CHAPTER - III

STRUCTURAL, MORPHOLOGICAL AND CHEMICAL COMPOSITION STUDIES

This chapter deals with PXRD, AFM, SEM and EDS analyses. The structure and phase of the TiO$_2$ nanoparticles are carried out by PXRD studies. The morphology of the synthesized TiO$_2$ nanoparticles is identified by AFM and SEM analysis. The EDS spectroscopy studies are carried out to find out chemical composition of TiO$_2$ nanoparticles.

3.1 Powder X-Ray Diffraction Studies

Powder X-Ray Diffraction (PXRD) is the primary tool for investigating the structure of crystalline materials and imperfections. Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. It is mostly used to characterize and identify phases and structures.

The great advantages of the technique are:

- Simplicity of sample preparation
- Rapidity of measurement
- The ability to analyze mixed phases, e.g. soil samples
- “In situ” structure determination

X-rays have a wavelength that is similar in magnitude to the spacing between the atoms in most inorganic materials. The dominant effect that occurs when an incident beam of monochromatic X-rays interact with a target material is scattering of those X-rays from atoms within the target material. This means that under certain
circumstances X-ray beams can be diffracted by crystal lattices. When the scattered radiation is collected on a flat plate detector, the rotational averaging leads to smooth diffraction rings around the beam axis rather than the discrete Laue spots observed in single crystal diffraction. The angle between the beam axis and the ring is called the scattering angle and in X-ray crystallography always denoted as $2\theta$. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interferences. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg’s Law, $2d \sin \theta = n\lambda$. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. However, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder. When a powder with randomly oriented crystallites is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected. An examination of the X-ray patterns produced will yield information regarding the arrangement of atoms within the lattice. X-ray diffraction is used for identification of compounds and phases, determination of crystal structures, determination of lattice parameters, and measurements of crystallite size. The schematic diagram of XRD is shown in figure (3.1). Since an X-ray diffraction pattern is determined by the atomic arrangement within a specimen, any material will produce diffraction pattern that is characteristic compounds or phases. Figure (3.2) shows the diffraction of X-rays from set of crystal planes.
Identification is aided by search and match software which compares experimental data with standard patterns from the ICDD reference database (JCPDS file). From this comparison, the compounds and phases of the synthesized materials can be identified. The broadening of X-ray diffraction peaks provides a convenient method for measuring particle sizes below 0.1 micrometer. The origins of the X-ray line broadening effects, like many other diffraction effects of crystals are best understood in terms of reciprocal lattices. Essentially, the width of the diffraction peak is inversely proportional to parameter, that is a measure of the size of the crystallites. When the size of the crystallites increases, the width of the peak decreases. If the crystallite gets too large, greater than 0.1 micron in average diameter, the peaks are so narrow that the width cannot be distinguished from the broadening in the X-ray diffraction instrument [1].

![Figure 3.1: Schematic diagram of PXRD system](image-url)
The effective crystallite sizes of the synthesized samples are calculated based on line broadening of X-ray diffraction peaks. The sizes of the crystallites (D) are obtained from the Debye-Scherrer’s equation,

\[ D = \frac{K\lambda}{\beta \cos \theta} \] ........................ (1)

where \( \lambda \) is the wavelength of the incident X-rays, \( \beta \) is full width half maximum, \( \theta \) is the half of the Bragg angle and \( K \) is a numerical constant and can be obtained by using the factor \( 2(\ln 2/\pi) = 0. 93 \) [2].

From the powder X-ray diffraction data, the angle of scattering and the corresponding intensities of diffracted beams for each reflection can be obtained. The lattice constants ‘a’ and ‘c’ values for tetragonal anatase phase of pure and metal ions doped TiO\(_2\) nanoparticles are calculated using the following equation [3],

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**Figure 3.2: Diffraction of X-rays from a set of crystal planes**

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The strain induced in powders due to crystal imperfection and distortion was calculated using the formula

\[ \varepsilon = \frac{\beta_{hkl}}{4 \tan \theta} \] ........................ (3)

From equations (1) and (3), it is confirmed that the peak width from crystalline size varies as \( \frac{1}{\cos \theta} \) and strain varies as \( \tan \theta \). Hence, sum of equations (1) and (3) simplify the breadth of the line,

\[ \beta_{hkl} = \frac{K \lambda}{D \cos \theta} + 4 \varepsilon \tan \theta \] ........................ (4)

Rearranging the above equation gives,

\[ \beta_{hkl} \cos \theta = \frac{K \lambda}{D} + 4 \varepsilon \sin \theta \] ........................ (5)

The above equations are called W-H equations. A plot is drawn with \( 4 \sin \theta \) along the x-axis and \( \beta_{hkl} \cos \theta \) along the y-axis for the prepared samples. From the linear fit to the data, the crystalline size is estimated from the y-intercept, and the strain, from the slope of the fit [4]. Equation (5) represents the uniform deformation model (UDM), where the strain is assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where the material properties are independent of the direction along which they are measured. In this present study, Powder X-ray diffraction data are recorded using X’PERT PRO.
PANalytical X-ray diffractometer. Photograph of X’PERT PRO PANalytical X-ray diffractometer is shown in figure (3.3).

![X'PERT PRO PANalytical X-ray diffractometer](image)

**Figure 3.3: Photograph of X’PERT PRO PANalytical X-ray diffractometer**

### 3.2 Powder X-Ray Diffraction (PXRD) Analysis

Figure (3.4) shows the PXRD pattern of pure TiO$_2$ nanoparticles prepared via Sol-Gel method. The 20 scans are recorded at several resolutions using Cu Kα-1 radiation of wavelength 1.54060 Å in the range of 10-80 degrees.

The PXRD patterns of the prepared pure TiO$_2$ nanoparticles show broad peaks. The broad peaks in the PXRD spectra indicate that the particles are of very small in crystalline size [5]. The data obtained are in good agreement with standard JCPDS file (JCPDS 21-1272) data of anatase crystalline phase of TiO$_2$ [6]. The
prepared TiO₂ nanoparticles (Figure 3.4) show the peaks at 2θ values of about 25.37, 37.93, 47.68, 53.96, 62.78, 68.91, and 75.34, which corresponds to the Miller indices of (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 0 4), (1 1 6) and (2 1 5) planes, respectively. At 30.8° very small peak is observed and is assigned to the (121) crystalline plane of the brookite phase [7]. Further this peak is confirmed by JCPDS file (JCPDS 29-1360) of brookite phase of TiO₂.

![X-ray diffraction pattern](image)

**Figure 3.4:** Powder X-ray diffraction patterns of prepared pure TiO₂ nanoparticles

Anatase phase TiO₂ nanoparticles with higher crystallinity is preferred for photocatalytic application [8, 9]. Hence, the prepared pure TiO₂ nanoparticles must be calcinated to higher temperature to improve the crystalline quality. However, calcination to higher temperature leads to phase transformation from anatase to rutile. According to the literature survey, anatase to rutile phase transformation occurs above
600˚C [10-13]. Hence, in order to get improved crystallinity and to maintain the anatase phase, the calcination temperature is fixed at 550˚C. Therefore, in the present work, all the pure and metal ions doped TiO₂ nanoparticles are calcinated to 550˚C for 3 hours.

The PXRD pattern of the calcinated pure TiO₂ nanoparticles is shown in figure (3.5).

![Figure 3.5: Powder X-Ray Diffraction patterns of pure TiO₂ nanoparticles calcinated at 550˚C](image)

When compared with prepared pure TiO₂ nanoparticles, crystallinity gets improved by calcination. This can be identified from the sharp diffraction peaks of calcinated pure TiO₂ nanoparticles [14]. The observed peaks corresponds to the anatase crystalline phase of TiO₂ with tetragonal crystal structure. The peak at 30.8˚ is also present after calcination. This peak is ascribed to brookite phase and is not suppressed or transformed to rutile phase by calcination.
From PXRD patterns, the crystallite size can be calculated using the width of the prominent peak by Scherrer equation [15-17],

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of X-ray radiation (Cu Kα-1 radiation = 1.54060 Å), \( K \) is a constant and usually taken as 0.9, \( \beta \) is the full width at half maximum (FWHM) after subtraction of equipment broadening, and \( \theta \) is the Bragg angle of the diffraction peak. Crystallite size measures the broadening of a particular peak in the diffraction pattern associated with a particular planar reflection from within the crystal unit cell. It is inversely related to the full width half maximum of an individual peak. It is known that narrower the peak, the larger is the crystallite size. Also, the periodicity of the individual crystallite domain reinforces the diffraction of the X-ray beam resulting in a tall narrow peak. If the crystals are randomly arranged or have low degrees of periodicity, the result is a broader peak. This is normally the case for nanomaterial assemblies. Thus, it is apparent that the full width half maximum of the diffraction peak is related to the size of the nanomaterials [18]. According to this, the crystallite size of all these samples are calculated from full width at half maximum of the (1 0 1) plane of the anatase peak [19]. From the PXRD spectrum the crystallite size of as-prepared pure TiO₂ nanoparticles is found to be approximately 20nm, using Scherrer equation. Moreover, the calculated value of crystallite size of calcinated pure TiO₂ nanoparticles is 22nm.

Figures (3.6-3.8) show the PXRD patterns of Fe²⁺ doped TiO₂ nanoparticles. When it is doped with Fe²⁺ ions, diffraction angle of the (1 0 1) plane shifted to
25.23°, 25.52° and 25.32° from 25.31° (calcinated pure) for 1, 3 and 5wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles, respectively. Moreover, the diffraction patterns of Fe$^{2+}$ doped TiO$_2$ nanoparticles did not show any peaks of iron or iron compounds, which suggest the formation of an iron-titanium solid solution, where the iron ion has been incorporated into the TiO$_2$ crystal structure substitutionally due to similar ionic radii (Ti (0.68 Å) and Fe (0.64 Å)) [20]. An increase in unit cell volume (Table 3.2) is the further evidence for the doped metal ion Fe$^{2+}$ present in the TiO$_2$ lattice.

Figures (3.9-3.11) show the PXRD patterns for Zn$^{2+}$ doped TiO$_2$ nanoparticles. The large difference between the ionic radii of Zn$^{2+}$ (0.88 Å) and Ti$^{4+}$ (0.68 Å) make it difficult for Zn$^{2+}$ to substitute Ti$^{4+}$. If a Zn$^{2+}$ ion replaces a Ti$^{4+}$ site, the TiO$_2$ host lattice would have to deform, and the volume of the unit cell would increase. It is noted that the calculated unit cell volume (Table 3.2) of the Zn$^{2+}$ doped TiO$_2$ nanoparticles increases when compared to pure TiO$_2$ nanoparticles. This suggests that the metal ion Zn$^{2+}$ replaces the Ti$^{4+}$ site and is incorporated into the TiO$_2$ crystal structure [21]. Here the peak shifting is observed at 25.32°, 25.25° and 25.36° for 1, 3 and 5wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles respectively.

The PXRD patterns of Ag$^+$ doped TiO$_2$ nanoparticles are shown in figure (3.12-3.14). The ionic radius of Ag$^+$ is very much larger than that of Ti$^{4+}$ (Ti$^{4+}$ = 0.68 Å, Ag$^+$ = 1.22 Å). It is found that the values of $a$, $c$ and $\nu$ for the Ag$^+$ doped TiO$_2$ nanoparticles (Table 3.2) significantly increase with Ag$^+$ doping. Compared with pure and other metal ions doped TiO$_2$ nanoparticles, there is a larger expansion for the anatase lattice with Ag$^+$ doping, suggesting that Ag$^+$ doping imposes an effect dominantly on the anatase phase in TiO$_2$. It is known that Ag$^+$ atoms can not
easily enter into the anatase or rutile lattice since the ionic radius of Ag$^+$ is greatly larger than that of Ti$^{4+}$ ion. As a result, most Ag$^+$ atoms are expected to locate in the grain boundary layers or the more porous regions [22-24]. Consistent evidence has been reported by Li et al. [25] in which the local concentrations of Ag$^+$ are found to be higher in the more porous region and lower in the denser regions. The shifting of peaks is listed in table (3.1). As a consequence of large ionic radii, the volume of the unit cell increases enormously. This is proved by the highest volume (Table 3.2) obtained by Ag$^+$ doped TiO$_2$ nanoparticles.

The PXRD patterns of Ni$^{2+}$ doped TiO$_2$ nanoparticles are shown in figure (3.15-3.17). The ionic radii of Ni$^{2+}$ (0.72 Å) is quite similar to that of host Ti$^{4+}$ (0.68 Å) ions. Hence, these ions can easily substitute Ti$^{4+}$ ion in TiO$_2$ lattice without distorting the crystal structure, thereby stabilizing the anatase phase for all the three dopant concentrations. The calculated lattice parameter values and volume (Table 3.2) are agreed with the previous reported values [26]. The shift in 2$\theta$ values of (1 0 1) reflection peak is observed at 25.57˚, 25.58˚ and 25.48˚ for 1, 3 and 5wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles respectively.

The PXRD patterns of Cu$^{2+}$ doped TiO$_2$ nanoparticles are shown in figure (3.18-3.20). The similarity in ionic radius of Cu$^{2+}$ (0.73 Å) to that of Ti$^{4+}$ (0.68 Å) enable copper to substitute Ti$^{4+}$ in the titanium lattice [27]. The decrease in the crystalline size with increased Cu$^{2+}$ loading and lattice expansion are observed (Table 3.2) [28]. The peak shifting is observed at 25.58˚, 25.55˚ and 25.64˚ for 1, 3 and 5wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles, respectively in the (1 0 1) reflection plane.
All these metal ions doped TiO₂ nanoparticles show either an increase or a decrease in the intensity of peaks when compared to calcinated pure TiO₂ nanoparticles. The changes in intensities and shift in peak positions are due to the distortion in the crystal lattice due to metal ions doping [22].

The calculated lattice parameter values for pure and metal ions doped TiO₂ nanoparticles are listed in table (3.2). Expansion or contraction in unit cell volume and variation in the lattice parameter values of doped TiO₂ samples confirm the presence of dopant in the TiO₂ lattice. The crystallite size values of metal ions doped TiO₂ nanoparticles calculated using Scherrer equation from the 2θ values of diffraction plane (1 0 1) are listed in table (3.3).

Moreover, for all the concentrations of Fe²⁺, Zn²⁺ and Ag⁺ doping suppresses the brookite peak whereas doping of Ni²⁺ and Cu²⁺ improve the intensity of the brookite peak. Thus, doping of Fe²⁺, Zn²⁺ and Ag⁺ leads to formation of single phase anatase TiO₂ which is important for photocatalysis [29].
Figure 3.6: Powder X-Ray Diffraction patterns of 1 wt% Fe\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles

Figure 3.7: Powder X-Ray Diffraction patterns of 3 wt% Fe\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles
Figure 3.8: Powder X-Ray Diffraction patterns of 5 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.9: Powder X-Ray Diffraction patterns of 1 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.10: Powder X-Ray Diffraction patterns of 3 wt% Zn\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles

Figure 3.11: Powder X-Ray Diffraction patterns of 5 wt% Zn\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles
Figure 3.12: Powder X-Ray Diffraction patterns of 1 wt% Ag$^+$ doped TiO$_2$ nanoparticles

Figure 3.13: Powder X-Ray Diffraction patterns of 3 wt% Ag$^+$ doped TiO$_2$ nanoparticles
Figure 3.14: Powder X-Ray Diffraction patterns of 5 wt% Ag\textsuperscript{+} doped TiO\textsubscript{2} nanoparticles

Figure 3.15: Powder X-Ray Diffraction patterns of 1 wt% Ni\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles
Figure 3.16: Powder X-Ray Diffraction patterns of 3 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.17: Powder X-Ray Diffraction patterns of 5 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.18: Powder X-Ray Diffraction patterns of 1 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.19: Powder X-Ray Diffraction patterns of 3 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.20: Powder X-Ray Diffraction patterns of 5 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles

Table 3.1: The shifts in 2$\theta$ values of TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>(h k l) value</th>
<th>2$\theta$ (Degree)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$ (prepared)</td>
<td>(1 0 1)</td>
<td>25.379</td>
<td>3.510</td>
</tr>
<tr>
<td>Pure TiO$_2$ (calcinated)</td>
<td>(1 0 1)</td>
<td>25.313</td>
<td>3.509</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt% Fe$^{2+}$</td>
<td>(1 0 1)</td>
<td>25.239</td>
<td>3.528</td>
</tr>
<tr>
<td>TiO$_2$: 3 wt% Fe$^{2+}$</td>
<td>(1 0 1)</td>
<td>25.524</td>
<td>3.489</td>
</tr>
<tr>
<td>TiO$_2$: 5 wt% Fe$^{2+}$</td>
<td>(1 0 1)</td>
<td>25.323</td>
<td>3.517</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt% Zn$^{2+}$</td>
<td>(1 0 1)</td>
<td>25.325</td>
<td>3.516</td>
</tr>
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<td>(1 0 1)</td>
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<td>3.526</td>
</tr>
<tr>
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<td>25.365</td>
<td>3.511</td>
</tr>
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<td>(1 0 1)</td>
<td>25.331</td>
<td>3.516</td>
</tr>
<tr>
<td>TiO$_2$: 3 wt% Ag$^+$</td>
<td>(1 0 1)</td>
<td>25.235</td>
<td>3.529</td>
</tr>
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<td>3.510</td>
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<td>TiO$_2$: 3 wt% Cu$^{2+}$</td>
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<td>3.482</td>
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<tr>
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<td>25.649</td>
<td>3.470</td>
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### Table 3.2: Lattice parameter values of pure and metal ions doped TiO₂ nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>a=b (Å)</th>
<th>c (Å)</th>
<th>Volume(Å³)</th>
</tr>
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<tbody>
<tr>
<td>Pure TiO₂ (prepared)</td>
<td>3.782</td>
<td>9.459</td>
<td>135.364</td>
</tr>
<tr>
<td>Pure TiO₂ (calcinated)</td>
<td>3.778</td>
<td>9.461</td>
<td>135.069</td>
</tr>
<tr>
<td>TiO₂: 1 wt % Fe²⁺</td>
<td>3.780</td>
<td>9.506</td>
<td>135.854</td>
</tr>
<tr>
<td>TiO₂: 3 wt % Fe²⁺</td>
<td>3.780</td>
<td>9.510</td>
<td>135.906</td>
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<td>TiO₂: 5 wt % Fe²⁺</td>
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<td>9.529</td>
<td>137.173</td>
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<tr>
<td>TiO₂: 3 wt % Ag⁺</td>
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<td>9.531</td>
<td>137.301</td>
</tr>
<tr>
<td>TiO₂: 5 wt % Ag⁺</td>
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<td>9.532</td>
<td>137.402</td>
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<tr>
<td>TiO₂: 1 wt % Ni²⁺</td>
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<td>9.453</td>
<td>135.521</td>
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<td>9.457</td>
<td>135.537</td>
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<td>9.459</td>
<td>135.464</td>
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<tr>
<td>TiO₂: 5 wt % Cu²⁺</td>
<td>3.785</td>
<td>9.468</td>
<td>135.686</td>
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</table>

### 3.3 Microstrain Analysis Using Williamson – Hall (W-H) Plot

Uniform deformation model (UDM) is considered to illustrate micro strain produced by imperfection in TiO₂ nanoparticles. In the uniform deformation model (UDM), the strain is assumed to be uniform in all crystallographic directions.
Williamson-Hall plot provides information about effective crystallite size and lattice strain through the following relation [30, 31],

$$\beta \cos \theta = \frac{K \lambda}{D} + 4\varepsilon \sin \theta$$

Where $\beta$ is the full width half maximum in radians, $\lambda$ is the wavelength of X-rays, $\theta$ is the diffraction angle, $D$ is the effective particle size and $\varepsilon$ is the effective strain. $\beta \cos \theta$ is plotted against $4 \sin \theta$ and after linear fitting the intercept gives the value of $D$ and the slope gives the value of $\varepsilon$. It is found that a negative slope in the plot indicates the presence of compressive strain whereas, the positive slope indicates the presence of tensile strain [32]. Horizontal slope indicates the homogeneity of the nanoparticles. ie, particles free from micro strain [33]. Figures (3.21-3.37) show the W-H plot for the pure and metal ions doped TiO$_2$ nanoparticles.

The micro strain and particle size values obtained from W-H plot and the crystallite size calculated from Scherrer equation are listed in table (3.3). From the table, it is noted that the as-prepared TiO$_2$ nanoparticles show the highest positive strain value. This is due to the presence of an excess number of atoms and defects on the amorphous grain boundary and will produce a stress field in this region and impose a strain in the system. The calcinated pure and metal ions doped TiO$_2$ nanoparticles show lowest micro strain value when compared to as-prepared pure TiO$_2$ nanoparticles. This is due to the gradual removal of grain boundary defects when the pure and metal ions doped TiO$_2$ nanoparticles are subjected to calcination [34].

Hence, it is concluded that the crystal imperfection is very much reduced by calcination. The crystallite size obtained from W-H plot is well matched with crystallite size calculated using Scherrer equation.
Figure 3.21: W-H plot for prepared pure TiO$_2$ nanoparticles

Figure 3.22: W-H plot for calcinated pure TiO$_2$ nanoparticles
Figure 3.23: W-H plot for 1 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.24: W-H plot for 3 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.25: W-H plot for 5 wt% Fe\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles

Figure 3.26: W-H plot for 1 wt% Zn\textsuperscript{2+} doped TiO\textsubscript{2} nanoparticles
Figure 3.27: W-H plot for 3 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.28: W-H plot for 5 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.29: W-H plot for 1 wt% Ag\textsuperscript{+} doped TiO\textsubscript{2} nanoparticles

Figure 3.30: W-H plot for 3 wt% Ag\textsuperscript{+} doped TiO\textsubscript{2} nanoparticles
Figure 3.31: W-H plot for 5 wt% Ag$^+$ doped TiO$_2$ nanoparticles

Figure 3.32: W-H plot for 1 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.33: W-H plot for 3 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.34: W-H plot for 5 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.35: W-H plot for 1 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.36: W-H plot for 3 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.37: W-H plot for 5 wt% Cu²⁺ doped TiO₂ nanoparticles

Table 3.3: Micro strain and crystallite size obtained from W-H plot

<table>
<thead>
<tr>
<th>Samples</th>
<th>Micro Strain (ε)</th>
<th>Crystallite Size (D) (nm) (W-H Plot)</th>
<th>Crystallite Size (D) (nm) Scherrer Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO₂ (prepared)</td>
<td>0.00384</td>
<td>11.23</td>
<td>20.29</td>
</tr>
<tr>
<td>Pure TiO₂ (calcinated)</td>
<td>0.00057</td>
<td>24.50</td>
<td>22.13</td>
</tr>
<tr>
<td>TiO₂: 1 wt % Fe²⁺</td>
<td>0.00230</td>
<td>43.80</td>
<td>44.26</td>
</tr>
<tr>
<td>TiO₂: 3 wt % Fe²⁺</td>
<td>0.00015</td>
<td>14.19</td>
<td>13.53</td>
</tr>
<tr>
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3.4 Atomic Force Microscopy (AFM) Studies

Morphology and size distribution are observed for all the prepared samples by atomic force microscopy (AFM) using a PARK SYSTEM XE-70 AFM instrument. The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscopy, with a resolution of fraction of a nanometer. The information is gathered by “feeling” the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements in response to an electric command enable a very precise scanning. The atom at the apex of the tip “senses” individual atoms on the underlying surface when it forms incipient chemical bonds with each atom. As these chemical interactions subsequently alter the tip’s vibration frequency, they can be detected and mapped. This principle is used to distinguish between atoms of silicon, tin and lead on an alloy surface [35]. It is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale.

There are three modes of operation: (i) Contact mode where the sample-tip distance is so small that the important force is the core-core repulsive one. (ii) Non-contact mode where the force is the Vander Waal’s one. It can achieve a resolution of ~1nm. (iii) Tapping mode where the forces are Van der Waals forces, dipole-dipole interactions, electrostatic forces, etc. The AFM can scan both hard and soft samples in ambient air or in a fluid environment. A block diagram, figure (3.38), illustrates the principle and operation of AFM.

Contact mode

The first and foremost mode of operation, contact mode is widely used. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface
corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height is present above the surface. It is this adjustment that is displayed as data. However, the ability to track the surface in this manner is limited by the feedback circuit. Sometimes the tip is allowed to scan without this adjustment, and one measures only the deflection. This is useful for small, high-speed atomic resolution scans, and is known as variable-deflection mode.

**Non contact mode**

Non contact mode belongs to a family of AC modes, which refers to the use of an oscillating cantilever. A stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but do not touch it (hence, non-contact). The forces between the tip and sample are quite low on the order of pN (10^{-12} N). The detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever.

**Tapping mode**

In tapping mode, the cantilever is driven to oscillate up and down at or near its resonance frequency. This oscillation is commonly achieved with a small piezo element in the cantilever holder, but other possibilities include an AC magnetic field (with magnetic cantilevers), piezoelectric cantilevers, or periodic heating with a modulated laser beam. The amplitude of this oscillation usually varies from several nm to 200 nm. In tapping mode, the frequency and amplitude of the driving signal are kept constant, leading to constant amplitude of the cantilever oscillation as long as there is no drift or interaction with the surface. The interaction of forces act on the cantilever when the tip comes close to the surface, Van der Waals forces, dipole-
dipole interactions, electrostatic forces, etc. cause the amplitude of the cantilever's oscillation to change (usually decrease) as the tip gets closer to the sample. This amplitude is used as the parameter that goes into the electronic servo that controls the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the cantilever is scanned over the sample. A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface [36]. Nowadays, tapping mode is the most frequently used AFM mode for operating in ambient conditions or in liquids. Figure (3.39) shows the photograph of a PARK SYSTEM XE-70 AFM instrument.

Figure 3.38: Principle and operation of AFM
3.5 Atomic Force Microscopy (AFM) Analysis

An AFM is used to examine the surface morphology of the TiO$_2$ nanoparticles. AFM images of pure and metal ions doped TiO$_2$ nanoparticles for selected samples are shown in figure (3.40-3.45). It is found that the surface morphologies and roughness of the pure and metal ions doped TiO$_2$ nanoparticles are obviously different. The pure and metal ions doped nanoparticles exhibited granular nanostructured morphology. The pure TiO$_2$ has granular microstructure and flat texture with lower surface roughness. However, metal ions doped samples show higher roughness than pure TiO$_2$. There are many larger aggregate particles (like many islands) dispersed on the surface. Therefore, it is suggested that metal ions doping probably caused aggregation of TiO$_2$ nanoparticles [37]. The particle size values of calcinated pure TiO$_2$ nanoparticles obtained from AFM is in the range of 150-300 nm. From the image of AFM, the particle size values for 1 wt% Fe$^{2+}$ doped
TiO$_2$ nanoparticles is obtained in the range between 150 and 250 nm. Similarly, the particle size values obtained for 1 wt% Zn$^{2+}$, Ag$^+$, Ni$^{2+}$ and Cu$^{2+}$ are in the range of 50-350 nm. In addition, the particle agglomeration and aggregation is clearly understood from the AFM images of pure and metal ions doped TiO$_2$ nanoparticles.

**Figure 3.40**: AFM image of calcinated pure TiO$_2$ nanoparticles

**Figure 3.41**: AFM image of 1 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.42: AFM image of 1 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.43: AFM image of 1 wt% Ag$^+$ doped TiO$_2$ nanoparticles
Figure 3.44: AFM image of 1 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles

Figure 3.45: AFM image of 1 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
3.6 Scanning Electron Microscopy (SEM) Studies

Nanostructured materials take an enormously rich variety of property and promising exciting new advances in micromechanical, electronic, and magnetic devices as well as in molecular fabrications. The structure-composition-processing-property relationships for these sub 100nm-sized materials can be understood by employing an array of modern microscopy and microanalysis tools. Scanning electron microscopes are advanced microscopes that provide topographical and elemental information at magnifications of 10x to 100,000x with virtually unlimited depth of field. The SEM also has much higher resolution, so that closely spaced specimens can be magnified at much higher levels [38]. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments for imaging and investigation of nanoparticles. The main components of the instrument and the optical system are shown schematically in figure (3.46).

An electron beam is generated by an electron gun at the top of the column. This beam is focused by two magnetic lenses inside the column and strikes the sample in the sample chamber in a very small spot. There is a wide selection of adhesives available for mounting the sample. Double coated conductive carbon tape is the one used most commonly. It requires no drying time, holds the sample firmly to the surface, and can be used as a ground strap from the sample surface to sample holder.

When electrons penetrate into the sample, some electrons are scattered back out of the sample and are collected by a suitable detector. These electrons are used to obtain information on the mean atomic number in the part of the sample from which they originated, relative to other part. Secondary electrons with very low energy also be released and are used to obtain information on the topography of the sample [39].
Figure 3.46: Schematic diagram of principle of Scanning Electron Microscopy

Usually, the electron beam is not left stationary on the sample, but scans across certain area in a raster pattern. The signal from one of the detectors is selected and used to modulate the intensity on a viewing screen, which is scanned synchronously with the primary beam in the column. Thereby an image is generated on the viewing screen with high brightness in areas with a strong signal from the detector, and darker areas where weak signals are detected [40]. On scanning, an enlarged image of the sample is obtained on the screen. To vary the magnification, the size of the scanned area of the sample is varied while the scanning width on the viewing screen is constant. The signals that derived from the electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample [41].
In this present study, JEOL JSM-6390LV Scanning Electron Microscope instrument model is used to take SEM micrographs. The Photograph of JEOL JSM-6390LV Scanning Electron Microscope is shown in figure (3.47).

Figure 3.47: The Photograph of JEOL JSM-6390LV Scanning Electron Microscope

3.7 Scanning Electron Microscopy (SEM) Analysis

The SEM micrographs of prepared and calcinated pure TiO$_2$ nanoparticles are shown in figure (3.48). The prepared TiO$_2$ nanoparticles show morphology of spherical particles and after calcination the particles become bigger in size without altering the morphology. Similar morphology with increase in particle size after calcination has been previously reported by a few authors using Sol-Gel method [42-44].
Figure (3.49) and figure (3.50) show the SEM micrographs of Fe\(^{2+}\) and Zn\(^{2+}\) doped TiO\(_2\) nanoparticles. The TiO\(_2\) nanoparticles exhibit irregular morphology due to the agglomeration of primary particles [45]. The particles are spherical in shape and have homogeneous clusters of size in the range between 1 \(\mu\)m and 1.5 \(\mu\)m.

The SEM micrographs of Ag\(^{+}\), Ni\(^{2+}\) and Cu\(^{2+}\) doped TiO\(_2\) nanoparticles are shown in figure (3.51-3.53). The morphology of Ag\(^{+}\), Ni\(^{2+}\) and Cu\(^{2+}\) doped TiO\(_2\) nanoparticles is significantly different from pure, Fe\(^{2+}\) and Zn\(^{2+}\) doped TiO\(_2\) nanoparticles. The SEM micrographs of Ag\(^{+}\), Ni\(^{2+}\) and Cu\(^{2+}\) doped TiO\(_2\) nanoparticles show uneven distribution of agglomerated particles like aggregated plates. However, they generally consist of spherical particles and many micro, mesopores are expected at the interstices of the particles [46, 47]. The grain sizes of these doped TiO\(_2\) nanoparticles are in the range from 9-16 \(\mu\)m.

From the SEM micrographs it is understood that pure, Fe\(^{2+}\) and Zn\(^{2+}\) metal ions doped TiO\(_2\) nanoparticles are aggregate whereas the Ag\(^{+}\), Ni\(^{2+}\) and Cu\(^{2+}\) doped TiO\(_2\) nanoparticles are agglomerate. The particle size obtained from SEM micrographs matches with the particle size obtained from AFM data.

![Figure 3.48: SEM micrographs of (a) prepared and (b) calcinated TiO\(_2\) nanoparticles](image)

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Figure 3.49: SEM micrographs of (c) 1 wt% Fe$^{2+}$ doped (d) 3 wt% Fe$^{2+}$ doped and (e) 5 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.50: SEM micrographs of (f) 1 wt% Zn$^{2+}$ doped (g) 3 wt% Zn$^{2+}$ doped and (h) 5 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.51: SEM micrographs of (i) 1 wt% Ag⁺ doped (j) 3 wt% Ag⁺ doped and (k) 5 wt% Ag⁺ doped TiO₂ nanoparticles
Figure 3.52: SEM micrographs of (l) 1 wt% Ni$^{2+}$ doped (m) 3 wt% Ni$^{2+}$ doped and (n) 5 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.53: SEM micrographs of (o) 1 wt% Cu$^{2+}$ doped (p) 3 wt% Cu$^{2+}$ doped and (q) 5 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
3.8 Energy Dispersive X-Ray Spectroscopy (EDS) Studies

Energy Dispersive X-ray Spectroscopy (EDS, EDAX) is an analytical technique used for the elemental analysis or chemical composition of a sample. Figure 3.54 shows the schematic diagram of an EDS system.

Energy Dispersive X-ray Spectroscopy (EDS, EDAX) is an analytical technique used for the elemental analysis or chemical composition of a sample. Figure 3.54 shows the schematic diagram of an EDS system.

It relies on the investigation of an interaction of some source of X-ray excitation and a sample. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating a hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in
the form of an X-ray. The number and energy of the X-ray emitted from a specimen can be measured by energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they are emitted, this allows the elemental composition of the specimen to be measured. EDS systems are controlled by computers and are used for the basic operations of spectrum collection and peak identification. The X-ray spectra give information on the types of elements present in a specimen from the wavelength of the X-ray emitted and the elemental concentration from the intensity of the particular peak [48].

3.9 Energy Dispersive Spectroscopy (EDS) Analysis

Energy Dispersive Spectroscopy (EDS) is used to identify composition of elements present in the synthesized nanoparticles [47].

The EDS spectra of prepared and calcinated (Figure 3.55) pure TiO$_2$ nanoparticles show three energy peaks around 0.2, 4.2 and 5 keV. The intense peaks are assigned to bulk TiO$_2$ and the less intense peaks are assigned to surface TiO$_2$ [49]. The elements, Ti and O are evidently seen in the EDS spectrum. No impurity peak is observed in the detection limit of EDS. This implies the high purity of prepared TiO$_2$ nanoparticles [50].

The EDS spectrum of Fe$^{2+}$ doped TiO$_2$ nanoparticles are shown in figure (3.56). The peaks of Fe$^{2+}$ are distinct in 0.4, 6.4 and 7 keV. This confirms the presence of Fe$^{2+}$ ion in the TiO$_2$ lattices. Moreover, further evidence is H. Moradi et al. [51] who have also reported similar peaks for 5 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles.
The EDS spectrum of Zn$^{2+}$ doped TiO$_2$ nanoparticles are shown in figure (3.57). The EDS spectrum of Zn$^{2+}$ doped TiO$_2$ nanoparticles shows two peaks of Zn$^{2+}$ around 8.6 and 9.6 keV. Also, D. V. Aware et al. [52] obtained these peaks at similar positions for 5 mole% Zn$^{2+}$ doped TiO$_2$ nanoparticles. This is the evidence for Zn$^{2+}$ metal ions present in the TiO$_2$ lattice.

Figure (3.58) shows the EDS spectrum of Ag$^+$ doped TiO$_2$ nanoparticles. In these spectra, the peaks of Ag$^+$ are obtained around 3, 3.2 and 3.4 keV. This proves the presence of silver ion in the surface of TiO$_2$. These results agree with the reports of few authors who have reported similar peaks of Ag$^+$ at the exact position for silver doped TiO$_2$ nanoparticles [53-55]. This proves the presence of Ag$^+$ in the silver ions doped TiO$_2$ nanoparticles.

Figure (3.59) shows the EDS spectrum of Ni$^{2+}$ doped TiO$_2$ nanoparticles. In the case of Ni$^{2+}$ doped TiO$_2$ nanoparticles, the EDS spectrum displays the peaks of Ni$^{2+}$ at 0.8, 0.9, 7.5 and 8.3 keV. These peaks are well matched with the previous reports [56, 57].

Figure (3.60) shows the EDS spectrum of Cu$^{2+}$ doped TiO$_2$ nanoparticles. The peaks of Cu$^{2+}$ are observed at 0.8, 1, 8 and 8.9 keV for all the three doping concentrations. Similar observations are reported by C. Karunakaran et al. [58] for Cu$^{2+}$ ions doped with TiO$_2$-P25 powders.

From all the above interpretations, the less intense peaks are assigned to metal ions in the TiO$_2$ lattices [49, 59] and metal dopants do not alter the structure of TiO$_2$, but they enter the lattice of TiO$_2$ by causing deformation in its lattice sites.
Figure 3.55: EDS spectra of (a) prepared and (b) calcinated pure TiO$_2$ nanoparticles

Figure 3.56: EDS spectra of (c) 1 wt% Fe$^{2+}$ doped (d) 3 wt% Fe$^{2+}$ doped and (e) 5 wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.57: EDS spectra of (f) 1 wt% Zn$^{2+}$ doped (g) 3 wt% Zn$^{2+}$ doped and (h) 5 wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.58: EDS spectra of (i) 1 wt% Ag⁺ doped (j) 3 wt% Ag⁺ doped and (k) 5 wt% Ag⁺ doped TiO₂ nanoparticles
Figure 3.59: EDS spectra of (l) 1 wt% Ni$^{2+}$ doped (m) 3 wt% Ni$^{2+}$ doped and (n) 5 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 3.60: EDS spectra of (o) 1 wt% Cu$^{2+}$ doped (p) 3 wt% Cu$^{2+}$ doped and (q) 5 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
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