Platinum Loaded Titania Nanostructures - Synthesis, Characterization, Optical and Photocatalytic Studies

7.1. Introduction

We have discussed in earlier chapters the results of our investigation on the effect of morphology of various nanotitania phases and also on the effect of Au, Ag and Pd loading on the photocatalysis of titania nanostructures. In an attempt to modify the optical properties of titania synthesized by microwave irradiation we were successful in loading Au, Ag and Pd into titania structures which shifted the absorption into visible region.

Titania is the most widely used photocatalyst, but its limited activity under visible light irradiation has motivated the quest for modified titania materials absorbing visible light [1-11]. To induce visible light activity in TiO$_2$, the band gap must be shifted to lower values. The visible light activity can be induced by loading TiO$_2$ with noble metals such as Au, Ag, Pd and Pt [12-26]. In this chapter, we report our investigation on the effect of Pt loading on the photocatalysis of nanotitania.

Loading of TiO$_2$ lattice with metal nanoparticles introduces new energy levels in the band gap. Depending on the nature of the metal loaded and its concentration, the band gap of TiO$_2$ can be tailored to extend the photoresponsiveness into the visible light region. Addition of metal ions to TiO$_2$ can change the photocatalytic properties by changing the distribution of electrons on the TiO$_2$ surface. The metal nanoparticles work as charge carrier
traps, effectively enhancing charge separation of the electrons and holes and resulting in an increase in the quantum yield of surface photoreactions [27].

The objective of our investigation is to enhance the efficiency of TiO$_2$-based photocatalysts, which directly depends on the ability to obtain nanostructured materials with tailored features to generate electron–hole pairs with a reduced recombination rate and to reduce the energy band gap sufficiently to absorb visible light.

In the present work, we could enhance the visible light photocatalysis of titania nanostructures by loading platinum by metal sol method [28]. In this chapter, the catalytic performances of three morphologically different nanotitania and their platinum loaded nanostructures (Pt/TiO$_2$) are studied for dye degradation of methylene blue under sunlight.

### 7.2. Synthesis and Characterization of Pt Loaded TiO$_2$ Nanostructures

#### 7.2.1 Experimental

All reagents were purchased from Merck, Germany. Titanium trichloride (15 wt% TiCl$_3$, 10 wt% HCl) was used as the titanium precursor. NH$_4$OH (1.5 M), NaCl (5 M), NH$_4$Cl (5 M), hexachloroplatinic acid (H$_2$PtCl$_6$), NaBH$_4$, and polyvinyl alcohol (PVA) were employed for the synthesis. A typical microwave oven (Whirlpool, 1200 W) operating at a frequency of 2450 MHz was used for the synthesis.

The three TiO$_2$ nanostructures with different morphologies viz., cube, sphere and rod (S1, S2, S3) synthesized as reported in the third chapter, were loaded with 0.75 wt% Pt employing metal sol method. For this a suitable amount of PVA solution (1 wt%) was added to an aqueous hexachloroplatinic acid solution (0.1 mg Pt/ml) under vigorous stirring. Then, a freshly prepared solution of NaBH$_4$ (molar ratio NaBH$_4$/Pt = 4) was slowly added drop wise
into the mixture. The TiO\textsubscript{2} samples were added after the pH of Pt sol was adjusted to 6.0 by NH\textsubscript{4}OH or HCl solution. The mixture was stirred at 60°C for 3 hrs, then filtered and washed until no Cl\textsuperscript{-} was detected by AgNO\textsubscript{3} solution. After being dried at 100°C overnight, the samples were calcined at 550°C in air for 4 hrs. The platinum loaded on samples S1, S2 and S3 are represented as PtS1, PtS2 and PtS3 respectively.

Photocatalytic activity of TiO\textsubscript{2} was evaluated by the degradation of the dye, methylene blue (MB) in aqueous solution under sunlight in the presence of synthesized TiO\textsubscript{2} and the Pt loaded TiO\textsubscript{2} nanostructures. The changes in the concentrations of methylene blue in the aqueous solution were examined by absorption spectra measured on a UV-2450 Shimadzu UV–visible spectrophotometer. Before examining the photocatalytic activity for the degradation of aqueous methylene blue, TiO\textsubscript{2} and Pt/TiO\textsubscript{2} sol was prepared. About 100 mg of the synthesized TiO\textsubscript{2} or Pt/TiO\textsubscript{2} was dispersed ultrasonically in 100 ml of 4 x10\textsuperscript{-5} M methylene blue solution in a quartz reactor. To maximize the adsorption of the dye onto the TiO\textsubscript{2} surface, the resulting mixture was kept in the dark for 30 min under stirring conditions [29]. The solution was then irradiated by exposing to sunlight for three hours, viz., from 11-14 hrs during the month of February when the sunlight with bright and constant intensity was abundantly available. We have checked the intensity of the sunlight using YSI 9500 Photometer (0.9 kW/m\textsuperscript{2}) and was found quite uniform during the month of February, when the experiments were done. The degradation of the dye was monitored by measuring the absorption maximum of methylene blue at 661 nm at 30 min intervals of reaction.
7.3 Results and Discussion

7.3.1. X-ray Diffraction Studies

![XRD pattern of bare and platinum loaded titania nanostructures](image)

**Fig. 7.1.** XRD patterns of bare and platinum loaded titania nanostructures

The X-ray diffraction (XRD) pattern (Fig. 7.1.) shows that anatase TiO$_2$ phase with lattice constants, $a = 3.777$ and $c = 9.501$ was formed (JCPDS file no. 89-4921) when NH$_4$OH was used as the medium (S1). All the diffraction peaks of nanotitania synthesized in NaCl medium (S2) and NH$_4$Cl medium (S3) correspond to rutile phase with lattice constants $a = 4.608$, $c = 2.973$ and $a = 4.548$, $c = 2.946$, respectively (JCPDS files, no. 76-0319 and 88-1173). It is clear from the X-ray diffractograms that all the samples are highly crystalline. There is
no phase change for the nanotitania after platinum loading on the samples S1, S2 and S3. Further, no platinum peaks were found in the XRD patterns and may be due to the low platinum content in these titania nanostructures. The average crystallite sizes of S1, S2, S3, PtS1, PtS2 and Pt S3 are 12, 10, 21, 11, 9 and 19 nm respectively which shows that there is only little effect on the crystallite size of TiO$_2$ nanoparticles on platinum loading. It is worth noting that no peak of platinum at $2\theta = 40^\circ$ was observed in the case of Pt/TiO$_2$, suggesting that the metal sol method yields highly dispersed platinum particles on the TiO$_2$ photocatalyst [30]. The X-ray diffraction patterns of platinum loaded TiO$_2$ samples almost coincide with that of bare TiO$_2$ indicating that the metal particles are below the concentration limit to be detected by X-ray analysis [31].

7.3.2. BET Surface Area Analysis

The crystallite size, BET surface area, pore size and pore volume values are summarized in Table 7.1. The surface area of S1, S2 and S3 are 96, 77 and 34 m$^2$ g$^{-1}$, respectively. The sample S1 has highest surface area and is due to its mesoporous nature with pore size around 4 nm. Platinum loaded TiO$_2$ particles show a decrease in surface area of the samples S1, S2 and S3 as is evident from the Table 7.1. The platinum nanoparticles inserted into the pores of mesoporous titania, reduced its surface area. However, this reduction is not detrimental to its photocatalytic activity. The platinum on the nanotitania surface act as a sink for electron capture and enhanced the photo catalysis by prolonging the lifetime of photogenerated electron-hole pairs. In spite of its low surface area, platinum loaded titania nanostructures exhibits well crystalline phases which are able to degrade the methylene blue reasonably. The pore volume of the platinum loaded titania nanostructures is comparatively less than that of titania nanostructures. This trend is consistent with surface area and pore size results [32].
Table 7.1  The crystallite size, BET surface area, pore size and pore volume values of bare and Pt loaded TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Crystallite Size (nm)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>12</td>
<td>96</td>
<td>4</td>
<td>0.37</td>
</tr>
<tr>
<td>S2</td>
<td>10</td>
<td>77</td>
<td>2.5</td>
<td>0.18</td>
</tr>
<tr>
<td>S3</td>
<td>21</td>
<td>34</td>
<td>2.0</td>
<td>0.10</td>
</tr>
<tr>
<td>Pt S1</td>
<td>11</td>
<td>91</td>
<td>2.4</td>
<td>0.28</td>
</tr>
<tr>
<td>PtS2</td>
<td>9</td>
<td>72</td>
<td>1.8</td>
<td>0.11</td>
</tr>
<tr>
<td>Pt S3</td>
<td>19</td>
<td>30</td>
<td>1.4</td>
<td>0.09</td>
</tr>
</tbody>
</table>

7.3.3. Electron Microscopic Analysis
7.3.3.1. Field Emission Scanning Electron Microscopic Analysis

FESEM images of bare and platinum loaded titania samples are given in Fig. 7.2. (a-c) S1, S2 and S3 show a cube-like morphology, spherical morphology and rod-like morphology, respectively. The elemental analyses of the samples were done by energy dispersive X-ray spectroscopy (EDX) experiments, which were carried out in the FESEM. The presence of 0.75 wt% platinum was confirmed from EDX analysis for all the three samples (PtS1, PtS2 and PtS3) (Fig. 7.2). Different concentrations of platinum in all the three samples were tried but optimum results were obtained with 0.75 wt% Pt.
Fig. 7.2.a FESEM of bare and Pt loaded titania (S1 and PtS1) and EDX of PtS1

Fig. 7.2.b. FESEM of bare and Pt loaded titania (S2 and PtS2) and EDX of PtS2
Fig. 7.2.c. FESEM of bare and Pt loaded titania (S3 and PtS3) and EDX of PtS3

7.3.3.2. Atomic Force Microscopic Analysis

Fig. 7.3. represents AFM images of platinum loaded TiO₂ samples. Platinum particles are not seen in FESEM images or AFM images and may be due to its small size.

Fig. 7.3. AFM images of the platinum loaded titania
7.3.3.3. **Transmission Electron Microscopic Analysis**

The high resolution TEM images of the bare and platinum loaded TiO$_2$ nanoparticles synthesized are shown in Fig.7.4. (a-c). TEM image of S1 (a) and PtS1 (a) shows the formation of nanocubes with particle size around 25 nm with pores. The HRTEM image S1 (b) shows lattice fringes of the anatase phase with $d = 0.34$ nm and PtS1 (b) shows lattice fringes of the anatase phase with $d = 0.33$ nm. Due to high symmetry in cubic morphology, lattice points are perfectly packed leading to the single crystalline nature which is evident from selected area electron diffraction pattern. The selected area electron diffraction pattern in the inset of the S1 (a) and PtS1 (a) confirms that the sample S1 is a single crystalline anatase phase. The high surface area observed for the sample S1 and PtS1 may be due to the highly porous nature of the cubes.

**Fig. 7.4. a.** HRTEM and corresponding lattice of bare and Pt loaded of titania nanocubes (S1 and PtS1)
Fig. 7.4. b. HRTEM and corresponding lattice of bare and Pt loaded of titania nanospheres (S2 and PtS2)

Fig. 7.4. c. HRTEM and corresponding lattice of bare and Pt loaded of titania nanorods (S3 and PtS3)
Sample S2 (a) and PtS2 (a) shows the formation of nanospheres of average size around 8 nm. Corresponding selected area electron diffraction pattern of S2 and PtS2 are shown in the inset. The pattern indicates the polycrystalline nature of the sample. Lattice image of S2 (b) of these nanospheres shows lattice fringes of the rutile phase with \( d = 0.32 \) nm and lattice image of PtS2 (b) shows lattice fringes of the rutile phase with \( d = 0.31 \) nm. S3 (a) and PtS3 (a) shows the formation of nanorods with an average aspect ratio of around 4 nm. Corresponding SAED pattern indicates a polycrystalline nature, which may be due to the diffraction in a bunch of nanorods. The HRTEM image of nanorod S3 (b) shows clear lattice fringes of the rutile phase with \( d = 0.32 \) nm and PtS3 (b) shows lattice fringes of the rutile phase with \( d = 0.31 \) nm. In all the three Pt loaded samples \( d \) spacing has decreased and can be ascribed to the effect of occupation of Pt particles in the lattice. Pt loaded samples showed the presence of very small, spherical and well dispersed platinum nanoparticles on the \( \text{TiO}_2 \) surface and it appears as black spots in Fig. 7.4. (PtS1 (a), PtS2 (a) and PtS3 (a)).

7.3.4. Optical Studies

7.3.4.1. UV–visible Absorption Studies

Fig. 7.5. shows the UV-vis absorption spectra of titania nanostructures S1, S2, and S3. The onset of absorption for the three samples is 382, 405 and 415 nm for S1, S2 and S3, respectively. It is clear from the figure that platinum loaded samples showed significant absorption in the visible region. The red shifted photoresponse of these samples may lead to high photocatalytic activity under visible region which helps in the enhancement of photocatalytic activity under sunlight. As for Pt loaded titania nanostructures, the surface plasmon resonance (SPR) peak is absent because Pt nanoparticles have no characteristic peak in the region of 300-800 nm [33].
Fig. 7.5. UV–visible absorption spectra of bare and platinum loaded TiO$_2$ samples

The band gap energies were calculated by the equation:

$$E_g = \frac{1239.8}{\lambda}$$

where $E_g$ is the band gap (eV) and $\lambda$ (nm) is the wavelength of the absorption edges in the spectrum. The band gap values of platinum loaded and bare TiO$_2$ samples are given in Table 7.2. The band gap of nanocubes (S1, 3.2 eV) is significantly higher compared to that of nanospheres (S2, 3.17 eV) and nanorods (S3, 3.15 eV). The band gap ($E_g$) of S1 is estimated to be 3.2 eV, which is in good agreement with the reported value for anatase (3.2–3.3 eV). However, rutile nanostructures show a slightly higher band gap than the
reported value (3.0–3.1 eV). The higher band gap may be due to the smaller particle size.

**Table 7.2** Band gap values of bare and Pt loaded TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.2</td>
</tr>
<tr>
<td>S2</td>
<td>3.17</td>
</tr>
<tr>
<td>S3</td>
<td>3.15</td>
</tr>
<tr>
<td>PtS1</td>
<td>2.88</td>
</tr>
<tr>
<td>PtS2</td>
<td>2.79</td>
</tr>
<tr>
<td>PtS3</td>
<td>2.78</td>
</tr>
</tbody>
</table>

The band gap values of platinum loaded TiO$_2$ samples are less than that of bare nanoTiO$_2$ samples. The lower band gap of platinum loaded TiO$_2$ can enhance the photocatalytic activity of these samples under visible light.

**7.3.4.2. Photoluminescence Studies**

The photoluminescence emission spectra (PL) of silver loaded and bare TiO$_2$ samples were studied in the range of 250-700 nm to investigate the separation efficiency of charge carriers and the results are shown in Fig. 7.6.

It is evident from the figure that the PL intensity of TiO$_2$ was decreased with platinum loading. The PL intensity reflects the recombination possibility of electrons and holes. As the PL intensity decreased with platinum loading, we can infer that the feasibility of recombination of photoexcited electrons and holes is low [34, 35]. The electrons are excited from valence band (VB) to conduction band (CB) of TiO$_2$ under irradiation and generate photoexcited
electrons and holes. Although loading with platinum narrows the band gap of TiO$_2$ samples, the recombination of electrons and holes are relatively slow which is evident from PL spectra. The plausible explanation for this observation is that pt loaded on the surface may also block part of the excitation light and the emission light.

![PL spectra](image)

**Fig. 7.6.** The photoluminescence (PL) emission spectra of bare and platinum loaded TiO$_2$ samples

For platinum loaded TiO$_2$ samples, platinum plays an important role in the interfacial charge transfer and in the decrease in rate of electron-hole recombination. Platinum particles could act as an effective electron scavenger to trap the photo induced electrons and holes of TiO$_2$ leading to
the reduction of electron–hole recombination and thus improving the photocatalytic efficiency. The decrease in PL intensity of platinum loaded samples are in the order PtS1>PtS2>PtS3 as evident from the figure which indicate that the electron–hole recombination is less for PtS1 than PtS2 and PtS3. This low electron–hole recombination result in the higher photocatalytic activity of PtS1 than PtS2 which in turn is greater than PtS3. The electrons trapped in platinum sites were subsequently transferred to the surrounding adsorbed O$_2$. The PL spectrum is used to investigate the fate of electron hole pairs in semiconductor particles, since PL emission results from the recombination of free carriers [34, 36].

7.3.5. Raman Spectral Studies

Raman spectroscopy is a powerful technique for the investigation of various phases of TiO$_2$ because it is capable of elucidating the structure as peaks from each material which are clearly separated in frequency and therefore, the phases are easily distinguishable. The expected vibrational modes of anatase TiO$_2$ are $A_{1g} + 2B_{1g} + 3E_g$ at 147, 197, 396, 515 and 638 cm$^{-1}$, and that of rutile are, $A_{1g} + B_{1g} + B_{2g} + E_g$ at 144, 238, 447 and 611 cm$^{-1}$ [37, 38]. Fig. 7.7. (a, b and c) shows the Raman scattering patterns of bare and Ag loaded TiO$_2$ powders. The Raman spectra of bare nanotitania (S1) in Fig. 7.7. a shows that the anatase is the predominant phase, which is in accordance with the XRD analysis. It is found that the spectra of bare and Pt loaded titania nanocube are similar. Both spectra show four Raman bands associated with the TiO$_2$ at around 146, 401, 514 and 638 cm$^{-1}$ [39]. The Raman peaks at 146 and 638 cm$^{-1}$ are assigned to the $E_g$ modes of anatase phase and the Raman peak at 401 cm$^{-1}$ is assigned to the $B_{1g}$ mode. The peak at 514 cm$^{-1}$ is a doublet of the $A_{1g}$ and $B_{1g}$ modes of anatase phase [40]. Raman peaks at 238($B_{2g}$), 447($E_g$) and 611($A_{1g}$) cm$^{-1}$ of spherical nanotitania (S2 and AgS2) and 446($E_g$) and 612($A_{1g}$) cm$^{-1}$ of rod
shaped nanotitania (S3 and AgS3) are assigned to rutile phase (Fig. 7.7. b and c) which are in accordance with the XRD analysis.

Fig. 7.7. Raman spectra of bare and Pt loaded TiO$_2$ samples
The Pt loaded TiO₂ powder shows much stronger vibration peaks due to the surface enhanced Raman scattering effect (SERS) [41,42]. The SERS effect includes electromagnetic and chemical enhancement. No electromagnetic field block between loaded Pt and TiO₂ can lead to the coupling of their electromagnetic fields. Since the 512 nm Ar⁺ laser line is in the region of the plasmon absorption of Pt particles, the electrons located at Pt particle surface could be excited to high energy states. Those electrons can couple with the laser light, leading to an obvious resonance and strong localized fields. As a result, the Pt loaded TiO₂ powder shows enhanced Raman scattering, indicating that Pt particles are tightly connected with TiO₂ grains [43]. Raman intensities of spectral lines increases on platinum loading [38, 43].

7.3.6. Photocatalytic Activity Studies
To investigate the photocatalytic activity of synthesized TiO₂ samples in solar light, the degradation of methylene blue was studied in presence of bare and platinum loaded TiO₂ nanoparticles under sunlight. For comparison, photocatalytic studies were also performed with commercially available photocatalyst, Degussa P25 and the results are depicted in Fig. 7.8. Methylene blue (MB) shows a maximum absorption at 661 nm. The absorption peak gradually diminishes upon solar light irradiation, illustrating the methylene blue degradation. It is clear that the anatase titania nanocubes (S1) shows higher photocatalytic activity than the other two rutile nanostructures (S2 and S3) [26]. The difference in activity of the synthesized samples is related to their surface area, particle size and phase. Small crystallite size and mesoporous texture produces high surface area TiO₂ and hence can provide more active sites and adsorb more reactive species. Since S1 is purely anatase phase and has the highest surface area among the three samples, it exhibits the highest photocatalytic activity. The
appreciable activity observed for the nanorods (34 m² g⁻¹) compared to Degussa P25 (50 m² g⁻¹) is due to the preferentially grown 110 planes in the nanorod morphology [25]. The activity of different samples in sunlight is in the order PtS1 > PtS2 > PtS3 > S1 > S2 > S3 > Degussa P25. The high photocatalytic activity of platinum loaded TiO₂ samples compared to bare titania is mainly attributed to the decrease in band gap so that visible light is enough to excite electron from valence band to conduction band. In our investigation, we have adopted a new strategy in which nanotitania was synthesized by microwave irradiation followed by platinum loading using metal sol approach.

**Fig. 7.8.** Photocatalytic activity of bare and platinum loaded TiO₂
7.4. Conclusions

Anatase nanocubes (S1), rutile nanospheres (S2) and nanorods (S3) were synthesized using a simple microwave irradiation technique by changing the pH of the media. The synthesized nanostructures were loaded with platinum in order to improve the photocatalytic activity of the samples under visible region. Structural and physicochemical characterization revealed the dependence of photocatalytic activity of nanotitania on different morphologies. Among bare samples anatase nanocubes (S1) exhibit a much higher BET specific surface area than rutile nanospheres (S2) and nanorods (S3). The band gap energy for anatase nanocubes is greater than that of the rutile nanospheres (S2) and nanorods (S3). Loading of platinum particles could improve the photocatalytic properties of the titania nanostructures under sunlight. Among the various titania nanostructures, Pt-loaded titania nanocubes exhibit enhanced photocatalytic activity compared to Pt-loaded titania nanospheres and nanorods. Irrespective of the morphology, titania nanocubes, nanospheres and nanorods showed improved photocatalytic activity compared with commercial Degussa P25 TiO₂ photocatalyst in the degradation of the dye, methylene blue in aqueous solution under solar light irradiation.
References

3. Y. Ding, Y. Wang, L. Zhang, H. Zhang, C. M. Li, Y. Lei, Nanoscale 3, 1149 (2011)