6.1. Introduction

This chapter details the synthesis, characterization, optical and photocatalytic studies of palladium loaded titania nanostructures. In the third chapter, we have already reported a simple microwave method to synthesize phase pure anatase and rutile nanotitania with different morphologies viz., cubes, spheres and rods. In an attempt to modify the optical properties of titania synthesized by microwave irradiation, we were successful in loading gold and silver into titania structures as discussed in the fourth and fifth chapters.

Heterogeneous photocatalysis based on TiO$_2$ has been the focal point of numerous investigations in recent years [1-4] because of its chemical stability of this material, its lack of toxicity and its potential utility for total destruction of organic compounds in polluted air and waste water. [5-6] Despite the positive attributes of TiO$_2$, there are a few drawbacks associated with its use; it has a high bandgap (E$_g$ > 3.0 eV) and it is excited only by UV light ($\lambda$ < 400 nm) to inject electrons into the conduction band and to leave holes into the valence band. Thus, this practically limits the use of sunlight or visible light as an irradiation source in photocatalytic reactions on TiO$_2$. In addition, the high rate of electron–hole recombination on TiO$_2$ particles results in a low efficiency of photocatalysis. For the purpose of overcoming these limitations of TiO$_2$ as a photocatalyst, numerous studies have been recently performed to enhance electron–hole separation and to extend the absorption range of TiO$_2$.
into the visible range. These studies include doping metal ions into the TiO$_2$ lattice, dye photosensitisation on the TiO$_2$ surface, addition of inert support and deposition of noble metals [7-19]. However, the efficiency of TiO$_2$-based photocatalysts directly depends on the ability to obtain nanostructured materials with tailored features and to generate electron–hole pairs with a reduced recombination rate.

In this chapter, we report the photocatalytic enhancement of nanotitania by loading palladium using metal sol method. To the best of our knowledge no one has reported previously the preparation of Pd loaded TiO$_2$ using TiO$_2$ synthesized by microwave irradiation technique. By applying microwave heating, the reaction mixture is heated rapidly and more uniformly through direct molecular interaction with electromagnetic radiation. This technique would also reduce reaction time and gives better yield. The major advantages of using microwaves are rapid heat transfer and selective heating [22]. The catalytic performances of three different crystalline titania and their palladium loaded structures (Pd/TiO$_2$) were studied for dye degradation of methylene blue under sunlight.

6.2. Synthesis and Characterization of Pd loaded TiO$_2$ nanostructures

6.2.1. 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) and NH$_4$Cl (5 M), PdCl$_2$, NaBH$_4$, and polyvinyl alcohol (PVA) were employed for the synthesis. Commercially available TiO$_2$ (P-25) from Degussa (Germany) consists of 70% anatase and 30% rutile with a specific BET surface area of 50 m$^2$ g$^{-1}$ and having particle size of 30 nm [23] was used throughout the experiments. This was used as a standard
photocatalyst without any further treatment. A typical microwave oven (Whirlpool, 1200 W) operating at a frequency of 2450 MHz was used for the synthesis. All chemicals were of reagent-grade quality and were used as received. Distilled water was used for all the experiments.

The TiO$_2$ nanostructures having cubical (S1), spherical (S2) and rod like (S3) morphology were synthesized as reported in third chapter [20] and loaded with 0.5 wt% Pd using metal sol method. For this a suitable amount of PVA solution (1 wt%) was added to an aqueous PdCl$_2$ solution (0.1 mg Pd/ml) under vigorous stirring. Then, a freshly prepared solution of NaBH$_4$ (molar ratio NaBH$_4$/Pd = 4) was slowly added drop wise into the mixture. The TiO$_2$ samples were added after the pH was adjusted to 6.0 by NH$_4$OH or HCl solution. The mixture was stirred at 60°C for 3 hrs, then filtered and washed until no Cl$^-$ was detected by AgNO$_3$ solution. After being dried at 100°C overnight, the samples were calcined at 550°C in air for 4 hrs. The Pd loaded on samples S1, S2 and S3 are represented as PdS1, PdS2 and PdS3 respectively.

The X-ray diffraction (XRD) patterns of the titania were recorded on a Brucker D8 advance diffractometer with CuK$_\alpha$ radiation. The crystallite size of TiO$_2$ was calculated using Debye Scherrer equation, $L = k\lambda/(\beta \cos \theta)$, where $L$ is the average crystallite size, $\lambda$ is the wavelength of the radiation, $\theta$ is the Bragg’s angle of diffraction, $\beta$ is the full width at half maximum intensity of the peak and $k$ is a constant usually applied as 0.89. A Jeol JSM 6500F scanning electron microscope was used for FESEM studies. High resolution transmission electron micrographs and electron diffraction patterns were recorded using a JEOL JEM-3010 HRTEM microscope at an accelerating voltage of 300 kV. The TEM specimens were prepared by drop casting the
sample on the surface of the carbon coated copper grid. The tapping mode AFM images of the samples deposited on a mica sheet were taken using Nanoscope-IV scanning probe microscope. The BET surface area, pore size distribution and pore volume of the samples were measured on a Micromeritics ASAP 2010 analyzer based on N$_2$ adsorption at 77 K in the pressure range from 0.1 to 760 mm Hg. The ultraviolet–visible absorption (UV–vis) spectra were recorded using a UV-2450 Shimadzu UV–visible spectrophotometer. The photoluminescence (PL) spectral measurements were made using Perkin Elmer LS-55 luminescence spectrometer at an excitation wavelength of 325 nm. Raman spectroscopic analysis was done using a HORIBA Jobin Yvon iHR550 spectrophotometer.

Photocatalytic activity of TiO$_2$ was evaluated by the degradation of the dye, methylene blue (MB) in aqueous solution under sunlight in the presence of as-synthesized TiO$_2$ and the Pd loaded TiO$_2$. 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 degradation of aqueous methylene blue, TiO$_2$ and Pd/TiO$_2$ sol was prepared. About 100 mg of the synthesized TiO$_2$ or Pd/TiO$_2$ was dispersed ultrasonically in 100 ml of 4 $\times$ $10^{-5}$M methylene blue solutions in a quartz reactor. To maximize the adsorption of the dye onto the TiO$_2$ surface, the resulting mixture was kept in the dark for 30 min under stirring conditions [24]. The solution was then irradiated for 180 min under sunlight. The degradation of the dye was monitored by measuring the absorption maximum of methylene blue at 661 nm at 30 min intervals of reaction.
6.3. Results and Discussion

6.3.1. X-ray Diffraction Studies

Fig. 6.1. XRD patterns of bare and Pd loaded titania

The X-ray diffraction (XRD) patterns (Fig. 6.1.) of the TiO$_2$ particles show that anatase phase with lattice constants, $a = 3.777$ and $c = 9.501$ was formed (JCPDS file no. 89-4921) in NH$_4$OH medium (S1). All the peaks in S2 (NaCl medium) and S3 (NH$_4$Cl medium) corresponds 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 figure that all the samples are highly crystalline and phase pure. It is also observed that there is no phase change due to palladium loading on the samples S1, S2 and S3. Further, no palladium peaks were found in the XRD patterns. The average crystallite sizes of S1, S2, S3, PdS1, PdS2 and PdS3 are 12, 10, 21, 11, 10 and 20 nm respectively. The X-ray diffraction patterns of palladium loaded TiO$_2$ samples almost coincide with that of bare TiO$_2$ showing no diffraction peaks due to
palladium species thus suggesting that the metal particles are well dispersed on the TiO$_2$ surface [25]. This result can presumably be ascribed to the combinations of low contents of loading Pd, small particle size, and homogeneous distribution [26].

6.3.2. BET Surface Area Analysis

The crystallite size, BET surface area, pore size, and pore volume values are summarized in Table 6.1. 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. Palladium loaded TiO$_2$ paritcles show a decrease in surface area of the samples as is evident from the table and this can be ascribed to the calcinations process used during the synthesis. The decrease in surface area after palladium loading is appreciable in the case of S1; this may be due to the blocking of pores of TiO$_2$ nanocube surface by palladium particles [26].

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Crystallite size from XRD (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>PdS1</td>
<td>11</td>
<td>76</td>
<td>2.5</td>
<td>0.29</td>
</tr>
<tr>
<td>PdS2</td>
<td>10</td>
<td>65</td>
<td>1.7</td>
<td>0.12</td>
</tr>
<tr>
<td>PdS3</td>
<td>20</td>
<td>33</td>
<td>1.2</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 6.1 The crystallite size, BET surface area, pore size, and pore volume values of bare and Pd loaded TiO$_2$ samples
6.3.3. Microscopic Analysis

6.3.3.1. FESEM Analysis

FESEM images of palladium loaded and bare titania samples and EDX are given in Fig. 6.2. 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 0.5 wt % Pd was confirmed from EDX analysis for all the three samples (PdS1, PdS2 and PdS3) (Fig. 6.2.a, 6.2.b and 6.2.c). Different concentrations of palladium in all the three samples were tried but optimum results were obtained with 0.5 wt% Pd.

Fig. 6.2.a FESEM of bare and Pd loaded titania (S1 and PdS1) and EDX of PdS1
**Fig. 6.2.b** FESEM of bare and Pd loaded titania (S2 and PdS2) and EDX of PdS2

**Fig. 6.2.c** FESEM of bare and Pd loaded titania (S3 and PdS3) and EDX of PdS3
6.3.3.2. Atomic Force Microscopic Analysis

Fig. 6.3. represents AFM images of palladium loaded TiO$_2$ samples. Palladium particles are not seen in FESEM images or AFM images and may be due to its small size.

Fig. 6.3. AFM images of the palladium loaded titania
6.3.3.3. TEM Analysis

The high resolution TEM images of the bare and palladium loaded TiO\textsubscript{2} nanoparticles synthesized are shown in Fig. 6.4. TEM images of S1 (a) and PdS1 (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 PdS1 (b) shows lattice fringes of the anatase phase with \( d = 0.31 \) nm. The selected area electron diffraction pattern in the inset of the S1 (a) and PdS1 (a) confirms that the sample S1 is a single crystalline anatase phase. The high surface area observed for the sample S1 and PdS1 may be due to the highly porous nature of the cubes. Sample S2 (a) and PdS2 (a) shows the formation of nanospheres of average crystallite size around 8 nm. Corresponding selected area electron diffraction pattern is shown in the inset. The pattern indicates the polycrystalline nature of the sample. Lattice image S2 (b) of these nanospheres shows lattice fringes of the rutile phase with \( d = 0.32 \) nm and lattice image PdS2 (b) shows lattice fringes of the rutile phase with \( d = 0.305 \) nm. Sample S3 (a) and PdS3 (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 S3 (b) of the rutile nanorods show clear lattice fringes of the rutile phase with \( d = 0.32 \) nm and PdS3 (b) show lattice fringes of the rutile phase with \( d = 0.302 \) nm. In all the three Pd loaded samples d spacing has decreased and can be ascribed to the effect of occupation of Pd particles in the lattice. Pd loaded samples showed the presence of very small, spherical and well dispersed palladium nanoparticles on the TiO\textsubscript{2} surface and it appears as black spots in Fig. 4 (PdS1(a), PdS2(a) and PdS3(a)).
Fig. 6.4.a. HRTEM of bare and palladium loaded TiO$_2$ (S1 and PdS1)

Fig. 6.4.b. HRTEM of bare and palladium loaded TiO$_2$ (S2 and PdS2)
**Chapter 6**

**6.3.4. UV–visible Absorption Studies**

Fig. 6.5. 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. The broad absorbance band in 450-550 nm region in the palladium loaded samples PdS1, PdS2 and PdS3 corresponds to the well reported plasmon resonance of nano palladium particles.

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**Fig. 6.4.c.** HRTEM of bare and palladium loaded TiO$_2$ (S3 and PdS3)
Fig. 6.5. UV–visible absorption spectra of bare and palladium loaded TiO$_2$

Table 6.2  Band gap values of bare and Pd 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>PdS1</td>
<td>2.95</td>
</tr>
<tr>
<td>PdS2</td>
<td>2.89</td>
</tr>
<tr>
<td>PdS3</td>
<td>2.91</td>
</tr>
</tbody>
</table>
It is clear from the figure that palladium 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. The band gap energies were calculated by the equation:

\[ \text{Eg} = \frac{1239.8}{\lambda} \]

where \( \text{Eg} \) is the band gap (eV) and \( \lambda \) (nm) is the wavelength of the absorption edges in the spectrum.

The band gap values of bare and palladium loaded TiO\(_2\) samples are given in Table 6.2. The band gap energy of nanocubes (S1, 3.2 eV) is significantly higher as compared to that of nanospheres (S2, 3.17 eV) and nanorods (S3, 3.15 eV). For anatase, the band gap (Eg) is estimated to be 3.2 eV, which is in good agreement with the reported value for anatase (3.2–3.3 eV). The absorption spectrum of rutile shows a lower absorption and the calculated band gap is around 3.17 and 3.15 eV respectively for the samples S2 and S3. 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. The band gap values of palladium loaded TiO\(_2\) samples are less than that of bare nanoTiO\(_2\) samples (Table 6.2). The lower band gap of palladium loaded TiO\(_2\) can enhance the photocatalytic activity of these samples under visible light.

**6.3.5. Photoluminescence Studies**

The photoluminescence emission spectra (PL) of bare and palladium loaded TiO\(_2\) samples were studied in the range of 200-700 nm to investigate the separation efficiency of charge carriers and the results are shown in Fig. 6.6.
It is evident from the figure that the PL intensity of TiO$_2$ was decreased with palladium loading. The lower PL intensity shows that the rate of recombination between electron and holes is low [27, 28]. The electrons are excited from valence band (VB) to conduction band (CB) of TiO$_2$ under UV irradiation and generate photoexcited electrons and holes. Although loading with palladium narrows the band gap of TiO$_2$ samples, the recombination of electrons and holes are relatively slow which is evident from PL spectra.

**Fig. 6.6.** The photoluminescence emission spectra (PL) of bare and palladium loaded TiO$_2$

For palladium loaded TiO$_2$ samples, palladium plays an important role in the interfacial charge transfer and in the decrease in rate of electron-hole
recombination. Palladium 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 palladium loaded sample is in the order PdS1>PdS2>PdS3 as is evident from the Fig. which indicates that the electron – hole recombination is less for PdS1 than PdS2 and PdS3. This also helps for the higher photocatalytic activity of PdS1 than PdS2 which in turn greater than PdS3. The electrons trapped in palladium sites were subsequently transferred to the surrounding adsorbed O$_2$. It can be supported by PL emission spectra which have been widely used to investigate the fate of electron hole pairs in semiconductor particles since PL emission results from the recombination of free carriers [27, 28].

6.3.6. Raman Spectral Studies

Fig. 6.7. (a, b and c) shows the Raman scattering patterns of bare and Pd loaded TiO$_2$ powders. 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$^{-1}$ [29]. The Raman spectra of S1 show (Fig. 6.7.a) that the anatase is the predominant phase, which is in accordance with the XRD analysis. It is found that the spectra of bare and Pd loaded are similar. Both spectra show four Raman bands associated with the TiO$_2$ at around 638, 514, 401, and 146 cm$^{-1}$ [29]. The Raman peaks at 146 and 638 cm$^{-1}$ are assigned to the Eg modes of anatase phase and the Raman peak at 401 cm$^{-1}$ is assigned to the B1g mode. The peak at 514 cm$^{-1}$ is a doublet of the A1g and B1g modes of anatase phase [30].
Fig. 6.7. Raman spectra of bare and Pd loaded titania
The Pd loaded TiO\textsubscript{2} powder shows much stronger vibration peaks due to the surface enhanced Raman scattering effect (SERS) [31]. The SERS effect includes electromagnetic and chemical enhancement. No electromagnetic field block between loaded Pd and TiO\textsubscript{2} can leads to the coupling of their electromagnetic fields. Because the 512 nm Ar + laser line is in the region of the plasmon absorption of Pd particles, the electrons located at Pd 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 Pd loaded TiO\textsubscript{2} powder shows enhanced Raman scattering, indicating that Pd particles are tightly connected with TiO\textsubscript{2} grains \textsuperscript{32}. Raman spectra of S2 and S3 are identical to rutile phase (Fig. 6.7.b and c). Raman intensities of spectral lines increase on palladium loading as in the case of S1 [33, 34].

### 6.3.7. Photocatalytic activity

To investigate the photocatalytic activity of synthesized TiO\textsubscript{2} samples in solar light, the degradation of methylene blue was studied in presence of bare and palladium loaded TiO\textsubscript{2} nanoparticles under sunlight. For comparison, photocatalytic studies were also performed with commercially available photocatalyst, Degussa P25 and the results are depicted in Fig. 6.8.

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) as we reported earlier [20]. 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 TiO\textsubscript{2} 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 m$^2$ g$^{-1}$) compared to Degussa P25 (50 m$^2$ g$^{-1}$) is due to the preferentially grown 110 planes in the nanorod morphology as reported in our paper [20]. The activity of different samples in sunlight is in the order PdS1 > PdS2 > PdS3 > S1 > S2 > S3 > Degussa P25. The high activity of palladium loaded TiO$_2$ samples than corresponding bare TiO$_2$ is mainly attributed to the decrease in band gap so that visible light is enough to excite electron from valence band to conduction band.

![Graph](image)

**Fig. 6.8.** Photocatalytic activity of bare and palladium loaded TiO$_2$ samples in solar light
6.4. 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 palladium 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 non-loaded 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 palladium particles could improve the photocatalytic properties of the titania nanostructures under sunlight. Among the various titania nanostructures, Pd-loaded titania nanocubes exhibit enhanced photocatalytic activity compared to Pd-loaded titania nanospheres and nanorods. Irrespective of the morphology, titania nanocubes, nanospheres and nanorods showed improved photocatalytic activity compared commercial Degussa P25 TiO₂ photocatalyst in the degradation of the dye, methylene blue in aqueous solution under solar light irradiation.
References


