CHAPTER 5
Polymorphic Phase Transformation of Degussa P25 TiO₂ by Nitrogen
Incorporation: Correlation of Anatase to Rutile ratio on Photocatalytic Activity.

5.1. Introduction:
The P25 is a well known commercial material containing anatase and rutile phases in the ratio of ~3:1 and their reported average crystallite sizes are 85 and 25 nm [1]. It is widely used in various technological applications such as solar energy storage cells [2,3], as a catalyst in synthesis of organic compounds [4,5] and also in the degradation of organic contaminants in gaseous phase and aqueous systems [6-8]. Photocatalytic activity of P25 is also extended for the abatement of the E. coli bacteria under solar simulated light [9]. The two major crystalline phases of TiO₂ are anatase and rutile. The co-presence of anatase and rutile shows synergistic effect compared to the isolated anatase and rutile particles [10]. P25 shows excellent photocatalytic activity because of the adsorptive affinity of organic compounds on the surface of anatase which is greater than that of rutile phase. In addition anatase exhibits lower rates of recombination in comparison to rutile due to its 10-fold greater rate of hole trapping capacity [10, 11]. However, the inherent limitation of P25 is the large band gap (3.2 eV), which hinders it being active under the visible region (λ > 400 nm). Many approaches have been made to improve the visible response of P25. Recently nonmetal doping has been proposed to be an efficient method for preparation of modified P25 TiO₂. There are three possible ways to incorporate nitrogen atoms in to the TiO₂ lattice: i) Replacement of lattice oxygen by an N atom, ii) Replacement of Ti atom by an N atom (These two mechanisms imply the rapture of Ti-O bonds that must be replaced either by Ti-N or by N-O bonds is called as substitutional doping), iii) Incorporation of N at an interstitial position which may occur with out inducing too much strain in the structure. It has been reported that the milling atmospheres with different oxygen partial pressures had an influence on the transformation kinetics. When the nanocrystalline TiO₂ powders was milled in oxygen, air and nitrogen atmospheres, the transformation rates of anatase to rutile in turn increased with a decrease in oxygen partial pressure of the milling atmosphere, due to the reducing concentration of oxygen vacancies in the milled TiO₂ lattice [12, 13]. Yin et al
prepared nitrogen doped rutile titania by ball milling P25 titania powder with hexamethylenetetramine and studied the effect of reaction condition on the phase composition [14]. This phase transformation of anatase to rutile was accelerated by increasing the mechanical energy of ball milling. But anatase to rutile ratio decreased by increasing the amount of hexamethylenetetramine. Kang et al reported the preparation of nitrogen doped titania using NH3 by a planetary milling [15]. They observed that grinding the samples in the presence of gaseous ammonia displays higher specific surface area. With in an increase the grinding time period the absorption edge was shifted to visible light region. However comparison of photocatalytic activity and determining the factors which influence their activity is greatly restricted. This is because the rutile is prepared as thermally stable phase and usually possesses much smaller surface area and larger crystallite size than anatase TiO2. In fact, some researchers have demonstrated that rutile titania with smaller crystalline size and with larger surface area posses high photocatalytic activity [16, 17]. Zhang et al have proposed that the contents of anatase and rutile phases in the TiO2 powders can be successfully controlled by simply changing the proportion of Cl− and SO42− ions in the aqueous phase of the micro emulsion. They proposed mechanism involving bidentately chelated sulfate ions [18]. Iodine doped TiO2 with a bicrystalline framework of anatase and rutile also shows a much better activity than anatase TiO2, where rutile phase has a similar crystal size to anatase phase [19]. The enhanced activity can be attributed to: (i) Transfer of electrons from the rutile to electron trapping / lattice trapping sites of anatase and also to the impurity level created by the defects or to the oxygen vacancies, (ii) Synergistic effect in the bicrystalline framework of anatase and rutile, (iii) Similar crystallite size and high intimate contact between both the phases as reported in our previous work [20- 22]. In present work, Diaminopyridine (DAP) is selected as the source of nitrogen. The phase contents of anatase and rutile in the P25 powders have been altered by simply changing the proportion of DAP. The details of the method of catalyst preparation using DAP as the nitrogen source is given in the section 2.2.3 and the photocatalytic experimental details are given in the section 2.5.3. The photocatalytic activity was tested for the photodegradation of Methylene Blue (MB). The effect of nitrogen doping on various aspects like the phase composition,
particle size, specific surface area, morphology and photocatalytic dye degradation capacity were investigated.

5. 2. Results and discussions:

5. 2. 1 PXRD studies

Figure 5. 1 shows the PXRD pattern of P25 and NTP25 samples. The anatase phase of titania shows a major peaks at $\theta = 25^\circ, 37^\circ, 48^\circ, 55^\circ, 56^\circ, 62^\circ, 71^\circ$ and $75^\circ$ and rutile phase shows the major peaks at $\theta = 28^\circ, 36^\circ, 42^\circ$, and $57^\circ$ indicated as A and R in the Figure 5. 1. The rutile fraction increases with increase in the concentration of DAP up to 0.15 at %, and further the intensity of the rutile peak decreases for 0.20 at %. The atomic fractions of rutile / anatase were calculated using the empirical formulae given in the Eq 2.11 and 2.12 [23]. Anatase-to-rutile phase content ratio of all the samples are given in the Table 5. 1. Anatase-rutile ratio decreases for NTP25-04 and gradually increase as the concentration of DAP increases and it reaches a maximum for the catalyst NTP25-15 as shown in the inset of the Figure 5. 2. Doping substitutional anion with valence higher than the $\text{O}^2-$ and with a larger ionic size would induce oxygen vacancies at the surface of anatase crystallites, favoring the band rupture, ionic and structural reorganization for the formation of rutile phase. Further the electrical imbalance caused by the incorporated dopant is neutralized by the creation of new oxygen vacancies (induced oxygen vacancies). For the sample NTP25-04 with 0.04 at % of N, induced oxygen vacancies may facilitate rutile nucleation. The anatase and rutile peaks are of almost equal intensity for the sample NTP25-10. With further increase in the DAP concentration to 0. 20 at % the rutile phase content decreases. The combination of TiO$_2$ powder with organic DAP molecule eased the mechanical stress and led to a large decrease in free energy for the phase transformation [15]. The average crystallite sizes (D) were calculated using the Scherer’s formula as mentioned in the Eq 2.10. The catalyst containing smaller crystallites will have large number of lattice defects. The atoms in the defect sites have higher energy than those in the main lattice and can favorably act as nucleation sites for the rutile phase formation at the surface of anatase crystallites.
Figure 5.2 The plot of Antase: Rutile ratios versus the concentration of nitrogen in at %. The decrease in crystallite size increases the total surface area. The increase in rutile content for the sample NTP25-04 is mainly due to its smaller crystallite size which is believed to contain higher density of surface defects on the anatase crystallite. Thus the high concentration of nucleation sites for the polymorphic phase transition from anatase to rutile exists at particle-particle interfaces in comparison to bulk materials. This might result in the increase of rutile fraction for NTP25-04. The variations in the lattice parameter are as shown in Table 5.1 indicating that the crystal lattices of the samples were locally destroyed by N doping [24, 25]. The above PXRD results revealed that nitrogen atoms were incorporated into the crystal lattice of TiO₂. The literature data show that the anatase-rutile phase transformation takes place at a temperature of 780° C for pure titania [25]. The temperature for the transformation can vary from 400-1200° C depending on various factors like: (a) The type and amount of additives. (b) Method of powder preparation and (c) Heating atmosphere and temperature. These processing variables would significantly change the transformation rate and activation energy and thus produce a transition temperature either higher or lower than that of pure titania [25].
Table 5.1: Summary of the data obtained by PXRD for P25 and NTP25 samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>P25</th>
<th>NP25-04</th>
<th>NP25-10</th>
<th>NP25-15</th>
<th>NP25-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase :Rutile</td>
<td>82</td>
<td>46</td>
<td>51</td>
<td>77</td>
<td>65</td>
</tr>
<tr>
<td>Anatase :Rutile</td>
<td>12</td>
<td>54</td>
<td>49</td>
<td>27</td>
<td>40</td>
</tr>
<tr>
<td>Fraction(wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average crystal size(nm)</td>
<td>25.56</td>
<td>50.11</td>
<td>51.06</td>
<td>70.15</td>
<td>43.83</td>
</tr>
<tr>
<td>Lattice parameter, a (nm)</td>
<td>85.59</td>
<td>88.09</td>
<td>58.69</td>
<td>70.44</td>
<td>58.69</td>
</tr>
<tr>
<td>Lattice parameter, c (nm)</td>
<td>0.3791</td>
<td>0.3617</td>
<td>0.3795</td>
<td>0.3795</td>
<td>0.3606</td>
</tr>
<tr>
<td>Lattice parameter, c (nm)</td>
<td>0.4604</td>
<td>0.4586</td>
<td>0.4618</td>
<td>0.4602</td>
<td>0.4601</td>
</tr>
<tr>
<td>Cell volume (cm³)</td>
<td>0.1365</td>
<td>0.1360</td>
<td>0.1307</td>
<td>0.1307</td>
<td>0.1356</td>
</tr>
<tr>
<td></td>
<td>0.0504</td>
<td>0.0531</td>
<td>0.0512</td>
<td>0.0517</td>
<td>0.0517</td>
</tr>
</tbody>
</table>

5.2.2 UV-visible absorption and diffuse reflectance spectra:
The band gap energies were calculated by using Kubelka-Munk plot of \((1 - R_\alpha)^2 / 2R_\alpha\) versus wavelength as shown in Figure 5.3, and corresponding band gap energies are illustrated in Table 5.2. The band gap shifts to longer wavelength upon nitrogen incorporation. The extent of red shift in the band gap was higher for NTP25-15 sample compared to other doped samples. The band gap in the visible region for the doped samples arises due to the electronic transition between the defect levels to the band gap states of P25. The observed absorptions for NTP25-04, NTP25-10, NTP 25-15 and NTP25-20 samples, were around 426, 436, 454 and 444 nm corresponding to the band gap states of 2.91, 2.84, 2.7 and 2.79 eV indicating that the doping of heteroatom results...
in the formation of additional energy levels above the valence band of P25. It is well known that valence and conduction band of P25 are mainly formed due to the major contribution by the completely filled O 2p orbital and the empty Ti 3d orbital respectively. The 2p orbital of the doped nitrogen atom significantly interacts with the 2p orbital of the oxygen and contribute to the increase in the width of the valence band. The thermal decomposition profile obtained by thermo gravimetric analysis (TGA) of P25, DAP, Ti-DAP and NTP25-20 in air are shown in Figure. 5.4. P25 showed 0.8% weight loss from room temperature to 150°C, 0.9 % between 150 and 500°C and weight remained constant there after. The pure DAP shows 10, 50 and 70 % weight loss at ~100, 125 and 175°C and there after there is continuous decrease in the weight with increase in temperature. The Ti-DAP complex shows 20, 30 % weight loss at150 and 350°C. Only 30 % of weight loss observed for Ti-DAP complex in 30- 500°C temperature range. It is believed that the weight loss in the first region is due to the adsorbed water and the second region is due to the decomposition of non-coordinated DAP molecule. NTP25-20 shows negligible weight loss in the measured region as shown in the Figure 5.4.

![Figure 5.4](image)

**Figure 5.3:** Kubelka-Munk plot for various photocatalysts mentioned. $X = (1-R_\alpha)^2/2R_\alpha$. $R_\alpha$ is ratio of the relative reflectance to reflectance of non absorbing medium; $(1-R_\alpha)^2$ is the molar absorption co-efficient and $2R_\alpha$ is the scattering coefficient.
5.2.3 XPS analysis

XPS spectra of P25 and NTP25 samples are shown in Figure 5.5. It could be observed from Figure 5.5 (i) that the broad N 1s peak was found at 396-399 eV implying the incorporation of nitrogen in the TiO₂ lattice. The peak at a binding energy of 396.6 eV can be assigned to the nitrogen incorporated substitutionally in the TiO₂ lattice [26-28]. Figure 5.5 (ii) displays O 1s XPS spectra. O 1s peaks were found at ~529 eV in N doped samples which could be assigned to the lattice oxygen of TiO₂. The peaks corresponding to NTP25-04, NTP25-10, NTP25-15 and NTP25-20 are shifted in the binding energy (indicated by the solid line marker in Figure 5.5 (ii)) compared to P25. The XPS spectra of Ti 2p regions are shown in Figure 5.5 (iii). The XPS spectrum of Ti 2p₃/₂ shows a peak at 458.6 eV and 457.9 eV for P25 and NTP25 samples. The XPS spectra of Ti 2p ₃/₂ for NTP25-04, NTP25-10, NTP25-15 and NTP25-20 shows a shift in the binding energies (indicated in solid line marker in Figure 5.5 (iii)). The shift of both O 1s, Ti 2p₃/₂ in the binding energy indicates the increase of the electron densities on the Ti atoms suggesting that some Ti³⁺ species may exist in all the four samples [29]. Miao et al have also assigned these shifted peaks to TiO₂ - Nₓ [30]. Based on the above XPS analysis, the broad peaks observed for N 1s, O 1s and the shift of Ti 2p peaks in the spectra provide strong evidence for the substitutional incorporation of nitrogen into the TiO₂ lattice. The observed shift in the binding energy is due to the surface strain and lattice distortion induced by the incorporation of the nitrogen dopant. When nitrogen substitutes for the oxygen in the initial O-Ti-O structure, the electron density around N is reduced, compared to that in a TiN crystal, because of the O atom on the Ti atom. Thus, the N 1s binding energy in an O-Ti-N environment is higher than that in an N-Ti-N environment where the N atom replaces the O atom. The structure of the P25 sample is such that the nitrogen perturbs the TiO₂ lattice and changes the Ti-O bond. Thus, the observed changes in the XPS spectra are providing consistent structural information for O-Ti-N formation, the substitutional doping of nitrogen for oxygen, which leads to the enhanced photocatalytic activity observed in NTP25 samples. The composition of Nitrogen in various doped catalysts as obtained from the XPS data are listed in the Table 5.2.
Figure 5.4: TGA curve of DAP, Ti-DAP complex and NTP25-20 samples.

Table 5.2: Nitrogen content (at. %) from XPS, BET surface area, pore size, absorption threshold, band gap energies of P25 and NTP25 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrogen Content (at. %)</th>
<th>BET surface area (m²/g)</th>
<th>Porosity (cm³/g)</th>
<th>absorption threshold (nm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>--</td>
<td>50.1</td>
<td>0.25</td>
<td>380</td>
<td>3.26</td>
</tr>
<tr>
<td>NP25-04</td>
<td>0.0386</td>
<td>57.56</td>
<td>0.28</td>
<td>426</td>
<td>2.91</td>
</tr>
<tr>
<td>NP25-10</td>
<td>0.0897</td>
<td>59.28</td>
<td>0.31</td>
<td>436</td>
<td>2.84</td>
</tr>
<tr>
<td>NP25-15</td>
<td>0.1395</td>
<td>66.23</td>
<td>0.34</td>
<td>454</td>
<td>2.72</td>
</tr>
<tr>
<td>NP25-20</td>
<td>0.1894</td>
<td>62.14</td>
<td>0.33</td>
<td>444</td>
<td>2.79</td>
</tr>
</tbody>
</table>

5.2.4 FTIR Studies:

Figure 5.6 and 5.7 show the infrared spectra of P25 and NTP25 samples. The absorption bands observed in the regions of 3420-3450 cm⁻¹ and 1630-1640 cm⁻¹ are assigned to the stretching and bending vibrations of the hydroxyl on the surface of P25
and NTP25 catalysts. The IR absorption band in the region of 520-580 cm\(^{-1}\) can be assigned to the stretching vibrations of Ti-O bond [31]. NTP25 samples show new absorption peaks ~ 3400, 1400 and 1646 cm\(^{-1}\) (Figure 5. 6). These peaks can be assigned to the N-H stretching and the N-H bending vibrations of NH\(_3\) [32- 33]. A new absorption peak observed at 1060 cm\(^{-1}\) indicates the replacement of the oxygen atoms by nitrogen atoms in the TiO\(_2\) crystal lattice to form yellow colored nitrogen-doped TiO\(_2\) solid. This absorption peak can be assigned to the N-Ti-O stretching vibration [31]. The stretching vibration peaks at 3458 and 569 cm\(^{-1}\) shifts to low wave numbers 3440 and 540 cm\(^{-1}\) due to the oxygen vacancies which are easily created at grain boundaries on nitrogen doping [34]. The above observed shifts can be attributed to the formation of N-Ti-O bond and also to the created oxygen vacancies. FT-IR spectra of the samples DP25, DAP, DP25+DAP (before calcinations) and DP25+DAP (after calcinations) in the range 200 to 2200 cm\(^{-1}\) are shown in Figure 5. 8. FT-IR absorption band around 1250-1100 cm\(^{-1}\) indicates the surface anchored –NH. The absorption band observed around 1170 cm\(^{-1}\) for DAP+ P25 (before calcinations) and 1119-1170 cm\(^{-1}\) for P25 +DAP (after calcinations) should be the characteristic band of the monodentately bonding -NH species on the surface of P25. The DAP and DAP+P25 (before calcinations) samples shows absorption bands at ~1600, 1580, 1500 and 1450 cm\(^{-1}\) that are particularly diagnostic of aromatic structure, in particular to aromatic C-C skeletal in plane vibrations and these vibrations are not shown by the P25 +DAP (after calcination) indicating that the DAP is monodentately bound to the surface of the catalyst and it disappears when it is calcined at 550° C. The bands observed at 1340-1250 cm\(^{-1}\) can be assigned to C-N bond (nitrogen attached to the aromatic carbon) in the DAP molecules, which completely disappear after calcinations. The absorption band at 1130 cm\(^{-1}\) increases as the concentration of N increases in the following order NTP25-05< NTP25-10< NTP25-15 < NTP25-20.
Figure 5.5: (i) N 1s, (ii) O 1s, (iii) Ti 2p XPS spectra of various N-doped and undoped P25 TiO$_2$. 

132
Figure 5.6: FT-IR Spectra of DP 25 and NTP25 samples in the region 0-4500 cm$^{-1}$ where 
Figure 5. 7: FT-IR Spectra of DP 25 and NTP25 samples in the region 350-1600 cm\(^{-1}\) where A) DP 25, B) NTP25-04, C) NTP25-10, D) NTP25-15 and E) NTP25-20.

Figure 5. 8: FT-IR Spectra of DP25, DAP, DP25+DAP (before calcination) and DP25+DAP (after calcination) samples in the region 200-2200 cm\(^{-1}\).
5. 2. 5 SEM Surface morphology and BET surface area studies:

Figure 5. 9 show SEM micrographs of DP25 and NT P25. The NTP25-04, NTP25-10, NTP25-15 (B, C and D in Figure 5. 9) shows the flat layered structure due the high concentration of the rutile where as in the case of NTP25-20 this flat layer structure collapses and shows a non uniform image (E and F in Figure 5. 9). This is because water and carbon dioxide molecules between the layers were lost during the process of calcinations at 550⁰ C. The retention of the layered structure in NTP25-04, NTP25-10, NTP25-15 implies the ionic bonds between the O and N in TiO₂ lattice. BET specific surface area of P25 to NTP25-15 increases from 50.1 to 66.23m²/g as shown in the Table 5. 2.

5. 2. 6 Fluorescence studies:

The decay profiles of the prepared samples were investigated by the fluorescence lifetime method. The fluorescence decay profiles of P25 and NTP25 under the excitation wavelength of 380 nm are shown in the Figure 5. 10. These decay profiles were traced using the extended exponential function [35].

\[
I = I_0 t^{\beta - 1} \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right]
\]  

(5.1)

Where \( \tau \) is the lifetime and \( \beta \) is the shape factor. This function has been widely used for the analysis of charge carrier dynamics in semiconductors [36]. Good fitting of the decay profiles of NTP25 using the above equation indicates the existence of carrier trapping sites at different energy levels, which lead to a distribution of the carrier transport rates. According to this equation, we can calculate the lifetime of the charge carriers for all the respective catalysts and the results are given in Table 5. 3. From Figure 5. 10, it can be observed that the decay profiles of NTP25 were quenched with the increase of the nitrogen dopant concentration. The extent of recombination decreases with increase in nitrogen. It can be seen from in set of the Figure 5. 10 that the lifetime of NTP25-15 is dependent on the excitation wavelengths. When the shorter wavelength (290 nm) is used to excite NTP25 the lifetimes are shortened compared to longer waveglength. The decay
profile is considered to be mainly determined by the migration of electrons to the surface of the photocatalysts [35, 37].

5. 2. 7 Mechanism of formation of different phase contents in DP25:

DAP acts as Lewis base $\phi$-(NH$_2$)$_2$ where $\phi$ is pyridine moiety. Grinding TiO$_2$ in presence of DAP accelerate the phase transformation. This may be due to the adsorption of Lewis base DAP on the fresh surface of TiO$_2$ since Ti$^{4+}$ in the lattice acts as Lewis acid sites. Titanium ion first increases its coordination by using its vacant d orbitals to accept the nitrogen electron pairs from nucleophilic ligands (such as -NH group of DAP). TiO$_2$ crystal structures consist of TiO$_6^{2-}$ octahedron, which share edges and corners in different manners that result in the formation of different crystal phases. Octahedron in anatase share four edges and are arranged in zigzag chains along the [221] plane, while rutile octahedron share only two edges and form linear chains parallel to the [001] plane [38-41]. The mechanism of formation of anatase and rutile phases in the presence of DAP is proposed in Scheme 5. 1. The placement of the third octahedron plays a very important role in the determination of rutile and anatase phase contents (Scheme 5. 1A) [38]. However, the presence of DAP would influence the orientation of the third octahedron. In the beginning at lower DAP concentration, DAP would interact with octahedral hydroxyls by static electricity and formation of rutile nucleation is more favored (Scheme 5. 1B). These results were substantiated by the IR spectroscopic techniques (confirmed from the presence of IR-peak $\sim$1100 cm$^{-1}$ for P25 + DAP after calcinations in the Figure 5.8). But at the higher concentrations of DAP, steric effect plays a major role, the third octahedron would polycondense along the converse direction in order to decrease the repulsion. This decreases the rutile content at higher DAP concentration (Scheme 5. 1C). It has been reported that the presence of nucleophilic ligands accelerates the growth of TiO$_2$ clusters to anatase [39]. By changing the concentration of DAP anatase / rutile ratios can be altered.
Table 5.3: Emission lifetime of fluorescence decay profile, apparent first-order rate constant \((k_{\text{app}})\) and percentage degradation of MB under UV/solar light for different photocatalysts, under the reaction conditions of [photocatalyst] = 200 mg/L, [MB] = 100 mg/L and volume = 250 ml.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Measured excitation wavelength, nm</th>
<th>Lifetime (ns)</th>
<th>(k_{\text{app}} \times 10^3) ((\text{min}^{-1}))</th>
<th>Percentage of degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>UV Solar</td>
<td>UV Solar</td>
</tr>
<tr>
<td>P25</td>
<td>380</td>
<td>2.15</td>
<td>2.25 0.98</td>
<td>52 29</td>
</tr>
<tr>
<td>NP25-04</td>
<td>380</td>
<td>2.46</td>
<td>1.85 1.12</td>
<td>35 38</td>
</tr>
<tr>
<td>NP25-10</td>
<td>380</td>
<td>2.22</td>
<td>1.78 2.12</td>
<td>28 46</td>
</tr>
<tr>
<td>NP25-15</td>
<td>380, 290</td>
<td>2.12, 1.87</td>
<td>1.67 3.22</td>
<td>27 86</td>
</tr>
<tr>
<td>NP25-20</td>
<td>380</td>
<td>2.15</td>
<td>1.84 2.82</td>
<td>39 59</td>
</tr>
</tbody>
</table>

5.2.8 Correlation of Anatase / Rutile ratio on the photocatalytic activity

The plot of \(C/C_0\) versus time for the degradation of MB under UV / solar irradiation are shown in Figure 5.11 and the corresponding rate constant and percentage degradation values are shown in Tables 5.3. 100 % dye degradation was observed in the presence of NTP25-15 under UV/ solar light in the time period of 5.5 h. While only 24, 52, 72 % degradation was observed for NTP25-04, NTP25-10 and NTP25-20. The catalyst NTP25-15 with bicrystalline framework showed higher efficiency compared NTP25-04, NTP25-10 and NTP25-20 which had different anatase and rutile phase ratios.
**Figure 5.9:** SEM micrographs of P25 (A), NTP25 samples where, (B) NTP25-04, (C) NTP25-10, (D) NTP25-15, (E) NTP25-20 and (F) NTP25-20 in higher magnification.
Figure 5. 10: Fluorescence decay profiles of P25 and NTP25 at excitation wavelength of 380 nm. The inset of the fig shows the fluorescence decay profiles of NTP25-20 photocatalyst under different excitation wavelengths: (A) 290 and (B) 380 nm.

The enhanced activity of NTP25-15 under UV/solar light was attributed to the bicrystalline framework of anatase and rutile which suggests the existence of synergistic effect. It is well known that, this pair of polymorphs can effectively reduce the recombination of photogenerated charge carriers to enhance the photocatalytic activity [20, 42, 43]. Scheme 5. 2(i): Under UV excitation, anatase in the mixed phase gets activated as it is a good absorber of UV light photons. Further transfer of electrons takes place from the conduction band edge of anatase to the trapping sites of rutile. Thus, rutile serves as a passive electron sink, hindering the recombination in the anatase phase and the hole originating from the anatase transfer to the surface, which accounts for the enhanced activity of P25 [20, 21, 44, 45].
Scheme 5.1: Mechanism proposed for the formation of anatase and rutile phases in NTP25: (A) the orientation of the octahedron determines the formation of rutile or an anatase phase; (B) Interaction between –NH group of DAP and TiO$_6^{5-}$octahedron and formation of rutile phase at low concentration of DAP; (C) Interaction of two –NH groups of DAP molecule with TiO$_6^{5-}$ octahedron and inhibition of rutile phase formation at high concentration of DAP.
**Scheme 5.2(ii):** A similar mechanism takes place in the case of NTP25-15 under UV irradiation. In comparison to P25, NTP25-15 possesses a defects level (Ti $^{3+}$/ oxygen vacancy) which is about 0.2 eV below the conduction band edge of anatase, which is even lower than the conduction band edge of rutile itself. Hence, subsequent electron transfer from the rutile trapping site to the defect level further favors the charge separation, which might account for the higher activity of NTP25-15. 

**Scheme 5.3 (i):** The band gap of rutile is favorable for visible light excitation as the conduction band edge of rutile lie 0.2 eV below the conduction band edge of anatase. Under solar excitation, rutile in the mixed phase gets activated as it is a good absorber of solar light photons. The transfer of electrons takes place from the conduction band edge of rutile to the trapping sites of anatase. 

**Scheme 5.3(ii):** A similar mechanism takes place in the case of NTP25-15 under solar light irradiation. In comparison to P25, NTP25-15 possesses an additional defect level (Ti$^{3+}$-V$_o$) and nitrogen dopant energy level. The Ti$^{3+}$-V$_o$ defect level is below the conduction band of anatase, which is even lower than the conduction band of rutile itself. Hence subsequent electron transfer from rutile trapping site to the defect level favors the charge separation which might account for higher activity of NTP25-15 [46]. The lattice trapping sites of anatase has energy less than the conduction band edge of rutile [47]. Thus by competing with the recombination, the charge separation activates the catalyst and the hole originating from the rutile valence band participates in the oxidative degradation of organic pollutants. The transfer of electron from rutile to anatase has an activation energy barrier of 8.3 x 10$^{-4}$ eV based on the measured rate of electron transfer [48]. Due to the low activation barrier, the effective inter particle electron transfer between the two polymorphs is quite possible only when they are in close proximity with similar crystallite sizes [20, 21]. The intimate contact between the two polymorphs depends mainly on their crystallite size. Hong et al reported that low photocatalytic performance of mixed phase titanium was due to larger rutile crystallite size [48]. P25 has anatase to rutile ratio of 85:15 with rutile crystallite size being 85.59 nm, larger than anatase crystallite size (25.56 nm). The sample NTP25-15 has anatase to rutile ratio of 77:27 and the crystallite sizes are in the ratio of 70.15:70.44 nm for two the phases. Since the crystallite size of both the phases is almost same, it can
be concluded that both the polymorphs are in intimate contact for NTP25-15 compared to all the other catalysts resulting in lower recombination of charge carriers and thereby accelerating the interfacial charge transfer process.

5. 2. 9 Kinetics and catalysis:

5. 2. 9. 1 Adsorption kinetics:

The effect of adsorption of the dye molecule at different concentration on the surface of P25 and NTP 25 catalysts are studied. The extent of adsorption shows the following order: NT P25-15 > NT P25-20 > NT P25-10 > NT P25-05 > P25. The extent of adsorption increases with the increase in the concentration of dye it also increases with increase in dopant concentration as shown in Figure 5. 12. The maximum adsorption was found for NTP25-15 and the least for P25. The Freundlich equation is used in the present case for heterogeneous surface energies in which the energy term. q_e strictly refers to the variation in the heat of adsorption is given by

\[ q_e = k_f C_e^{1/n} \]  \hspace{1cm} (5.2)

The linear form of the Eq 5.2 is

\[ \log q_e = \log k_f + \frac{1}{n} \log C_e \]  \hspace{1cm} (5.3)

Where \( C_e \) is the equilibrium concentration (mg / L) and \( q_e = x / m \), \( x \) is the amount of adsorbate and \( m \) is the amount of adsorbent at equilibrium time and \( k_f \) and \( n \) are Freundlich constants. \( n \) gives an indication of the favorability (\( n<1 \)) and \( k_f \) is the capacity of the rate of adsorption. The plot of \( \log q_e \) versus \( \log C_e \) is shown in Figure 5. 13. The intercept and slope gives the values of \( \log k_f \) and \( n \) values (Table 5. 4).
Scheme 5.2: Charge transfer mechanism in a mixed phase under UV light irradiation: (i) P25 (ii) NTP25-15 (as per references 20, 21 and 44).
Scheme 5.3: Charge transfer mechanism in a mixed phase under solar light irradiation: (i) P25 (as per reference 20, 21 and 46), (ii) NTP25-15.
Figure 5.11: Plot of $C/C_0$ versus time under UV/solar light irradiation for the degradation of MB using various photocatalysts under the experimental conditions of $[\text{MB}] = 40 \text{ mg} / \text{L}$, $[\text{Photocatalyst}] = 400 \text{ mg} / \text{L}$, where A) Under UV irradiation Solar B) Under Solar irradiation.
Table 5.4: Values of $k_f$ and $n$ from the plot of log $C_e$ versus log $q_e$ (Freundlich isotherm) for the adsorption of MB dye molecule as obtained by Eq. (5.2) on NTP25-15.

<table>
<thead>
<tr>
<th>Adsorbent dose (mg/L)</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_f$</td>
</tr>
<tr>
<td>15</td>
<td>7.413</td>
</tr>
<tr>
<td>20</td>
<td>11.22</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>11.48</td>
</tr>
</tbody>
</table>
Figure 5.12: Plot of percentage adsorption versus initial concentration of MB on the surface of different photocatalysts.

Figure 5.13: Plot of log $C_e$ versus log $q_e$ for the adsorption of MB on different photocatalysts.
5. 3. Conclusion

Nitrogen doped P25 TiO₂ photocatalysts with bicrystalline framework of high surface area and different anatase / rutile phase contents were prepared using DAP as an nitrogen source. The phase content in the powders could be controlled precisely by varying the DAP concentration. The orientation of the third octahedron plays a very important role in the determination of rutile and anatase phase contents. The catalyst NTP25-15 containing 77 % of anatase showed the highest photocatalytic activity for photodegradation of MB, which is due to the: (i) The defect states introduced by the dopant serving as trap sites for the charge carriers, (ii) The similarity in the crystal sizes of anatase and rutile in NTP25-15 reduces the recombination of charge carriers by accelerating the interfacial charge transfer process due to the close proximity of crystal phases and (iii) Synergistic effect is observed between anatase and rutile phases under both UV and solar light facilitating efficient photodegradation.

5. 4. References:

(2005).
(2009).