Chapter III

PHOTOCATALYSIS
## CONTENTS

### CHAPTER III: PHOTOCATALYSIS

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3.1. Introduction

Titanium dioxide is a versatile material which is being investigated extensively due to its unique optoelectronic and photochemical properties such as high refractive index, high dielectric constant, excellent optical transmittance in the visible and near IR regions as well as its high performance as a photocatalyst for water splitting and degradation of organics [1]. Since Frank and Bard [2] first examined the possibilities of using TiO$_2$ to decompose cyanide in water, there has been an increasing interest in environmental applications. However with a band gap of 3.0-3.3 eV, titanium dioxide has been photocatalytically active only under ultraviolet light [3]. The development of photocatalyst exhibiting high reactivity under visible light ($\lambda > 400$ nm) would allow main part of the solar spectrum to be used, hence several attempts for TiO$_2$ modification have been proposed:

(i) transition metal-ion doped TiO$_2$

(Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt) [4-15]

(ii) reduced TiOx photocatalysts [16-19]

(iii) non-metal doped TiO$_2$ (N, C, S, I, P, F, B) [20-24]

(iv) composites of TiO$_2$ with semiconductor having lower band energy

(e.g. Cd-S particles) [25]

(iv) sensitizing of TiO$_2$ with dyes (e.g. thionine) [26]

(v) TiO$_2$ doped with upconversion luminescence agent [27,28].
Since TiO$_2$ is chemically and biologically inert, photocatalytically stable, easy to produce and use without risks to environment and human, it is the well researched material for:

(i) waste water treatment from industries, factories, laboratories

(ii) degradation of textile dyes, pesticides [30]

(iii) antimicrobial studies [31].

Degradation of dyes in industrial wastewaters has received an increasing attention due to toxic effects of the dye to aquatic life and human beings. In photocatalytic degradation of dyes some of the parameters that affect the process are

- pH of the solution to be degraded
- pH of the precursor solution
- oxidizing agent
- calcination temperature
- dopant content
- catalyst loading.

The effect of pH on dye degradation is related to the ionization state of the surface according to the following reactions

$$\text{TiOH} + \text{H}^+ = \text{TiOH}_2^+ \quad [32]$$

$$\text{TiOH} + \text{OH}^- = \text{TiO}^- + \text{H}_2\text{O} \quad [33]$$

as well as to that of reactant dye [34]. Secondly hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered to be predominant species at neutral or high pH values [35].
It is also observed that TiO$_2$ particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption gets reduced [36]. Oxidizing agents also have a great deal of influence on the photocatalytic degradation of dyes since oxygen is required as electron scavenger to keep the photocatalytic reaction [37].

TiO$_2$ also presents excellent antibacterial activity [38-41]. It has been reported that the catalytic and bactericide properties of TiO$_2$ can be improved by growing particles of a noble metal (Ag, Au or Cu) over its surface [42], or inside its matrix as reported by Thiel et al [43].

Many methods have been reported for the production of TiO$_2$ photocatalyst such as chemical solution deposition, chemical vapor deposition, two step wet chemical method, ultrasonic irradiation, sol-gel, thermal and hydrothermal etc. reviewed by various research groups [44-47].

Various operational parameters affect the effectiveness or activities of TiO$_2$ –based photocatalysts. Hence it is important to study the nature of the sample to be degraded. In our work we have studied the photocatalytic effect of the prepared catalysts for degradation of dyes.
3.2. Experimental

3.2.1. Catalyst Preparation

The catalysts were synthesized by:

a) thiourea precursor method as discussed earlier in section 2.2.2. and 2.2.3.

The list of the synthesized catalysts is presented in Table 3.1.

b) hydrolysis method as discussed earlier in section 2.10.

The list of the synthesized catalysts is presented in Table 3.2.

3.2.2. Catalyst Characterization

The catalysts were characterized by XRD, BET surface area, BJH pore analysis, PZC, photoluminescence, EDAX, SEM and TEM

Table 3.1: Catalysts synthesized by thiourea precursor method

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Code</th>
<th>Method</th>
<th>Phase (% Anatase)</th>
<th>Scherrer crystallite size (nm)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R1</td>
<td>TiCl₃: HNO₃</td>
<td>52</td>
<td>14</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>R2</td>
<td>TiCl₃ (HNO₃):Tu (1:2)</td>
<td>82</td>
<td>13</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>R2a</td>
<td>TiCl₃ (HNO₃):Tu (1:4)</td>
<td>34</td>
<td>09</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>R3</td>
<td>TiCl₃ (HNO₃):Tu:Oa (1:2:1)</td>
<td>100</td>
<td>12</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>R3a</td>
<td>TiCl₃ (HNO₃):Tu:Oa (1:4:1)</td>
<td>100</td>
<td>08</td>
<td>94</td>
</tr>
<tr>
<td>Sr. No.</td>
<td>Catalyst Code</td>
<td>Method</td>
<td>Hydrolysis time</td>
<td>% Rutile *</td>
<td>Scherrer crystallite size (nm)</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>--------</td>
<td>-----------------</td>
<td>------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Degussa</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>Aldrich</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>A1 TiCl₃: H₂O</td>
<td>48 hrs</td>
<td>89</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>A2 TiCl₃: H₂O: Degussa P-25 ‘seed’</td>
<td>3 hrs</td>
<td>68</td>
<td>18</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>A3 TiCl₃: H₂O: Aldrich TiO₂ ‘seed’</td>
<td>2.5 hrs</td>
<td>57</td>
<td>16</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>A4 TiCl₃:H₂O: A3 ‘seed’</td>
<td>2.5 hrs</td>
<td>83</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>A5 TiCl₃:HNO₃:H₂O at 60°C</td>
<td>1 hr</td>
<td>19</td>
<td>10</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>A6 TiCl₃:HNO₃:H₂O: Aldrich TiO₂ ‘seed’ at RT</td>
<td>1 hr</td>
<td>49</td>
<td>16</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>A7 TiCl₃:HNO₃:H₂O: Aldrich TiO₂ ‘seed’ at 60°C</td>
<td>1hr</td>
<td>35</td>
<td>14</td>
<td>83</td>
</tr>
<tr>
<td>10</td>
<td>A8 TiCl₃:HNO₃:H₂O: without seed at RT</td>
<td>10 hrs</td>
<td>100</td>
<td>16</td>
<td>103</td>
</tr>
</tbody>
</table>

* Percentage of the phase is inclusive of the phase content in the seed
3.2.2.1. UV-Vis Diffuse Reflectance Spectroscopy

Figure 3.1 shows the diffuse reflectance spectra of the titania samples. The absorption edges and band gaps were determined from the onset of diffuse reflectance spectra of the samples measured using UV-Vis spectrophotometer (Shimadzu UV-2450).

![Diffuse reflectance spectra of synthesized titania samples](image)

**Figure 3.1**: Diffuse reflectance spectra of synthesized titania samples
R1 [TiCl$_3$ (HNO$_3$), R2 [TiCl$_3$ (HNO$_3$):Tu (1:2)], R3 [TiCl$_3$ (HNO$_3$):Tu (1:2:1)], and Degussa P-25

It is clear that all these samples showed absorption edge in the visible region. The band gap of the samples was determined by the equation $E_g = \frac{1239.8}{\lambda}$ [48], where $E_g$ is the band gap energy (eV) and $\lambda$ (nm) is the wavelength of the absorption edges in the spectra. The calculated band gaps of the prepared titania samples are summarized in Table 3.3.
Table 3.3: The calculated band gaps of the prepared titania samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R1</th>
<th>R2</th>
<th>R2a</th>
<th>R3</th>
<th>R3a</th>
<th>Degussa P-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method of synthesis</td>
<td>TiCl$_3$</td>
<td>TiCl$_3$</td>
<td>TiCl$_3$</td>
<td>TiCl$_3$</td>
<td>TiCl$_3$</td>
<td>-</td>
</tr>
<tr>
<td>% Anatase</td>
<td>52</td>
<td>82</td>
<td>34</td>
<td>100</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>3.09</td>
<td>2.43</td>
<td>2.32</td>
<td>3.03</td>
<td>2.98</td>
<td>3.14</td>
</tr>
</tbody>
</table>
3.2.2.2. Energy Dispersive X-ray spectroscopy (EDAX)

The elemental compositions of the prepared catalytic systems determined by EDAX analysis is given in Figure 3.2 for R2a and Figure 3.3 for R3a.

The results clearly indicate the presence of Nitrogen and Sulphur in the prepared titania samples.

Figure 3.2: EDAX elemental analysis of sample R2a [TiCl$_3$ (HNO$_3$):Tu (1:4)]

Figure 3.3: EDAX elemental analysis of sample R3a [TiCl$_3$ (HNO$_3$):Tu:Oa (1:4:1)]
3.2.2.3. Transmission Electron Microscopy (TEM)

The morphology of the TiO$_2$ samples investigated by transmission electron microscopy for R3 and R3a is presented in Figure 3.4 and Figure 3.5 respectively. The TEM image shows that the sample R3 [TiCl$_3$ (HNO$_3$):Tu:Oa (1:2:1)] and R3a [TiCl$_3$ (HNO$_3$):Tu:Oa (1:4:1)] is composed of clusters of particles having well defined spherical morphology.

Figure 3.4: TEM image of sample R3  
Figure 3.5: TEM image of sample R3a
The particle size distribution of the 35 selected particles of R3 and R3a is shown in Figure 3.6 and 3.7 respectively.

R3 particles showed an average size of 12.5 nm, whereas R3a showed an average particle size of 8.5 nm.

**Figure 3.6:** Particle size distribution of R3

**Figure 3.7:** Particle size distribution of R3a
3.2.2.4. Photoluminescence

Figure 3.8 shows the photoluminescence (PL) emission spectra of titania nanostructures measured at room temperature. The PL emission spectra are observed with an excitation wavelength around 325 nm, exhibiting a strong structural emission band around 398 nm due to surface excitation. It was confirmed that the peaks marked with “*” in the spectra correspond to artifacts arising due to scattering of the excitation light by sample [49].

![Figure 3.8: PL emission spectra of titania samples R1, R2 and R3](image)

Further the peak intensity showed correlation with photocatalytic activity. R3 showed highest peak intensity as well highest photocatalytic activity. The undoped sample R1 showed lowest peak intensity as well as lowest activity (section 3.3.1.).
3.3. Methylene Blue degradation

Methylene Blue (MB) is an inexpensive and common dye used in textile industry. It is a cationic dye with chemical structure given in scheme 3.1.

![Scheme 3.1: Chemical structure of Methylene Blue dye](image)

Konstantinou and Albanis [50] reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. The release of coloured waste in water can form dangerous by-products through oxidation, hydrolysis or other chemical reactions taking place in the wastewater phase. These by-products can have toxic effects and also reduce light penetration in contaminated water. Methylene blue is known to cause irritation to gastrointestinal tract with symptoms of nausea, vomiting, diarrhea if swallowed and also methemoglobinemia, cyanosis, convulsions etc.

A lot of research has been done on the removal of methylene blue from waters. In our study, photocatalytic activity of the synthesized samples was investigated for the degradation of methylene blue in visible light.
3.3.1. Experimental procedure

The experiments were carried out simultaneously for all the catalysts in bright sunlight between 10.00 a.m. to 12.00 noon. Experiments were repeated for all the catalysts simultaneously on three different days in order to confirm the consistency of results. In a typical run 50 mL of aqueous dye solution and 0.2 g of the activated catalyst was exposed to sunlight for the duration of the experiment. The solutions thus exposed to sunlight were stirred intermittently. After every 30 minutes, 2 mL aliquots were pipetted out, centrifuged and the absorbance of the clear supernatants was determined at 660 nm wavelength for methylene blue against appropriate blanks. The resulting profiles are shown in Figure 3.9.
Figure 3.9: Photocatalytic degradation profiles of the TiO$_2$ catalysts R1, R2 and R3

It is clear from the Figure that, the anatase TiO$_2$ catalyst R3 as expected showed highest photocatalytic activity and was quite comparable to that of Degussa P-25. This was followed by R2 and R1 as the presence of anatase phase decreased in these samples. However both the S-doped rutile as well as anatase showed higher photocatalytic activity than the undoped rutile TiO$_2$. Similar observations were made when catalyst R2a and R3a were used. The band gap in R2 and R2a being lower, it is possible that the higher rate of electron-hole recombination resulted in relatively lower activity of rutile samples than the S-doped anatase samples.
As the decolourisation of methylene blue precedes time dependent UV-Vis spectra was recorded. Figure 3.10 shows the UV-Vis spectra of MB dye as a function of time in presence of sample R3 [TiCl$_3$ (HNO$_3$):Tu:Oa (1:2:1)]

**Figure 3.10:** Time dependant UV-Vis spectra of MB in presence of sample R3
As described earlier (section 2.10.) TiO$_2$ samples were also prepared by hydrolysis method. The photocatalytic activity of these samples synthesized by hydrolysis of TiCl$_3$ in aqueous medium was also evaluated using degradation of methylene blue as test reaction.

It is particularly noteworthy, as these samples were prepared by a novel rapid synthesis method using Degussa or Aldrich commercial catalysts as seeds. Their activity in general was lower than these commercial catalysts, probably because most of them were mixed phase catalysts. A8 is a particular case of titania obtained by room temperature hydrolysis of TiCl$_3$. It showed a 100 % rutile phase, yet it showed photocatalytic activity comparable to Degussa P-25 and better than the Aldrich anatase phase (Figure 3.11). This is probably the first report of a rutile phase showing such a high photocatalytic activity.

This sample also had a special morphological feature. Its TEM showed a unique assembly of flower like nanotubular structures (section 2.10.5.).
This excellent photodegradation using A8 can be due to the presence of favourable parameters such as particle size, nanorod shape of the particles, crystalline phase and very high surface area. It is earlier reported that for each titanium dioxide phase some optimum size and shape exists where each phase presents high photocatalytic activity [51]. It was also observed that the photocatalytic activity of rutile phase TiO$_2$ (A8) was higher in comparison to the anatase phase TiO$_2$ (R3).
3.4. Congo Red degradation

Congo red (CR) is an example of azo dye with molecular formula, $C_{32}H_{22}N_6Na_2O_6S_2$ which has extensively been used in industry for applications such as textiles, paper, leathers, additives and in analytical chemistry. The chemical structure of the dye is shown in scheme 3.2.

![Scheme 3.2: Chemical structure of Congo Red dye](image)

Physical and chemical techniques such as coagulation, adsorption on activated carbon, ultra filtration and reverse osmosis are generally used efficiently to remove dyes from textile wastewater. However these processes merely transfer the dye from liquid phase to solid wastes. Consequently the technique for degradation of dyes and many other organics in wastewater and effluents is essential. In order to achieve more effective photocatalytic degradation, it is necessary to consider the surface charge property of semiconductors and nature of dye molecules. In this work the effects of some parameters such as aggregation feature of congo red, pH and type of catalysts on degradation rate of dye solution was examined.
3.4.1. Photocatalysis

Figure 3.12 shows that the congo red solution gives three absorption peaks at 498 nm, 347 nm and 235 nm, in UV-Vis absorbance spectra, attributed to the N=N, benzoic and naphthalene rings respectively.

![Figure 3.12: UV-Vis spectra of congo red dye solution](image)

The degradation of congo red dye was studied by a similar procedure described in section 3.3.1 using $3.5 \times 10^{-6}$ M congo red solution for S-doped samples prepared by thiourea precursor method. It was observed that with the addition of S-doped TiO$_2$ catalysts to congo red dye solution, the red colour of the solution turned blue due to red shift in the 498 nm peak (as seen in Figure 3.13). This peak is assigned to N=N group of the dye.
This red shift is believed to be due to formation of dimer or aggregation of the congo red dye molecule on the catalyst surface. These S- doped samples generally had low pzc values. The representative data is shown in Table 3.4. Thus implying that they could release protons in solution very easily. These protons then protonate the dye molecule. When protonation occurred at the amino moiety causing NH$_3^+$ species dimerisation or further aggregation could occur by binding at the sulphonyl site of the dye. However when protonation could occur at the nitrogen of the azo group, the latter would be polarized causing red shift in the spectrum which is also responsible for the appearance of the blue colour. Similar observation has also been made in case of congo red degradation by other workers [52].
Table 3.4: The pH-pzc values of the prepared titania samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method of synthesis</th>
<th>R1</th>
<th>R2</th>
<th>R2a</th>
<th>R3</th>
<th>R3a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiCl₃ (HNO₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(HNO₃):Tu (1:2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiCl₃ (HNO₃):Tu (1:4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiCl₃ (HNO₃):Tu:Oa (1:2:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiCl₃ (HNO₃):Tu:Oa (1:4:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Degussa P-25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Anatase</td>
<td>52</td>
<td>82</td>
<td>34</td>
<td>100</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>pzc</td>
<td>6.57</td>
<td>6.65</td>
<td>4.37</td>
<td>3.79</td>
<td>3.34</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Further the freshly prepared congo red solution at different pH neutral, basic and acidic was analyzed by UV-Vis absorption spectra. While neutral and basic congo red dye solution did not influence the UV-Vis spectra, aggregation of the dye was seen in acidic solution.

Thus the S-doped TiO₂ samples were more effective for adsorption of the congo red dye than its photodegradation under the given condition of pH. However as described in the preceding section, the S-doped TiO₂ samples had high activity for degradation of methylene blue dye.
Further, the photocatalytic activities of these samples synthesized by hydrolysis of TiCl$_3$ in aqueous medium were also evaluated for degradation of congo red.

Figure 3.14a shows the degradation profiles of some representative samples. The red colour of the congo red disappeared within 30 minutes in case of sample A8 as compared to other samples synthesized by this method.

Figure 3.14b shows time dependant UV-Vis spectra of CR dye in presence of catalyst A8. This sample was also most active for degradation of methylene blue (section 3.3.1).
Thus, this investigation resulted in rapid synthesis of a nano rutile catalyst having excellent efficacy for degradation of cationic dye methylene blue as well as anionic dye congo red.
3.5. Conclusions:

(i) Both rutile as well as anatase samples synthesized by thiourea precursor method showed higher photocatalytic activity as compared to the undoped TiO$_2$ sample.

(ii) The relatively lower activity of S-doped rutile sample as compared to S-doped anatase is attributed to higher rate of electron hole recombination.

(iii) All samples synthesized by hydrolysis of TiCl$_3$ were active for the photodegradation of methylene blue.

(iv) Rutile TiO$_2$ synthesized by hydrolysis of TiCl$_3$ in nitric acid medium at room temperature showed excellent efficacy for degradation of cationic dye methylene blue as well as anionic dye congo red.
References:


