CHAPTER 3

RESULTS AND DISCUSSION

This chapter deals with the results obtained from the experimental methods as discussed in Chapter 2.2 and Chapter 2.3. The obtained results were used to explore the particle size, morphology, optical, structure and textural properties of Titanate Nano Tubes (TNTs), Titanate Nano Ribbons (TNRs) and mesoporous TiO₂/CNT nanocomposites. Evaluation of the physico-chemical properties of the above-said were correlated with the photocatalytic degradation of Rhodamine-B and Methyl orange dye.

3.1 TITANATE NANOTUBES (TNTs) AND NANORIBBONS (TNRs)

3.1.1 Morphology of Nanotube and Nanoribbon

Figure 3.1 shows the SEM images of nanotubes, nanoribbons and commercial TiO₂. Figure 3.1(a) and (b) shows the morphology of the samples synthesized at 100°C for 24 h and 72 h respectively. Sample (a) was anomalistic since titania nanoparticles are partially transformed into tubular morphology this is in good agreement with XRD and Raman analysis. Increasing the hydrothermal time to 72 h, led the formation (sample (b)) of nanotubes. Figure 3.1(c) and (d) showed that the nanotubular images synthesized at 150°C for 24 h and 72 h respectively. In which sample (d) demonstrated well developed and high yield of nanotubes due to increasing the hydrothermal temperature. Peng et al (2009) studied the similar effect and obtained anomalistic morphology of the product by treating the sample at
180°C for 12 h and one dimension structures after 24 h hydrothermal treatment duration. Figure 3.2(e) and (f) showed the formation of nanoribbon like morphology synthesized at 200°C for 12 h and 72 h respectively. At longer reaction time, dense nanoribbons are formed with wider widths and

![Images of SEM images of as-synthesized TNTs](image)

**Figure 3.1 SEM images of as-synthesized TNTs** (a) 100°C/24h (b) 100°C/72h (c) 150°C/24h and (d) 150°C/72h.

lengths. These different morphologies imply that the hydrothermal reaction temperature and time acts as a significant role in the formation of nanotubes and nanoribbons. It can be evidenced from Jiang *et al* (2012), who reported the treatment duration has a strong effect on the change in product morphology from hollow nanotubes into nanoribbons. Since the nanotubes does not retain their morphology in the strong alkaline solution for extended period of time, at longer treatment duration of 72 h yielded bundles of very
long and wide nanoribbons having lengths of several tens of micrometers. It is clear from these results that the hydrothermal treatment duration and treatment temperature has a strong effect on the morphological features of the resulting products (Figure 3.2f).

The more detailed microstructure of the TNTs can be seen from the TEM images of the sample (a) as in Figure 3.3 shows the hollow open ended nanotubes with almost uniform inner diameter around 4 nm and outer diameter around 8–9 nm, and the length ranging from several tens to several hundreds of nanometers. These results were in good agreement with the
previous studies (Xiong et al 2010). In addition to nanotubes, some other flat sheets (marked as circles) and rolled-up sheets were also found in the sample (a), revealed that the partial transformation of precursor. Further, the layered nanosheets coexisting with some partially developed nanotubes are observed at 100°C, which confirms that the 1D nanostructures are formed from the intermediate layered nanosheets. The nanotubes are adhered among themselves forming a bunch of nanotubes and oriented in a particular direction. The bunching of adjacent parallel nanotubes into larger bundles can be explained by the oriented attachment (OA) theory (Zhang et al 2006).
According to the OA theory, when structurally similar surfaces approach, atoms of opposing surfaces may combine chemically with each other and results in nanotube bundles bunching along identical crystal faces.

HRTEM image of sample (b) exhibited well crystalline titanate nanotubes with multiple shells of 4–5 layers, and an interlayer distance was about 0.8 nm. No major difference was observed from samples (c) and (d), both illustrating the nanotubular morphology. The TEM images of TNTs prepared under different condition shows scrolls with unequal number of walls on the tube sides consisted of 3–4 layers and found no correlation of diameter of TNTs between the time and temperature of the hydrothermal treatment. Besides, a slight decrease in inner and outer diameters. Similar results were reported by Mozia et al (2010).

![Figure 3.4 TEM and HRTEM images of TNRs (e) 200°C/24h and (f) 200°C/72h.](image)

The SAED pattern of sample (c) (inset) were distinct compared with the sample (a) (inset) indicating an improvement in crystallinity. Crystalline layered structure were observed in the titanate nanoribbons (as
shown in Figure 3.4 sample (e) and (f) when increase the hydrothermal temperature. In both the samples long and wide width nanoribbons ranging from 10-400 nm were identified (Viana et al 2009a). Moreover, high yield and dense nanoribbons were observed in sample (f) compare to sample (e) due to larger reaction time. In Figure 3.4(e) (inset) illustrate a solo nanoribbon with stacked nanosheets, which may be attributed to the thicker nanosheet

Figure 3.5 TEM and HRTEM images of TNTs and TNRs after calcination. layers of the nanoribbon particles, at the longer hydrothermal reaction duration. These nanoribbons with crystalline structure, is as reflected by the selected area electron diffraction pattern shown in inset of Figure 3.4(f). The nanotubes and nanoribbons morphologies can be stable after calcinations at
400°C as shown in Figure 3.5(a), (c) and (e), and the inset pictures corresponding to the samples (b), (d) and (f). However, the structure was changed after calcination which is illustrated by the XRD analysis.

3.1.2 X-ray Diffraction Analyses and EDX

The XRD pattern of starting TiO₂ precursor and as synthesized samples washed with HCl aqueous solutions are shown in Figure 3.6. The starting TiO₂ nanoparticles are well-crystallized anatase with minor rutile titania phase. These nanoparticles are spherical in shape (see Figure 3.2TiO₂). At higher reaction temperature in the samples (e) and (f), the intense characteristic peaks appeared at around 2θ = 11°, 27° and 48° for the titanate nanoribbon products, the characteristic peak at around 2θ = 11° indicates that the nanoribbons are composed of a layered titanates with interlayer distance.

The peak-shift from 10° to 11° means the decrease of the interlayer spacing compared with titanate nanotubes. Formation of layered titanate patterns with relative intensities and position of the first peak (interlayer distance) dependent on the degree of proton exchange. The general chemical formula for obtained layered titanate nanotubes and nanoribbons described as NaₓH₂₋ₓTi₃O₇·nH₂O (Sun & Li 2003; Morgado et al 2006; Morgado et al 2007a). these residual Na⁺ ions in the TNTs and TNRs was confirmed by Raman peaks (Figure 11, peak at 707 cm⁻¹ and Figure 12, peak at 196 cm⁻¹). It was evident that the amount of chemically bound water, intercalated between layers, was proportional to the existing sodium in this layered structure. Also,
Na⁺ may not be completely ion-exchanged by H⁺ during acid washing, prepared TNTs and TNRs exhibited existence of water in the samples; these findings can be confirmed by FT-IR spectroscopy. Consequently, sharp peaks were observed at higher reaction time as in sample (f), which implied the well crystalline formation of nanoribbons (Peng et al 2009).

In the connection of crystalline formation, Poudel et al (2005) reported that the crystallinity of nanotubes was slightly better using anatase TiO₂ phase as precursor. On the other hand, Papa et al (2009) showed that nanotubes were obtained regardless of the size and structure of the precursor or the starting materials. Moreover EDX measurements of the TNTs and TNRs indicating the presence of sodium as an layered cation containing
Figure 3.7 EDX Spectra of selective samples (b) 100°C/72h (d) 150°C/72h and (f) 200°C/72h.
water(n), even after acid washing. Presence of Na+ for the tube like samples (b), (d) and ribbon like sample (f) are 4.79 wt%, 2.17 wt% and 3.24 wt% respectively (Table 3.1), and the corresponding precursor components spectra are presented in Figure 3.7.

Interestingly, Figure 3.8 shows the XRD pattern of samples after calcined at 400°C for 2 h, the intensity of diffraction peak around at $2\theta = 10^\circ$ for titanate nanotubes is not present in the calcined samples (a), (b), (c) and (d), instead the anatase peak at ca. 25° appeared, indicating titanates decomposes into anatase TiO₂ by calcinations (Morgado et al 2007b; Wang et al 2012). In contrast, Zhang et al (2004) confirmed that the nanotube morphology and crystalline form remain unchanged at annealing temperature ($T) \leq 500^\circ$C except all shift in peak, related to dehydration of interlayered
OH groups. Notably, for the nanoribbons samples (e) and (f) can be indexed to metastable form of titanium dioxide, TiO$_2$ (B) (Sasaki et al 1992; Armstrong et al 2004). Consequently, both samples exhibited a layered structure with such lower interlayer distance (2 ≈14°) due to dehydration. Of course, titania exists in a large number of crystalline polymorphs. Its phase diagram contains anatase, brookite, rutile, TiO$_2$(B), TiO$_2$(H) and TiO$_2$(R) at ambient pressure and many other high pressure forms. Some of the titania polymorphs can be modeled as edge- and corner-linked structures with Ti cations coordinated octahedrally by oxygen anions. In particular, our prepared samples after post treatment has anatase and TiO$_2$ (B) contain chains of edge-sharing octahedra in one orientation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample (b)</th>
<th>Sample (d)</th>
<th>Sample (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>52.29</td>
<td>53.53</td>
<td>49.91</td>
</tr>
<tr>
<td>Na K</td>
<td>04.79</td>
<td>02.17</td>
<td>03.24</td>
</tr>
<tr>
<td>Ti K</td>
<td>42.92</td>
<td>44.30</td>
<td>46.86</td>
</tr>
</tbody>
</table>

3.1.3 X-ray Photoelectron Spectroscopy Analyses

The XPS study was performed in order to infer the chemical composition and electronic state of the precursor. In general, XPS has rarely been used in the examination of titania nanotubes, though it has been used to examine other titania nanostructures, especially for metal-doped and composites (Ruan et al 2005; Hwang et al 2003). Typical XPS survey
patterns for the samples (a), (c) and (e) are shown in Figure 3.9, all the standard photoelectron lines of titanate Ti 3p, Ti 3s, Ti 2p, Ti 2s and O 1s, are presented. It can be seen that, the nanotube samples are predominately titanium and oxygen, with trace of sodium due to solvent incorporation in hydrothermal process.

Figure 3.10, is the high resolution spectra of Ti 2p with Na 1s (inset), it was found that the two characteristic peaks of Ti 2p\textsubscript{1/2} was at ~467.05 eV and Ti 2p\textsubscript{3/2} was at ~461.34 eV, are attribute to the spin–orbit splitting of the Ti 2p components, with a peak separation of 5.71 eV, which are in good agreement with the titanium (IV) species (Huang et al 2007; Erdem et al 2001). The peaks are asymmetric indicating the presence of lower valent Ti ions. Meanwhile, Seo et al (2008) investigated XPS spectra corresponding to ion-exchanged and annealed titanate film. The peak
positions of the samples were standard photoelectron lines of titanate Ti 3p, Ti 2p, Ti 2s, O 1s and Na 1s are obtained. The sample after annealing treatment at 600°C, exhibited little increase in intensity of Na 1s peak than the ion-exchanged titanate, indicates exposure of intercalated sodium in the titanate as a result of deterioration of the tubular structure.

![Figure 3.10 High resolution XPS spectra of Ti 2p and Na 1s (inset).](image)

The peak located at 38.5 eV and 64 eV are assigned to Ti 3p and Ti 3s respectively as in Figure 3.9, meaning that the influence of Ti ions. The presences of O 1s core level XPS spectra of samples are located at 531.39 eV. Moreover, Zhang et al (2013) revealed that apart from main peak at 529.9 eV of O 1s, the shoulder peak at 531.5 eV corresponds to the oxygen vacancy – Ti$^{3+}$, surface state, ascribed to lattice oxygen in titanate (Gopel et al 1984). Similar results were observed by Zhu group (Zhu et al 2007), reports that to get reliable data, the O 1s signal modeled with two Pseudo-Voigt functions. After modeling the O 1s signal shows two contributions at 530.1 eV and 532.3 eV could be attributed to lattice oxygen in TiO$_2$, and to
OH groups respectively. Further, observation of sample (e) (inset of Figure 3.10), the peak located at around 1072.6 eV, is correlated to Na 1s, present in the as-synthesized titanate, this result was supporting with EDX observations (Martin et al 1978).

3.1.4 Vibrational Spectroscopy Analyses

Figure 3.11 shows the Raman spectra of raw material TiO₂ and synthesized nanotubes. Anatase active modes at 145, 198, 398, 517 and 641 cm⁻¹ were observed for TiO₂. The sample (a) suggesting the mixture of anatase and nanotubular titanates were present (Qian et al 2005), since both TiO₂ and TNTs peaks were observed. This was not entirely a TiO₂ phase, because the transformation of TiO₂ nanostructure is not completely converted into TNTs phase. This is in good agreement with XRD analysis where both the phases were present (see Figure 3.6(a)). The major peaks were observed at 278, 448 and 707 cm⁻¹ for the sample (b), these peaks are identical to titanate nanotube phase. This is confirmed with reported article which exhibited broad bands at 145, 195, 280, 450, 640, 700 and 920 cm⁻¹ for nanotubes and evidently, Raman bands at 280, 448, 668 and 917 cm⁻¹ for titanate nanotubes (Jacome et al 2007). Our samples showed nearly corresponding vibrating bands of TNT except the peak at 917 cm⁻¹ related to Ti-O-Na vibrations in the interlayer regions of the nanotube walls (Peng et al 2010) and the peak at 668 cm⁻¹ is shifted to 707 cm⁻¹. The disappearance of 917 cm⁻¹ vibrating band is due to less content of Na⁺ ions in nanotubes, which is associated with exchange of Na⁺ ions to H⁺ ions by acid washing procedure. Evidently, sample (b) contains 4.7 wt % of Na⁺ ions detected by EDX measurement. Therefore, when the reaction time increased with the same temperature, the intensity of the peak at 278 and 448 cm⁻¹ raised. These peaks correspond to Ti-O and Ti-O-Ti vibrating modes of
titanates respectively (Mozia et al 2010). Remarkably, these results revealed that the transformation of anatase TiO$_2$ to titanate phase begins at 100°C/24h. Figure 3.12 shows the Raman spectrum collected from the samples (c), (d), (e) and (f). The three main characteristic peaks at 278, 448 and 686 cm$^{-1}$ were observed for the samples (c) and (d) synthesized at 150°C/24h and 150°C/72h respectively. In which, no major difference obtained between two spectrums. Obviously, this set of spectrum was similar to the peaks obtained in sample (b) for titanate nanotube.

Viana et al (2009b) reported that Raman spectrum of titanate nanoribbon produced better atomic ordering in the layers due to their layer size and less distortion of the layers compared with titanate nanotube, also better crystallinity because of more vibrational peaks. Indeed, in our case the peaks at 152, 196, 276, 385, 437 and 682 cm$^{-1}$ observed for the sample (e), synthesized at 200°C/24h and peaks at 162, 196, 276, 376, 430, 465 and
684 cm$^{-1}$ observed for the sample (f), synthesized at 200°C/72h, the peaks are nearly consistent for both obtained spectrums. Peaks at 152 and 162 cm$^{-1}$

![Figure 3.12 Raman spectra of TNTs (c) 150°C/24h (d) 150°C/72h and TNRs (e) 200°C/24h (f) 200°C/72h.](image)

...corresponding to $E_g$ phonon mode of anatase, is shifted compared to that in TiO$_2$ spectrum by 7–10 cm$^{-1}$. The peak at 196 cm$^{-1}$ assigned to Na-O-Ti modes. The spike at 276 cm$^{-1}$ is correspond to Ti-O bonds in sodium titanate with layer structure and the bands at 682 and 684 cm$^{-1}$ for the samples treated for 24 h and 72 h respectively were assigned to a Ti-O-Ti vibration (Hodos et al 2004; Kolenko et al 2006; Kukovecz et al 2005). However, the significant peak identified by Bavykin et al (2006) at 917 cm$^{-1}$ assigned to Ti-O-Na vibrations was not clearly detected in our samples. When the reaction time increases the vibrational mode of 437 cm$^{-1}$ split into 430 and 465 cm$^{-1}$ cause, high crystallinity which are assigned to Ti-O-Ti vibration. Thus, obtained nanoribbons might be of layered titanate structure (Ma et al 2005) origin similar to nanotubular structure.
On the basis of group theory predictions, FT-IR spectra characterized the titanate nanotube, nanoribbon and demonstrated the existence of large amount of water and hydroxy groups. In Figure 3.13, the broad peak at 3405 cm\(^{-1}\) corresponded to stretching vibrations of O-H group of physisorbed water and the peak at 1627 cm\(^{-1}\) might be associated to the bending vibration of H-O-H group on the TNTs and TNRs (Sun & Li 2003). The peak at about 491 cm\(^{-1}\) can be assigned as bending modes of TiO\(_6\) octahedra (Wang et al 2008; Viana et al 2011a). Notably, the presence of water in the titanate nanotubes was higher compared with nanoribbons because of considerably enhanced specific surface area and pore volumes with reference to the BET results (Peng et al 2010). Qamar et al (2006) evaluated that the presence of the interlayer water decreases the covalent character of the O-H bond, and consequently the Bronsted acidity increases, resulting in high ion-exchange capacity of the layered structure and easy acid catalyzed condensation of OH groups during the heat treatment. However, the
spectral characteristics of TNTs and TNRs synthesized at different hydrothermal temperature and time were coinciding with similar peaks, suggesting the structure morphologies are coexist such as all samples are titanate structure. This result is in good agreement with a morphological phase diagram of titanate nanostructures derived from alkaline hydrothermal method (Viana et al 2011b).

3.1.5 \( \text{N}_2 \) Adsorption-Desorption Isotherm Study

The nitrogen adsorption-desorption isotherms of TNTs and TNRs synthesized under different conditions are presented in Figure 3.14. All the TNTs and TNRs showed the type IV isotherms with type H3 hysteresis loop according to IUPAC classifications (Sing et al 1985), suggesting the presence of mesopores (2–50 nm). Further, the observed hysteresis loop approaches \( P/P_0=1 \), indicating the presence of macropores (>50 nm) (Bavykin et al 2004) presumed that TNTs are multiwall scrolls through the formation mechanism of sheet folding or wrapping, which is believed to be, exhibited the H3 loop and non-rigid aggregates of plate-like particles giving rise to slit-shaped pores formation. Textural parameters derived from isotherm data are summarized in Table 3.2. The significant increase in the specific surface area and pore volume were observed from starting TiO\(_2\) to titanate nanotube, when the hydrothermal temperature and time increased such as \( S_{\text{BET}} \) from 27 to 247 m\(^2\)/g and pore volume 0.16 to 1.0 cm\(^3\)/g. A similar result has been evidenced by Mozia et al (2010). Indeed, the titanate nanoribbons could not possess mesopores however; obtained values of mesopores and pore volume can be attributed to the formation of aggregates (Yu et al 2006b). The BET specific surface area was determined by multipoint BET method using adsorption data in the relative pressure \( (P/P_0) \) range of 0.05–0.3 and the pore volume, average pore diameter were determined by BJH (Barrett-Joyner-Halenda) method and presented in the Table 3.2. It can be seen that the average
Figure 3.14 N₂ adsorption-desorption isotherms of TNTs and TNRs synthesized under different conditions (a) 100°C/24h (b) 100°C/72h (c) 150°C/24h (d) 150°C/72h and TNRs (e) 200°C/24h (f) 200°C/72h.

inner diameter of TNTs revealed by TEM measurements was around 4 nm, whereas the average pore diameter obtained by N₂ adsorption method at the relative pressure 0.99 was overestimates. This is because of pores between the tubes are usually bigger than the inner diameter (Peng et al 2010), so that these pores cause to made agglomeration into nanotube bundles.

Figure 3.15 shows the pore size distribution plot of as synthesized TNTs and TNRs determined by BJH method from desorption isotherm data. It would be reasonable to think that the hysteresis loops can be attributed to the total contribution of both intra-particle pores and inter-particle pores. BJH desorption isotherm show a bimodal pore size distributions consist of smaller (3–4 nm) intra-particle pores and larger (6–11 nm) inter-particle pores. The intra-particle pore size is in range of 3–4 nm with mean pore diameter
distribution at 3.5 nm, as was observed from HRTEM (see Figure 3.3d). The peak within the narrow region (3–4 nm) attributed to the inner diameter of TNTs, while the broad region of diameter from 11 nm to 100 nm is ascribed to the voids generated from the aggregation of nanotubes (Morgado et al 2007a). The samples (e), (f) and TiO$_2$ exhibited disappearance of bell shape peaks, which strongly prove the absence of porous structure for those samples (Nguyen-Phan et al 2010). After annealed at 400°C for 2 h, the specific

![Figure 3.15 Pore size distribution (BJH) curves of TNTs and TNRs synthesized under different conditions.](image)

surface area was decreased. Obviously around 98 to 111 m$^2$/g for all the nanotubes prepared under different conditions, indicates the disappearance of some large pores in the nanotubes. A similar result was also demonstrated by Yu et al (2006a) and they further observed higher pore volume due to aggregation of TiO$_2$ particles with small size, after hydrothermal post treatment at 150°C for 24 h, this formation of pores by the dehydration of the titanate layers (Yu et al 2006b). Despite, Lee et al (2007) showed that the
pore size distribution strongly depend on hydrothermal post treatment. Moreover, the result of the present work could not find remarkable changes in the specific surface area of nanoribbons.

Table 3.2 Textural parameters of TNTs and TNRs from isotherms

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Average pore size (nm)</th>
<th>Average pore size (nm)*</th>
<th>( S_{\text{BET}} ) (m(^2)/g) after post treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2) (a)</td>
<td>27</td>
<td>0.16</td>
<td>3.2</td>
<td>24.9</td>
<td>-</td>
</tr>
<tr>
<td>TiO(_2) (b)</td>
<td>177</td>
<td>0.60</td>
<td>6.8</td>
<td>12.7</td>
<td>109</td>
</tr>
<tr>
<td>TiO(_2) (c)</td>
<td>215</td>
<td>0.76</td>
<td>6.8</td>
<td>13.4</td>
<td>113</td>
</tr>
<tr>
<td>TiO(_2) (d)</td>
<td>235</td>
<td>0.82</td>
<td>8.1</td>
<td>13.9</td>
<td>93</td>
</tr>
<tr>
<td>TiO(_2) (e)</td>
<td>247</td>
<td>1.00</td>
<td>9.9</td>
<td>16.2</td>
<td>102</td>
</tr>
<tr>
<td>TiO(_2) (f)</td>
<td>28</td>
<td>0.06</td>
<td>3.5</td>
<td>8.9</td>
<td>29</td>
</tr>
<tr>
<td>TiO(_2) (g)</td>
<td>33</td>
<td>0.17</td>
<td>3.2</td>
<td>21.3</td>
<td>26</td>
</tr>
</tbody>
</table>

* determined at \( P/P_0 = 0.99 \)

3.1.6 UV/Vis Diffuse Reflectance Spectroscopy

In Figure 3.16 all the samples showed obvious absorbing band-edge, which means that the samples have semiconductor characteristics. The absorption spectrum of commercial TiO\(_2\), as synthesized TNTs and TNRs consists of a single broad absorption at ca. 366–381 nm due to the charge-transfer from the valence band to conduction band. The band gap energy (\( E_g \)) values were calculated from the relation \( E_g = 1240/\lambda \) (Gratzel 1988; Li et al 2011). For that the absorption edge and band gap energy of TiO\(_2\) were 380 nm and 3.26 eV respectively, this is consistent with the literature results (Peng et al 2010). The band gap of TNTs and TNRs prepared under various conditions were calculated to be 3.24 eV (382 nm), 3.34 eV (371 nm), 3.22 eV (385 nm), 3.38 eV (366 nm), 3.56 eV (348 nm) and 3.65 eV (340 nm) for the samples (a), (b), (c), (d), (e) and (f) respectively. It has been observed that the \( E_g \) of TNRs slightly higher than that TNTs. Yu and Yu (2006) reported that the \( E_g \) of TNTs lies between 3.03 to 3.15 eV with respect to hydrothermal treatment
time, such low values were associates with high rutile content in the prepared samples. Interestingly, Yu et al (2006b) estimated to be 3.08 eV prior to

![Absorbance vs Wavelength](image)

Figure 3.16 Solid diffuse reflection UV-Vis spectra of TiO₂, (a) 100°C/24h (b) 100°C/72h (c) 150°C/24h (d) 150°C/72h (e) 200°C/24h and (f) 200°C/72h.

hydrothermal post-treatment of TNRs and lowest value of 2.93 eV was obtained after post-treatment due to the partial phase transition of TNRs. Moreover, Liu group (Liu et al 2011) attributed, the absorbing of wide range of visible light with lower reflectance intensity by co-doping Gd/TNT and N/TNT, indicates the survival of rare earth elements. Thus, the different band gap energies can be attributed to the difference in the hydrothermal temperature and time and, surface microstructure of the TNTs and TNRs.
3.1.7 Evaluation of Photocatalytic Activity

The photocatalytic activities of different samples are evaluated with the degradation of well known pollutant rhodamine B and methyl orange aqueous solution under UV-light irradiation, and starting TiO$_2$ nanoparticles were used under the same reaction conditions for comparison. Degradation reaction can be monitored by UV-visible spectroscopy and the selective results are shown in Figure 3.18 after hydrothermal post-treatment. Before irradiation the system was kept in the dark for reaching an adsorption-desorption equilibrium state. When the reaction system was irradiated by the light, the absorption of rhodamine B decreased gradually and irradiation time were recorded from the absorbance measured at $\lambda=553$ nm for rhodamine B and 465 nm for methyl orange. The colour of the dispersion disappeared after the reaction, indicating that the chromogenic aromatic structure of the dye was destroyed (Xie et al 2009). No appreciable photodegradation can be observed prior to calcination of as-prepared TNTs and TNRs samples (Yu et al 2006b; Kiatkittipong et al 2013) as depicted in Figure 3.19. After calcined
the samples at 400°C for 2 h, the efficiency of photodegradation for nanotubes and nanoribbons were observed due to the formation of photoactive crystalline phase during calcination, this is confirmed by our XRD patterns. Subsequently the specific surface area was reduced around 105 m²/g for TNTs and very less variation in TNRs after calcination. The photodegradation of rhodamine B aqueous solution in the presence of nanotubes and nanoribbons with different specific surface area is illustrated in Figure 3.20. The reaction rate of as synthesized nanotubes significantly higher (76–93%) than the
nanoribbons (60–66%) subsequently, the reaction rate of both nanotubes and nanoribbons are higher compare with TiO$_2$ after 5 h irradiation. Degradation efficiency reached 93.2%, 89.5%, 87.3%, 76.1%, 66.7% and 60.5% rhodamine B for 150°C/24h, 150°C/72h, 100°C/72h, 100°C/24h, 200°C/72h, and 200°C/24h respectively. Figure 3.21 shows the degradation efficiency of methyl orange, after calcinations. The efficiency of degradation of methyl orange aqueous solution shows 60.5%, 39.4%, 36.1%, 31.5%, 29.7%, and 27% for the samples (c), (d), (b), (a), (f) and (e) respectively. This dye also higher (32–61%) than the nanoribbons (27–30%) subsequently, the reaction rate of both nanotubes and nanoribbons are higher compare with TiO$_2$ after 5 h irradiation. Therefore, the enhancement of photocatalytic activity of nanotubes and nanoribbons can be ascribed to the presence of anatase phase.

It is noted that the large surface area allows better contact between organic molecules and TNTs and TNRs surfaces what might be responsible
for better activity of 150°C/24h than the others. Since the particle size of the sample is very small, the surface area is large, so that the reactive sites formed on the surface of the catalyst are adequate to absorb the organic pollutants. From these, obviously high specific surface area is the dominating factor.

Figure 3.20 Degradation efficiency of rhodamine B, after post-treatment.

Figure 3.21 Degradation efficiency of Methyl Orange, after post-treatment.
(Lee et al 2007) in the determination of photocatalytic activity. However, recombination of photogenerated electron-hole pair is one of the significant factors that deteriorate the photoactivity (Qamar et al 2009).

Low-dimensional nanostructured materials have attracted considerable attention recently due to their unique physical properties and their potential applications. Dimensionality is a crucial factor in determining the properties of nanomaterials and, thus, the control of size and shape is of great interest. In contrast to size control, shape control of particulates is a more difficult and challenging topic. The tubes, flakes or fibers with the size range in the nanometer region are expected to possess novel properties. Many efforts are being devoted to develop new methods for synthesizing one-dimensional nanomaterials such as nanowires and nanotubes. Activity of some TiO$_2$ nanoparticles with different shapes and some nanocomposites are accounted towards the degradation of rhodamine B aqueous solution as shown in Table 3.3.

Organic dyes are generally present in the industrial wastewaters, which cannot be readily degraded, resulting in potentially environmental problems. Rhodamine B (RhB) and methyl orange (MO) are the two most used dyes with different molecular structures and functional groups. Due to their good stabilities and special color characteristics, RhB and MO are widely used in the printing, textile, and photographic industries. In this study, TiO$_2$ nanotubes and TiO$_2$(B) nanoribbons, were synthesized by the hydrothermal method. Photocatalytic activity of as-prepared nanomaterials was evaluated by degrading RhB and MO in aqueous suspensions under UV-light irradiation at room temperature. Both calcined catalysts exhibited remarkable photocatalytic activities in RhB and MO decomposition. Due to their specific properties, these products have taken advantage over commercial TiO$_2$ on the photocatalytic activities. Based on the remarkable
<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Method of Preparation</th>
<th>Photocatalytic Measurements</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase TiO₂</td>
<td>Low &amp; high temperature heating process</td>
<td>Rutile &gt; anatase TiO₂, Brookite &lt; anatase &amp; rutile TiO₂</td>
<td>Jing et al (2011)</td>
</tr>
<tr>
<td>Rutile TiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brookite TiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ thin film</td>
<td>Sol-gel</td>
<td>Much higher than Degussa P-25</td>
<td>Ma &amp; Yao (1998)</td>
</tr>
<tr>
<td>TiO₂ nanotubes</td>
<td>Hydrothermal</td>
<td>% of removal is higher than P-25</td>
<td>Guo et al (2011)</td>
</tr>
<tr>
<td>TiO₂ nanowires</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ coated non-woven paper</td>
<td>Commercially received</td>
<td>High degradation rate</td>
<td>Barks et al (2008)</td>
</tr>
<tr>
<td>Ti/TiO₂ mesh</td>
<td>Anodizing</td>
<td>Excellent adsorption</td>
<td>Li et al (2002)</td>
</tr>
<tr>
<td>TiO₂ nanotubes, TiO₂(B) nanoribbons</td>
<td>Hydrothermal</td>
<td>Higher than commercial TiO₂</td>
<td>Present thesis work</td>
</tr>
<tr>
<td>Some composites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂/SBA-16</td>
<td>Hydrothermal</td>
<td>Much higher than pure TiO₂</td>
<td>Ma et al (2010)</td>
</tr>
<tr>
<td>Carbon/TiO₂ nanotubes</td>
<td>Electrospinning</td>
<td>Fast adsorption with high capacity than P-25</td>
<td>Im et al (2012)</td>
</tr>
<tr>
<td>Mesoporous TiO₂/CNT</td>
<td>EISA</td>
<td>Higher than mesoporous TiO₂</td>
<td>Present thesis work</td>
</tr>
</tbody>
</table>
photocatalytic performance, these nanostructures could act as the promising materials in the field of photocatalysis and environmental remediation.

It is also shown that TiO$_2$ nanotubes have higher photocatalytic activity than TiO$_2$(B) nanoribbons. The morphology and surface area of the photocatalysts greatly influence the photocatalytic activity. The tubular structure promotes the diffusion of reactants and products, enhancing the photocatalytic activity by facilitating access to the reactive sites on the surface of the photocatalysts. Meanwhile, the tube-like structure can help rapid mass transfer of the adsorbed molecules from bulk solution onto the catalyst surface, causing the photocatalytic process to be accelerated. In addition, TiO$_2$ nanotubes have a large surface area and open mesoporous morphology, which provide an extremely high adsorption capacity. This is beneficial to the collection of organic pollutant molecules like those of RhB and MO. The strong adsorption of organic contaminants would contribute to high photodegradation efficiency. The similar photocatalytic procedure was followed for mesoporous TiO$_2$/CNT nanocomposites prepared by EISA method, for the degradation of Rhodamine B aqueous solution (Chapter 3.2.6). Observation shows that the addition of appropriate amount of CNTs can greatly improve the photocatalytic activity of mesoporous TiO$_2$.

**Mechanism:** The mechanism of the photo-degradation of pollutants is based on the absorption of the UV light with greater photonic energy than the band gap; semiconductors can generate electron-hole pairs, which initiate simultaneously oxidative and reductive reactions with surface species before recombination. Thereby the so-called semiconductors-mediated heterogeneous photocatalysis has received considerable attention. TiO$_2$ has been demonstrated as one of the most preferable semiconductors for photocatalysis due to its adequate band gap and position, high quantum efficiency, nontoxicity, low cost, and long-term stability. This heterogeneous
photocatalysis for environmental cleanup has been one of the most active areas, which considered being a green approach without creating harmful by-products (Pelaez et al 2012). Evidently, Zhang et al (2010) employed the high crystalline mesoporous TiO₂ synthesized via the surfactant sulfuric acid carbonization method for the degradation of rhodamine B (RhB) under UV light irradiation. Higher photocatalytic activities are achieved than that from the commercial P25, which can be attributed to the higher surface area of the ordered mesoporous TiO₂.

The photocatalytic properties of TiO₂ are derived from the formation of photogenerated charge carriers (hole and electron) which occurs upon the absorption of ultraviolet (UV) light corresponding to the band gap (Fujishima et al 2008). The absorption leads to a charge separation due to promotion of an electron (e⁻) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h⁺) in the valence

\[ TiO_2 + hν \rightarrow h^+ + e^- \]  \hspace{1cm} (3.1)

band. Charge carriers can be trapped as Ti³⁺ and O⁻ defect sites in the TiO₂ lattice, or they can recombine, dissipating energy (Tachikawa et al 2007). Alternatively, the charge carrier can migrate to the catalyst surface and initiate redox reactions with adsorbates (Cozzoli et al 2003). However, the ultimate goal of the process is to have a reaction between the generated holes with a reductant to produce an oxidized product and also a reaction between the activated electrons with an oxidant to produce a reduced product.

Oxidation

\[ TiO_2 + H_{(_{\text{vb}})}^+ + H_2O \rightarrow TiO_2 + H^+ + OH^* \]  \hspace{1cm} (3.2)
\[ TiO_2 + h_{(\gamma_b)}^+ + OH^- \rightarrow TiO_2 + OH^* \]  \hspace{1cm} (3.3)

Reduction

Molecular oxygen acts as an acceptor species in the electron transfer reaction

\[ TiO_2 + e_{(c_b)}^- + O_2 \rightarrow TiO_2 + O_2^- \]  \hspace{1cm} (3.4)

Superoxide anions can subsequently be involved in the following reactions

\[ O_2^-* + H^+ \rightarrow H_2O_2^* \]  \hspace{1cm} (3.5)

\[ H^+ + O_2^- + H_2O_2^* \rightarrow H_2O_2 + O_2 \]  \hspace{1cm} (3.6)

\[ H_2O_2 + h\nu \rightarrow 2OH^* \]  \hspace{1cm} (3.7)

The OH* free radicals are very reactive and attack the pollutant molecule

\[ \text{rhodamine B} + OH^* \rightarrow \text{degraded products} \]  \hspace{1cm} (3.8)

An interesting use of one dimensional (1D) titania nanostructure in photocatalytic applications is the growth of freestanding flow-through membranes. The transient studies of photogenerated charged carries in titanate and TiO_2 (B) nanotubes have revealed that the lifetime of trapped electrons is longer than that of TiO_2 nanoparticles, suggesting an improved charge separation due to the elongated morphology. Further, conventional TiO_2 photocatalysts are operated based on this principle.

3.2 MESOPOROUS TiO_2/CNT NANOCOMPOSITES

Synthesis strategies of mesoporous titania through evaporation induced self assembly (EISA) method, and preparation of mesoporous titania with carbon nanotubes composites, are described in Chapter 2.3. This section 3.2
describes the various physico-chemical properties of synthesized materials and their composite materials, further behaviour of these materials towards photo catalytic reactions are also demonstrated.

3.2.1 X-Ray Diffraction Studies of Mesoporous Titania and its CNT composites

Among the three polymorph of TiO₂ phases, i.e. anatase, rutile and brookite, only the first two have been widely studied and compared either as powders or as thin films. On the contrary, only a few recent papers dealing with the preparation of pure brookite powders or films can be found in the literature. The scarcity of results is due to various reasons among which the most relevant is the difficulty of synthesizing pure brookite because it usually forms as a secondary minority phase along with rutile and/or anatase, depending on the experimental conditions adopted.

XRD pattern of mesoporous TiO₂ prepared by EISA method is shown in Figure 3.22. The diffraction pattern exhibits peaks (JCPDS 21-1272) of

![Figure 3.22 XRD patterns of mesoporous TiO₂.](image)
anatase, rutile and brookite. Anatase is the major crystalline phase as indicated by the peaks occurring at 2θ = 25.3°, 37.0°, 44.0°, 54.3°, 62.7° associated with anatase phase (Reyes-Coronado et al 2008; Haiying et al 2011). The lower intensities of diffraction peaks located at 2θ = 27.5°, 36.1°, 41.3° associated with rutile and at 2θ = 30.5° with brookite phase (Reyes-Coronado et al 2008). As prepared sample also shows the high intensity anatase peaks which suggest that anatase is the highly crystalline phase in the sample after preparation. Strong hump at around 4° in the low-angle region indicated the presence of mesostructure. Mesostructures with more or less regular diameter channel packed at random often display a single peak in low-angle. Average size of the mesoporous TiO₂ was found to be 5.19 nm calculated using the Scherrer-Debye formula. Although, a high intensity anatase peaks suggest that well crystalline phase in the sample. Zhang & Banfield (2000) had proved that though rutile is the most stable phase for bulk materials, when a large amount of surface is present (such as for nanoparticle smaller than 14 nm), anatase is stabilized, minimizing the total free energy of the system. Moreover, the presence of interagglomerate pores can also prevent the anatase grain growth. Therefore, the stabilization of the anatase phase and mesostructure upon calcinations or reflux probably can be ascribed to the present specific synthesis conditions.

However, Figure 3.23 shows XRD patterns of the mesoporous TiO₂/CNT nanocomposites catalysts which are very similar to the pattern of mesoporous TiO₂ as in Figure 3.22. In particular, no characteristics peaks of CNTs (2θ = 26.0° and 43.4°) were found in these composites (Lee et al 2003). This may be attributed to the overlap of highest intensity peak for CNTs at 26.0° with anatase TiO₂ at 25.3°, as well as crystallinity of CNTs was much lower than that of anatase TiO₂, causing the shielding of the CNT peaks by those of mesoporous TiO₂ (Yu et al 2005a; Da Dalt et al 2013). This pattern matched with graphite pattern with a slightly shift to lower
diffraction angle due to the curvature of side walls, which causes higher distance between two adjacent (002) planes. CNTs in composite cannot be detected by XRD due to the overlapping (002) peak of CNT with (101) peak of anatase and existence of CNT in trace amount in composite. Further, the average crystallite size of the composite was ca. 4-8, 4-7, 4-7 and 4-8 nm for the samples CT20, CT40, CT60 and CT80 respectively.

3.2.2 The Morphological Studies

Figure 3.24 shows typical TEM micrograph of as-synthesized mesoporous titania, confirmed the nanoscale size range. The average size of the mesoporous TiO₂ nanoparticles (Figure 3.24a) is approximately 5–20 nm, which is consistent with crystallite size estimated from XRD analysis, indicates that there is no significant agglomeration of mesoporous TiO₂ nanoparticles. The distinguished ring patterns of selected-area electron
diffraction (SAED) in the inset of Figure 3.24b suggested that these mesoporous structures consisted of crystalline titania phases. The presence of clearly resolved lattice fringes demonstrates that the framework of the mesopores is composed of anatase nanocrystals. Thus HRTEM and XRD indicated the presence of mesopore network with a highly crystalline matrix between the mesopores. Figure 3.25(a-d) illustrates the TEM images of TiO$_2$/CNT nanocomposites for catalyst ratios 1:20, 1:40, 1:60, and 1:80 respectively. All the images revealed that the mesoporous TiO$_2$ are dispersed on the surface of CNTs, although a partial agglomeration with embedded CNTs confirming the contact between the CNTs and mesoporous TiO$_2$. Moreover, the composite micrograph showing non-uniformly covered tubular bodies with large mesoporous TiO$_2$ clusters at the ends (Gao et al 2009), as shown in Figure 3.25 a and b.

It can be considered that the better dispersion provides a larger number of active catalytic centers for the photocatalytic reaction, if TiO$_2$ particles were uniformly distributed on the whole CNTs surface. However, it can be seen that in the high resolution micrographs Figure 3.25 c and d, some
Figure 3.25 TEM images of mesoporous TiO$_2$/CNT nanocomposites for the samples a-CT20, b-CT40, c-CT60 and d-CT80.

mesoporous TiO$_2$ particles have aggregated to clusters and edges on bunch of CNTs, which resulted in the presence of a dense mesoporous TiO$_2$. There is no major deviation in specific surface area, due to coverage of mesoporous TiO$_2$ on the surface of CNT. Whereas, Song et al (2012) recently reported that
the specific surface area of the composites gradually decreased, when the catalyst ratios were increased. Additionally in Figure 3.26, EDX spectra analysis of mesoporous TiO$_2$/CNT for the composite CT20 confirms the presence of Ti, O and C elements (Ti: 40.75, O: 25.17, C: 21.20, and Cu: 12.88 wt %). Oxygen and Ti were the major elements in the composite series due to mixing ratio of composites. Also, the presence of Cu element is originated from sample grid.

3.2.3 Nitrogen Adsorption- Desorption Measurements

Figure 3.27 shows the N$_2$ adsorption-desorption isotherm of mesoporous TiO$_2$, a clear hysteresis at high relative pressure is observed, which is related to capillary condensation associated with large pore channels, indicating the presence of mesopores ascribed to type IV with H2 hysteresis-loop, suggests the embedding of large mesopores in a matrix with smaller pores (Kruk & Jaroniec 2001). The pore size distribution plot (inset Figure 3.27)
exhibits a narrow pore size centred at 6.88 nm. All the textural properties of mesoporous titania and its various CNT composites are listed in Table 3.3. Where, the specific surface area was determined by multipoint BET method using the adsorption data in the relative pressure (P/P₀) range of 0.05–0.3. And the pore volume, average pore diameter were determined by BJH (Barret-Joyner-Halenda) method.

N₂ adsorption-desorption isotherms of the composites are shown in Figure 3.28. All the samples display similar nitrogen sorption isotherms. These isotherms exhibit a Type IV adsorption/desorption shape with a H2 hysteresis loop, at high relative pressure range between 0.4 and 0.8 indicating the abundance of mesopores in samples. The composites still have mesoporous structure, although the shape of the hysteresis-loops remains unchanged by inclusion of slit like porous materials such as H3 type loop of CNTs. This may cause, the inner cavities of raw CNTs do not make an
important contribution to adsorption due to closed ends. However, inner cavities become accessible to adsorption when the nanotube tips may be broken by oxidation (Anson *et al* 2004).
Figure 3.29 shows the BJH pore-size distribution of composites, suggesting that the presence of CNTs do not make great changes in the pore size, and exhibited narrow pore-size centred at around 6.8 nm. Further, the pore size distribution of CNTs becomes broader in the range 10 to 100 nm.

3.2.4 UV/Vis Diffuse Reflectance Spectroscopy

The diffuse reflectance UV-vis spectra of different nanocomposites and the mesoporous TiO$_2$ are shown in Figure 3.30. The prepared mesoporous TiO$_2$ exhibited (inset Figure 3.30) an absorption edge with strong absorption in the UV light region below 380 nm. A unique absorption were observed for the nanocomposites and shows the lower absorption intensity of UV light than mesoporous TiO$_2$, suggests that the composites are different from the mesoporous TiO$_2$ (Song et al 2012). However, Xu et al (2010) mentioned that the method of preparation of composites is important on forming structure.

Figure 3.30 UV-Vis spectra of nanocomposite samples (inset mesoporous TiO$_2$).
and thereby affecting the photocatalytic properties significantly. Moreover, due to the interaction of mesoporous TiO$_2$ with CNTs, may lead to modify the process of e$^-$/h$^+$ formation while photocatalytic process under illumination (Sun et al. 2004). Since the CNTs did not significantly affect morphology of mesoporous TiO$_2$, this could be related to the increase in conductivity and homogeneous distribution of charge carriers in the composite containing CNTs, which reduces the interaction of charge carriers with incident photons. The band gap energy values were calculated by the formula expressed as $E_g = 1240/\lambda$, and the results are listed in Table 3.4.

### Table 3.4 Textural properties of CNT and various Titania/CNT nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$D_p$(nm)</th>
<th>$E_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso TiO$_2$</td>
<td>149</td>
<td>0.309</td>
<td>6.88</td>
<td>3.33</td>
</tr>
<tr>
<td>CNT</td>
<td>155</td>
<td>0.859</td>
<td>29.97</td>
<td>--</td>
</tr>
<tr>
<td>CT20</td>
<td>145</td>
<td>0.343</td>
<td>6.89</td>
<td>3.35</td>
</tr>
<tr>
<td>CT40</td>
<td>142</td>
<td>0.324</td>
<td>6.88</td>
<td>3.33</td>
</tr>
<tr>
<td>CT60</td>
<td>141</td>
<td>0.331</td>
<td>6.87</td>
<td>3.33</td>
</tr>
<tr>
<td>CT80</td>
<td>145</td>
<td>0.339</td>
<td>6.86</td>
<td>3.33</td>
</tr>
</tbody>
</table>

#### 3.2.5 Effect of Photoluminescence

Photoluminescence (PL) analysis is a tool in the characterization of surface and interfaces, involving the electron–hole pair of semiconductor particles (Yu et al. 2003; Fujihara et al. 2000). Figure 3.31 shows the PL spectra of mesoporous TiO$_2$ and nanocomposites at excitation wavelength of 297 and 300 nm respectively. These excitation wavelengths have been chosen since, it is close to the maximum absorption spectra for mesoporous TiO$_2$ and nanocomposites (see Figure 3.30). Gfroerer et al (2000) reported that photoluminescence excitation (PLE) and optical intensity is quite important to
study different regions and recombination mechanisms near interface, since absorption of incident light depends on the excitation energy, and determines the depth of the PL probe.

Titania has two main emissions at around 400 and 580 nm due to the band gap transition and conversion of Ti$^{4+}$ to Ti$^{3+}$ in surface states, respectively. Here, the green emission is strong and participated in charge transfer mechanisms. In order to examine the effect of CNTs on the recombination of electron-hole produced by mesoporous TiO$_2$, the PL spectra are detected for the different photocatalysts. Mesoporous TiO$_2$ and nanocomposites shows PL emission band corresponding to the peak position of about 603 nm. A small peak shifts are caused by the trapping of electrons at defect sites prior to recombination (Fujihara et al 2000). The composites mesoporous TiO$_2$/CNT shows significantly diminished PL intensity as compared to mesoporous TiO$_2$, indicating that the electron-hole

![Figure 3.31 The Photoluminescence (PL) spectra of mesoporous TiO$_2$ and nanocomposite catalysts.](image)
recombination rate of self-trapped excitations in mesoporous TiO$_2$ is reduced by the introduction of CNTs (Yu et al 2005b; So et al 2002). Therefore, it has been confirmed that, $e^-$ transfer happens in the mixture of mesoporous TiO$_2$ and CNT.

3.2.6 Performance of Photocatalysis

To examine the photocatalytic efficiency of mesoporous TiO$_2$ and mesoporous TiO$_2$/CNT composites, the photodegradation of rhodamine B aqueous solution under visible light irradiation at room temperature was conducted. The heterogeneous photocatalytic degradation of RhB solution under visible light irradiation is detected with UV–vis spectrophotometer after adsorption–desorption equilibrium. The characteristic absorption bands of RhB located at 553 nm steadily decrease with increasing irradiation times and the representative photograph (inset Figure 3.32) for the RhB solution using CT60 as catalyst clearly shows the decolouration process of RhB solutions along with irradiation time. Therefore, the concentration of RhB is evolved using the linear part of the absorbance–concentration curve (Beer’s Law) and measuring absorbance to figure out the corresponding concentration. The photocatalytic activity of mesoporous TiO$_2$ was also measured under the same condition for the purpose of comparison. Figure 3.32 shows the kinetic behaviours of the photocatalytic RhB degradation of mesoporous TiO$_2$ and mesoporous TiO$_2$/CNT composites. Compared with the mesoporous TiO$_2$, enhanced photocatalytic properties of mesoporous TiO$_2$/CNT nanocomposite can be observed. About 76% of RhB is degraded after 210 min irradiation in the presence of mesoporous TiO$_2$, while maximum of 97% of the RhB is
Figure 3.32 Photodegradation of RhB aqueous solution over mesoporous TiO$_2$ and nanocomposites (inset UV-Vis absorbance spectra of RhB for CT60 composite).

degraded in the presence of mesoporous TiO$_2$/CNT composite. The photodegradation of RhB in aqueous suspensions containing mesoporous TiO$_2$/CNT nanocomposites obeyed the pseudo first-order kinetics (Kuvarega et al 2012; An et al 2007) as shown in Figure 3.33, which displays the time profiles of $C/C_0$ under visible light irradiation for different nanocomposites, where $C$ is the concentration of RhB at the irradiation time $t$ and $C_0$ is the initial concentration. After light on, the concentration of RhB decreased with irradiation time and the pseudo-first-order reaction is observed. The reaction rate after the adsorption equilibrium can be expressed as,

$$\ln \left( \frac{C}{C_0} \right) = kt$$

where $C$ and $C_0$ are the reaction concentration at time $t = t$ and $t = 0$ respectively. The apparent first order rate constant was calculated from the slopes of a straight lines corresponding with the plot of $\ln \left( \frac{C}{C_0} \right)$ verses time,
the observed pseudo first-order rate constant are listed in Table 3.5. From the calculated reaction rate constant on the basis of the kinetic plot, the 80% mesoporous TiO\textsubscript{2}/CNT composite shows the highest rate constant as compared to other samples; indicating synergistic reaction happened between mesoporous TiO\textsubscript{2} and CNT. Incorporation of CNT with mesoporous TiO\textsubscript{2}.

![Figure 3.33 Apparent first-order linear transforms of RhB degradation - kinetic plots.](image)

Table 3.5 Calculated rate constant values for Pseudo first order reaction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(k_{\text{app}}\times10^{-3}) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso TiO\textsubscript{2}</td>
<td>0.726</td>
</tr>
<tr>
<td>CT20</td>
<td>1.122</td>
</tr>
<tr>
<td>CT40</td>
<td>1.722</td>
</tr>
<tr>
<td>CT60</td>
<td>1.883</td>
</tr>
<tr>
<td>CT80</td>
<td>1.951</td>
</tr>
</tbody>
</table>
reduces the band gap by forming states in the inter-gap region and CNT can trap photogenerated electrons, emitted by mesoporous TiO₂ due to irradiation of visible light, thus enhancing electron-hole separation on the surface of the photocatalyst and increasing photocatalytic activity. Further, the enhancement of catalytic activity, the mesoporous TiO₂ can be attributed to the shift of optical response to visible region and the high surface area of mesoporous structure.

Moreover, CNTs with a large surface area are usually associated with large amounts of crystalline defects, which favor the recombination of photo-generated electrons and holes and would lead to poor photoactivity. Therefore, a large surface area is not a decisive factor in the photo-degradation of RhB. Considered reasonable explanation for the enhanced adsorption capacity of CNTs/TiO₂ would be that RhB molecules have a strip shape, and with the CNTs/TiO₂ composite, it was easier to be adsorbed in the parallel direction to the pore path and more side oriented adsorption occurred. Such a way that, as studied in previous works (Oh et al 2009; Chen et al 2009),

![Image of RhB solution in the presence of CT60 at different time intervals.](image-url)

**Figure 3.34 The photo of RhB solution in the presence of CT60 at different time intervals.**
MWCNTs can act as an electron sensitizer and donator in the composite photocatalysts to accept the photo-induced electron(e−) into the conduction band of the TiO2 under UV irradiation, thus increase the amount of electron. Therefore, the high degree of recombination of e−/h+ is a major rate-limiting factor controlling the photocatalytic efficiency. Further, other researchers have found positive photocatalytic effect from simply mixing CNTs with TiO2 (Jitianu et al 2004; Yu et al 2005b; Wang et al 2005a; Kang et al 2007).

**Mechanism:** A proposed mechanism of enhanced photocatalysis of mesoporous TiO2/CNT composite is shown schematically in Figure 3.35. The reasons for incorporating increasing the catalytic activities of mesoporous TiO2 inhibited the particle growth significantly and resulted in porous structure with larger surface area, which would lead to higher photocatalytic efficiency. In general, idea of oxidation potential the hydroxyl radical, OH•, exhibits the main characteristic of being able to attack to every organic compound; after the fluorine, it is the most powerful oxidizing agent and reacts 10⁶–10¹² times faster than alternative agents, as O₃ (Calgon 1996). Since, photocatalytic reaction proceeds via a series of chemical events, following the initiation step of pair electron-hole formation. This leads to the utilization of both the electron(e−)–hole(h+) for oxidation processes and eventually to the capture of the e− for the reduction processes (Equation (3.9)), as well as the potential formation of super oxides anions and hydrogen peroxide from oxygen (Equation (3.11)).

Molecular oxygen acts as an acceptor species in the electron transfer reaction

\[ e^- + O_2 \rightarrow O_2^- \text{ or } O_2^{*} \] (3.9)

Super-oxide anions can subsequently be involved in the following reactions
\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^* \] (3.10)

\[ \text{H}^+ + \text{O}_2^- + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \] (3.11)

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}^* \] (3.12)

The OH* free radicals are very reactive and attack the pollutant molecule to degrade it into mineral acids including CO$_2$ and water (Al-Ekabi & Serpone 1993). The mixing of mesoporous TiO$_2$/CNT composite possesses higher photocatalytic activity than that of mesoporous TiO$_2$. We speculate that is relative to the formation of chemical bond between mesoporous TiO$_2$ and CNT and their large surface area. Also the formation of a semiconductor-metal junction (Schottky barrier) where there is a space-charge separation region. This Schottky barrier will result in the metal possessing an excess negative charge and the semiconductor an excess positive charge (Linsebigler et al 1995). Thus, e$^-$ may migrate into the nanocylinder of CNTs and the chance of recombination of e$^-$/h$^+$ is greatly reduced.

![Figure 3.35 Schematic mechanisms for mesoporous TiO$_2$/SWCNT composite.](image-url)
Consequently, CNT acts as photosensitizer and transfer $e^-$ to the mesoporous TiO$_2$. As shown in Figure 3.35, the photogenerated $e^-$ is injected into the conduction band of the mesoporous TiO$_2$ allowing for the formation of super oxide radicals by absorbed molecular oxygen as shown in Equation (3.9). Further, simultaneous electron back-transfer to CNT with the formation of a hole in the valence band of mesoporous TiO$_2$. The now positively charged mesoporous TiO$_2$ can then react with adsorbed water to form hydroxyl radicals which are responsible for the degradation of the organic compound. Similar to previous findings, the same mechanism could explain the enhanced photocatalytic activity of MWCNTs/TiO$_2$ composite tested for the degradation of phenol under UV and visible light irradiation (Wang et al 2005b). In which, synergetic effect, induced by a strong interphase interaction between MWCNT and TiO$_2$, was ascribed to MWCNT acting as photosensitizer rather than as adsorbent or dispersing agent in the composite catalysts.