Chapter 3

Samarium ion (Sm$^{3+}$) doped TiO$_2$ synthesis, characterization and photodegradation.

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3.1 Introduction

In this chapter an efficient and straight-forward method for the preparation of samarium ion (Sm$^{3+}$) doped photocatalytically active, anatase TiO$_2$ is discussed. TiO$_2$ has mainly two drawbacks in achieving high photocatalytic efficiency, the fast electron hole recombination and the limited absorption in the solar spectrum. To reduce the recombination of photogenerated electrons and holes on TiO$_2$, and also to extend its light absorption into the visible region, TiO$_2$ has been doped with transition metal ions, coupled semiconductor systems, noble metals deposition, nonmetals and rare earth ions. Various synthetic routes like sol–gel method, hydrothermal method, co-precipitation-peptization method have been studied for the preparation of metal ion doped TiO$_2$ nanocrystals. Rare earth metals having incompletely occupied 4f and empty 5d orbitals often serve as catalyst or promoter for catalysis. It has been already discussed that the photocatalytic activity of TiO$_2$ can be improved by doping with rare earth metals. Liang et.al. reported the photocatalytic activity of rare earth ions (Sm$^{3+}$, Nd$^{3+}$, Pr$^{3+}$) doped TiO$_2$ catalysts for Orange I degradation under both UV and visible light irradiations. Xiao et.al. reported the synthesis of Sm$^{3+}$ doped TiO$_2$ nanocrystallites under visible light by auto-combustion technique shift to longer wavelengths as compared to bare TiO$_2$ sample. Shi et.al. developed a series of Sm$^{3+}$ doped TiO$_2$ for the photocatalytic degradation of methyl orange. Park et.al. reported that the
photoluminescence emission of Sm$^{3+}$ doped TiO$_2$ nano tubes with UV light irradiation. However, all these methods required expensive chemicals, templates for structure direction of TiO$_2$, harsh chemical/heat treatment for removal of the template to obtain pure TiO$_2$ and induce crystallinity into TiO$_2$. In this work a simple modified sol-gel method was used to synthesize TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ and characterized with XRD, FTIR, DRS, SEM and TEM. Photocatalytic activity of these samples was studied by photo degradation of methylene blue under UV and direct sun light. The effect of calcination temperatures on the photocatalytic activity was also been discussed. This modified sol-gel method using acetic acid as a stabilizing agent leads to a highly homogeneous distribution of the Sm$^{3+}$ dopant in the TiO$_2$ host matrix with nano sized powders. This method also offers a uniform particle size distribution and other advantages such as excellent compositional control, homogeneity of dopant distribution on the molecular level due to the mixing of liquid precursor and lower crystallization temperature for the formation of TiO$_2$.

3.2 Results and Discussion

3.2.1 FT-IR Spectroscopy

The FTIR spectra of TSm1, TSm2, TSm5, TSm10 and bare TiO$_2$ calcined at 300, 500 and 700 °C were recorded. A representative example of the FTIR spectra of TSm2 dried at 100 °C and 500 °C and bare TiO$_2$ calcined at 500 °C was shown in Figure 3.1. In both spectra of TiO$_2$ and TSm2, the absorption band at 3500-3000 cm$^{-1}$ indicates hydroxyl group stretching vibration and surface adsorbed water molecule. The peak at 1627 cm$^{-1}$ indicates the hydroxyl group bending vibration and the peak at 2920 and 2855 cm$^{-1}$ is the asymmetric C-H
stretching vibration.\textsuperscript{28} Absorbed CO\textsubscript{2} on the surface is indicated by the peak at 2338 cm\textsuperscript{-1}.\textsuperscript{29} The presence of peak at 1120 cm\textsuperscript{-1} in Sm\textsuperscript{3+} doped TiO\textsubscript{2} sample is due to the Ti-O-Sm stretching vibrations. The peak at 1425 and 1532 cm\textsuperscript{-1} in both TiO\textsubscript{2} and Sm\textsuperscript{3+} doped TiO\textsubscript{2} is due to the symmetric and asymmetric stretching vibration of acetate groups. Both TiO\textsubscript{2} and Sm\textsuperscript{3+} doped TiO\textsubscript{2} sample possess strong and broad band in the range of 400-700 cm\textsuperscript{-1} which were attributed to Ti-O stretching and Ti-O-Ti bridging stretching modes, which is a characteristic peaks of anatase phase of TiO\textsubscript{2}.\textsuperscript{30} The peak at 477 cm\textsuperscript{-1} for Sm\textsuperscript{3+} doped TiO\textsubscript{2} is due to the vibration modes of anatase skeletal O-Ti-O and Ti-O-Sm bonds.\textsuperscript{31,32,33,34} A new band at 478 cm\textsuperscript{-1} was observed in the spectra of Sm\textsuperscript{3+} doped TiO\textsubscript{2} samples. This band is attributed to the Sm–O bond.\textsuperscript{35} Similar type of observation was also seen in the FTIR spectra of TiO\textsubscript{2} and Sm\textsuperscript{3+} doped TiO\textsubscript{2} calcined at 500 and 700 °C.

![FTIR spectra of TiO\textsubscript{2} calcined at 500 °C, TS\textsubscript{M2} dried at 100 °C, and TS\textsubscript{M2} calcined at 500 °C.](image)

**Figure 3.1.** FTIR spectra of a) TiO\textsubscript{2} calcined at 500 °C b) TS\textsubscript{M2} dried at 100 °C c) TS\textsubscript{M2} calcined at 500 °C.
3.2.2 XRD

XRD patterns of pure TiO$_2$ and TSm1, TSm2, TSm5, TSm10 calcined at 300, 500 and 700 °C were recorded. The XRD of TiO$_2$ and TSm2 at 300, 500 and 700 °C were shown in Figure 3.2 A, 3.2 B and 3.2 C respectively. From the figure it is clear that all samples are in the anatase phase. The particle characteristics of the TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ samples under different weight percentage and temperature are summarized in Table 3.1 A. The relative intensity of (101) peaks were broadened and reduced in the Sm$^{3+}$doped TiO$_2$, in comparison with pure TiO$_2$ calcined at the same temperature (Figure.3.3). It can be seen that no peaks from samarium oxide (Sm$_2$O$_3$) were observed in any of the doped sample which implies that Sm$^{3+}$ ions are incorporated in the crystal lattice of TiO$_2$. When the crystallite sizes of the Sm$^{3+}$ doped TiO$_2$ samples were calculated using the Scherrer formula (Table 3.1), it was found that the crystallite size was reduced by Sm$^{3+}$ ion doping. It is due to the segregation of the dopant cations at the grain boundary of TiO$_2$, and the growth of nanocrystalline TiO$_2$ is then prevented. These smaller crystallite of TSm2 may delay the transformation of anatase to rutile structure and also have the larger surface area compared to pure TiO$_2$.\textsuperscript{36,37} which is accordance to the data obtained from the BET surface area isotherm (Figure 3.2 D & 3.2 F, Table 3.1 B), where TSm2 shows a surface area of 68.07 m$^2$/g while that of TiO$_2$ is only 1.14 m$^2$/g.
Figure 3.2 A) XRD patterns of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 300 °C.

Figure 3.2 B) XRD patterns of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 500 °C
Figure 3.2 C) XRD patterns of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 700 °C

Figure 3.2 D) BET adsorption Isotherm of TiO$_2$ calcined at 500 °C.
Figure 3.2 E) BET adsorption Isotherm of TSm2 calcined at 500 °C.

Table 3.1 A. Crystal size of anatase TiO$_2$, TSm1, TSm2, TSm5 and TSm10 calcined at 300, 500 and 700 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>300 °C</th>
<th>500 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>8.4</td>
<td>12.6</td>
<td>21.7</td>
</tr>
<tr>
<td>TSm1</td>
<td>7.79</td>
<td>10.6</td>
<td>15</td>
</tr>
<tr>
<td>TSm2</td>
<td>7.7</td>
<td>10.5</td>
<td>12.4</td>
</tr>
<tr>
<td>TSm5</td>
<td>6.96</td>
<td>8.4</td>
<td>11.4</td>
</tr>
<tr>
<td>TSm10</td>
<td>6.5</td>
<td>7.6</td>
<td>11.1</td>
</tr>
</tbody>
</table>
Table 3.1 B. BET surface Area Analysis of TiO₂ and TSm2 at 500 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>1.14 m²/g</td>
</tr>
<tr>
<td>TSm2</td>
<td>68.07 m²/g</td>
</tr>
</tbody>
</table>

3.2.3 Raman Spectroscopy

Raman spectra of TSm1, TSm2, TSm5, TSm10 and pure TiO₂ calcined at 300, 500 and 700 °C were recorded. A representative example of the Raman spectra of TiO₂ and TSm2 calcined at 500 °C was shown in Figure 3.3. The spectrum reveals the anatase phase purity of synthesized TiO₂ nanoparticles. The peaks are present at 145 (E₉), 395 (B₁ₑ), 514 (B₁ₑ) and 639 cm⁻¹ (E₉) which are the characteristics of anatase phase of TiO₂.³⁸ The major peak of anatase is decreasing as the doping was introduced confirms the incorporation of Sm³⁺ into the crystal lattice and thereby decrease in crystallinity which has been explained in XRD spectra (Figure 3.2). It can also be confirmed that, in addition to decrease in peak intensity the peak broadening increases, which attributes to the oxygen vacancies and thereby Ti³⁺ doping occurred as a result of doping.³⁹
3.2.4 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) studies were carried out (Figure 3.4) to investigate the amorphous to crystalline transition of the TiO$_2$ precursor samples of both TiO$_2$ and TSm$_2$ samples. Endothermic peak at 92 °C was observed for the TiO$_2$ sample and 94 °C for the TSm$_2$ and these peaks are due to the removal of adsorbed water molecules. The exothermic peak at 309 °C of TSm$_2$ sample shows the amorphous to crystalline transition. The presence of an endothermic peak at 405 °C shows desorption of water molecules from the TiO$_2$. 

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**Figure 3.3.** Raman Spectra of a) TiO$_2$ and b) TSm$_2$ calcined at 500 °C.
Figure 3.4. Differential scanning calorimetry of a) TiO$_2$ b) TSm.

3.2.5 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy (DRS) in the range 200-800 nm of TiO$_2$ and TSm1, TSm2, TSm5 and TSm10 calcined at different temperature were investigated to study the optical absorption properties. The DRS spectra of TiO$_2$ and TSm2 calcined at 500 and 700 °C were shown in the Figure 3.5, and it is clear that TSm2 shows an absorption band in the range 400-500 nm. It also observed that when doping concentration increased 1 to 10 percent, the absorption edge of sample shifts to higher wavelength. This red shift can be attributed to the charge-transfer transition between the $f$ electrons of Sm$^{3+}$ ion and the TiO$_2$ conduction band$^{33,34}$ which help in the generation of electron and hole under visible light irradiation. Which is in accordance with the Photoluminescence spectra obtained (Figure 3.6), where it can be observed that the intensity of the emission peak is
quenched. Similar red shift absorption profile is observed with an increase in calcined temperature. The band gap energies were calculated by using UV-Vis DRS spectra with Tauc equation are shown in the Table 3.2. The band gap energies of Sm$^{3+}$ doped samples are lower than that of TiO$_2$ due to the red shift that occurred as a result of Sm$^{3+}$ doping.

**Table 3.2. Band gap energies of TSm1, TSm2, TSm5, TSm10 and TiO$_2$ calcined at different temperatures.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 °C</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.1</td>
</tr>
<tr>
<td>TSm1</td>
<td>2.54</td>
</tr>
<tr>
<td>TSm2</td>
<td>2.50</td>
</tr>
<tr>
<td>TSm5</td>
<td>2.54</td>
</tr>
<tr>
<td>TSm10</td>
<td>2.59</td>
</tr>
</tbody>
</table>

**Figure 3.5** A) Absorbance of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 500 °C.
Figure 3.5 B) Absorbance of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 700 °C.

Figure 3.5 C) Reflectance of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 500 °C.
Figure 3.5 D) Reflectance of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 700 °C.

Figure 3.5 E) Tauc plot of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 500 °C.
Figure 3.5 F) Tauc plot of a) TiO₂ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 700 °C.

Figure 3.6 PL spectra of a) TiO₂ and b) TSm2 calcined at 500 °C.
3.2.6 X-ray Photoelectron Spectroscopy (XPS)

XPS of TiO₂ and TSm2 calcined at 500 °C were recorded. Spectrum reveals the incorporation of Sm³⁺ into the lattice of TiO₂. Notable peak changes are occurred on the surface of TiO₂. The 2p³/2 and 2p₁/₂ peaks of TiO₂ were observed at 460.2 eV and 466 eV for bare TiO₂ (Figure 3.7A). The peak 460.2 eV is attributed to the oxygen richness.⁴² The splitting was found in both the samples at 5.8 eV, which attributes the anatase phase purity of both TiO₂ samples.⁴³ Surface defects originate when Sm³⁺ enters into the lattice of TiO₂ and which is confirmed by the blue shifting in the binding energy i.e. 457.6 eV (2p³/2) and 463.2 eV (2p₁/₂). The peak at 457.6 eV reveals the presence of Ti³⁺.⁴² At the same time the decrease in valency of Ti explain the presence of oxygen vacancies. These relevant explanations reveal the transformation of oxygen rich environment to oxygen deficient environment. From the O1s XPS (Figure 3.7B) it can be seen that the peak at 531.5 eV blue shifted to 528.7 eV indicates the change in oxygen environment.³⁰ Figure 3.7C, the Sm3d XPS reveals the incorporation of Sm³⁺ into the crystal lattice. As evidenced from XRD, even though the ionic radius of Sm³⁺ (109.8pm) is far greater than Ti⁴⁺ (74.5pm), Sm³⁺ entered into the crystal lattice of TiO₂ and those ions occupy the interstitial position of TiO₂. The distinct doublets at 1081.5 and 1106 eV coming from Sm3d₅/₂ and Sm3d₃/₂ attribute the presence of Sm-O-Ti bond.⁴⁴
3.2.7 Scanning Electron Microscopy (SEM)

The morphology of the TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ sample was analyzed using Scanning Electron Microscopy (SEM). SEM images of TiO$_2$ and TSm2 doped TiO$_2$ calcined at a temperature 500 °C showed in the Figure 3.8A. SEM analysis indicates that the particles undergo agglomeration in both TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ samples. It is clear from Figure 3.8A that the particle size of Sm$^{3+}$ doped TiO$_2$ sample is lower than that of TiO$_2$. This observation is in agreement with the
crystalline size calculation from XRD where TiO$_2$ showed a crystalline size of 12.6 nm whereas TSm2 showed only 10.6 nm (Table 3.2) at a calcination temperature 500 °C. That means the Sm$^{3+}$ ion doping could hinder the increase of crystallite size during calcinations. Also SEM images showed the uniform nature of particles with no change in particle morphology due to Sm$^{3+}$ doping with well-defined clear boundaries. EDS analysis (Figure 3.8B and Table 3.3) was carried out for the TiO$_2$ and TSm2 to determine the chemical composition. Strong X-ray peaks associated with Ti and oxygen are present in TiO$_2$ whereas strong peaks of samarium were found in the Sm$^{3+}$ doped TiO$_2$ along with Ti and oxygen. Quantitative analysis by the EDS software package was used to determine the respective weight percentages of each element in the TiO$_2$ and TSm2 shown in Table 3.3 confirms the presence of both Ti and Sm in the lattice of Sm$^{3+}$ doped TiO$_2$.

![SEM images of TiO$_2$ and TSm2 calcined at 500 °C.](image)

**Figure 3.8A.** SEM image of a) TiO$_2$ b) TSm2 calcined at 500 °C.
Figure 3.8 B. Energy Dispersive Spectroscopy (EDS) of a) TiO$_2$ and b) TSm$_2$ at 500 °C.

Table 3.3. Energy Dispersive Spectroscopy (EDS) elementary analysis TiO$_2$ and TSm$_2$ calcined at 500 °C.

<table>
<thead>
<tr>
<th>Element</th>
<th>TSm$_2$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Atomic%</td>
</tr>
<tr>
<td>TiK</td>
<td>57</td>
<td>80.03</td>
</tr>
<tr>
<td>OK</td>
<td>42.40</td>
<td>19.88</td>
</tr>
<tr>
<td>SmL</td>
<td>0.61</td>
<td>0.09</td>
</tr>
</tbody>
</table>

3.2.8 Transmission Electron Microscopy (TEM)

TEM images of TiO$_2$ and TSm$_2$ calcined at 500 °C were recorded. TiO$_2$ shows a particle size of 19-23 nm (Figure. 3.9a) at 500 °C. On the other hand, the TSm$_2$ has a particle size of 10-12 nm (Figure. 3.9b), and thus the TEM observations support the conclusions derived from the XRD data. The selected area electron diffraction (SAED) image of Sm$^{3+}$ doped TiO$_2$ calcined at 500 °C shows broad band due to the Scherrer line broadening which is attributed to the small crystalline size.$^{45,46}$
however TiO₂, at same temperature, showed distinct spots due to the high crystallinity and larger size of the crystals.

![TEM images](image)

**Figure 3.9. TEM images of a) TiO₂ and b) TSm2 at 500 °C.**

### 3.3 Photocatalysis

Photocatalytic activity of both TiO₂ and TSm2 calcined at 500 °C for methylene blue degradation under UV and sunlight were carried and the rate constant obtained from the degradation kinetics were summarized in Table 3.4. Figure 3.10 shows the degradation efficiency of methylene blue under the UV and sunlight irradiation using TiO₂ and TSm1, TSm2, TSm5 and TSm10 calcined at 500 °C. From Table 3.4 it can be seen that calcined temperature influence on photocatalytic activity of pure TiO₂ and TSm. The optimum calcination temperature was at 500 °C. Rate of degradation under direct sunlight irradiation is more compared to UV light irradiation. This is because upon Sm³⁺ ion doping, the light absorption capacity of TiO₂ increases from UV to visible region in accordance with band gap narrowing. From the Table 3.4, it is observed that TSm sample shows greater photocatalytic activity than TiO₂ under UV light except the lower temperature and
lower concentration of Sm$^{3+}$ (TSM1). The rate constant obeys the first order kinetics and the values are summarized in the Table 3.4, among the different TSM, highest activity was obtained for TSM2 calcined at 500 °C, with a rate constant of 0.092 min$^{-1}$, which is 2.5 times higher than the bare TiO$_2$ (0.037 min$^{-1}$). Absorption spectra of methylene blue dye degradation under UV light using TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ at 500 °C were shown in Figure 3.11 and 3.12. TSM2 calcined at 500 °C degraded completely within 40 minutes. From the results it can be concluded that the TSM2 calcined at 500 °C is the best photocatalyst among the samples under UV light irradiation.

The visible light activity of TiO$_2$ and TSM under direct sunlight using the methylene blue degradation experiment was carried out and the time taken for degradation of methylene blue using TiO$_2$ and TSM under sunlight was also shown in Table 3.4. From the Table 3.4, it is found that Sm$^{3+}$ doped TiO$_2$ sample undergo methylene blue degradation much faster than compared to TiO$_2$ at all calcinations temperatures under sunlight irradiation. The rate constant was calculated from the first order kinetics and is shown in Table 3.4. Among the doped samples highest activity was obtained for TSM2 sample calcined at 500 °C with a rate constant of 0.103 min$^{-1}$ which is 10 times higher than the pure TiO$_2$ (0.013 min$^{-1}$). Absorption spectra of methylene blue dye degradation under visible light using TiO$_2$ and 2% Sm$^{3+}$ doped TiO$_2$ at 500 °C were shown in Figure 3.13 and 3.14. TSM2 calcined at 500 °C degraded completely within 25 minutes. The results point out that TSM2 calcined at 500 °C is the best photocatalyst among samples under visible light irradiation.
Figure 3.10. Degradation curve of a) TiO$_2$ b) TSm1 c) TSm2 d) TSm5 and e) TSm10 calcined at 500 °C. A) UV light B) Sunlight.

Table 3.4. Rate constant (min$^{-1}$) of TiO$_2$ and TSm calcined at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>300 °C</th>
<th>500 °C</th>
<th>700 °C</th>
<th>Sample</th>
<th>300 °C</th>
<th>500 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.021</td>
<td>0.036</td>
<td>0.002</td>
<td>TiO$_2$</td>
<td>0.007</td>
<td>0.013</td>
<td>0.004</td>
</tr>
<tr>
<td>TSm1</td>
<td>0.007</td>
<td>0.03</td>
<td>0.014</td>
<td>TSm1</td>
<td>0.003</td>
<td>0.059</td>
<td>0.28</td>
</tr>
<tr>
<td>TSm2</td>
<td>0.007</td>
<td>0.092</td>
<td>0.073</td>
<td>TSm2</td>
<td>0.004</td>
<td>0.103</td>
<td>0.091</td>
</tr>
<tr>
<td>TSm5</td>
<td>0.009</td>
<td>0.051</td>
<td>0.066</td>
<td>TSm5</td>
<td>0.005</td>
<td>0.024</td>
<td>0.026</td>
</tr>
<tr>
<td>TSm10</td>
<td>0.012</td>
<td>0.028</td>
<td>0.023</td>
<td>TSm10</td>
<td>0.013</td>
<td>0.025</td>
<td>0.020</td>
</tr>
</tbody>
</table>
Figure 3.11. Absorption spectra and Kinetic study of methylene blue dye degradation under UV using TiO$_2$ sample calcined at 500 °C.

Figure 3.12. Absorption spectra and Kinetic study of methylene blue dye degradation under UV using TSm2 calcined at 500 °C.
Figure 3.13. Absorption spectra and Kinetic study of methylene blue dye degradation under direct sunlight using TiO$_2$ sample calcined at 500 °C.

Figure 3.14. Absorption spectra and Kinetic study of methylene blue dye degradation under direct sunlight using TSm2 sample calcined at 500 °C.
3.3.1 Proposed photocatalytic mechanism of Sm$^{3+}$ doped anatase TiO$_2$

TSM doped sample showed higher visible light activity than the TiO$_2$ can be explained as follows. The methylene blue dye gets adsorbed as well as complexes with the Sm$^{3+}$ ions on the surface of the anatase TiO$_2$ catalyst. When the dye molecule get excited by absorption of a suitable visible light photon, the electrons of excited dye molecule can be injected into conduction band (CB) of TiO$_2$ as shown in Scheme 3.1. The Sm$^{3+}$ species can act as an effective electron scavenger to trap the conduction band electrons of TiO$_2$, which were injected from the excited dye molecule. The electrons trapped in Sm$^{2+}$ sites were subsequently transferred to the adsorbed O$_2$ by oxidation process leading to generation of effective oxidative superoxide radical species (O$_2^-$) capable of attacking the nearby dye molecules. Since Sm$^{2+}$ with six f-electron is unstable; the electrons can be easily de-trapped and transferred to the oxygen molecules. Therefore it reduced the recombination rate of the photogenerated electron and hole, which enhanced the photocatalytic degradation rate of methylene blue dye. Ti2p XPS clearly explains the presence of Ti$^{3+}$ species originated after Sm doping. Presence of Ti$^{3+}$ means the oxygen vacancy rich environment. The defective surface always results in the VB maxima increase and conduction band minima decrease. As a result of Sm doping there must be VB tailing i.e. the presence of surface oxygen vacancy states arise due to O2s states.$^{47}$ The Ti$^{3+}$ can also form a defect level and act as the hole-trap to promote the charge transfer. These defects on the TiO$_2$ surface can suppress the recombination of
electron–hole pairs and hence extend their lifetime and thereby improves the photocatalytic efficiency. The aforementioned processes can be summarized as

\[ \text{Dye} + h\nu \rightarrow \text{Dye}^* \]

\[ \text{Dye}^* + \text{TiO}_2 \rightarrow \text{Dye} + \text{TiO}_2 (e^-) \] (electron injection)

\[ \text{Sm}^{3+} + e^- \rightarrow \text{Sm}^{2+} \] (electron trapping)

\[ \text{Sm}^{2+} + \text{O}_2 \rightarrow \text{Sm}^{3+} + \text{O}_2^- \] (electron trapping)

\[ \text{O}_2^- + 2 \text{H}^+ \rightarrow 2 \cdot \text{OH} \] (Generation of oxidative species)

\[ \text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+} \]

\[ \text{Ti}^{3+} + h^+ \rightarrow \text{Ti}^{4+} \]

As shown in scheme 3.1, there is a possibility for the light absorption directly by the anatase titania photocatalyst leading to the photoexcitation of electron from the valence band to the conduction band. The process provides electron-hole separation and thereby effective photocatalysis as shown in Scheme 3.1. In this case the holes that are generated get react with water molecules forming \( \cdot \text{OH} \). Also the electrons that are present in the conduction band of anatase simultaneously react with oxygen molecules directing towards \( \text{O}_2^- \) (super oxide radical anion). The so formed \( \cdot \text{OH} \) and \( \text{O}_2^- \) mineralize the methylene blue dye facilitate effective photocatalysis. In the case of \( \text{Sm}^{3+} \) doped TiO\(_2\) the photoexcitation is more feasible due to the narrowed band gap arose due to the donor levels that are formed by
Sm$^{3+}$ doping and thus photodegradation rate was more as depicted in Figure 3.14.

![Scheme 3.1. Photocatalytic mechanism of Sm$^{3+}$ doped anatase TiO$_2$.](image)

**Scheme 3.1. Photocatalytic mechanism of Sm$^{3+}$ doped anatase TiO$_2$.**

### 3.4 Conclusions

A modified sol-gel strategy has been developed for the synthesis of TiO$_2$ and Sm$^{3+}$ doped TiO$_2$ nanoparticles. On introducing Sm$^{3+}$ into the crystal lattice of oxygen rich TiO$_2$ nanocrystals environment was changed from oxygen richness to oxygen deficiency *i.e.* Sm$^{3+}$ induced oxygen deficiency in the crystal lattice of TiO$_2$. These TiO$_2$ nanoparticles with oxygen richness and oxygen deficiency (doped and undoped) were subjected photocatalytic degradation of methylene blue dye under UV and solar illuminations and degradation kinetics were
systematically examined. It was found that TSm2 calcined at 500 °C has shown the maximum photoactivity under both UV and sunlight illumination. The augment activity was connected to the change of surface structure of TiO$_2$, the raise of OH radicals produced by the unbalance charge, and the production of sub-band gap by doping Sm$^{3+}$. 
3.5 References


