Chapter

Dysprosium ion ($\text{Dy}^{3+}$) doped TiO$_2$ via modified sol-gel method.

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4.1. Introduction

In this chapter a photocatalytic active, thermally stable dysprosium ion (Dy$^{3+}$) doped anatase TiO$_2$ synthesized using modified sol-gel method is discussed. TiO$_2$ is an ample photocatalytic material for photochemical water splitting and environmental purification due to its prime properties, such as low cost, availability, nontoxicity, long-term stability and high oxidative power.$^{1,2,3}$ As is generally known, anatase and rutile are the two most closely examined phases of TiO$_2$. Besides, anatase shows higher photocatalytic activity than that of rutile, and thus is the most commonly practiced crystal phase of TiO$_2$ for photocatalysis.$^{4,5}$ Though, a large intrinsic band gap of TiO$_2$ (3.2 eV for the anatase structure$^6$ and 3.0 eV for the rutile structure$^7$) allows only the UV portion ($\lambda<385$ nm) of the solar spectrum to be absorbed, which persuades to a poor solar energy utilization. Different efforts have been made to modify the electronic properties of TiO$_2$, so that it could expand its response to visible light and enhance its visible-light photocatalytic activity.

Rare earth ions are well known for their capability to form complexes with various Lewis bases in the interaction of these functional groups with the f-orbital.$^8$ Thus, the incorporation of the rare earth ions into TiO$_2$ crystal matrices could provide a potential means to inhibit the photohole and photoelectron combination and to expand the light adsorption of the semiconductor, and therefore to enhance the visible light photocatalytic activity, such as Eu-TiO$_2$ nanocrystalline.$^9$
Ln$_2$O$_3$/TiO$_2$ (Ln = Eu, Pr, or Yb),$^{10}$ La-TiO$_2$, Pr-TiO$_2$, Nd-TiO$_2$, $^{11}$ N-Ce/TiO$_2$. $^{12}$ The results indicate that the photocatalytic activity of TiO$_2$ could be significantly enhanced by doping with the rare earth ions because the doped rare earth ions can form complexes with various organic molecules by f-orbital.

In this work, TiO$_2$ and Dy$^{3+}$doped TiO$_2$ were synthesized via modified sol-gel method. The photocatalytic effect under both UV and direct sunlight were studied using the bare and doped TiO$_2$ calcined at 300, 500 and 700 °C.

4.2 Results and Discussion
4.2.1. FTIR Spectroscopy

FTIR spectra of the samples calcined at 300, 500 and 700 °C have been recorded. A representative example of the FTIR spectra of TDy1 dried at 100 °C and 500 °C and bare TiO$_2$ calcined at 500 °C was shown in Figure 4.1. The absorption band at 3500-3000 cm$^{-1}$ in both spectra indicates hydroxyl group stretching vibration and surface adsorbed water molecule. The peak at 1635 cm$^{-1}$ indicates the hydroxyl group bending vibration. The peak at 2910 and 2855 cm$^{-1}$ is the asymmetric C-H stretching vibration. $^{13}$ The bands at 1422 cm$^{-1}$ are due to the vibration of CO$_3^{2-}$ anions, indicating the absorption of CO$_2$ molecules on the surface of the samples. $^{14}$ The broad peak in the range 400-700 cm$^{-1}$ is due to Ti-O stretching vibration modes, which can be observable in the anatase phase of TiO$_2$. $^{14}$ The peak at 410 cm$^{-1}$ for Dy$^{3+}$ doped TiO$_2$ is due to the vibration modes of anatase skeletal O-
Ti-O and O-Ti-O-Dy bonds. Band at 543 cm\(^{-1}\) observed, attributes the Dy-O bond.

Figure 4.1 FTIR spectra of a) TiO\(_2\) calcined at 500 °C b) TDy1 dried at 100 °C c) TDy1 calcined at 500 °C.

4.2.2. XRD

XRD patterns of pure TiO\(_2\) and 1, 2, 5 and 10% Dy\(^{3+}\)-TiO\(_2\) powders calcined at 300, 500, 700 °C were showed in Figure 4.2 A, 4.2 B and 4.2 C. From the figure it is clear that all catalysts were dominated by the anatase structure, which indicates that Dy\(^{3+}\) doping inhibits the crystal phase transformation of TiO\(_2\). Comparing the relative intensity of 101 peaks of Dy\(^{3+}\) doped TiO\(_2\) and pure TiO\(_2\) calcined at the same temperature, the relative intensity of (101) peak get broadened in doped sample. However, XRD did not show any peaks for dysprosium
oxide (Dy₂O₃). This implies that Dy³⁺ ions are incorporated into the crystal lattice of TiO₂. When the crystallite size of the Dy³⁺-TiO₂ samples were calculated using the Scherrer formula, it was found that the crystallite size was reduced by doping. It may be ascribed to the segregation of the dopant cations at the grain boundary, and the growth of nanocrystallite in the nanoparticles is prevented. The particle characteristics of the samples under different weight percentage and temperature used in this study are summarized in Table 4.1. It was concluded that Dy³⁺ ion doping could hinder crystal transformation and decrease crystallite size generally. This smaller crystalline size for Dy³⁺ could lead to larger surface area,¹⁶,¹⁷ which will improve the photocatalytic performance of Dy³⁺ doped TiO₂ compared to bare TiO₂.

**Figure 4.2 A.** XRD patterns of a) TDy0.5 b) TDy1 c) TDy2 d) TDy5 and e) TDy10 calcined at 300 °C.
Figure 4.2 B. XRD patterns of a) TDy0.5 b) TDy1 c) TDy2 d) TDy5 and e) TDy10 calcined at 500 °C

Figure 4.2 C. XRD patterns of a) TDy0.5 b) TDy1 c) TDy2 d) TDy5 and e) TDy10 calcined at 700 °C
Table 4.1. Crystal size of anatase TiO₂, TDy0.5, TDy1, TDy2, TDy5 and TDy10 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>TiO₂</td>
<td>7.84</td>
<td>12.6</td>
<td>21.7</td>
</tr>
<tr>
<td>TDy0.5</td>
<td>8.26</td>
<td>11.8</td>
<td>20.7</td>
</tr>
<tr>
<td>TDy1</td>
<td>7.20</td>
<td>9.80</td>
<td>15.6</td>
</tr>
<tr>
<td>TDy2</td>
<td>7.19</td>
<td>9.80</td>
<td>11.1</td>
</tr>
<tr>
<td>TDy5</td>
<td>7.01</td>
<td>8.60</td>
<td>11.1</td>
</tr>
<tr>
<td>TDy10</td>
<td>6.90</td>
<td>8.10</td>
<td>9.90</td>
</tr>
</tbody>
</table>

4.2.3 Raman Spectroscopy

Raman spectra of TDy0.5, TDy1, TDy2, TDy5, TDy10 and pure TiO₂ calcined at 300, 500 and 700 °C were recorded. Raman spectra of TiO₂ and TDy1 calcined at 500 °C were shown in Figure 4.3. The spectrum reveals the anatase phase purity of synthesized TiO₂ nanoparticles. The peaks are present at 146 (E₉), 397 (B₁₉), 517 (B₁₉) and 639 cm⁻¹ (E₉) which are the characteristics of anatase phase of TiO₂.¹⁸,¹⁹ The major peak of anatase is decreasing as the doping was introduced confirms the incorporation of Dy³⁺ into the crystal lattice of TiO₂ and thereby decrease in crystallite size which has been explained in XRD spectra (Figure 4.2). It can also be confirmed that, in addition to decrease in peak intensity the peak broadening increases, which attributes to the presence of oxygen vacancies as a result of Dy³⁺ doping.²⁰
Figure 4.3. Raman Spectra of a) TiO$_2$ and b) TDy1 calcined at 500 °C.

4.2.4 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy (DRS) in the range 200-900 nm of TiO$_2$ and Dy$^{3+}$ doped TiO$_2$ calcined at different temperature were investigated to study the optical absorption properties. The DRS spectra of TiO$_2$ and TDy1 at 500 and 700 °C were shown in the Figure 4.4. From the Figure 4.4 Dy$^{3+}$ doped TiO$_2$ shows an absorption band higher than pure TiO$_2$. It was also observed that at calcination temperature of 500 °C, TDy1 shows the maximum absorption edge and shifts to higher wavelength. This red shift can be attributed to the charge-transfer transition between the $f$ electrons of Dy$^{3+}$ ion and the TiO$_2$ conduction band which help in the generation of electron and hole under visible light irradiation. The red shift absorption profile is observed with an increase in calcined temperature from 300 to 700 °C. The band gap energies were calculated by using DRS spectra with Tauc equation and condensed in the Table 4.2. The
band gap energies of $\text{Dy}^{3+}$ doped samples are lower than that of TiO$_2$ due to the red shift that occurred as a result of $\text{Dy}^{3+}$ doping.

**Table 4.2.** Band gap energies of TiO$_2$, T Dy0.5, T Dy1, T Dy2, T Dy5 and T Dy10 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>T Dy0.5</td>
<td>2.86</td>
</tr>
<tr>
<td>T Dy1</td>
<td>2.85</td>
</tr>
<tr>
<td>T Dy2</td>
<td>2.65</td>
</tr>
<tr>
<td>T Dy5</td>
<td>2.54</td>
</tr>
<tr>
<td>T Dy10</td>
<td>2.42</td>
</tr>
</tbody>
</table>

**Figure 4.4.** A) Absorbance plot of a) TiO$_2$ b) T Dy0.5 c) T Dy1 d) T Dy2 e) T Dy5 and f) T Dy10 calcined at 500 °C.
Figure 4.4 B) Absorbance plot of a) TiO$_2$ b) TDy0.5 c) TDy1 d) TDy2 e) TDy5 and f) TDy10 calcined at 700 °C.

Figure 4.4 C) Tauc plot of a) TiO$_2$ b) TDy0.5 c) TDy1 d) TDy2 e) TDy5 and f) TDy10 calcined at 500 °C.
Figure 4.4 D) Tauc plot of a) TiO$_2$ b) TDy0.5 c) TDy1 d) TDy2 e) TDy5 and f) TDy10 calcined at 700 °C.

4.2.5. X-ray Photoelectron Spectroscopy (XPS)

XPS of TiO$_2$ and TDy1 calcined at 500 °C were recorded. Spectrum reveals the association of Dy$^{3+}$ ion into the lattice of TiO$_2$. There is some peak changes are occurred on the surface of TiO$_2$. The 2p$_{3/2}$ and 2p$_{1/2}$ peaks of Ti$^{4+}$ were observed at 460.2 eV and 466 eV for bare TiO$_2$ (Figure 4.5A) whereas for Sm$^{3+}$ doped TiO$_2$ peaks are obtained at 459 and 465 eV. The peak 460.2 eV (in bare TiO$_2$) attributes to the oxygen richess.\textsuperscript{21} The splitting difference was found around 6 eV almost similar for bare and Sm$^{3+}$ doped TiO$_2$, which attributes the anatase phase purity of both TiO$_2$ samples.\textsuperscript{22}Surface defects originate when Dy$^{3+}$ enters in to the lattice of TiO$_2$ and which is confirmed by the blue shifting in the binding energy \textit{i.e.} 459 eV (2p$_{3/2}$) and 465 eV (2p$_{1/2}$). The peak at 459 eV reveals the presence of Ti$^{3+}$.\textsuperscript{21}The decrease in valency of Ti explains the presence of oxygen vacancies, which
reveal the transformation of oxygen rich environment to oxygen deficient environment. From the O1s XPS (Figure 4.5B) it can be seen that the peak at 531.5 eV blue shifted to 530.3 eV indicates the change in oxygen environment. Figure 4.5C, the Dy4d XPS reveals the incorporation of Dy\(^{3+}\) into the crystal lattice. The Dy4d peak had a greater degree of complex peak shape than based on the simple spin–orbit splitting, due to final state multiplet splitting effects arising from interactions of 4d and 4f states,\(^{23}\) very large due to the same principal quantum number of the two shells.\(^{24,25}\) The main band was centered at an average BE of 158.2 eV. The BE of the absolute maximum is relatively close to the values reported for Dy (III) oxide.\(^{23,25}\) As evidenced from XRD, even though the ionic radius of Dy\(^{3+}\) (105.2 pm) is far greater than Ti\(^{4+}\) (74.5 pm), Dy\(^{3+}\) entered into the crystal lattice of TiO\(_2\) and those ions occupy the interstitial position of TiO\(_2\).

Figure 4.5. XPS of A) Ti2p, B) O1s and C) Dy4d.
4.2.6. Transmission Electron Microscopy (TEM)

Figure 4.6 shows TEM images of TiO$_2$ and TDy1 calcined at 500 ºC. TiO$_2$ shows a particle size of 20-28 nm (Figure 4.6a) at 500 ºC. On the other hand, the Dy$^{3+}$ doped TiO$_2$ has a particle size of 7-12 nm (Figure 4.6b), and thus the TEM observations support the conclusions derived from the XRD data that the particle size will decrease as a result of Dy$^{3+}$ doping into TiO$_2$ lattice. The electron diffraction image of TDy1 calcined at 500 ºC shows broad band due to the Scherrer line broadening which is attributed to the small crystalline size\textsuperscript{26,27} however TiO$_2$, at same temperature, showed distinct spots due to the high crystallinity and larger size of the crystals.

![TEM image of TiO$_2$ and TDy1 at 500 ºC.](image)

4.2.7. Energy Dispersive Spectroscopy (EDS)

Chemical composition of TiO$_2$ and TDy1 was determined using EDS analysis (Figure 4.7). Strong X-ray peaks associated with Ti and oxygen are present in TiO$_2$ where as strong peaks of Dy were found in
the TDy1 along with Ti and oxygen confirms the presence of both Ti and Dy in the lattice of TDy1.

![Energy Dispersive Spectroscopy (EDS) of a) TiO$_2$ and b) TDy1 at 500 °C.](image)

**Figure 4.7. Energy Dispersive Spectroscopy (EDS) of a) TiO$_2$ and b) TDy1 at 500 °C.**

### 4.3 Photocatalysis

Photocatalytic activity of both TiO$_2$ and TDy1 calcined at 500 °C for methylene blue degradation under UV and sunlight were carried out and the rate constant obtained from the degradation kinetics were briefed in Table 4.3. From Table 4.3 it can be seen that photocatalytic activity of pure TiO$_2$ and TDy is influenced by the calcination temperature. Rate of degradation under direct sunlight irradiation and UV light irradiation of Dy$^{3+}$doped TiO$_2$ is more than that of bare TiO$_2$ except in lower temperature. This is because upon Dy$^{3+}$ ion doping, the light absorption capacity of TiO$_2$ increases from UV to visible region in accordance with band gap lowering. The rate constant obeys the first order kinetics and the values are summarized in the Table 3, among the different TDy, highest activity was obtained for TDy1 calcined at 500 °C, with a rate constant of 0.145 min$^{-1}$ and is approximately 4 times
higher than the bare TiO$_2$ (0.036 min$^{-1}$). Absorption spectra of methylene blue dye degradation under UV light using TiO$_2$ and Dy$^{3+}$ doped TiO$_2$ at 500 $^\circ$C were shown in Figure 4.8 and 4.9. TDy1 calcined at 500 $^\circ$C degraded completely within 25 minutes. From the results it can be concluded that the TDy1 calcined at 500 $^\circ$C is the best photocatalyst among the samples under UV light irradiation.

The visible light activity of TiO$_2$ and TDy 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 TDy under sunlight were also shown in Table 4.3. From the Table 4.3, it is found that Dy$^{3+}$ 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 4.3. Among the doped samples highest activity was obtained for TDy1sample calcined at 500 $^\circ$C with a rate constant of 0.141 min$^{-1}$ which is almost 11 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 TDy1 doped TiO$_2$ at 500 $^\circ$C were shown in Figure 4.10 and 4.11. TDy1 calcined at 500 $^\circ$C degraded completely within 25 minutes. The results point out that TDy1 calcined at 500 $^\circ$C is the best photocatalyst among samples under sunlight irradiation.
Table 4.3. Rate constant of TiO$_2$ and TDy calcined at different temperatures.

<table>
<thead>
<tr>
<th>UV light</th>
<th>Sunlight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>300 °C</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.021</td>
</tr>
<tr>
<td>TDy0.5</td>
<td>0.038</td>
</tr>
<tr>
<td>TDy1</td>
<td>0.008</td>
</tr>
<tr>
<td>TDy2</td>
<td>0.009</td>
</tr>
<tr>
<td>TDy5</td>
<td>0.007</td>
</tr>
<tr>
<td>TDy10</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Figure 4.8. Absorption spectra and Kinetic study of methylene blue dye degradation under UV using TiO$_2$ sample calcined at 500 °C.
Figure 4.9. Absorption spectra and Kinetic study of methylene blue dye degradation under UV using TDy1 sample calcined at 500 °C.

Figure 4.10. Absorption spectra and Kinetic study of methylene blue dye degradation under direct sunlight using Ti sample calcined at 500 °C.
Figure 4.11. Absorption spectra and Kinetic study of methylene blue dye degradation under direct sunlight using TDy1 sample calcined at 500 °C.

4.4 Conclusions

A modified sol-gel strategy was developed for the synthesis of TiO$_2$ and Dy$^{3+}$ doped TiO$_2$ nanoparticles. As synthesised nanomaterials are well characterised with XRD, FT-IR and Raman spectroscopy, DRS, XPS, SEM and TEM. Crystallite size calculation from XRD showed that the crystallite size is decreased as a result of Dy$^{3+}$ doping and is further supported by TEM also. XPS result showed that on introducing Dy$^{3+}$ into the crystal lattice of oxygen rich TiO$_2$ nanocrystals the environment was changed from oxygen richness to oxygen deficiency. Dy$^{3+}$ doping induced oxygen deficiency in the crystal lattice of TiO$_2$. These TiO$_2$ nanoparticles and Dy$^{3+}$ doped TiO$_2$ with doped and undoped were subjected to various calcination temperatures and their photocatalytic degradation under UV and solar illuminations were systematically examined. Among the various samples TDy1 calcined at 500 °C has shown the maximum photoactivity under both UV and sunlight illumination.
4.5 References


