The Effect Of Heat Treatment On Phase Transformation And Morphology Of Nano-Crystalline Titanium Dioxide (Tio_2)

Yadanar Win Myint, Tun Tun Moe, Wint Yi Linn, Anjae Chang, Phyu Phyu Win

Abstract: Effect of heat treatment on different properties of Titanium dioxide(TiO_2) nanocrystal is being reported. Nanocrystalline TiO_2 was synthesized via chemical precipitation methods using $TiCl_3$ as starting material with two types of precipitants: NaOH and NH_4OH. The effect of calcination temperatures (300,500 and 900˚C) on the crystalline structure, phase formation and morphology of synthesized TiO_2 were investigated by Xray diffraction (XRD) and Scanning electron microscope (SEM). For precipitation method using $TiCl_3$ + NaOH, the structure and phase determination using XRD analysis were confirmed the small crystallite size in the range of 11nm to 31nm with rutile phase. In the case of $TiCl_3$ + NH_4OH, phase transformation from anatase to rutile was clearly observed at annealing temperature of 900˚C. The SEM range revealed that almost of the nanocrystals are in spherical shape and effect of heat treatment on particle size was observed. According to the results, pH does not influence the TiO_2 morphology but the agglomeration becomes higher when the temperature calcination is increased.

Key Words: Nanocrystalline TiO_2, Precipitation method, Heat treatment, Phase transformation

1. Introduction

Titanium dioxide (also known as titanium (IV) oxide or titania) is the naturally occurring oxide of titanium with chemical formula TiO_2. It is most widely used white pigment because of its brightness and a high refractive index[1]. TiO_2 nanoparticles can be used for a variety of applications including self-cleaning, water treatment, antibacterial, and air purification due to their effective photocatalytic activity [2]. In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light. Since then, enormous efforts have been devoted to the research of TiO_2 material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo/electrochromics and sensors [3,4]. It is also the most preferred semiconductor photocatalytic material due to its favorable properties like non toxicity, chemical inertness and stability over a wide pH range under irradiation condition and its relatively favourable disposition of band edges [5]. TiO_2 is widely used because of its strong oxidizing power, non-toxicity and long-term stability [6]. The efficacy of materials and devices on the basis of titania is highly dependent on both their dimension and crystallinity [7]. TiO_2 exists in three different crystalline phases which are anatase, rutile, and brookite. Anatase and rutile have a crystalline structure that corresponds to the tetragonal system while brookite has an orthorhombic crystalline structure.

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As a bulk material, rutile is the stable phase. However, anatase is the generally favour for solution-phase preparation. Anatase and brookite are a metastable phase and readily transform to rutile when heated. After synthesis at any relatively low temperature below 600°C, anatase phase of TiO_2 is normally obtained and then transform to rutile phase above 800°C. In spite of this general effect, the starting material, its composition, deposition method and annealing temperature also play an important role in the formation of the resulting TiO_2 crystal phases [8]. Nanostructured titanium dioxide can be obtained by chemical methods: sol-gel, chemical bath deposition, chemical vapour deposition and physical methods such as physical vapour deposition. TiO_2 powder was obtained by chemical methods using as precursor $TiCl_3$ [9]. Ookubo et al reported the formation of hydrated titanium oxide from the precipitation of $TiCl_3$ and urea; they obtained double oxides, Ti_6O_{11} and Ti_7O_{13}, or a mixture of rutile and brookite. Ragai et al have shown the formation of a TiO_2 gel by reaction of $TiCl_3$ with ammonia which leads, depending on the pH, to the formation of rutile or anatase after heating at 500˚C. Pedraza et al. have shown that pure nanorods of rutile could be obtained with a length around 100 nm by $TiCl_3$ oxidation by air in aqueous medium followed by calcination[10,11,12,13].Calcination temperature is especially important for removing organic molecules from the final products and completing the crystallization. Moreover, very high calcination temperature results in aggregation, phase transformation and the properties of Ti The aim of present study is to synthesize the TiO_2 nanocrystals through precipitation process of titanium tetrachloride ($TiCl_3$) with sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH) under different annealing temperatures. The synthesized TiO_2 nanoparticles properties were studied through XRD, FESEM, and UV-Visible spectroscopy characterization techniques.

2. Experimental

2.1 Synthesis

Nanocrystalline TiO_2 was prepared using the precursor titanium tetrachloride ($TiCl_3$) solution. Sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH) were used as precipitants for TiO_2 synthesis. In precipitation method using NaOH, a $TiCl_3$ solution in 10-15% HCl was introduced to deionized water under vigorous stirring at 700 rpm for 1.5 to 2hrs, producing a final solution strength of 0.3M. A blue–violet solution was obtained at room temperature [15]. The pH was adjusted between 0.7 and 3.4 with 5M sodium hydroxide (NaOH) solution. The solutions are divided into two portions. The first solution (pH 0.7) was then dried at 60˚C in an oven for 24 h. In the second solution, the solid obtained are then centrifuged, washed with HCl solution (pH = 1) and deionized water in order to remove salts and dried at 60˚C for overnight. Finally, the white powder was calcined at different temperatures 300, 500 and 900˚C for 2 hours in high temperature programmable furnace. In the precipitation using NH_4OH, 40ml $TiCl_3$ solution was hydrolyzed with 40 ml deionized H_2O. A solution of 0.2M NH_4OH was added drop wise under continuous stirring in order to obtain alkaline pH. Finally 10 ml hydrogen peroxide 3% was added for the increasing of the oxidation rate. While adding ammonium hydroxide, the formation of a dark blue precipitate was observed. The solution obtained was treated with concentrated 30% H_2O_2 for rapid oxidation. The precipitate was left for a few days for aging in order to form a gel. Finally, the gel was vigorously washed with distilled water several times for removing the impurities (ammonia and chlorine ions) [16].The gel was dried at 60˚C for 24h, and calcined at 300, 500 and 900˚C for 2 hours.

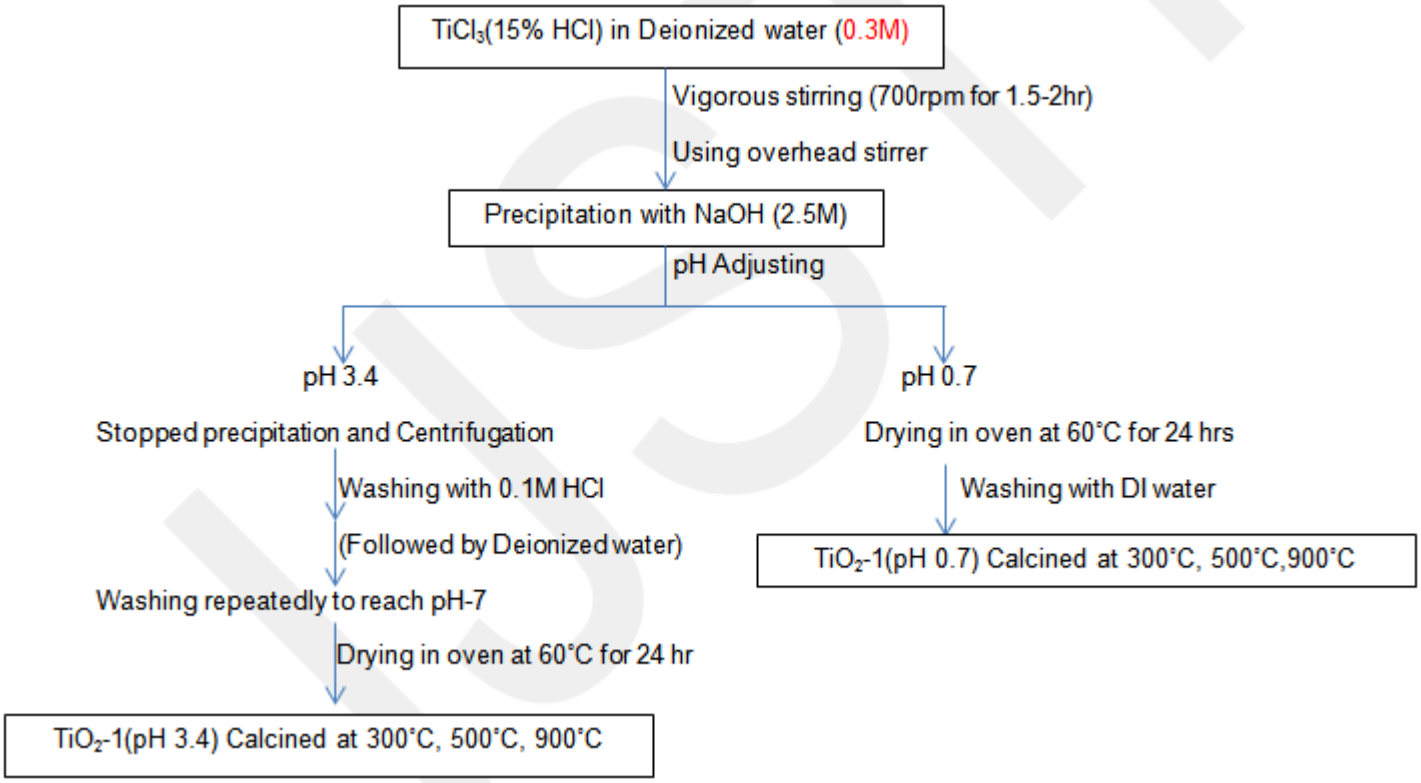


Fig 1(a) *TiO_2 synthesis with $TiCl_3$ + NaOH method*

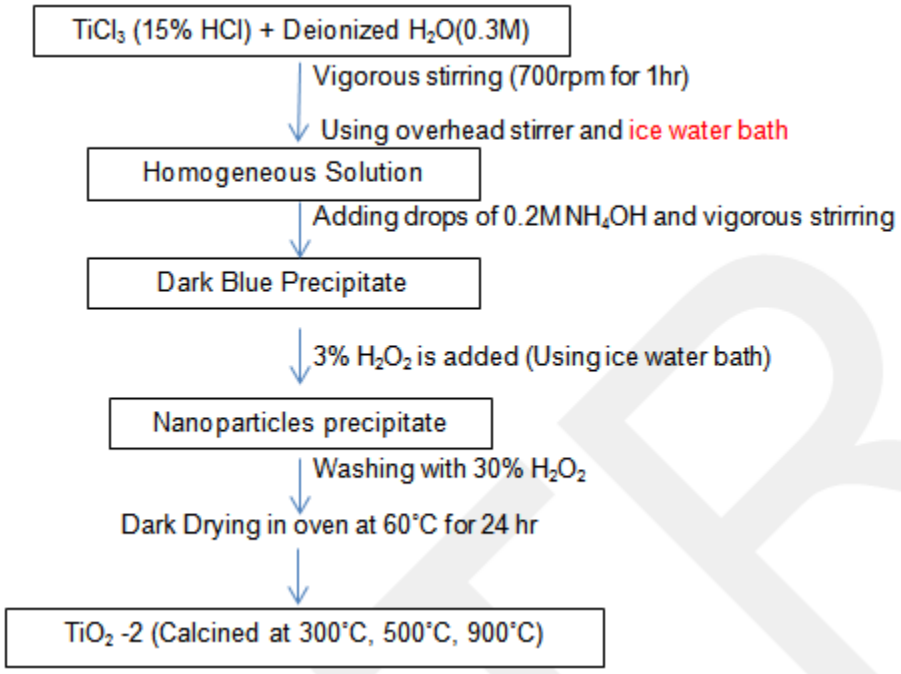


Fig 1(b) *TiO_2 synthesis with $TiCl_3$ + NH_4OH method*
Figure. *Process for synthesis of TiO2 nanoparticles by using two precipitants*

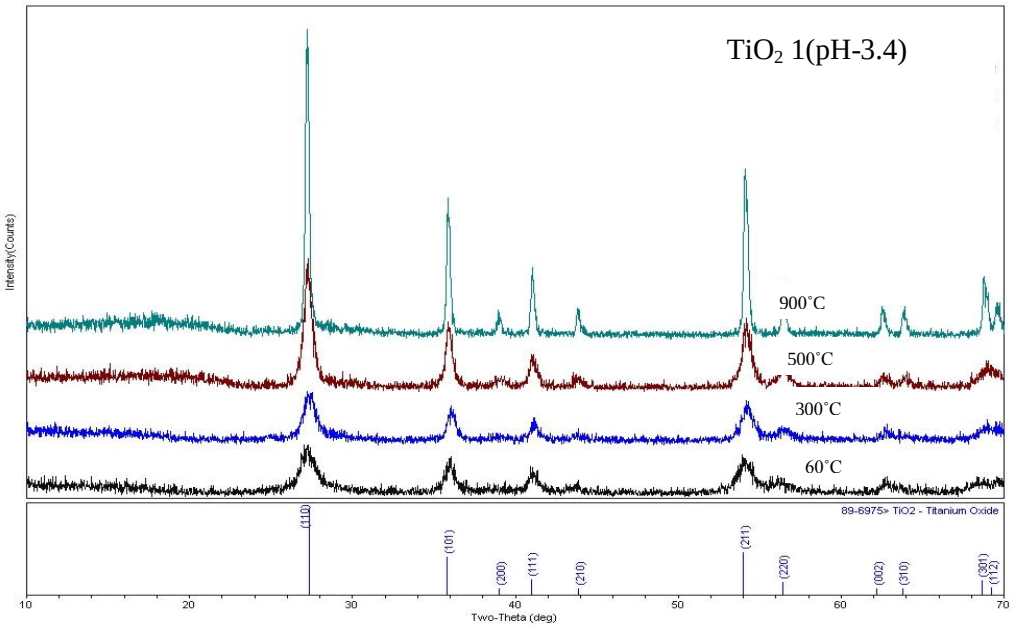
Several techniques are employed for characterization of TiO_2 nanocrystals, X-ray Diffraction (XRD) was used to identify the crystal phase and to estimate the average crystallite size as well. The particle size and morphology of the powder was observed by Field emmision Scanning electron microscope (FeSEM).

3. Results and Discussion

The X-ray diffraction measurement has been done to investigate the nanostructure and crystallinity of synthesized TiO_2 nanocrystals. The XRD patterns of the nanoparticles obtained by precipitation method of $TiCl_3$ with NaOH and $TiCl_3$ with NH_4OH are shown in Fig. 2(a), (b) and (c) respectively. The higher the annealing temperature, the stronger the crystallinity. The primary formed structure observed at low temperature are amorphous structures in both methods, especially in precipitaton method of $TiCl_3$ + NH_4OH, amorphous phase with broadening peak was also found at calcination temperature of 300˚C.The existence of this peak broadening may possibly be due to the small crystal size resulted by lower temperature and short duration of calcination.This diffraction peak broadening can be minimized by increased their calcined temperature. From XRD spectrum of TiO_2 sample calcined at 300˚C from $TiCl_3$ + NaOH method , the rutile phase only was observed and that peaks are quite wide, which indicates incomplete crystallization because it has amorphous component. When the calcined temperature increased to 500˚C, the crystallinity of TiO_2 was improved without any change in the rutile phase Fig 2(a) and (b). Rutile can be formed at lower temperatures, with an increasing tendency to form anatase at progressively increased temperature in chemical precipitation method. The temperature and molar ratio of the reactants of precipitation reaction have effect on the phase and crystal size of the product [17]. In the case of precipitation method using ammonium hydroxide, the rutile peaks become significant when temperature increased to 900˚C and the amount of rutile was calculated about 100%[Fig. 2(c)].The intensities of the strongest peaks of anatase (101)(2θ= 25.4˚) and rutile(110)(2θ= 27.4˚) were used to make a relative comparison of phase content between the synthesized TiO_2 powders. XRD patterns were acquired to determine crystal properties and grain size. Associated with peak intensities and widths, particle size is generally assumed to induce peak broadening below ca. 200 nm. The larger the full width at half maximum (FWHM) of the peak, the smaller the grain size. Crystallite size was obtained by Debye-Scherrer's formula given by equation (1)

$$D=K\lambda/(\beta\cos\theta) \quad (1)$$

where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the full-width at half-maximum height; and θ is the diffraction angle [18]. When the temperature rose to 300 and then 500 ˚C, the size of formed crystallites has increased which could be attributed to the thermally promoted crystallite growth. The size of crystallites increases from 11.6 to 31.5 nm when calcination temperature has been elevated to 900 ˚C (see Table 1). At 900 ˚C, apart from anatase, sharp rutile peaks was also observed in the XRD result of $TiCl_3$ +NH_4OH method. The formed rutile showed quite different behavior having larger size than the remained anatase particles. This, in fact, reveals that nucleation and growth of rutile phase would have been initiated at temperature somewhere from 500 to 900 ˚C.


TiO2 1(pH-3.4)
Intensity(Counts)
900˚C
500˚C
300˚C
60˚C
89-6975> TiO2 - Titanium Oxide
(110)
(101)
(200)
(111)
(210)
(211)
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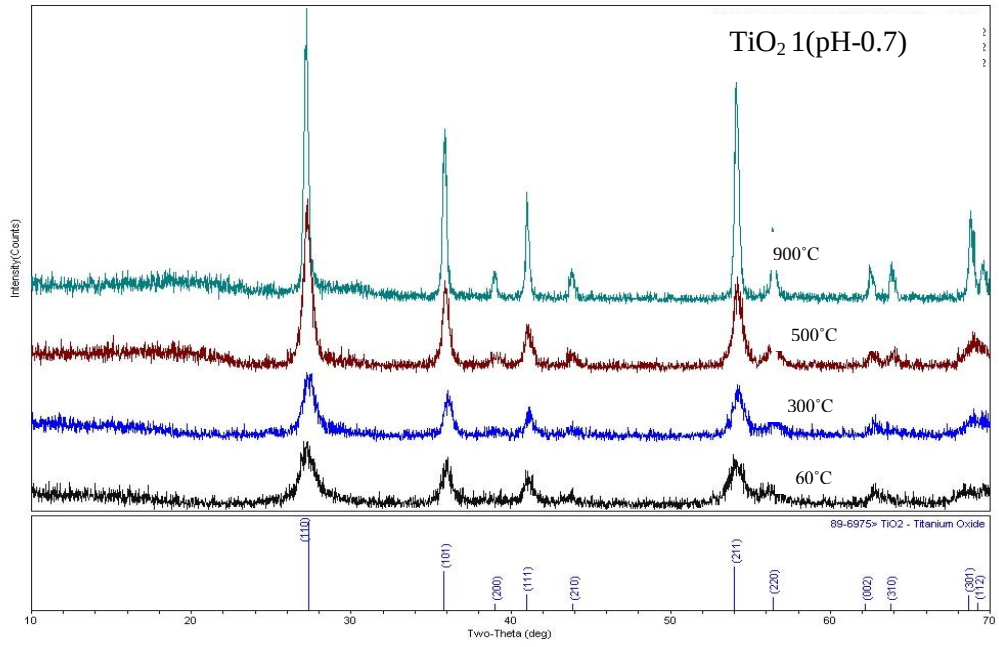
Two-Theta (deg)

(a).


TiO2 1(pH-0.7)
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900˚C
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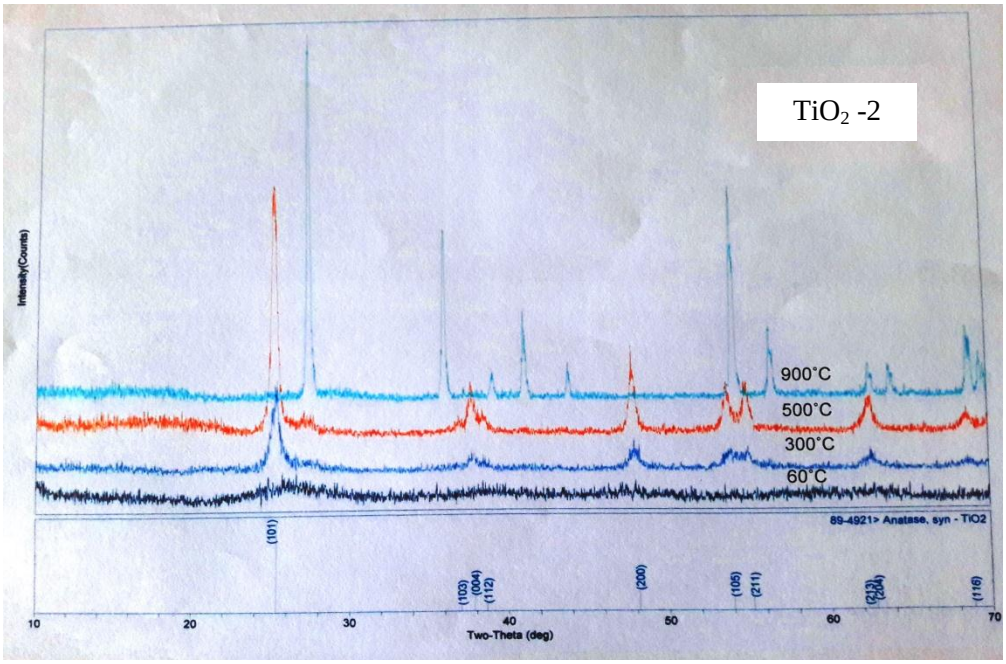

(c)

Figure 2. *XRD pattern of the TiO_2 nanocrystal obtained from (a) $TiCl_3$ + NaOH (pH0.7)(b) $TiCl_3$ + NaOH (pH 3.4) and (c)$TiCl_3$ + NH_4OH precipitation methods at various calcining temperatures.*

Fig. 3 shows surface morphology of the TiO_2 nanoparticles at different calcination temperatures. Fig.3(a) and (b) represent the images of TiO_2 nanoparticles prepared by $TiCl_3$ + NaOH (pH 7 and pH 3.4) method at different calcination temperatures 60,300, 500 and 900˚C, which illustrate the particle sizes grow bigger as the calcined temperature was increased. According to the results, pH does not influence the TiO_2 morphology but the agglomeration becomes higher when the temperature calcination is increased. It is observed that, in the higher calcination temperatures, the larger particle size with irregular morphology is obtained for the sample calcined at 300 and 500˚C, the particle size is almost 100 nm. This result confirmed that width of the rutile peak diffraction from XRD indicating the smaller crystalline size at 60˚C. An increase of the temperature up to 300˚C, the size becomes bigger than 60˚C and the agglomeration become significant. The particle size grow bigger as the calcined temperature was increased to 900˚C, which explained the effects of heat treatment on particle size of TiO_2 nanoparticles as shown in Fig.3. A thermal treatment is necessary to improve the crystallinity of amorphous compounds. When TiO_2 powders are calcinated at higher temperature, crystal structure transformations may occur. The amorphous-anatase and anatase-rutile transitions depend strongly on the method preparations, the nature of the precursor and calcination conditions. Generally, the complete transformations of amorphous to anatase has been found to be completed between 300 and 500˚C, the anatase-rutile transformation has been reported to occur in different temperature ranges from 600 to 1100˚C [19]. In a system with two or more metallic compounds, the composition of the precipitate depends on the differences in solubility between the components and the chemistry occurring during precipitation. Generally, under the conditions of either a slow precipitation rate or poor mixing within the reaction medium, co-precipitation is selective and the co-precipitate is heterogeneous in composition. Subsequent to formation of the co-precipitate, hydrothermal treatments that transform amorphous precipitates to crystalline materials with improved thermal stability and surface acidity may be carried [20]. The SEM images illustrate that almost of the particle in spherical shape and effect of heat treatment on particle size was considerable. An increase of particle size with calcination temperature was increased from 60 to 900˚C, attributed to the crystal growth. The SEM results were not in good agreement with XRD data measured using Scherrer's equation(1).

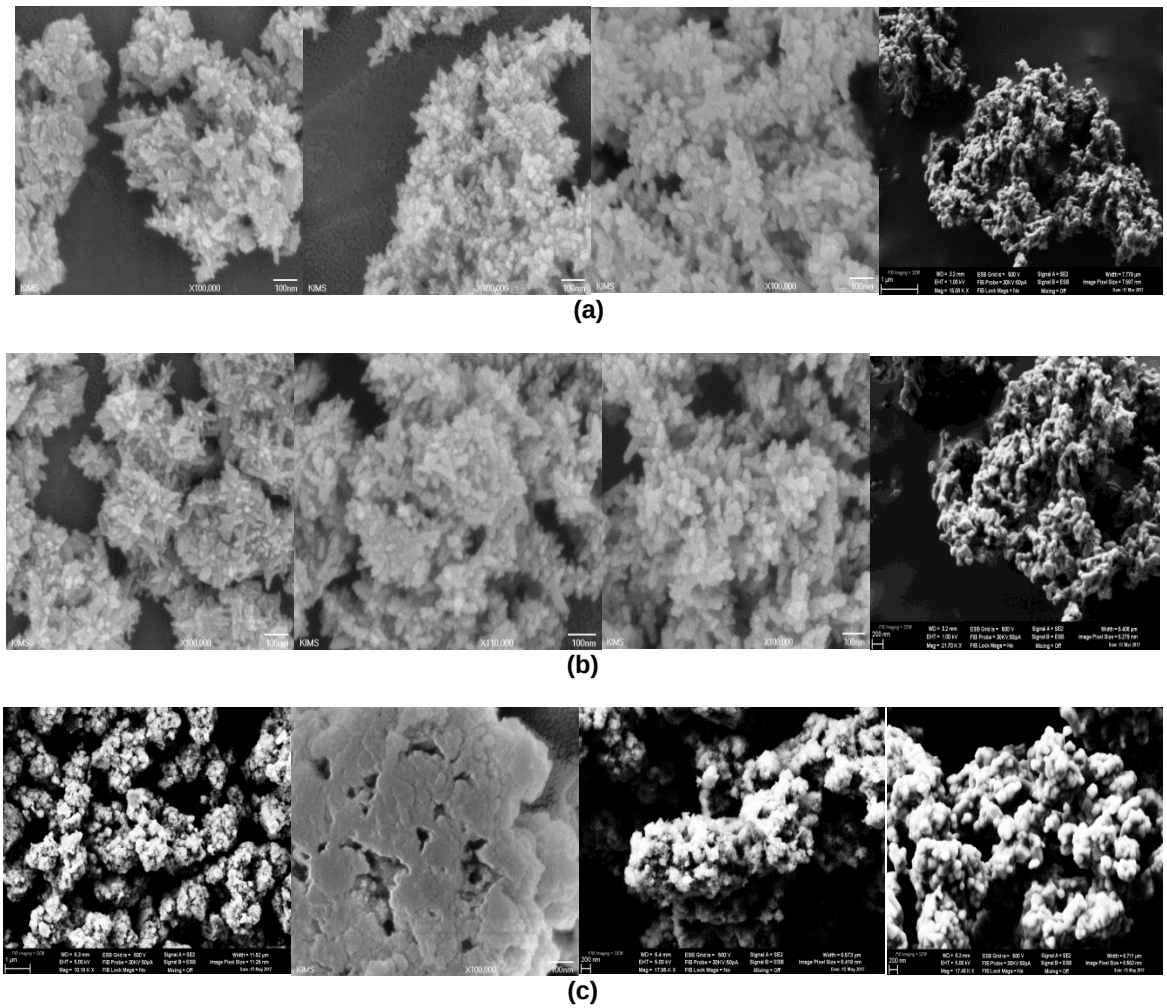

Figure 3. *SEM micrographs of TiO_2 nanoparticles prepared by (a) $TiCl_3$ + NaOH (pH 3.4) method (b) $TiCl_3$ + NaOH (pH 0.7) method (c) $TiCl_3$ + NH_4OH method at different calcination temperatures 60˚C, 300˚C, 500˚C and 900˚C respectively (from the left to the right)*

Table 1.*Summary of the properties of TiO_2 nanoparticles*

Sample preparation method		Calcination Temperature (˚C)	Phase	Crystallite size
$TiCl_3$ + NaOH	pH 3.4	60	Rutile	11.1
		300	Rutile	11.7
		500	Rutile	15.7
		900	Rutile	31.5
$TiCl_3$ + NaOH	pH 0.7	60	Rutile	11.6
		300	Rutile	12.6
		500	Rutile	15.6
		900	Rutile	26.7
$TiCl_3$+ NH_4OH		60	Anatase	18.2
		300	Anatase	20.0
		500	Anatase	23.4
		900	Rutile	34.9

4. Conclusion

TiO_2 nano-crystals were prepared by chemical precipitation method of using $TiCl_3$ + NaOH and $TiCl_3$ + NH_4OH and the structure and morphology were characterized using different techniques. The typical composition of TiO_2 nanoparticles under various calcination temperatures was investigated. From XRD characterization, all the samples obtained by $TiCl_3$ + NaOH indicate rutile with crystallite size in range 11.1 to 31.5 nm.The largest crystallite size can be seen at the highest calcination temperature. At 900 ˚C, apart from anatase, sharp rutile peaks was also observed in the XRD result of $TiCl_3$ +NH_4OH method. The formed rutile showed quite different behavior having larger size than the remained anatase particles. Scanning electron microscope picture displayed that the particles was clear sphere like structure and was relatively well-distributed. It can be concluded from the measurement of SEM and XRD that an increase in particle size of TiO_2 is associated with the increase in the calcination temperature. After calcination

operation, the crystals size increase because OH links are broken and crystals begin to growth. This may be due to the heat induced TiO_2 aggregation and phase transformation. The experimental findings concluded in this work allows for better understanding of the parameters that control the growth of TiO_2 nanocrystals while synthesizing with chemical precipitation method.

Acknowledgements

The authors appreciate the support provided by Department of Research and Innovation, Ministry of Education, Myanmar where the entire bench work was carried out.

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