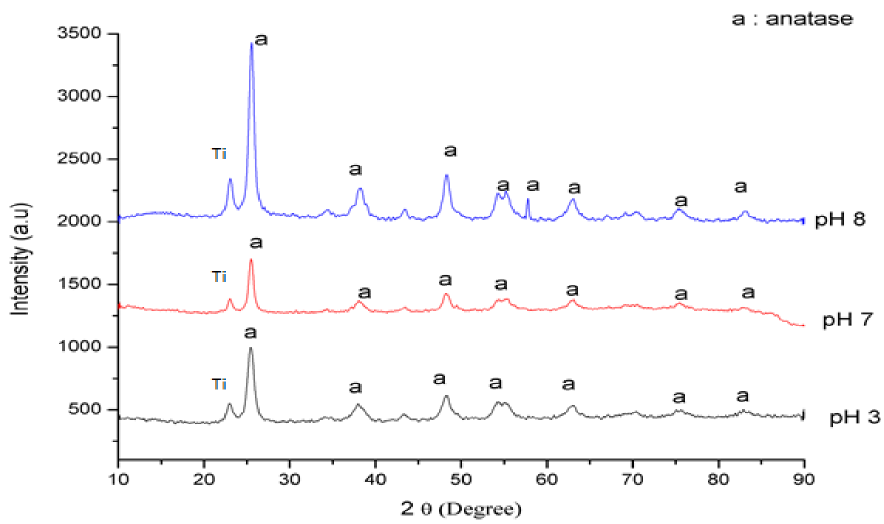


**Figure 5 :** XRD pattern of titanium dioxide particles calcined at 350 $^{o}$C for pH 3, 7 and 8.

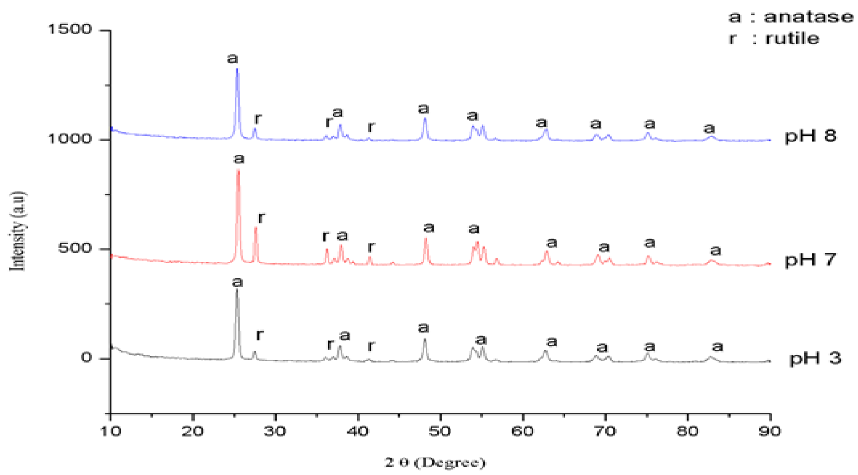


**Figure 6:** XRD pattern of titanium dioxide particles calcined at 550 $^{o}$C for pH 3, 7 and 8.

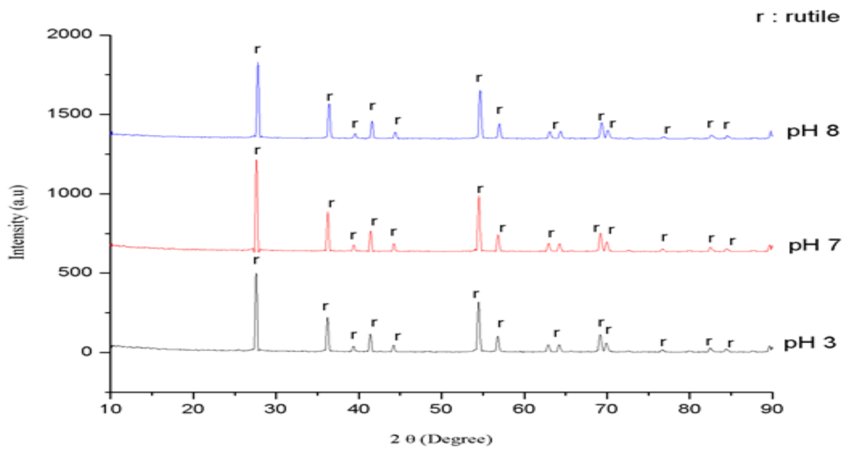


**Figure 7 :** XRD pattern of titanium dioxide particles calcined at 750 $^{o}$C for pH 3, 7 and 8.

## 4. Conclusions

Titanium dioxide nanoparticles were successfully synthesized via sol-gel process using titanium tetraisopropoxide (TTIP) as the precursor, hydrochloric acid (HCL) as the catalysts, and ethanol with deionized water as a solvent. The synthesized titanium dioxide powders were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The morphology was studied using FE-SEM. The phase transformation was investigated by X-ray Diffraction (XRD).The morphology analysis from FE-SEM confirms an agglomeration of particles from the sol-gel method by different pH value. At pH 3, 7 and 8 the phase transformation from XRD pattern shows the phase of titanium dioxide transform from anatase to rutile after calcination. The titanium dioxide phase for pH 3 before calcination shows had a peak but it was amorphous. Whereas, the titanium dioxide phase for pH 7 and 8 before calcination shows the amorphous phase. It was observed that pH and temperature plays an important role toward the phase transformation of titanium dioxide.

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