Morphology of titanium dioxide synthesized via precipitation technique: Effect of calcination and reflux on the surface morphology

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Abstract. - Globally, the use of titanium dioxide (TiO2) for photocatalytic activities has a tremendous attention because of the numerous advantages which can be obtain from photocatalysts. The usage of TiO2 was verified to be nontoxic, biologically inert, physically and chemically stable against corrosion. The TiO2 photocatalyst was prepared via a simple precipitation method using titanium tetrachloride (TiCl4) in the presence of ammonium sulfate was used to obtain samples of mesoporous titanium dioxide with anatase structure. In the work discussed in this paper, titanium dioxide (TiO2) nanoparticles were synthesized by wet precipitation method under different conditions. Prepared TiO2 powders were characterized by XRD, FESEM and UV Vis-DRS. Different conditions, for example reflux time (2 and 4 hours) and calcination temperature (350°C), were changed to achieve to best nanocrystallite material. It was found that variation of all these conditions could strongly affect crystallinity, morphology, and crystallite size. The crystallite sizes of nanoparticles, calculated by using the Scherrer equation, were from approximately 11 to 15 nm.

1. Introduction

Titanium dioxide (TiO2) has been extensively used globally in manufacture of photocatalysts, gas sensors, and dielectric ceramics [1]. The photocatalytic activity and reactivity of TiO2 can be determined by its phase composition, size, shape of particles, structure and size of pores [2]. To control the phase composition and texture properties is primarily determined by the wide variety of starting substances used and diversity of affecting factors and synthesis methods [3]. The size of the TiO2 particles is an important factor affecting the performance of the materials. Therefore, there are a lot of research has been done upon the reduction of the particle size. There are several methods used to synthesis titanium dioxide. The most widely employed method for the preparation of TiO2 nano-powders, including sol gel route, homogeneous precipitation, hydrothermal methods, flame synthesis and new molten salts method [4]. The main advantage of this precipitation method is the possibility of controllably varying the synthesis conditions, which yields titania.
According to several researches, it was found that different techniques often produces different results. Even for the same technique but varying the conditions for instance using different amount of the starting materials, the obtained powder size can be different [5]. Besides that, it is believed that calcination method as well as reflux can cause a change in the size and morphology of the TiO₂ produced.

Subsequently, particle size and the morphology are significant parameters that affect the physical properties of the TiO₂. In order to determine the morphology and particle size, numerous methods could be used for the study. It can be done by direct observation of particles by transmission electron microscopy (TEM) or scanning electron microscope techniques (SEM), where we are able to obtain the vital information on the shape of particles. Besides that, information on particle size can be obtained by conducting the X-ray diffraction (XRD) method as the particle size is associated to the diffraction peak broadening. TEM, SEM and XRD not only used to measure the particle size, whereas it also able to determine the crystalline phases [6].

Besides SEM and XRD, UV-visible diffuse reflectance spectroscopy will be used to characterize TiO₂ in order to determine the absorbance and band gap value. The optical band gap (Eg) of TiO₂ differs depending on the structure, particle size and morphology but with the value for amorphous TiO₂ is ~3.5 eV [7]. The band gap value for crystalline anatase is 3.2 eV whereas rutile will be 3.0 eV respectively [8]. Generally, rutile TiO₂ is able to absorb light of a wider wavelength range and it is assumed that the photocatalytic performance of rutile would be greater than anatase. However, anatase provides higher photocatalytic activity owing to the higher density of localized states, consequent surface-adsorbed hydroxyl radicals, and slower charge carrier recombination rate relative to rutile [9,10]. Thus, there is growing interest in understanding the unique photocatalytic activity of anatase.

The main aim of this study was to determine the effect of the structure and photocatalytic performance of titanium dioxide synthesized by precipitation of titanium tetrachloride in the presence of ammonium sulfate additives under different conditions such as calcination and reflux.

2. Materials and Methodology

2.1 Materials

All chemicals were used as received. Those chemicals are titanium tetrachloride (TiCl₄, 99.90%), ammonia solution (NH₃ (aq), 25%), ammonium sulfate ((NH₄)₂SO₄, 99.90%).

2.2 Synthesis of TiO₂

TiO₂ photocatalyst was synthesized using TiCl₄ as the Ti-precursor without any further purification. The TiO₂ was prepared via hydrolysis of TiCl₄ in an aqueous system with ammonium sulfate (NH₄)₂SO₄ as a precursor and followed by precipitation with NH₃(aq). The mixture was dried in an oven (~80°C) overnight and grounded to fine powder giving the amorphous as-synthesized TiO₂. Different conditions, for example reflux time and calcination temperature, were changed to achieve the best nanocrystalline material. The sample are categorized as in table 1 below. The pure as-synthesized sample were calcined at 350 °C as well as refluxed for 2 hours and 4 hours.
Table 1. Samples prepared under four different experimental conditions.

| Sample Label | Conditions          |
|--------------|---------------------|
| TiO₂_Raw     | As-synthesized      |
| TiO₂_350     | Calcined at 350°C   |
| TiO₂_2       | Refluxed for 2 hours|
| TiO₂_4       | Refluxed for 4 hours|

2.3 Characterization of TiO₂

The UV-visible diffuse reflectance (DRUV-Vis) spectra of all photocatalysts were recorded using Cary 100 (Agilent) spectrophotometer and spectralon was used as a reference. XRD (Bruker D8 Advance) conducted with CuKα radiation (40 kV, 40 mA) at 20 angles from 2º to 80º and a scan speed of 4º·min⁻¹. This technique is used to identify the type of TiO₂ phases. The morphology of the TiO₂ photocatalysts was determined by using Zeiss Supra 35VP by conducting the Emission Scanning Electron Microscope (FESEM). The samples were scanned at 100 kX magnification. The image formed from the interaction of the electrons transmitted through the sample is magnified and focused onto an imaging device.

3. Results and Discussions

3.1 Structures and morphologies

The structural analysis of TiO₂ particles was carried out using XRD instrument. The diffractograms were recorded in the 20 range of 10-80º. Figure 1 shows the representative of XRD patterns taken from as-synthesized TiO₂, TiO₂ calcined at 350ºC, refluxed TiO₂ at 2 hours and 4 hours respectively. The crystalline nature was observed in the powder XRD of TiO₂ and diffraction peaks belong to the anatase phase of TiO₂. The broad lines were comparatively broad for all the samples representing nano sized crystals. The XRD patterns exhibited diffraction peaks which indicates that the TiO₂ in anatase phase with the corresponding (101), (103), (200) and (105), (204) planes respectively [11, 12]. The peaks were compared with the standard TiO₂ in rutile phase with the corresponding (110), (111), (220) and (301) planes respectively [13]. The XRD spectra also shows no detectable peaks related to TiO₂ rutile phase for TiO₂_Raw, TiO₂_2 and TiO₂_4 however there is one peak which indicates rutile at 27.42º (110) for TiO₂_350. Thus, all observed peaks are in good agreement with the standard spectrum (JCPDS no.: 21-1272 and 21-1276). Varshney et al, reports that the absence of spurious diffractions indicates the crystallographic purity [14]. There is no spurious diffraction peak found in the sample. Anatase exhibits higher photocatalytic activity compared to rutile TiO₂ [15]. The crystalline size in Table 2 was calculated using Scherrer equation as below:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

Where;
- \( D \) = Crystallite size
- \( \lambda \) = Cu Kα radiation Wavelength, 1.549 Å
- \( K \) = Shape factor, 0.94
- \( \beta \) = Broadening at half the maximum intensity
- \( \theta \) = Bragg angle (in degree)
Figure 1. XRD pattern of the photocatalysts

The full-width at half maximum (FWHM) were determined using Highscore Expert software. Table 2 tabulates the crystalline size of the prepared photocatalyst under different conditions. The changes in crystalline size of the synthesized samples were in line with the changes in the peak sharpness and intensity, suggesting that variation of crystallinity of synthesized samples was mainly determined by the size of crystallites and FWHM of the diffraction peak [16]. The results show that the FWHM of the diffraction peak decreases and become narrower for TiO$_2$ calcined at 350ºC and TiO$_2$ which was refluxed for 4 hours suggesting that the average crystallite size has become bigger correspondingly. This shows that the enhancement of the crystallinity, stems from the increment of the crystalline volume ratio due to the size enlargement of the nuclei [17]. An increasing trend of peak intensity and crystalline size was observed in sample TiO$_2$-2, TiO$_2$-Raw, TiO$_2$-4 and TiO$_2$-350, suggesting that the calcined sample resulted in further growth of crystalline size, hence favoring the formation of TiO$_2$ with higher crystallinity.

Table 2. Crystallite size of the prepared photocatalysts.

| Sample   | 2θ (degree) | Average Crystallite (nm) |
|----------|-------------|-------------------------|
| TiO$_2$-Raw | 25.6        | 12.40                   |
| TiO$_2$-350 | 25.6        | 15.91                   |
| TiO$_2$-2   | 25.7        | 11.04                   |
| TiO$_2$-4   | 25.4        | 14.62                   |
Further structural study of the prepared TiO$_2$ powder was characterized using FESEM image analysis. Figure 2 (a), (b), (c) and (d) shows the FESEM images of synthesized TiO$_2$ powder under different conditions as stated below. The size obtained from the FESEM results are slightly higher than that calculated crystallite size using the Scherrer formula. The FESEM images shows the high degree of crystallinity of the TiO$_2$ nanoparticles. The FESEM image in Figure 2 (b), particles were spherical in shape and surface morphology was found homogenous in most of the regions with no aggregates. Agglomeration of the particles was seen in Figure 2(a), (c) and (d). The FESEM image of Figure 2(d) have formation of lump due to particles sticking together in a spherical shape causing a high average particle size of 18.90 nm. Aggregates of white substance has been spotted on the FESEM image of the particles as referred to Figure 2 (a) and (c). The morphological results using FESEM, it was observed that the grown products are nanoparticles with an average diameter of ~10 to 22 nm. It is observed that when TiO$_2$ is refluxed, the agglomeration of the particle increases as suggested by the diffraction pattern in Figure 1 [18, 19].

Figure 2. FESEM images of (a) TiO$_2$-Raw, (b) TiO$_2$-350, (c) TiO$_2$-2, (d) TiO$_2$-4 at 100kX magnification
3.2 DRUV-Vis spectroscopy

The absorption spectra of all synthesized TiO$_2$ samples with different conditions are shown in Figure 3. The absorption spectrum for all synthesized TiO$_2$ shows an absorption edge at 400 nm and no significant absorbance from 400 nm onwards. However, in Figure 4, it is observed that a significant shift in the band gap of synthesized TiO$_2$ were detected from the variation of $(ahv)^2$ with photon energy $(hv)$ compared to the standard pure TiO$_2$ sample which has a band gap of 3.20 eV. The extrapolated line drawn (Figure 4) for all the synthesized TiO$_2$ corresponds to the bandgap of 3.17 to 3.12 eV, respectively (table 4). This indicates that the bandgap of the synthesized TiO$_2$ has been reduced significantly compared to standard pure anatase TiO$_2$ [20]. In addition, electron-hole pairs can be generated, even though the particle is irradiated with longer wavelength visible light. In order to improve the photocatalytic activity of TiO$_2$ under visible light irradiation, enhancement of light absorption in the visible region is vital. Therefore, doping TiO$_2$ with a metal could generate sub band states in the band gap of TiO$_2$ which can then be easily excited to produce more electron-hole pairs under visible light irradiation, hence resulting in higher photocatalytic activity compared to TiO$_2$ which is not doped with metal. This phenomenon could be due to many factors such as morphology, crystallite size and phase structure [21].

![Figure 3. DRUV-Vis spectra](image)

Table 3. Particle size of the prepared photocatalysts.

| Sample          | Particle Size Range (nm) |
|-----------------|--------------------------|
| TiO$_2_{\text{Raw}}$ | 13.02-21.33              |
| TiO$_2_{\text{350}}$ | 10.29-15.29              |
| TiO$_2_{\text{2hr}}$  | 14.21-18.72              |
| TiO$_2_{\text{4hr}}$  | 14.98-22.61              |
To calculate the band gap energy of the photocatalyst, reflectance \( [F(R)] \) spectra using Kubelka-Munk formalism and Tauc plot was used for each synthesized photocatalyst [20]. Using the Tauc plot of \([F(R)\cdot h\nu]^n\) vs. \( h\nu \) whereby \( h\nu \) is the photon energy and \( n = \frac{1}{2} \) for direct band gap of the photocatalyst, for which the value of \( n \) gives a straight line in the band edge region. By taking the solitary linear behavior as an evidence for the direct transition between valence and conduction bands, the optical energy band gap (\( E_g \)) of the photocatalyst was estimated [21]. The extrapolation of this straight line will intercept the photon energy \((h\nu)\)-axis to give the value of the indirect optical energy gap (\( E_i \)) to deduce the band gap energy of the respective photocatalyst. The band gap of the TiO\(_2\)_raw was 3.17 eV, calcined TiO\(_2\) at 350ºC was 3.12 eV whereby the band gap values were reduced. Upon refluxing the photocatalyst for 2 hours and 4 hours, the band gap was 3.19 eV and 3.16 eV respectively. As the Reflux duration increases, the band gaps decrease, indicating some synergistic effect [22]. According to Mogyorosi et al [23], the increase in band gap in the TiO\(_2\) refluxed at 2 hours comparing it with TiO\(_2\)_Raw could be due to a higher effective electron

**Figure 4.** Band Gap Shift spectra

**Table 4.** Band Gap of the prepared photocatalysts.

| Sample        | Band Gap (eV) |
|---------------|---------------|
| TiO\(_2\)_Raw | 3.17          |
| TiO\(_2\)_350 | 3.12          |
| TiO\(_2\)_2   | 3.19          |
| TiO\(_2\)_4   | 3.16          |
mass, a higher Fermi energy level and a greater charge mobility in anatase, which eventually rise to a larger band gap. The calcined TiO$_2$ at 350°C gave the highest reduction to the band gap (3.12 eV). To further decrease the band gap size, it is advice to dope the TiO$_2$ with appropriate metal as it has the ability in decreasing the band gap energy resulting in an increase in the absorbance in the visible region. This occurs when the metal is doped on the TiO$_2$ and cause the generation of electron-hole pairs, which can cause the charge transfer phenomena to take place between metal ions and TiO$_2$ [24].

4. Conclusion

This study is on the synthesis and characterization of TiO$_2$ nanoparticles via precipitation technique. From the results obtained, anatase TiO$_2$ with small crystallite size from 11 nm to 15 nm was successfully synthesized using titanium tetrachloride (TiCl$_4$) as the precursor in the presence of ammonium sulfate. FESEM images characterization shows that the nanoparticles are in nano-range. The results evidently show that the sample synthesized and calcined at 350ºC (TiO$_2$$_{350}$) has smaller average particle sizes and the surface morphology was found homogenous in most of the regions with no aggregates which may contribute to a better photocatalytic performance. In addition, the TiO$_2$ calcined at 350ºC was able to reduce the band gap from 3.20 eV to as low as 3.12 eV. The lowering of band gap is a sign of shifting the absorption edge to visible light region, which is vital for photocatalysts to harvest energy from the free and abundant sunlight. According to research, to further enhance the photocatalytic performance, it is necessary to incorporate metal onto TiO$_2$ nanoparticles. Metal doping TiO$_2$ is one of the significant approaches to keep the electron–hole pairs separated, delaying its fast recombination, and shift the absorbance of TiO$_2$ to the visible region resulting in enhancement of the photoactivity of TiO$_2$ under visible light illumination.

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