

Preparation and Photocatalytic Activity of Mixed Phase Anatase/rutile TiO₂ Nanoparticles for Phenol Degradation

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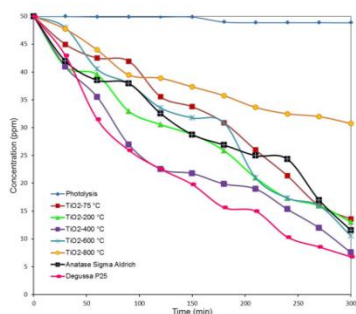
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Graphical abstract



Abstract

The evolution of desirable physico-chemical properties in high performance photocatalyst materials involves steps that must be carefully designed, controlled, and optimized. This study investigated the role of key parameter in the preparation and photocatalytic activity analysis of the mixed phase of anatase/rutile TiO₂ nanoparticles, prepared via sol-gel method containing titanium-n-butoxide Ti(OBu)₄ as a precursor material, nitric acid as catalyst, and isopropanol as solvent. The prepared TiO₂ nanoparticles were characterized by means of XRD, SEM, and BET analyses, and UV-Vis-NIR spectroscopy. The results indicated that the calcination temperature play an important role in the physico-chemical properties and photocatalytic activity of the resulting TiO₂ nanoparticles. Different calcination temperatures would result in different composition of anatase and rutile. The photocatalytic activity of the prepared mixed phase of anatase/rutile TiO₂ nanoparticles was measured by photodegradation of 50 ppm phenol in an aqueous solution. The commercial anatase from Sigma-Aldrich and Degussa P25 were used for comparison purpose. The mixed phase of anatase/rutile TiO₂ nanoparticles (consists of 38.3% anatase and 61.7% rutile) that was prepared at 400°C exhibited the highest photocatalytic activity of 84.88% degradation of phenol. The result was comparable with photocatalytic activity demonstrated by Degussa P25 by 1.54% difference in phenol degradation. The results also suggested that the mixed phase of anatase/rutile TiO₂ nanoparticles is a promising candidate for the phenol degradation process. The high performance of photocatalyst materials may be obtained by adopting a judicious combination of anatase/rutile and optimized calcination conditions.

Keywords: Mixed phase anatase/rutile; TiO₂ nanoparticles; phenol degradation; calcination temperature; photocatalytic

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1.0 INTRODUCTION

The ability to degrade organic and inorganic pollutants comes from redox environment that is generated from photoactivation, and this makes the semiconductor TiO₂ to be intensively utilized as a photocatalyst in wastewater treatment [1–3]. The photoactivation of TiO₂ photocatalyst occurs when the absorption of UV irradiation onto TiO₂ particles surface takes place. The UV irradiation absorption can be equal or higher than the band gap value of 3.2 eV for anatase or 3.0 eV for rutile [4, 5]. The TiO₂ exists in three distinct polymorphs, which are anatase, rutile (both tetragonal crystal systems), and brookite (orthorhombic crystal system) [6, 7]. Among these three TiO₂, anatase possesses the best photocatalytic properties, followed by rutile, and brookite.

The study on the band gap alignment of rutile and anatase TiO₂ has proven that the mixed phase of anatase/rutile TiO₂ would have synergistic effects and higher photocatalytic activity as compared to pure phase of either in anatase or rutile [4].

Degussa P25 and Aeroxide TiO₂ P25 are the common commercial mixed phases of anatase/rutile TiO₂ with 80% anatase and 20% rutile. The reason for the synergistic effects of the mixed phase of anatase/rutile TiO₂ nanoparticles in photocatalytic properties has still remained elusive. It is believed that the mixed phase of anatase/rutile TiO₂ can improve the charge carrier separation through electron trapping in rutile and reduce the electron recombination. As a result, the formation of radical species for oxidation of substrate molecules can be maintained [8].

Sol-gel is one of the most prominent methods used to prepare mixed phase of anatase/rutile TiO₂ nanoparticles since it provides simplicity and low equipment requirements. The preparation of TiO₂ from sol-gel gives some advantages, such as the production of high purity nanocrystalline through precipitation, and the flexibility to control the synthesis process [9]. There are three main chemical reagents required in the preparation of TiO₂ via sol-gel method, which are precursor or the starting material for Ti source, acid catalyst, and solvent as

dispersing media. The most common precursor used in the preparation of anatase nanocrystalline are titanium-n-butoxide [9–11], titanium (IV) isopropoxide [12, 13], and tetrabutyl orthotitanate [14]. The highly crystalline TiO₂ nanoparticles can be prepared via sol-gel, and followed by heat treatment that ranges from 0 to 600°C [11, 15]. It has been reported that the high quality of mixed phase of anatase/rutile TiO₂ nanoparticles, which contributes to high photocatalytic activity, can also be obtained by manipulating the types of reagents and heat treatment conditions [7, 16, 17].

Therefore, the aim of this research was to prepare a mixed phase of anatase/rutile TiO₂ nanoparticles with high photocatalytic properties via sol-gel method by manipulating the calcination temperature. In this study, the titanium-n-butoxide, Ti(OBu)₄ was used as Ti precursor, nitric acid as catalyst, and isopropanol and distilled water as the dispersing media. The photocatalytic activity of the prepared TiO₂ nanoparticles was evaluated by using the photodegradation of phenol in aqueous solution.

2.0 EXPERIMENTAL

2.1 Materials

In this study, titanium-n-butoxide Ti(OBu)₄ from Sigma-Aldrich was used as a titanium precursor. Nitric acid was used as catalyst. Isopropanol and distilled water were used as the dispersing media. The commercial TiO₂ that consists of Degussa P25 and pure anatase purchased from Sigma-Aldrich, was used in the control experiment. All the chemicals used were of analytical reagent grade and used as received.

2.2 Preparation of Titanium Dioxide (TiO₂) Nanoparticles

The titanium precursor (Ti(OBu)₄) was added dropwise in isopropanol solution and stirred until a homogenous mixture was obtained. The mixture was then added dropwise into distilled water and vigorously stirred for several minutes. After that, the nitric acid was added into the mixture and vigorously stirred for about 30 min. The prepared mixture was aged in tight air for several days until the formation of white sol-gel was observed. The white sol-gel was then dried at 75°C for 74 h in vacuum oven until white powder was obtained. The dried powder was ground to get fine powder and denoted as T75. In order to study the mixed phase of anatase/rutile TiO₂ formation, the dried sample was subjected to calcination treatment. Four new samples were prepared after they were calcined at 200, 400, 600, and 800°C and denoted as T200, T400, T600, and T800, respectively. Calcination treatment was carried out in furnace at 5°C min⁻¹ heating rate for 2 h. All the samples were preserved in a desiccator until further use.

2.3 Characterization Methods

X-ray diffraction (XRD) was used to analyze the crystallinity of the TiO₂ samples. Measurements were carried out at 40 kV and 40 mA that employed a CuK α radiation at a wavelength of 0.15418 nm. The diffracted intensity was measured at the scan range of $2\theta = 20\text{--}80^\circ$ with a scan step speed of 1 °/min. The average sizes of the crystallites of anatase and rutile were estimated with the Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is Scherrer constant, K is 1 if the spherical shape is

assumed [16]. β , λ and θ are the full-width-at-half-maximum (FWHM) in radian [18], radiation wavelength, and the incident angle of the X-rays, respectively.

The surface morphologies of the catalyst samples were characterized by electron scanning microscopy (SEM). The surface areas were calculated by the BET single point method. The UV-Vis spectra were used to indicate the optical responses of the prepared TiO₂ nanoparticles at different calcination temperatures. All the optical absorption spectra of the samples were recorded in a wavelength, ranging between 200 to 600 nm, using a UV-Vis-NIR spectrophotometer Model UV-3101PC Shimadzu.

2.4 Photocatalytic Activity Measurements

The photocatalytic activity of the prepared TiO₂ nanoparticles was evaluated via degradation of 50 ppm phenol in aqueous solution. The photodegradation process was conducted in a self-designed photocatalytic reactor that consisted of 500 ml glass beaker, and was irradiated using ultraviolet (UV) lamp (Vilber Laurmat, 312 nm, 30 watt). The photocatalyst (0.8 g) was added in the 400 ml phenol solution and sonicated for 15 min. The mixture was stirred continuously with a magnetic stirrer in the dark for 30 min to achieve the adsorption/desorption equilibrium. After that, 1 mL was taken as a blank sample before irradiation. Then, the mixture was irradiated using UV lamp. Air diffuser was used to provide sufficient O₂ for the reaction. The suspensions (5 ml) were then collected at 30 min interval using 0.45 μm syringe filter to eliminate excess catalysts prior to analysis. The clear liquid from each suspension was subjected to UV-Vis Spectroscopy to measure the concentration change of phenol throughout the experiment. The photocatalytic activity was indicated in percentages for phenol degradation according to the following equation;

$$\text{Degradation of phenol} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (2)$$

where A_0 is the initial concentration and A_t is concentration at time t (0, 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min). A similar experiment was carried out for the commercial anatase TiO₂ from Sigma-Aldrich and Degussa P25. Meanwhile, a blank experiment was also carried out with direct photolysis of phenol, irradiated under UV lamp and without the presence of photocatalyst.

3.0 RESULTS AND DISCUSSION

3.1 X-ray Diffraction Pattern of the Synthesized TiO₂

The XRD technique is often used to identify the existence of amorphous, anatase, or rutile TiO₂ nanoparticles. Figure 1 shows the XRD pattern of TiO₂ prepared at different calcination temperatures. As presented in Figure 1, the intensity of XRD pattern of T75 was increased with the increase of the calcination temperature from 200 to 800°C. Generally, high intensity of the XRD pattern exhibited high crystallinity. Based on the XRD pattern, a summary of crystalline properties of the TiO₂ nanoparticles prepared at different calcination temperatures is presented in Table 1.

From Table 1, it can be seen that T75 exhibited a mixed phase of anatase/rutile TiO₂ at the drying stage, as low as 75°C, with the percentage of anatase and rutile produced 95% and 5%, respectively. Although the mixed phase of anatase/rutile TiO₂ can be formed at 75°C, the crystallinity was low. The crystallinity

of the mixed phase of anatase/rutile TiO_2 was enhanced gradually as a function of calcination, as clearly shown by the intensity of the diffraction peak, that had become higher and sharper. Furthermore, Figure 1 visibly shows the intensity of the diffraction peak of anatase plane at (101) significantly decreased, while the diffraction peak of rutile crystal plane at (110) increased as the calcination temperature increased.

By increasing the calcination temperature up to 800°C , the pure phase of rutile TiO_2 with high crystallinity was completely formed as the disappearance of (101) diffraction peak was observed. Hence, it can be concluded that the phase of transition of TiO_2 nanoparticles depended on the calcination temperature. This phase of transition was irreversible, in other words, rutile was prohibited to transform back into the anatase phase although the rutile was recalcined at a lower temperature. In the present work, pure and highly crystalline rutile TiO_2 nanoparticles were obtained at calcination temperature of 800°C . The diffraction peak signals of the brookite phase were observed in the sample calcined at 75°C , 200°C , and 400°C at 2θ of 30.77° , 30.82° , and 30.85° , respectively.

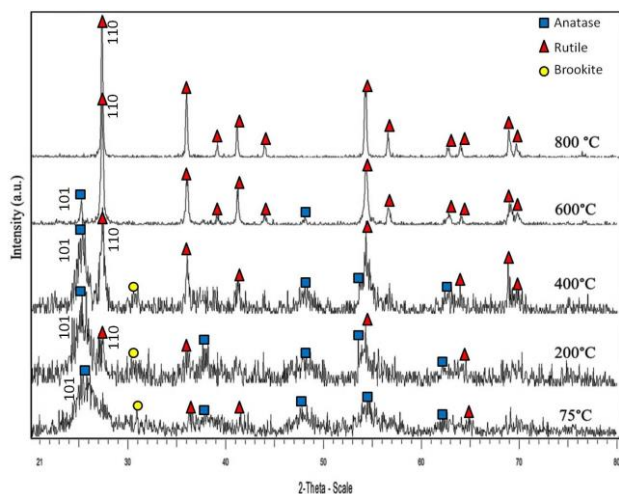


Figure 1 XRD patterns of the TiO_2 nanoparticles treated at different calcination temperature

The average crystallite sizes of the anatase and rutile in each sample were estimated using the Scherrer equation. The average crystallite size estimations are tabulated in Table 1. From Table 1, the average crystallite sizes of anatase and rutile increased as calcination increased, and this result has also been found elsewhere [19]. The lowest average size of anatase crystallite was estimated at 4.3 nm, which was calcined at 75°C . As the calcination temperature increased to 200, 400, and 600°C , the average crystallite size increased to 5.7, 9.4, and 49.4 nm, respectively. Figure 1 shows that the width of the diffraction peak of anatase (101) at $2\theta = 25.4^\circ$ became narrower as the calcination temperature increased from 75°C to 400°C . The same pattern of diffraction peak of TiO_2 rutile (110) at $2\theta = 27.5^\circ$ was also observed as the calcination temperature increased from 200°C to 800°C . Thus, it can be concluded that the crystallites sizes reduced as the XRD peak got broader [20].

Table 1 Crystalline properties of the TiO_2 nanoparticles prepared at different calcination temperature

Sample	Calcination Temperature ($^\circ\text{C}$)	Anatase (%)	Rutile (%)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Crystalite Size (nm)	
					Anatase	Rutile
T75	-	95.0	5.0	204.27	4.3	-
T200	200	52.8	47.2	200.73	5.7	24.7
T400	400	38.3	61.7	73.56	9.4	30.3
T600	600	12.0	88.0	27.95	49.4	35.3
T800	800	0	100	2.69	-	56.7
Anatase Sigma-Aldrich Degussa P25	-	100	0	15.16	89.8	-
	-	78	14	52.12	22.4	31.0

3.2 Scanning Electron Microscopy and BET Analysis

The morphological structure and the crystallinity of the prepared TiO_2 powder before and after calcination were observed by SEM. Figure 2(a) shows very fine powder and small particle size. However, as shown in Figure 2(b), the TiO_2 powder that was calcined at 800°C exhibited the aggregation phenomenon, which led to the formation of large TiO_2 particles. This was proved by the BET analysis, as shown in Table 1. It indicated that TiO_2 calcined at 800°C exhibited the lowest surface area of $2.69 \text{ m}^2 \text{g}^{-1}$. Meanwhile, the TiO_2 dried at 75°C revealed the highest surface area of $204.27 \text{ m}^2 \text{g}^{-1}$ as compared to the commercial anatase TiO_2 with surface area of $15.16 \text{ m}^2 \text{g}^{-1}$.

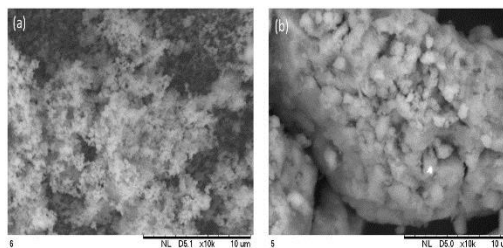


Figure 2 SEM images of the TiO_2 nanoparticles: (a) TiO_2 dried at low temperature of 75°C (b) TiO_2 calcined at 800°C

3.3 Optical Properties

In order to study the effect of calcination temperature on optical response of prepared TiO_2 , UV-Vis absorption spectra were characterized, as shown in Figure 3. This figure shows the UV-Vis spectrum of TiO_2 powder at different calcination temperatures, ranging from 75 to 800°C . It was interesting to find that the UV-Vis spectra indicated that all of the prepared TiO_2 obviously exhibited excellent optical responses to UV and visible region, especially sample T600. We obtained different optical responses as compared to previous studies' [12, 13, 21–25].

In the previous studies, a dopant material was introduced in the preparation of visible light active photocatalyst, such as multi wall carbon nano tubes (MWCNTs), sulphur, natural dyes, vanadium, and nitrogen. In the present study, almost all the TiO_2 sample prepared activated in the visible light, which might be ascribed to the N doping during the preparation of process due to HNO_3 [26]. However, as the calcination temperature

increased, the optical absorption of all the samples decreased, except T600. The strong absorbance in UV region of all the TiO₂ samples was due to the high tendency of electron excitation from the valence band to the conduction band. Sample T600, which consisted of 12% anatase and 88% rutile, exhibited the highest absorbance in the visible region, followed by T800, T400, T200, and T75.

From the spectrum, it could be observed that there were obvious absorbance differences in the UV light region and visible region between the samples. In the UV region, sample T600 also exhibited the highest absorbance, followed by T75, T400, T200, and T800. The highest optical absorption in both regions for T600 might be attributed to the electron affinity within the anatase and rutile phases. It has been proved that electron affinity of anatase is higher than rutile [27]. The rapid photogenerated conduction electron flows from anatase to rutile, and thus, limits the electron recombination rate [8].

The sample calcined at 800°C showed a relatively low absorbance rate due to the increase in particles size. Previous studies have suggested that this may be attributed to the combined effect of particles size and crystallinity [11, 28]. A lower absorbance rate at the UV range led to low responses to the UV light. It can be concluded that as the particles are low in crystallinity and large in particles size, the tendency to absorb UV light is limited, which is due to the smaller surface in the limit areas [27]. The increment in calcination temperature led to this aggregation phenomenon, as shown in Figure 3, as it turned to be more severe, and roughly corresponded to the result of UV/Vis spectrum, whereby the UV responses of the samples decreased as the calcination temperature was increased.

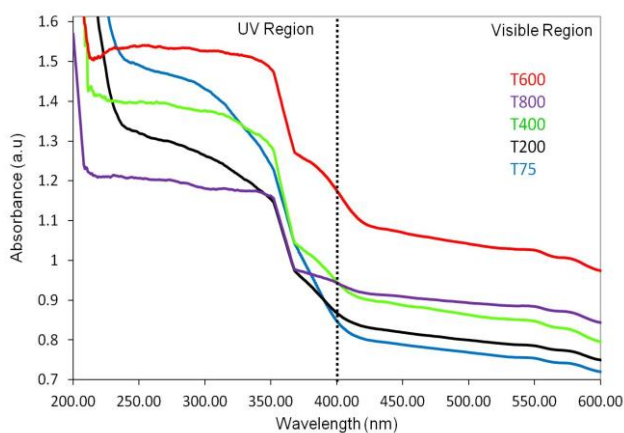


Figure 3 UV-Vis spectrum of the TiO₂ nanoparticles prepared at different calcination temperature

3.4 Photocatalytic Activity Measurements

The photocatalytic activity of the prepared catalyst was measured by the percentage of photodegradation of phenol in aqueous solution. The blank experiment was conducted to study the stability of phenol in aqueous solution towards UV irradiation. Figure 4 demonstrates phenol degradation in aqueous solution using TiO₂ nanoparticles as a function of irradiation time. The concentration of phenol decreased as the time of UV irradiation increased. Besides, it was found that after 130 min of irradiation by UV, the degradation of phenol in aqueous solution achieved 50% with samples of Degussa P25 and T400.

The direct photolysis without photocatalyst that was present in the reactor showed the lowest degradation of phenol

in aqueous solution, which was only 2.3% after it was irradiated by UV at 312 nm for 180 min. This value of degradation of phenol remained unchanged as the UV irradiation time reached up to 300 min, as shown in Figure 4. From the result, it can be proved that phenol was considered stable under UV irradiation without the presence of photocatalyst.

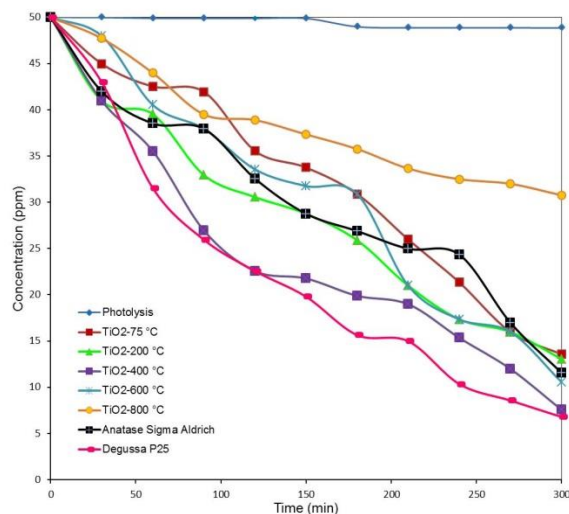


Figure 4 The phenol degradation in aqueous solution using TiO₂ nanoparticles as a function of irradiation time

The summary of the photocatalytic activity for all the samples for the degradation of phenol after 300 mins are tabulated in Table 2. It was revealed that the degradation of phenol in aqueous solution by using T400 exhibited the highest photocatalytic activity. It showed that 84.88% of phenol degradation was achieved. This result is comparable with the standard Degussa P25 by 1.54% difference in phenol degradation. Therefore, it was believed that T400 demonstrated similar properties of Degussa P25.

The lowest photocatalytic activity in the degradation of phenol, 38.48%, was obtained from T800. This was due to the low surface area created for the photodegradation reaction to take place. This result is in agreement with the UV-Vis spectroscopy data, whereby low optical response to UV was observed for the samples calcined at 800°C. A low optical response to UV leads to insufficient energy to excite electron from valence band to the conduction band [28]. The excitation of the electron is crucial since it leads to the formation of positive holes and has a positive charge [29]. This positive hole has strong oxidation power to promote the degradation of phenol molecules in aqueous solution.

Table 2 Photocatalytic activity of the TiO₂ nanoparticles prepared at different calcination temperature

Sample	Calcination Temperature (°C)	Degradation of phenol (%) after 300 min irradiation time
T75	-	72.88
T200	200	73.88
T400	400	84.88
T600	600	78.88
T800	800	38.48
Anatase Sigma-Aldrich	-	76.88
Degussa P25	-	86.42
Photolysis (control)	-	2.3

In addition, the photocatalytic activity of pure anatase TiO₂ (referring to commercial anatase from Sigma-Aldrich) and pure rutile TiO₂ (referring to TiO₂-800°C) can also be observed in Figure 4. As comparison to these results, the prepared mixed phase of TiO₂ showed higher photocatalytic activity than pure anatase and rutile TiO₂. Similar results could be found elsewhere [30]. The energy barrier between anatase and rutile phases facilitates the photogenerated electrons to transfer from anatase to rutile as the electron affinity of anatase is higher than rutile [4, 31]. Previous study on the band alignment of rutile and anatase TiO₂ indicated that the band alignment of approximately 0.4 eV drives force for the increased photocatalytic activity of anatase/rutile composites material over their individual counterparts [4]. There were significant differences in their photocatalytic activities, which were observed as the anatase phase exhibited higher photocatalytic activity than the rutile phase. Similar results were also obtained by other researcher [19].

4.0 CONCLUSION

The mixed phase of anatase/rutile TiO₂ nanoparticles was successfully prepared by using titanium-n-butoxide Ti(OBu)₄, nitric acid, and isopropanol as a precursor material, catalyst, and solvent, respectively. The preparation of the mixed anatase/rutile TiO₂ nanoparticles with controllable heating treatment had been a very simple approach and was energy saving. The effects of calcination temperature on the physicochemical properties and photocatalytic activity were studied. The results showed that the calcination temperature played important roles in the crystallites' growth and the crystallites' phase transition in the preparation of the mixed phase of anatase/rutile TiO₂ nanoparticles. Based on the XRD pattern, it can be concluded that the increment in calcination temperature leads to rapid crystallites' growth and a decrease in the particles size. Furthermore, the composition of anatase decreased while rutile increased in the mixed phase of anatase/rutile TiO₂ as the calcination temperatures increased. On top of that, the BET analysis revealed a decrease in the TiO₂ surface area, which was also due to the elevated calcination temperature. From the UV-Vis spectra, all the TiO₂ samples prepared in the laboratory exhibited excellent optical responses to UV and visible region. The highest photocatalytic activity was demonstrated by the mixed phase of anatase/rutile TiO₂ nanoparticles prepared at 400°C. The degradation of approximately 84% was achieved after 300 min of operation. This result was comparable with the photocatalytic activity obtained from the commercial anatase TiO₂ (Degussa P-25). The

mixed phase of anatase/rutile TiO₂ nanoparticles prepared in this study can be used as an appropriate photocatalyst material with effective performance for phenol degradation applications.

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