Preparation of TiO$_2$ nanoparticles by hydrolysis of TiCl$_4$ using water and glycerol solvent system

N Rab$^1$, F K Chong $^1$, H I Mohamed$^2$ and W H Lim$^3$

$^1$Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
$^2$Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
$^3$Advanced Oleochemical Technology Division, Malaysian Palm oil Board, Bandar Baru Bangi, Kajang Selangor, 43000, Malaysia

*Corresponding authors: rab_17000005@utp.edu.my, chongfaikait@utp.edu.my

Abstract. The anatase phase TiO$_2$ nanoparticles (NPs) were synthesized by precipitation method using TiCl$_4$ as a precursor in a new reaction medium containing water and glycerol. The as-synthesized photocatalysts were characterized by Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). The Raman spectra indicate the formation of crystalline anatase phase TiO$_2$ NPs after calcination at 300 and 400$^\circ$C. TiO$_2$ NPs formation was confirmed by observing the major characteristic, FT-IR vibration bands of Ti-O network. The band gap calculated from UV-Vis DRS spectra ranged from 3.02-3.28 eV. FESEM images exhibit spherical shape TiO$_2$ NPs in the form of nano-clusters with crystallite sizes ranged from 9.50-26.14 nm. FESEM images show that as the calcination temperature increases, the sizes of the TiO$_2$ NPs also increase. The inclusion of glycerol promotes the formation of smaller particles and lowers the band gap of TiO$_2$ NPs.

1. Introduction
Titanium dioxide (TiO$_2$) is considered as a nearly perfect material because of its remarkable and unique optical properties. It has acquired humongous research interest and has been widely investigated for a range of applications such as H$_2$ production as a fuel using solar energy [1], chemical sensors, dielectric material for ultrathin-film capacitors, as pigments in dyes and paints, self-cleansing surfaces [2], solar cells [3] desulfurization [4] and photo-acoustic signals to name a few [5]. TiO$_2$ is well-known for its strong oxidizing abilities, low cost, thermal and chemical stability, widespread availability, noncorrosive property and high efficiency toward degradation of organic pollutants. As a result, these benefits have led to the utilization of TiO$_2$ for multiple applications including environmental purification, especially water and air [6, 7].

Several state of the art reviews have been written on the preparation methods, physical and optical properties and applications of TiO$_2$ [8, 9]. Over the past two decades, a variety of methods such as hydrothermal, solvo-thermal, sol-gel, direct oxidation, chemical vapor deposition (CVD) electrodeposition (ED), sono-chemical, micro emulsion, microwave and precipitation method have been used for synthesis of TiO$_2$ [10, 11]. Among these synthetic approaches, precipitation method is considered to be the best technique because of its ease, pure phase formation of compounds, ambient operating conditions, low cost, minimal chemicals usage and high purity and yield of nanoparticles [12].
Additionally, the precipitation method has the potential to produce high quality photoactive material on industrial scale.

The present paper reports on the synthesis of TiO$_2$ NPs by hydrolysis of TiCl$_4$ using water and glycerol as solvent system instead of different types of acid and alcohol. Glycerol is utilized because it is non-toxic, can be easily handled and stored and it is produced in large quantities as a byproduct of biodiesel. The effects of water/glycerol ratio (v/v) and calcination temperature on morphology, particle size, crystalline phase formation and band gap energy were examined.

2. Experimental

2.1 Chemicals
Titanium (IV) Chloride (TiCl$_4$) (purity: 99.9%), ammonium hydroxide (NH$_4$OH, 30%) and glycerol (purity: 99.5%) were purchased from Merck. All the chemicals were of highest purity grade and were used without further purification. Deionized water was used throughout the experiments.

2.2 TiO$_2$ synthesis
Chemical precipitation method was followed for synthesis of TiO$_2$ nanoparticles. TiO$_2$ NPs were synthesized by hydrolyzing TiCl$_4$ in a reaction media with and without glycerol (table 1). 18.96778 g (0.100 moles) of 9.1117 M TiCl$_4$ was transferred drop wise to the solution containing water and glycerol at different ratios in an ice-bath under vigorous stirring. Upon the completion of the reaction, 300 mL of 2.5 M NH$_4$OH (as precipitating agent) was added drop by drop to the solution until the pH reached to 10. At pH 10, white precipitates of TiO$_2$ were appeared in the solution. Afterwards, the liquid phase was decanted from the solid phase. Then, the resulting precipitates were centrifuge at 4000 rpm for 10 mints and washed several times until the Cl$^-$ ions were completely eliminated. All the prepared samples were dried overnight in an oven at 80$^\circ$C. Then the samples were manually grounded into fine powder using pestle and mortar. In some cases, the TiO$_2$ powder were calcined at 300 and 400$^\circ$C for 1 hour at a heating rate of 10$^\circ$C/min separately, producing an off-white and black powders.

Table 1. Samples prepared at various experimental conditions.

| Sample no | Sample label | Water/Glycerol volume ratio | Calcination Temperature |
|-----------|--------------|----------------------------|------------------------|
| 1.        | T0_1:0       | 1:0                        | Uncalcined             |
| 2.        | T300_1:0     | 1:0                        | 300 $^\circ$C          |
| 3.        | T400_1:0     | 1:0                        | 400 $^\circ$C          |
| 4.        | T0_1:1       | 1:1                        | Uncalcined             |
| 5.        | T300_1:1     | 1:1                        | 300 $^\circ$C          |
| 6.        | T400_1:1     | 1:1                        | 400 $^\circ$C          |
| 7.        | T0_2:1       | 2:1                        | Uncalcined             |
| 8.        | T300_2:1     | 2:1                        | 300 $^\circ$C          |
| 9.        | T400_2:1     | 2:1                        | 400 $^\circ$C          |
| 10.       | T0_9:1       | 9:1                        | Uncalcined             |
| 11.       | T300_9:1     | 9:1                        | 300 $^\circ$C          |
| 12.       | T400_9:1     | 9:1                        | 400 $^\circ$C          |

2.3 TiO$_2$ Characterization
The TiO$_2$ photocatalyst was characterized by Raman spectroscopy, FT-IR, FESEM and UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS). Raman spectrophotometer was used to identify crystalline phase. Raman spectrum analysis was carried out using a portable Raman system’s (Inspector 500) spectrometer with a solid-state diode laser operated at 532 nm. The Raman system’s having incident power of 25 mW and a wavelength in the range of $\sim$200-3000 cm$^{-1}$. TiO$_2$ was further characterized by FTIR spectrum using spectrometer (iS50 FT-IR) to study the functional group and chemical bonds. UV-Vis DRS spectra were characterized on Agilent Carry-100 UV-Vis spectrophotometer using Spectralon as a reference sample within the range of 200-800 nm. FESEM images at a magnification of 50 kx were taken to study the surface morphology and particle sizes of the as-prepared photocatalyst using Carl Zeiss (SUPRA 55VP) instrument.

3. Results and discussion

3.1 Raman spectroscopy

The crystalline phases of TiO$_2$ samples were sensitively identified using Raman spectroscopy. All the Raman spectra were obtained at room temperature. The Raman spectra of TiO$_2$ samples, prepared at different water/glycerol ratios and calcined at 300 and 400$^\circ$C are presented in figure (1). Uncalcined samples did not display anatase crystalline structure and were excluded from the analysis. Major characteristic Raman bands of anatase crystalline phase are observed at (167, 399, 515, 519, and 638 cm$^{-1}$) for all the samples calcined at 300 and 400$^\circ$C, which are consistent with the earlier works by Li and Zeng [13]. Sharp peak is observed around 638 cm$^{-1}$ for the photocatalysts, indicating higher crystallinity in solid nanoparticles. This can minimize charge recombination during photoreaction [14]. The samples also show a fraction of rutile phase. The weak rutile peaks were observed at 795 cm$^{-1}$ and 300 cm$^{-1}$ for the samples calcined at 400$^\circ$C and samples calcined at 300$^\circ$C, respectively. The higher calcination temperature results in anatase phase of TiO$_2$ NPs [15]. The presence of glycerol has no distinct effect on the crystalline phase formation of TiO$_2$ NPs. However, it can be noted that higher the water concentration in the system, the higher the crystallinity.

![Figure 1](image-url)  
**Figure 1.** Raman spectra of the samples prepared different (water/glycerol) and calcined at 300 and 400$^\circ$C.
3.2 Fourier transform infra-red spectroscopy
The FT-IR spectra of the TiO₂ NPs, prepared under different experimental conditions were in the range of 400-4000 wavenumber (cm⁻¹), which identifies the functional group as well as chemical bonds in the compound (figure 2). The strong absorption bands observed in the frequency region of 800-1000 cm⁻¹ corresponds to Ti-O-Ti bonding which confirm the formation of titanium metal complex. As shown in figure (2), the broad intense band below 1000 cm⁻¹ is due to Ti-O-Ti stretching vibrations. The typical vibrations centered around 3410 and 1640 cm⁻¹, identifies the broad bands of O-H group. Peak observed at 1644.6 cm⁻¹ shows stretching vibrations of –C=C– bond alkenes and peak around 2361.8 cm⁻¹ corresponds to the (C-H) stretching vibrations. The sharp peak at 1410.3 cm⁻¹ shows stretching vibrations of (Ti-O-Ti) bonds its means that the sharp peaks which has been observed at around 1400cm⁻¹ in the spectrum it identify the characteristics of (Ti=O) bond formation which is matched with vibrations of (Ti=O) tetragonal structure. FT-IR spectra and the general appearance of all the samples was in good agreement with earlier reported results [12].

![Figure 2. FTIR spectra of the samples prepared under various experimental conditions.](image)

3.3 UV-Visible spectroscopy
The optical properties of the as synthesized TiO₂ samples were determined using UV-Vis DRS. The optical absorption spectra of samples were recorded at room temperature in the wavelength range of 200 to 800 nm. Based on the spectrum obtained (figure 3), TiO₂ NPs showed maximum absorption peaks (λmax) in the UV region (<380 nm). The band gap energy was determined by employing Kubelka-Munk function and Tauc’s plot. Band gap was obtained by plotting (αhv)² against hv by extrapolating the linear portion of the curve to X-Axis at α=0. The band gap calculated for the samples are given in table 2. As can be seen from table (2), the band gap values are low as compared to bulk band gap value of 3.84 eV. The band gap energy calculated for the sample (T0_2:1) was the lowest (3.02 eV) among all the samples. The band gap was reduced by the inclusion of glycerol into the reaction medium. However, when the water content was lowered in the system and the samples were calcined, the band gap energy again started increasing. TiO₂ NPs having smaller band gap can be suitable for photocatalytic application [12]. The typical band gap energy for pure anatase is 3.2 eV.
[16]. The samples prepared without glycerol and calcined at 300°C (T300_1:0) shows the highest band gap.

![UV-Vis DRS spectra of the samples prepared under various experimental conditions.](image)

**Figure 3.** UV-Vis DRS spectra of the samples prepared under various experimental conditions.

### 3.4 Field emission scanning electron microscopy

By employing FESEM, images for of the samples were taken at a magnification of 50 kx. Based on figure 4, all the samples display smooth planes and uniform morphology in the form of TiO₂ nano clusters. However, their sizes varied significantly (table 2). The particle sizes estimated from FESEM were in the range of 9.50-26.14 nm. It was found that the TiO₂ prepared at water/glycerol (1:0) and calcined at 400°C shows the lowest particle size as compared to samples prepared to other samples. This phenomenon is not very common. It has been reported that the particle size increases with increase in calcination temperature because of the agglomeration of smaller particle at high temperature. Low temperature leads to better boundaries between nanoparticles. Consequently, the morphology of the NPs changed to sphere [17]. It is evident that the presence of glycerol promotes the formation of smaller particles.
Figure 4. FESEM images of the samples prepared under various experimental conditions.
Table 2. Band gap and particle size of the TiO$_2$ nanoparticles.

| Sample no | Sample label | Band gap (eV) | Particle size range (nm) | Color | % Yield |
|-----------|--------------|--------------|--------------------------|-------|---------|
| 1.        | T0_1:0       | 3.18         | 14.90-23.31              | White | 84.64   |
| 2.        | T300_1:0     | 3.28         | 14.90-15.99              | White |         |
| 3.        | T400_1:0     | 3.11         | 14.98-24.51              | White |         |
| 4.        | T0_1:1       | 3.24         | 11.04-15.79              | White | 98.33   |
| 5.        | T300_1:1     | -----        | 14.56-26.14              | White |         |
| 6.        | T400_1:1     | 3.11         | 09.50-12.73              | Black |         |
| 7.        | T0_2:1       | 3.02         | --------------           | White | 95.82   |
| 8.        | T300_2:1     | -----        | 14.56-24.05              | Black |         |
| 9.        | T0_9:1       | 3.17         | --------------           | White | 96.88   |
| 10.       | T300_9:1     | -----        | 16.48-22.33              | Black |         |

4. Conclusion

TiO$_2$ nanoparticles of anatase phase were successfully synthesized from hydrolysis of TiCl$_4$ by utilizing a new reaction media (water/glycerol) instead of other existing solvents such as alcohol and acid. Different characterization techniques such as Raman, FESEM, FT-IR and UV-Vis DRS were used for crystalline phase identification, surface morphology and particles size, functional groups and optical band gap estimation, respectively. TiO$_2$ having spherical shape, average sizes ranged from 9.50-26.14 nm were obtained. Glycerol inclusion into the solvent system showed positive effect on particle size. The lower band gap energy (3.02 eV) was achieved at optimum ratio (2:1) of water and glycerol. This method can be easily fabricated and carried out at ambient condition and the utilization of glycerol in synthesis of TiO$_2$ NPs is a win-win situation as it is nontoxic, can be easily handled and more important it’s a cheap commodity. Further work will focus on the effect of glycerol in the photocatalytic activity of TiO$_2$ NPs towards degradation of organic compounds.

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