Synthesis of a compound with desired properties depends on its method of preparation and its characterisation. These are functionalized by various qualitative, quantitative, sensitive and specific techniques. Quantitative determination of composition and structure on the atomic scale is one of the major advantages of characterisation techniques. The research work behind the area of photocatalysis is mainly focused on the synthesis and characterisation of titania and its modified material with variety of applications. The main aim of characterisation is to correlate between structure and physiochemical properties with its the photocatalytic activities.
3.1 Introduction

In heterogeneous catalysis, the reactions most probably occur on its surface. Therefore it is necessary to characterize the catalyst to get a correct correlation between its physio-chemical properties and catalytic performance (1). In this chapter we discuss the results of characterisation techniques carried out on the prepared catalysts. The techniques are X-ray diffraction analysis (XRD), UV-Visible Diffuse reflectance spectroscopy (UV-Vis. DRS), CHNS elemental analysis, Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDX), Transmission electron microscopy (TEM), High resolution TEM analysis (HRTEM), Selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), Raman spectra analysis (RAMAN), and thermo gravimetric analysis (TG).

3.2 Optimization of catalyst

In the initial stages of the research focused on the preparation of pure titania and non-metal doped titania. In this purpose we used titanium tetraisopropoxide as the precursor for titania with isopropyl alcohol as the solvent source. We used several dopants sources such as urea, thiourea, ammonium chloride, liquid ammonia, triethylamine, diphenylamine, triethanolamine, orthophenylene diamine, aniline, ammonia etc for the preparation of non-metal doped titania. All the prepared catalysts were characterized by CHNS elemental analysis for the presence of dopant content, UV-Vis. DRS for the calculation of band gap and XRD analysis for the phase purity and crystallite nature. From these, we selected nitrogen doped titania catalyst obtained from urea and nitrogen sulphur co-doped titania catalyst obtained from thiourea as the dopant source for further studies. The preparations are repeated with same experimental conditions for the selected catalysts. The same characterisation techniques are also repeated and show a very good correlation results.
We also prepared different pure and modified catalyst with variations in amount of dopants concentration, amount of precursor concentration and different calcination temperature. The photocatalytic ability of all the prepared catalysts was evaluated by studying the degradation of aqueous solution of methylene blue in sunlight. From the activity studies we optimized nitrogen doped and nitrogen sulphur co-doped titania catalyst calcined at 400 °C by using 1:10 volume ratio of titanium isopropoxide to isopropyl alcohol with 10% aqueous solution of urea and 1% aqueous solution of thiourea respectively. And these are denoted as N-TiO$_2$ and NS-TiO$_2$. For the comparative study we also selected two other catalysts, for each optimized doped system with higher and lower amount of dopant source. Thus for nitrogen doped titania we used 5% and 12.5% aqueous urea solution, and for nitrogen sulphur co-doped titania we used 0.5% and 2.0% aqueous thiourea solution respectively. These are denoted as N-TiO$_2$ (l), N-TiO$_2$ (h), NS-TiO$_2$ (l) and NS-TiO$_2$ (h). For the preparation of pure titania same experimental conditions are repeated without adding the dopant source and it is denoted as L-TiO$_2$.

The physical appearance such as colour of the pure titania, nitrogen doped titania, nitrogen sulphur co-doped titania are white, yellow and slight less deep yellow respectively. The colour change in modified catalyst compared to pure titania indicates that the presence of some impurities incorporated into the network of titania. Later it is confirmed from other characterisation techniques that nitrogen and sulphur are these impurities.

### 3.3 X-ray Diffraction Analysis (XRD)

The crystallographic phases present in a sample are well understood from its X-ray diffraction pattern. X-ray diffraction analysis provides a powerful tool to understand the phase purity of the samples. It is widely used for determining the three dimensional structure of solid materials. It also provides the information such as crystallite nature, crystallite size, unit cell...
dimensions etc. (2). Fig. 3.1 shows the XRD pattern obtained for the samples of nitrogen doped titania (N-TiO$_2$), nitrogen sulphur co-doped titania (NS-TiO$_2$), pure titania (L-TiO$_2$) and commercial anatase titania (A-TiO$_2$) using Bruker AXS D8 advance X-Ray Diffractometer with Ni filtered Cu K$_\alpha$ radiation source ($\lambda = 1.5406$ Å) by recording 2$\theta$ in the range of 10-70$^\circ$ at a scan rate of 0.5$^\circ$/min.

![Fig. 3.1. XRD spectra of pure and modified titania](image)

The spectra showed that all the prepared catalyst give peaks at 2$\theta$ values around 25.4, 37.8, 55.1 and 62.8. These values correspond to the peaks of anatase phase (compared with standard value obtained from JCPDS data). Thus it is clear from the spectrum that all the prepared catalysts are in purely anatase with main peak at 2$\theta$ value of 25.4 corresponding to the (101) plane. The absence of peaks corresponding to the other phases indicated that all the prepared catalysts are purely anatase. There are no characteristic peaks corresponding to dopants due to their very small concentration. This reveals that the incorporation of dopants in the titania lattice do not make change on the its structure.
It is also noted from the spectra that all the prepared catalysts are well crystalline in nature. Crystallite size is determined by measuring the broadening of a major peak in a diffraction pattern associated with a particular planar reflection within unit cell of the crystal. It is inversely related to the FWHM (full width at half-maximum) of an individual peak. If the crystallite sizes are small then it can be randomly arranged or have low degrees of periodicity which results in the broadening of peak. If the crystallites are big, the periodicities of the individual crystallite domains reinforced resulting in a tall narrow peak (3). Thus larger the crystallite size, narrower the peak.

Crystallite size is a measure of the size of a coherently diffracting domain. The presence of poly crystallite aggregates show that crystallite size is not generally the exactly same as particle size. The average crystallite size is calculated from the broadening of the (101) XRD peaks of anatase using the Scherrer* equation and are reported in Table 3.1. It is clear from the Table that prepared samples are the nano sized particles with in the range of 10-12 nm. The broadening of the peaks in the prepared samples indicated that the particles size is decreased compared to commercial sample, having sharp peak (4,5). It was worth to note that the crystallite size in the range of 11-13 nm contributed to the optimum for photocatalytic activity mentioned by Wang et. al. This is because a very small crystallite size causes a blue shift in the absorption spectrum and favours surface recombination of the photo-excited holes and electrons while a larger crystallite size exhibits lower surface area and thus a smaller number of catalytic active sites per unit mass of catalyst (6-9).

* Scherrer equation, \[ D = \frac{K \lambda}{\beta \cos \theta} \]

Where \( D \) is the crystallite size, \( \theta \) and \( \lambda \) are the Bragg angle and the wavelength of the X-ray used. \( K \) is a constant approximately equal to 0.89; \( \beta \) is the full width half maximum of the strongest peak at \( \theta \) value.
Table 3.1. Crystallite size, bandgap and surface area of the prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Band gap (eV)</th>
<th>S.A BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-TiO2</td>
<td>10.0</td>
<td>2.3</td>
<td>100.9</td>
</tr>
<tr>
<td>N-TiO2</td>
<td>9.6</td>
<td>2.3</td>
<td>122.9</td>
</tr>
<tr>
<td>L-TiO2</td>
<td>11.6</td>
<td>3.1</td>
<td>85.7</td>
</tr>
<tr>
<td>A-TiO2</td>
<td>36.2</td>
<td>3.2</td>
<td>12.7</td>
</tr>
</tbody>
</table>

3.4 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis.DRS)

UV-Vis Diffuse reflectance spectroscopy is one of the spectroscopic techniques used for the insoluble solid materials. This technique allows the analyst to take advantage of the reflection of the incoming beam rather than using standard absorption configuration. Since only the surface of the sample is responsible for reflection and absorption of the incident radiation, it is used in the surface science of chemistry and physics. The most appropriate theory behind the diffuse reflections and transmission of light scattering layers is
developed by Kubelka and Munk (9-11). For an infinitely thick, opaque layer the Kubelka-Munk equation can be written as

\[ F(R_\alpha) = \frac{(1-R_\alpha)^2}{2R_\alpha} = \frac{k}{s} \]

Where \( R_\alpha \) is the diffuse reflectance of the layer relative to a non absorbing standard such as BaSO\(_4\), \( k \) is molar absorption coefficient of sample and \( s \) is the scattering coefficient.

A classical semiconductor exhibits minimal optical absorption for photons with energies smaller than the bandgap and high absorption for photons with energies greater than the bandgap. As a result, there is a sharp increase in absorption at energies close to the bandgap that manifests itself as an absorption edge (or reflection threshold) in the UV-Vis. absorption spectrum. For titania which has a bandgap between 3.0-3.2 eV, this absorption edge occurs at about 385-400 nm (see Fig. 3.3). That is charge transfer from the valence band (mainly formed by 2p orbitals of the oxygen anions) to the conduction band (mainly formed by 3d orbitals of titanium cation) (12, 13).

The band gap of catalyst is calculated using following equation.

\[ E = \frac{h\nu}{\lambda} = \frac{hc}{\lambda} \quad \text{or} \quad E = \frac{1240}{\lambda} \text{ (nm)} \]

\( E \) is the band gap in eV and \( \lambda \) is the wavelength from which reflection taken place

(This relation is called one of the simple version of KM (Kubelka-Munk) equation. The \( \lambda \) value obtained from the spectrum as shown in Fig.3.3).
Fig. 3.3 shows the UV-Vis diffuse reflectance spectra of the samples measured in the range of 200-900 nm using on Labomed UV-VIS Double beam UVD-500 spectrophotometer equipped with an integrating sphere assembly, using BaSO₄ as reflectance standard with a CCD detector.

From the figure it is clear that both the modified catalyst (N-TiO₂ and NS-TiO₂) gives a shift in absorption in the visible region compared to the pure samples. This indicated that the incorporation of impurities such as N and S in titania system, which responsible for the visible light absorption of the catalyst. The calculated values of band gap of all the catalysts are shown in Table 3.1. The decrease of bandgap may be attributed to the incorporation dopants energy states between the energy states of titania. That is the energy states of dopants such as 2p level of Nitrogen and 3p level of sulphur creates an intermediate energy level within the valence band and conduction band of pure titania. The two absorption edges in the modified catalyst are attributed to the pure titania and impurities such as nitrogen and sulphur are incorporated states of titania.
3.5 CHNS Elemental analysis

The presence of dopants elements in the modified catalyst were also confirmed from their elemental analysis. The CHNS elemental analysis was performed using a Elementar Vario EL III apparatus.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Nitrogen</th>
<th>% Sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-TiO₂ (l)</td>
<td>0.41</td>
<td>--</td>
</tr>
<tr>
<td>N-TiO₂</td>
<td>0.69</td>
<td>--</td>
</tr>
<tr>
<td>N-TiO₂ (h)</td>
<td>0.73</td>
<td>--</td>
</tr>
<tr>
<td>NS-TiO₂ (l)</td>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td>NS-TiO₂</td>
<td>0.18</td>
<td>1.14</td>
</tr>
<tr>
<td>NS-TiO₂ (h)</td>
<td>0.19</td>
<td>1.28</td>
</tr>
</tbody>
</table>

The results are shown in Table 3.2. The results indicated that the dopants such as nitrogen and sulphur are incorporated in the modified catalysts. It also noted that the percentage of dopant increases with increase in the dopant source concentration. At higher concentration of dopants source, the increase of dopant incorporated in the catalyst is not much significant. From the initial activity study we selected N-TiO₂ and NS-TiO₂ for further studies.

3.6 Scanning Electron Microscopy

The catalytic morphology can affect the transport of reactants and products to or from its active sites, its light absorption power and generation of photo excited species (9). Studies of the catalytic morphologies are an important parameter for interpreting the photocatalytic activity. The morphologies are noticeably dependent on the preparation procedure and the composition. Surface morphology of the catalysts is also observed from its TEM images.
The scanning electron microscopic images of the nitrogen doped and nitrogen sulphur co-doped titania are shown in Figure 3.4 and 3.5 respectively. The images show that the particles are somewhat spherical in nature and some are rectangular in shape. Most of them are shapeless due to the agglomerated crystallite powder morphology.

![Fig. 3.4. SEM images of N-TiO$_2$](image1)

![Fig. 3.5. SEM images of NS-TiO$_2$](image2)

### 3.7 Energy Dispersive X-ray analysis

The energy dispersive X-ray analysis gives both qualitative and quantitative information about the elemental composition of the materials. From the EDX spectra we can conclude that the presence other materials such as impurities or adducts in the samples. These impurities occur either accidently with the reagents molecules or added for modification of the
basic materials. The intensity of the spectra correlates with the amount of elements present in it. The EDX spectra of catalysts nitrogen doped titania and nitrogen sulphur co-doped titania are shown in fig. 3.6 and 3.7 respectively. The presence of doped elements such as nitrogen and sulphur in modified samples are clearly shown in the spectra of these catalysts. This indicates the incorporation of dopants such as nitrogen and sulphur in the titania network. As per the in efficiency of the instrument for the quantification elements of atomic number less than eleven, we can only give the qualitative information (not shown here) about the elemental composition of catalysts. The chemical compositions of the catalysts were obtained from JEOL Model JED-2300, energy dispersive X-ray analyzer used in conjunction with SEM.

Fig. 3.6. EDX spectra of N-TiO₂
3.8 Transmission Electron Microscopy

![Fig. 3.8. TEM image of N-TiO₂](image1)

![Fig. 3.9. TEM image of NS-TiO₂](image2)
Fig. 3.10. Particle size histogram of N-TiO₂

Fig. 3.11. Particle size histogram of NS-TiO₂

Fig. 3.12. HRTEM image of N-TiO₂

Fig. 3.13. HRTEM image of NS-TiO₂

Fig. 3.14. SAED image of N-TiO₂

Fig. 3.15. SAED image of NS-TiO₂
The Transmission Electron Microscopic (TEM) images of the modified catalysts N-TiO$_2$ and NS-TiO$_2$ are shown in Fig. 3.8 and 3.9 respectively. It can be noted from the images that the particles are agglomerated and exhibit both spherical and rectangular shapes. These are also in agreement with results of SEM images. Further observations indicate that the morphology of modified TiO$_2$ powders is very rough and may be beneficial for enhancing the adsorption of reactants due to its great surface roughness and high surface area.

Fig. 3.10 and 3.11 indicates the particle size histogram of the modified catalysts N-TiO$_2$ and NS-TiO$_2$ respectively. The results showed that both the catalysts give an average particle size of 7-13 nm. This result roughly indicated very good correlation of crystallite size obtained from XRD analysis. This crystallite size is believed to be correlated with the optimum size for better photocatalytic results (6).

The High resolution TEM images of the both catalysts are shown in Fig. 3.12 and 3.13. Particles in nano size range are clearly observed from the images. Both catalysts give around the same d value (d=0.357nm) obtained from their respective HRTEM images. These values give very good correlation with the d value obtained from the XRD spectrum of the respective catalyst, and this corresponds to the major anatase 101 planes. This result once again confirms the formation of purely anatase phase of the prepared samples. The images also indicated that the particles are well ordered and highly crystalline nature.

Fig. 3.14 and 3.15 show the selected area electron diffraction (SAED) pattern of the modified catalyst N-TiO$_2$ and NS-TiO$_2$ respectively. Electron diffraction reveals that each particle is composed of many small crystal nuclei, which is a convincing proof that the particles grow in aggregation model. The
well clarified electron diffraction pattern (used for the identification of crystallographic spacing) indicates that those particles are highly crystalline and well ordered. The d value corresponding to each pattern is calculated using the following equation.

\[ d = \frac{L \cdot h}{R \sqrt{2ME}}. \]

Where

- \( L \) = Camera constant
- \( h \) = Plank’s constant
- \( E \) = Energy of electron beam
- \( M \) = Mass of electron
- \( R \) = Radius of the diffraction circle.

Thus the d value obtained from the main diffraction circle is approximately equal to 0.357 nm, which corresponds to the anatase 101 plane. Thus this result indicates that the prepared catalysts are purely anatase with major 101 planes, which is also good agreement with that obtained from the XRD results.

### 3.9 X-ray Photoelectron Spectroscopy (XPS)

The atomic concentration values derived from the XPS data are presented in Table 3.3–3.6. For oxygen the 1s XPS spectra was de-convoluted using Gaussian multi-peak fitting program and peak area of 529.3 eV peak was taken for atomic ratio calculation purpose. Peak areas for corresponding peaks were divided by the sensitivity factors in these calculations. The values of sensitivity factors used in these calculations are given in Table 3.7. It may be noted that at some places C 1s peak with binding energy value of 284.8 eV is referred as standard value for the surface adventitious carbon. Thus if we include this correction the B.E. values observed in present study will be shifted to higher side by 0.2 eV.
Fig. 3.16 and 3.17 represents the Ti 2p XPS spectra of catalyst N-TiO$_2$ and NS-TiO$_2$ respectively. In each case there are two peaks. For N-TiO$_2$ peaks appear at 458.2 and 464.7 eV and for NS-TiO$_2$ peaks appear at 458.4 and 464.1 eV respectively. These are assigned to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ states. These doublet peaks are due to the spin-orbit splitting of Ti 2p (14). The above value indicates that titanium exists as Ti$^{4+}$ with stable Ti-O bond in the prepared catalysts. There is no evidence for the existence of Ti$^{3+}$ states. But for the pure titania (from literature) these peaks are observed at 458.9 and 464.7 eV respectively, which are contributed by O-Ti-O in TiO$_2$ (4,15,16). Compared with this, the Ti 2p peaks for both modified catalysts show a smaller shift in the binding energy. These shifts of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ core level signals suggesting the successful incorporation of the dopant into the titania lattice, which are attributed to Ti 2p peaks of N-Ti-N or O-Ti-N in modified titania (17).

**Table 3.3.** Atomic ratio derived from XPS data of Ti 2p$_{3/2}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ti 2p$_{3/2}$ peak</th>
<th>Ti:O:N/ Ti:O:N:S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>N-TiO$_2$</td>
<td>458.2</td>
<td>1.07</td>
</tr>
<tr>
<td>NS-TiO$_2$</td>
<td>458.4</td>
<td>1.13</td>
</tr>
</tbody>
</table>

**Table 3.7.** Sensitivity factor obtained from XPS analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>XPS peak</th>
<th>Sensitivity Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2p3/2</td>
<td>5.22</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>2.85</td>
</tr>
<tr>
<td>N</td>
<td>1s</td>
<td>1.74</td>
</tr>
<tr>
<td>S</td>
<td>2s</td>
<td>1.25</td>
</tr>
</tbody>
</table>
The O 1s XPS spectrum of catalyst N-TiO$_2$ and NS-TiO$_2$ are shown in Fig 3.18 and 3.19. The valence band of titania is mainly constructed with O 2p state, which is hybridized with the Ti 3d states (18,19). It shows a strong peak at 529.3 eV corresponding to bulk oxygen bonded to titanium where as weak band at 531 eV is due to oxygen attached to N. The weak shoulder at higher binding energy is associated with hydroxyl groups or sulphate ions adsorbed on the TiO$_2$ surface. But in the case of catalyst NS-TiO$_2$ shows another weak shoulder at higher binding energy of 532.2 eV (not shown here) due to the effect of sulphur which exists as S $^{6+}$ by replacing some of Ti.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>O 1s peak</th>
<th>Ti:O:N/ Ti:O:N:S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>N-TiO$_2$</td>
<td>529.2</td>
<td>1.07</td>
</tr>
<tr>
<td>NS-TiO$_2$</td>
<td>529.4</td>
<td>1.05</td>
</tr>
</tbody>
</table>
The N 1s XPS spectrum of catalyst N-TiO$_2$ and NS-TiO$_2$ are shown in Fig. 3.20 and 3.21. The assignment of the XPS peak of N 1s has still been under debate, and controversial hypotheses have been provided. Since the preparation methods and conditions largely affect N XPS spectral features, the peak position may be different for the same compounds prepared by different methods. In addition, the N source is different, which could probably influence the characteristics of the N state. Asahi et.al. (20) assigned the atomic beta N peak at 396 eV to substitutional N, which may be related to the active sites in photocatalysis. Most researchers also agree on N 1s peak at 396.0 - 397.5 eV responsible for substitutional doping of N atoms into the TiO$_2$ lattice indicates the characteristic peaks of Ti-N-Ti type linkage (4,15,16,21). Both the substitutional and interstitial N could affect the electronic band structure of TiO$_2$ and improve the photocatalytic activity in visible light region (22). Some researchers attributed the N 1s peaks at binding energies at 400 and 402 eV to molecularly adsorbed nitrogen species. Burda et.al. (15) observed a N 1s core level at 401.3 eV in N-doped titania nano particles and suggested that it is attributed to the N atoms in the environment of O-Ti-N, based on the comparison with the
N 1s electron binding energy of TiN (397.2 eV). Viswanath et al. and Ma et al. (4, 23) supported the above assignment and they concluded that the observed N 1s core level peak at 398-399 eV attributed to O-Ti-N linkage in the crystalline TiO$_2$ lattice.

The peak at 399.7 eV is also attributed to N-O bonds (24). It has also been reported that N 1s peak at around 400 eV can be assigned to molecularly chemisorbed gamma Nitrogen (25). Many researchers pointed out that the presence of oxidized nitrogen such as Ti-O-N and/or Ti-N-O linkages should appear above 400 eV (4,15,16,19,20,21). Di Valentin et al. reported that there are two types of N species in N-TiO$_2$ using electron paramagnetic resonance spectroscopy measurements and DFT calculations (26). Their spin-Hamiltonian parameters were consistent with calculations for both substitutional and interstitial N impurities. The N 1s peak observed at 399.6 – 399.9 eV, may also be attributed to the formation of hyponitrite(17,27).

Thus the main peak which appears around 399 eV can be assigned to either substitutional N replaced O atom of the TiO$_2$ lattice or the interstitial N bound to one lattice oxygen and formed as NO species. None of the catalysts shows the peak at 396-397 eV attributed to atomic nitrogen (18). Therefore, the peak around 399.6 eV in Fig 3.20 is assigned to the O-Ti-N linkage. These can be further evidenced by the positively shifted binding energy of N 1s core level to 400.2 eV in NS-TiO$_2$ (Fig. 3.21). The shift of binding energy to higher values indicated a decrease in the electron density of N atom. In other words, some N atoms become more positive when the S incorporated. It is likely that nitrogen species coordinate to S in the form of O-S-N linkage, similar to the O-Ti-N as in the case of doped only with nitrogen.
Table 3.5. Atomic ratio derived from XPS data of N 1s

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N 1s peak</th>
<th></th>
<th>TiO:N/ TiO:N:S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>FWHM (eV)</td>
<td>B.E. (eV)</td>
<td></td>
</tr>
<tr>
<td>N-TiO₂</td>
<td>399.5</td>
<td>3.0</td>
<td>89.3</td>
<td>1 : 1.80 : 0.27</td>
</tr>
<tr>
<td>NS-TiO₂</td>
<td>400.3</td>
<td>2.41</td>
<td>485.9</td>
<td>1 : 1.86 : 0.09 : 0.18</td>
</tr>
</tbody>
</table>

Fig. 3.20. N 1s XPS spectra of N-TiO₂   Fig. 3.21. N 1s XPS spectra of NS-TiO₂

Fig. 3.22. represents the S 2p XPS spectrum of catalyst NS-TiO₂. T. Ohno and others reported that the peak of S 2p around 168.0 – 170.0 eV corresponds to the S atom incorporated as cation in the form of S⁶⁺ in titania network and are expected to replace with Ti ions. The peak around 160.0 – 163.5 eV corresponds to S atom in Ti-S state (14,28). Therefore, the absence of peak at 160-163.5 eV indicates that sulphur does not replace oxygen atoms in the TiO₂ lattice. And the peak at 168.5 eV could be assigned to S⁶⁺ state (as SO₄²⁻). These sulphate ions can form S=O and S-O-S bonds on the TiO₂ surface, creating unbalanced charge on Ti and vacancies/defects in the titania network (14).
Table 3.6. Atomic ratio derived from XPS data of S 2p

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N 1s peak</th>
<th>Ti:O:N/ Ti:O:N:S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>N-TiO₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NS-TiO₂</td>
<td>168.3</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Fig. 3.22. S 2p XPS spectra of NS-TiO₂

3.10 Raman Spectroscopy

Raman spectra of the prepared catalyst are shown in Fig. 3.23. The results show that all the prepared catalysts give the peaks around 145, 397, 515 and 641 cm⁻¹ which are the characteristic peaks of anatase. No other peaks correspond to the rutile phase indicating that the prepared catalysts are purely anatase. The absence of more additional bands except those corresponding to anatase also verified that the lattice distortion is minor, since a severe lattice distortion to a lower symmetry usually leads to the splitting of Raman modes.

From a measurement of the maximum of low frequency Raman band, it is possible to determine the nano particle size (not shown here). Since the particle size can cause large shifts in the location of the scattered Raman peaks and their widths, namely the quantum size confinement effect. Consequently,
compared with the lowest frequency peak at 145 of different samples, it can be evidently seen that the intensities of this peak are dramatically increased and its widths are broadened after the dopants introduced (14,29-31). It indicates that the crystallite nature is enhanced, phase purity is retained and the particle size is decreased, which correlates the results obtained from XRD and TEM results.

![Raman spectra of the prepared catalyst](image)

**Fig. 3.23.** Raman spectra of the prepared catalyst

### 3.11 Thermal Analysis

The thermo gravimetric analysis is a well established technique for evaluating the thermal stability of the materials. It finds widest applications in the determination of different parameters depending on preparation of catalyst. These are nature and composition of active phase, effect of added promoters or presence of impurities on the catalyst, dispersion of active phase and active phase support interactions, nature and heterogeneity of active sites on catalyst surface, mechanistic aspects of the reaction under investigation, transient chemical changes that occurs on the surface, catalyst deactivation and regeneration etc. This can also be used for quality
control and catalyst characterisation through fingerprint spectra of different batches of the same catalyst. The techniques involve the pursuit of weight of sample over a period of time while its temperature is raised linearly. Recording analytical data and the temperature curve with provision for controlled heating of sample is carried out. In a thermo gravimetric curve (TG), horizontal portions point out regions where there is no weight change, whereas weight loss is indicated by curved portions.

Thermo gravimetric analysis was done on a Perking Elmer Pyris Diamond thermo gravimetric/differential thermal analyzer instrument under nitrogen atmosphere at heating rate of 10 °C/min from room temperature to 700 °C with samples mounted on a alumina sample holder. The thermo gravimetric analysis of the both modified catalyst N TiO$_2$ and NS-TiO$_2$ are shown in Fig. 3.24. The results indicated that both the catalysts give a very good thermal stability above the temperature of 400 °C. Initially there is a loss of weight due to removal of water molecules and above the temperature of 350 °C both compounds show no apparent loss of weight. So the catalysts can be prepared at a lower temperature.

![Thermo gram of N TiO$_2$ and NS-TiO$_2$](image)

**Fig. 3.24.** Thermo gram of N TiO$_2$ and NS-TiO$_2$
References


Results and Discussions


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