CHAPTER - III

PRISTINE ANATASE TiO₂ NANOPARTICLES
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3.1. Introduction

As for many oxides, properties of TiO₂ are directly determined by its polymorphs. TiO₂ occurs in nature in three different phases, namely, rutile, anatase and brookite [Guangshe et al., (2011)]. The unit cell structures of the polymorphs together with their basic parameters are reported in earlier literature [Diebold (2003)]. The rutile is the most stable structure of TiO₂, whereas the anatase and brookite are considered as metastable forms. Nevertheless, the highest photocatalytic activity is attributed to the anatase phase. From this perspective, the titania crystallinity plays a crucial role and influencing the overall photoefficiency of the layers. On the other side, while the pure form of the anatase and rutile is relatively easy to obtain, in case of brookite it is much more difficult [Kment et al., (2012)]. Among these polymorphs, rutile and anatase have been widely studied. Bookite is rarely studied due to its complicated structure and difficulties in sample preparation [Hu et al., (2009)]. These three phases can be commonly described as constituted by arrangements of the same building block-Ti–O₆ octahedron in which Ti atom is surrounded by six oxygen atoms situated at the corners of a distorted octahedron. In spite of the similarities in building blocks of Ti–O₆ octahedra for these polymorphs, the electronic structures are significantly different [Guangshe et al., (2011)].

Nanostructural titania is one of the most widely studied materials due to its unique and excellent properties in optics, electronics, photochemistry and biology, as well as its applications in photovoltaic cells, photocatalysis, and sensors [Lixia et al., (2010), Grimes and Mor (2009), Jiang et al., (2001), Varghese et al., (2006)]. A significant amount of research on TiO₂ has been performed over the last five decades
and a number of reviews on various aspects of TiO$_2$ have been published [Diebold (2003), Fujishima et al., (2000), Carp et al., (2004), Mor et al., (2006), Chen and Mao (2007), Thompson and Yates (2006), Linsebigler et al., (1995)] to understand and summarize the progress in this field. TiO$_2$ is a large band gap semiconductor, with band gaps of 3.2, 3.02, and 2.96 eV for the anatase, rutile and brookite phases, respectively [Wunderlich et al., (2004)]. Anatase TiO$_2$ is considered to be the active photocatalytic component based on charge carrier dynamics, chemical properties and the activity of photocatalytic degradation of organic compounds [Mital and Manoj (2011)]. In the present work, we report on the synthesis and characterization of nanocrystalline TiO$_2$ having narrow size distribution and minimal agglomeration. Besides, the prepared nano-titania was examined using various analytical techniques. We also investigate and discuss the structure and properties of the prepared TiO$_2$.

3.2. Results and Discussion

3.2.1. Phase and crystallite size analysis

Powder X-ray diffraction pattern of pure TiO$_2$ nanoparticles annealed at 450°C with miller indices (hkl) showing the crystal family of planes for each diffraction peaks were shown in Fig.3.1. From the synthesized (Fig.3.1) product, several diffraction peaks appeared and all of them could be clearly attributed to the characteristic peaks of TiO$_2$ and it can be well indexed to anatase phase (JCPDS-ICDD card: 21-1272). The intense diffraction peaks appearing at about 2θ of 25.28°, 37.81°, 47.99°, 53.95°, 55°, 62.9° and 75° corresponding with those from (101), (004), (200), (105), (211), (204) and (215) orientations, respectively.

The average crystallite size has been inferred from 2θ and the full width at half maximum (FWHM) of the (h k l) peaks using Debye–Scherrer relation,

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

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Where \( D \) is the average crystallite size in Å, \( K \) is the shape factor (0.9), \( \lambda \) is the wavelength of X-ray (1.5406 Å) CuK\( \alpha \) radiation, \( \theta \) is the Bragg angle, and \( \beta \) is the corrected line broadening of the nanoparticles [Zhang (2012)]. The result shows that the mean crystallite size of nano-TiO\(_2\) is about 15.31 nm. However, a smaller crystallite size could lead to larger surface area, which would be beneficial for increasing the photocatalytic activity of the material. Estimation of the crystallite sizes using this relation are depicted in Table 3.1.

The lattice parameters ‘\( a \)’ and ‘\( c \)’ for the tetragonal structure (\( a = b \neq c \), \( a = \beta = \gamma = 90^\circ \)) can be calculated by the following equation,

\[
S = \frac{\alpha^2 (h^2 + k^2)}{4a^2} + \frac{\alpha^2 l^2}{4c^2} \Delta
\]

Where \( h, k \) and \( l \) are the Miller indices of the peak. From the values of ‘\( a \)’ and ‘\( c \)’, the unit cell volume (\( V \)) can be determined [Chauhan et al., (2012)]. The calculated lattice parameters for anatase phase of TiO\(_2\) are \( a = b = 3.7881 \) Å, \( c = 9.5132 \) Å and \( V \) (= \( a^2c \)) = 136.51 Å\(^3\). Hence, the standard JCPDS pattern of anatase (21-1272), tetragonal, body centred, \( a = b = 3.785 \) Å, \( c = 9.513 \) Å, \( V = 136.31 \) Å\(^3\) matches well with the recorded XRD (Fig.3.1). The calculated results were shown in Table 3.2. The obtained diffraction pattern shows that only anatase TiO\(_2\) crystalline formation (neither rutile nor brookite structure was observed). The signal to noise ratio indicates that the synthesized nanoparticles are crystalline. It was reported that the anatase to rutile transformation in the annealing process does not occur at temperatures below 600°C [Khakpash et al., (2012)]. Calcination is a common treatment used to improve the crystallinity [Chauhan et al., (2012)] of TiO\(_2\) powder, however increasing the annealing temperature to 450°C resulted in the formation of anatase TiO\(_2\) with high crystallinity.
Figure 3.1: X-Ray diffractogram of pure anatase TiO$_2$ nanoparticles
Table 3.1: Calculated crystallite sizes of the bare TiO$_2$ nanoparticles
(Mean: 15.31 nm) by Debye–Scherrer method

<table>
<thead>
<tr>
<th>2θ deg</th>
<th>FWHM β</th>
<th>d-spacing Å</th>
<th>cos θ</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.28</td>
<td>0.68</td>
<td>3.52</td>
<td>0.9757</td>
<td>11.97</td>
</tr>
<tr>
<td>37.81</td>
<td>0.35</td>
<td>2.38</td>
<td>0.9460</td>
<td>23.99</td>
</tr>
<tr>
<td>47.99</td>
<td>0.6</td>
<td>1.89</td>
<td>0.9135</td>
<td>14.48</td>
</tr>
<tr>
<td>53.95</td>
<td>0.4</td>
<td>1.70</td>
<td>0.8912</td>
<td>22.28</td>
</tr>
<tr>
<td>55</td>
<td>1</td>
<td>1.67</td>
<td>0.8870</td>
<td>8.95</td>
</tr>
<tr>
<td>62.9</td>
<td>0.6</td>
<td>1.47</td>
<td>0.8530</td>
<td>15.52</td>
</tr>
<tr>
<td>75</td>
<td>1</td>
<td>1.26</td>
<td>0.7933</td>
<td>10.01</td>
</tr>
</tbody>
</table>

Table 3.2: Evaluated crystal parameters for pure TiO$_2$ nanoparticles with reference of JCPDS Card: 21-1272

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>JCPDS</td>
</tr>
<tr>
<td>Anatase</td>
<td>Tetragonal</td>
<td>a = b = 3.7881, c = 9.5132</td>
<td>136.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = b = 3.785, c = 9.513</td>
<td>JCPDS 136.31</td>
</tr>
</tbody>
</table>
3.2.2. Fourier transform infrared spectroscopy

The FTIR transmission spectrum of TiO$_2$ nanoparticles synthesized at the temperature of 450°C in air for 4h was shown in Fig.3.2. The reaction between precursor materials of TiO$_2$ resulted in the white powdered product. For clarifying whether TiO$_2$ particles have corresponding functional groups, the chemical structures of TiO$_2$ were characterized with FTIR spectroscopy. The FTIR study of TiO$_2$ nanoparticles shows the characteristics of the formation of high purity product and depicts the peaks correspond to TiO$_2$. From the FTIR spectrum, (Table 3.3) several peaks at 3391.72, 2920.55, 2849.32, 1747.95, 1627.28, 1342.47, 728.77 and 463.88 cm$^{-1}$ can be observed.

TiO$_2$ nanoparticles have significant hydroxyl groups on the surface. Moreover, small crystallites could result in the broadness of the peaks. The spectroscopic band is observed at around 3391.72 cm$^{-1}$, which is described to the both symmetric and asymmetric stretching vibrations of the hydroxyl group (Ti–OH) [Wei et al., (2008)]. A broad band observed in between 3600 and 3000 cm$^{-1}$ is related to the O–H stretching mode of hydroxyl group, indicating the presence of moisture in the sample. The characteristic peak at 1627.28 cm$^{-1}$ is associated with the O–H bending vibrations of the absorbed water molecules. Therefore, the two observed peaks at 3391.72 and 1627.28 cm$^{-1}$ correspond to the surface adsorbed water and hydroxyl groups [Kathiravan and Renganathan (2009)] and the presence of OH bands in the spectrum was owing to chemically and physically adsorbed H$_2$O on the surface of nanoparticles [Oluoro and Neelgund (2012)]. It was reported that the broad band from 1000 to 400 cm$^{-1}$ region is ascribed to the Ti–O stretching and Ti–O–Ti bridging stretching modes [Hongbin et al., (2012)]. For the pure TiO$_2$, the peaks at 463.88 and 728.77 cm$^{-1}$ in the range of 400–800 cm$^{-1}$ are the contributions from the anatase titania. A broad absorption band
between 450 and 800 cm\(^{-1}\) region is ascribed to the vibration absorption of the Ti–O–Ti linkages in TiO\(_2\) nanoparticles [Lu et al., (2008)]. According to the standard spectra of TiO\(_2\), the peak at 463.88 cm\(^{-1}\) would be attributed to the vibration of Ti–O bond in TiO\(_2\) (anatase titania) lattice, it indicates that the organic ligand was completely eliminated after annealing at 450°C. At the same time, the metal oxide TiO\(_2\) was formed by thermolysis of the powdered product [Chuan Xu et al., (2004)]. The IR absorption band at 728.77 cm\(^{-1}\) was attributed to the Ti–O–Ti stretching vibrations [Wei et al., (2008)].

The prepared product has some weak absorption bands correspond to the vibrational modes of organic species such as hydroxyl, carboxilate and alkane groups. Two weak bands at 2920.55 and 2849.32 cm\(^{-1}\) could be ascribed to the characteristic frequencies of residual organic species, which was not completely removed by ethanol and distilled water washing are assigned to C–H stretching vibrations of alkane groups. The peaks at 1340–1520 cm\(^{-1}\) region could be attributed to carboxyl (C=O) and methylene groups. The carboxyl and methylene groups might also be resulted from residual organic species [Sheng Guo et al., (2007)].

The peak at 1747.95 cm\(^{-1}\) can be associated to the asymmetric stretching mode of titanium carboxilate. The alkane and carboxilate groups come from TIOT and 2–propanol precursors used in the synthesis process. The intensity of the bands associated with the organic groups is considerably weak because the synthesized product was annealed at 450°C, indicating the elimination of organic species [Serrano et al., (2009)]. The absence of peak at 900 cm\(^{-1}\) proves the absence of peroxyo groups. The FTIR spectrum firmly suggests the presence of Ti–O bonds, OH groups and the absence of peroxyo groups in the final product [Rao and Dutta (2007)].
Figure 3.2: FTIR spectrum of anatase TiO$_2$ nanoparticles indicating relative functional groups

Table 3.3: The infrared absorption frequencies (cm$^{-1}$) and tentative vibrational assignments of pure TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Wavenumbers (cm$^{-1}$)</th>
<th>Tentative vibrational assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3391.72</td>
<td>O–H stretching</td>
</tr>
<tr>
<td>2920.55</td>
<td>C–H stretching</td>
</tr>
<tr>
<td>2849.32</td>
<td></td>
</tr>
<tr>
<td>1747.95</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1627.28</td>
<td>O–H bending</td>
</tr>
<tr>
<td>1342.47</td>
<td>Carboxyl and methylene groups</td>
</tr>
<tr>
<td>728.77</td>
<td>Ti–O–Ti stretching</td>
</tr>
<tr>
<td>463.88</td>
<td>Anatase titania</td>
</tr>
</tbody>
</table>
Hence, the experimental results of FTIR spectrum indicate that the relative functional groups are presented in TiO$_2$ nanoparticles. It is well known that the rapid condensation reactions between the large amounts of uncondensed Ti–OH, existed on the surface of the amorphous mesoporous TiO$_2$, would cause the walls of mesoporous TiO$_2$ to collapse during calcinations [Xiao et al., (2006)]. The TiO$_2$ nanoparticles prepared for the present study are of good quality and can be used for further characterizations. The infrared absorption frequencies and the corresponding vibrational assignments are represented in Table 3.3.

3.2.3. UV-VIS-DRS analysis

3.2.3.1. Determination of band gap energy

The diffuse reflectance spectrum of prepared anatase TiO$_2$ was illustrated in Fig 3.3. The TiO$_2$ material showed an intense absorption in the UV region and the absorption edge of titania can be easily discerned. Compared with bulk TiO$_2$ [Zhai and Wang (2007)], a shift of the reflectance spectrum of nano TiO$_2$ towards the lower wavelength region was observed. The band gap energy ($E_g$) of pure TiO$_2$ was obtained from the wavelength value corresponding to the intersection point of the vertical and horizontal part of the spectrum, using the equation [Zhao et al., (2010)]:

$$E_g = \frac{hc}{\lambda} \varepsilon V \quad ; \quad E_g = \frac{1240}{\lambda} \varepsilon V$$

The band gap energy corresponds to the absorption limit and can be roughly evaluated by the above relation. Whereas $E_g$ is the band gap energy (eV), $h$ is the Planck’s constant ($6.626 \times 10^{-34}$ Js), $c$ is the light velocity ($3 \times 10^8$ m/s) and $\lambda$ is the wavelength (nm).
Figure 3.3: UV-Vis-Diffuse reflectance spectrum of bare TiO$_2$ nanoparticles
The absorption edge of nano TiO$_2$ was at 345.49 nm, corresponding to a band gap of 3.5891 eV, which is usually ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d$_{x^2-y^2}$ orbitals of the Ti$^{4+}$ cations) [Ravichandran et al., (2009)], while the absorption edge of bulk TiO$_2$ was at 385 nm, corresponding to the band gap of 3.2 eV [Kathiravan and Renganathan (2009)]. It clearly shows that the calculated band gap energy of the nano TiO$_2$ is higher than that of bulk TiO$_2$. The valence band edge of TiO$_2$ is mainly determined by O 2p states, while the conduction band edge is of Ti 3d character predominantly; The Fermi level is at the top of the valence band. Therefore, the absorption edge corresponds to the electron transition from p states to d states. The increase in band gap of nano TiO$_2$ from bulk is due to the size effect [Shown et al., (2010)] of the synthesized TiO$_2$ nanoparticles ($\leq$ 25 nm). Notably, the band gap depends on the crystalline structure and the defects in the network of TiO$_2$.

3.2.3.2. Direct and indirect band gap energy

The absorption edge of the nano-TiO$_2$ was blue-shifted about $\leq$40 nm, compared with that of bulk TiO$_2$. Manifacier model is used to determine the absorption coefficient from the absorbance data [Manifacier et al., (1997)]. The fundamental absorption, which corresponds to the transmission from valence band to conduction band, is employed to determine the band gap of the material. The direct band gap energy can be estimated from a plot of $(a\nu)^2$ vs. photon energy ($\nu$) by using the relationship,

$$a\nu = A (\nu - E_g)^n$$

The optical absorbance coefficient ($a$) of a semiconductor close to the band edge can be expressed by the following equation,

$$a = A (\nu - E_g)^n/\nu$$
Where $\alpha = 4\pi k/\lambda$ (k is the absorption index or absorbance) and A depicts constant factor. The exponent n depends on the nature of the transitions; n may have values 1/2, 2, 3/2 and 3 corresponds the allowed direct and allowed indirect, forbidden direct and forbidden indirect transitions. In this case n=1/2 for the allowed direct transition. The plot of $(a\nu)^2$ vs. $\nu$ was presented in Fig.3.4. The value of band gap energy was determined by extrapolating the straight line portion of $(a\nu)^2 = 0$ axis (i.e. the zero co-efficient); as shown in Fig.3.4, which is calculated from the above equation. The intercept of the tangent to the plot will give a good approximation of the direct band gap energy of the material [Chauhan et al., (2012)] and it was calculated to be 3.5810 eV. Therefore, the band gap increases with decreasing particle size and the absorption edge is shifted to the higher energy region. Considering the blue shift of the absorption position from the bulk TiO$_2$, the absorption onset of the present material can be assigned to the direct transition of electrons in the TiO$_2$ nanocrystals [Vijayalakshmi and Rajendran (2012)].

The indirect band gap energy of TiO$_2$ nanoparticles can be estimated from plot of the square root of Kubelka–Munk function $F(R)$ vs. $\nu$. The reflectance data was converted to the absorption coefficient $F(R)$ values according to the Kubelka–Munk equation [Lin et al., (2006)],

$$F(R)_{KM} = (1 - R)^2 / 2R$$

Where $F(R)_{KM}$ is equivalent to the absorption coefficient ($a_{KM}$), which can be expressed as,

$$a_{KM}(\nu) = C_{1}(\nu - E_g)^2$$

Where $C_{1}$ is the absorption constant for indirect transition. In this case n=2 for the allowed indirect transition.
Figure 3.4: The plot for $(\alpha h\nu)^2$ vs. $h\nu$ to evaluate the direct band gap energy of nano-TiO$_2$

Figure 3.5: Kubelka–Munk plot: $(\alpha_{KM} h\nu)^{1/2}$ vs. $h\nu$ for indirect band gap energy of TiO$_2$ nanoparticles
The Fig. 3.5 shows the plot of Kubelka–Munk function (i.e., relationship of \((\alpha_{K\text{M}}h\nu)^{1/2}\) vs. \(h\nu\)) and the linear segment of the spectra is extrapolated to intersect the \(h\nu\) axis to obtain the band gap value of allowed indirect transition of the material. The nano TiO\(_2\) exhibit the indirect band gap value of 3.5806 eV. This result was consistent with the fact that the conduction band edge of nano TiO\(_2\) is about 0.38 eV more positive than that of bulk anatase. It indicates that the content of anatase in TiO\(_2\) would influence the indirect band gap value of nano TiO\(_2\). Hence, Ti atoms rearrange to an octahedral structure when converted from amorphous titania to crystalline TiO\(_2\). It is evident that TiO\(_2\) shows large optical absorbance in the UV region. Hence, the direct and indirect band gap values were larger than the value of 3.2 eV for the bulk TiO\(_2\) and validates our crystallite size result obtained from XRD (15.31 nm) analysis according to which smaller crystallite size would have larger band gap.

3.2.3.3. Determination of crystallite size (Brus model)

The particle size of the prepared TiO\(_2\) nanoparticles has been determined from the relationship between band gap shift \((\Delta E_g)\) and radius \((R)\) of nanoparticles using following expression [Kathiravan and Renganathan (2009)],

\[
\Delta E_g = \frac{\pi^2\hbar^2}{2\mu R^2} - \frac{1.6\varepsilon_0^2}{\varepsilon R} + \text{Polarization terms}
\]

where \(\hbar\) is Planck’s constant, \(R\) is the radius of the particle, \(\varepsilon\) is the dielectric constant of the semiconductor material and \(\Delta E_g\) is the band gap shift (i.e. \(\Delta E_g = E_{g(nano)} - E_{g(bulk)}\)), the calculated band gap shift for the nano-anatase TiO\(_2\) (3.58 eV) is 0.38 eV, as compared to bulk anatase (3.2 eV). This shift typically follows the Brus model or the effective mass approximation approach, which provides a quantitative interpretation of the shift in onset of absorption energy as a function of crystallite dimension and effective mass of the electrons and holes. The onset of absorbance provides insight into the band gap of the TiO\(_2\) semiconductor material, which can be significantly different.
from that of the bulk material [King et al., (2008)]. ‘μ’ is the reduced mass of the exciton, i.e., the reduced effective mass of the electron and the hole \((1/\mu=1/m_e^*+1/m_h^*)\) in the semiconductor. As the reported effective mass of the electron, \(m_e^*\) was in the range of 5–13 \(m_e\). The effective mass of the hole, \(m_h^*\) was reported to be \(-2 \ m_e\), ‘e’ is the electron charge (1.6×10^{-19} \text{ C}). The shifts in band gap were significantly affected by the reduced mass of exciton and the dielectric constant of the semiconductor (ε). The value of \(\mu = 1.63 \ m_e\) (\(m_e\) is the electron rest mass = 9.1×10^{-31} \text{ Kg}) and range between 1.43 and 1.73 \(m_e\). The dielectric constant of TiO\(_2\) anatase crystalline was reported to be between 23 and 184 [Lin et al., (2006)]. Since the optical dielectric constant of bulk titanium dioxide is very large (ε = 170), the cumbolic and polarization terms in the equation were neglected. The calculated \(\Delta E_g = 0.38 \text{ eV}\) of this blue shift compared to bulk anatase TiO\(_2\), indicated a size of TiO\(_2\) nano-crystallites was smaller than 25 nm. However, the particle size of TiO\(_2\) is calculated from both the reflectance spectrum as well as by analysis of the XRD data. The calculated crystallite size of the prepared TiO\(_2\) (Brus model) is 24.49 nm. Hence, the crystallite size evaluated from XRD (Debye-Scherrer) is around 15.31 nm, which is lower than the value obtained from Brus model; this may be due to aggregation of nanoparticles. The comparison of band gap energies by direct and indirect methods and crystallite size measurement by DRS analysis with XRD are depicted in Table 3.4.

**Table 3.4: Comparisons of band gap energies and crystallite size measurements**

<table>
<thead>
<tr>
<th>Bulk TiO(_2) [Zhai and Wang (2007)]</th>
<th>Anatase TiO(_2) nanoparticles</th>
<th>Calculated Band gap energy (eV)</th>
<th>Band gap shift (ΔE(_g))</th>
<th>Calculated Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_g=1240/\lambda)</td>
<td>Direct</td>
<td>Indirect</td>
<td>(E_g=3.2 \text{ eV})</td>
<td>3.5891</td>
</tr>
</tbody>
</table>
3.2.4. Photoluminescence spectroscopy

Information on the structural defects and the extent of charge carrier recombination was determined by PL study in order to provide rationale for the photocatalytic efficiency of the TiO$_2$ material. The photoluminescence spectrum of pure TiO$_2$ nanoparticles excited at 345 nm and the emission bands originating from the excited level was monitored in the spectral region between 350–640 nm as depicted in Fig.3.6. The wavelength corresponding to various transitions were calculated based on the Daude model [Daude et al., (1977)]. The energy of the trap level identified in this spectrum at 587 nm is attributed to Ti$^{4+}$ ions adjacent to oxygen vacancies (intra gap surface states). In addition, TiO$_2$ nanoparticles could exhibit a strong PL signal at about 431 nm (400–450 nm range), possibly mainly resulting from band edge free excitons and this surface emission is attributed to indirect transition X$_{1a}$ to Γ$_{1b}$ and linked to exciton recombination in shallow trapped surface state [Koliyat Parayil et al., (2012)]. From the emission spectrum, a band at 373 nm is attributed to the first vibronic fluorescence band (i.e. symmetry forbidden 0–0 band (I$_1$)) [Shown et al., (2010)]. The high PL intensity of bare TiO$_2$ is indicative of emissions resulting from electron hole recombination.

There were many oxygen vacancies on the surface of TiO$_2$ nanoparticles, and the size of particles (15.31 nm, from XRD) was fine so that the average distance the electrons could move freely was very short. These factors could make the oxygen vacancies very easily bind electrons to form excitons. Thus, the exciton energy level near the bottom of the conduction band could come into being, and the PL band of the excitons showed in Fig.3.6 could also occur. In general, the smaller the crystallite size, the larger the oxygen vacancy content, the higher the probability of exciton occurrence and stronger the PL signal.
Figure 3.6: Photoluminescence emission spectrum of anatase TiO$_2$ nanoparticles excited at 345 nm
As the used excited energy was lower than the band gap energy of TiO$_2$, the PL signal mainly resulted from the electron transitions related to surface defects or surface state energy level other than the electron transitions between the conduction band and valence band [Li qiang et al., (2004)]. During the process of PL, oxygen vacancies and defects could bind photoinduced electrons to form free or binding excitons so that PL signal could easily occur. However, the morphology could make impacts on the intensity of luminescence. The possible reasons are: the luminescence intensity is significantly enhanced due to the specific surface area and due to abundant local defects of the nanoparticles. Moreover, the interface effect of the nanomaterial resulted that less resonant energy could migrate to the quenching center existing at the surface of the nanoparticles, which resulted in higher luminescence intensity [Li et al., (2011)]. The PL intensity was more in case of the sintered (450°C) nanoparticles, so that the TiO$_2$ material needs to be sintered at higher temperature to remove the binders and to get the crystalline nanoparticles.

3.2.5. Morphological characterization

Nanostructural analysis using SEM supplemented by EDX were carried out for the anatase TiO$_2$ to establish the grain size, shape and confirm their chemical composition. To obtain information about morphology of the product, the synthesized powder was investigated by scanning electron microscopy. SEM observation of the nano-sized TiO$_2$ grains, large surface area, well-defined mesopores and the images were shown in Figs.3.7. From the Figs. 3.7 (a, b & c) showed the micrographs of nano-TiO$_2$ with different magnifications, confirm that the nanoparticles were grown in a very high density. From SEM micrographs, non-uniform distribution of particles was found and they consist of either some single particle or cluster of particles.
Figure 3.7: SEM images of pure TiO\(_2\) nanoparticles calcined at 450°C with different magnifications (a, b, c) and the corresponding energy dispersive X-ray analysis (d)

Figure 3.8: Particle size distribution in anatase phase of TiO\(_2\) nanoparticles
A closer examination of these figures reveals a well-defined particle-like morphology, having abundance of spherical shaped particles. The average agglomerated particle size in the range 16.25–22.36 nm with mean particle size of 18.98 nm and it could be suggested that the nanospheres obtained were homogenous. This average size value of nanoparticles was obtained for ×20,000 magnification (Fig.3.7-c). The particle size distribution is illustrated in Fig.3.8. It can be seen that the nanoparticles of TiO₂ have a well-defined shape with weak agglomeration, though the problems of agglomeration are common and expected in sol–gel synthesis. The actual size of the nanoparticles cannot be determined from the SEM images as the resolution of the SEM instrument used was limited. It was clearly seen that the surface of the pristine TiO₂ was smooth and porous in nature, which resulted from the growth of nanoparticles and each particle was approximately 18.98 nm (Fig.3.7-c) in diameter and it is near agreement with the size estimated from XRD (15.31 nm). Higher magnification of the uniform surface area of TiO₂ was shown in Fig.3.7-b and it can be estimated that TiO₂ has large specific surface area. However, it cannot be ruled out that some TiO₂ particles are too small to be observed at the resolution of the used microscope. Therefore, it is possible to assess that the pristine anatase grains have rounded shape and form sponge-like aggregates. The shape stability of TiO₂ nanoparticles is highly dependent on surface chemistry and the synthesis conditions play a key role [Caratto et al., (2012)]. However, the shape is more angular and a little more elongated in the view of higher magnifications. Energy dispersive X-ray spectroscopy (EDX) was employed here to examine the crucial information regarding the chemical composition of the titania nanoparticles as demonstrated in Fig.3.7-d. The EDX analysis clearly showed that the elements such as Ti and O were found in the spectrum, indicating that the TiO₂ matrix has composed of titanium and oxygen only.
The strong X-ray peaks associated with Ti Kα and O Kα in the EDX spectrum (Fig. 3.7-d), from that we noticed that the atomic and weight percentages of the elements Ti and O are 39.59 at.%, 66.24 wt.% and 60.41 at.%, 33.76 wt.% respectively.

3.3. Conclusions

The nanocrystals of TiO₂ were successfully synthesized by Sol–gel method. The XRD results reveal that the synthesized nanocrystals were of anatase phase with crystallite size of 15.31 nm. The existence of functional groups was identified by FT-IR measurement. The optical cut off wavelength was evaluated from UV-VIS-DRS analysis and the band gap energy was found to be 3.58 eV. The PL analysis shows the existence of both UV and visible emissions. This large band gap value and potential luminescence properties make TiO₂ as a suitable material for its usage in semiconductor and optoelectronic devices. The morphological analysis of pure TiO₂ nanostructures indicates that the mesoporous spherical shaped with non-uniform distribution of particles. The elemental identification was performed by EDX analysis and it represents the TiO₂ has relative atomic and weight percentages of titanium and oxygen.