Chapter 5
CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF TiO$_2$-ZnFe$_2$O$_4$ NANOCOMPOSITES

In this chapter we have successfully discussed results of TiO$_2$-ZnFe$_2$O$_4$ nanocomposite. Here ethylene glycol is used as a solvent as well as reducing agent. TiO$_2$-ZnFe$_2$O$_4$ nanocomposite is directed towards extending the photoresponse of TiO$_2$ from UV to visible wavelengths. The TiO$_2$-ZnFe$_2$O$_4$ nanocomposites were characterized by XRD, EDX, BET surface area measurements, N$_2$ adsorption desorption isotherm, SEM and HRTEM, FTIR, XPS, UV-DRS, room temperature-PL (RT-PL). From all these characterizations it is confirmed that mesoporous TiO$_2$-ZnFe$_2$O$_4$ nanocomposite is successfully formed. The visible light photoactivity for a TiO$_2$-ZnFe$_2$O$_4$ coupled system follows a bell curve with the maximum degradation being achieved with X equal to 3 (where X is the % of ZnFe$_2$O$_4$ in 100% TiO$_2$). TiO$_2$-ZnFe$_2$O$_4$ nanocomposite has been proved to be an efficient photocatalyst for degradation of organic compounds like phenolic or azo dyes.
5.1. Introduction

The primary objective for this study is to increase the anatase content while maintaining an adequate amount of ZnFe$_2$O$_4$ to create a composite with the potential of visible light absorption. The fundamental obstacle to couple ZnFe$_2$O$_4$ with TiO$_2$ is that, as the concentration of ZnFe$_2$O$_4$ increases, the anatase-to-rutile transformation will begin to occur at a lower onset temperature [414, 415]. By coupling TiO$_2$ with ZnFe$_2$O$_4$, one can increase the separation efficiency of electrons and holes so that their recombination can be minimized. TiO$_2$-ZnFe$_2$O$_4$ nanocomposites, on the other hand are difficult to prepare because of the differences in synthetic procedures. ZnFe$_2$O$_4$ is typically prepared in alkaline conditions while anatase TiO$_2$ requires slightly acidic conditions. Conventional approaches to the synthesis of titania microstructures are based on the hydrolysis of sol-gel precursors such as Ti(RO)$_4$ and TiCl$_4$. Therefore during synthesis of TiO$_2$ - ZnFe$_2$O$_4$ nanocomposites, pH plays an important role, which needs to be maintained. Enhancement of anatase to rutile transformation of TiO$_2$ by substitutional presence of Fe$^{3+}$ ions is another problem. However, polyol process via hybridization of metal precursor using ethylene glycol has been developed as a powerful alternative to form various materials [416, 417, 134]. In this chapter we have discussed a successful synthesis of TiO$_2$-ZnFe$_2$O$_4$ nanocomposite by processing TiO$_2$ and ZnFe$_2$O$_4$ separately, by polyol process and mixing the measured amount of colloidal ZnFe$_2$O$_4$ (ZF) solution in TiO$_2$ solution. Here ethylene glycol is used as a solvent as well as reducing agent. Jiang et al. have synthesized nanowires from the complexation of titanium butoxide and ethylene glycol at 170°C in which the chain-like species spontaneously aggregate into nanowires with uniform diameters [134]. This polyol process has been used recently for creating novel secondary morphologies such as titania tubes, titanate sheets, and metal-ion doped titania rods with high photocatalytic activity [418, 419]. But synthesis of coupled semiconductors by polyol process is not yet reported to the best of our knowledge. Therefore we are reporting for the first time, the successful coupling of TiO$_2$ with lower band gap ZnFe$_2$O$_4$ semiconductor by novel sonochemically assisted polyol method.
5.2. Results and Discussion

Further the samples were characterized thoroughly by XRD, BET surface area, \( \text{N}_2 \) adsorption isotherm, SEM, TEM, HRTEM, SAED pattern, FTIR, XPS, UV-DRS and RT-PL.

5.2.1. X-ray diffraction (XRD)

![X-ray diffraction pattern](image)

**Figure 5.1**: Overlay of a) bare TiO\(_2\), b-e) TiO\(_2\)-ZnFe\(_2\)O\(_4\) (at 1, 3, 5, 10% ZF v/v) and f) ZnFe\(_2\)O\(_4\) sample, all samples annealed at 300°C. Where $=$ spinel ZnFe\(_2\)O\(_4\) phase, A = Anatase phase and R = Rutile phase of TiO\(_2\).

Pristine samples have very small crystallite size and shows mixed phases (anatase and rutile phases) of TiO\(_2\) (XRD pattern of pristine STZF-3 sample is shown in Figure 5.2a). Figure 5.1 shows XRD patterns of bare TiO\(_2\), TiO\(_2\)-ZnFe\(_2\)O\(_4\) composite at 1, 3, 5 and 10% ZF sol in titania sol and bare
ZnFe$_2$O$_4$ sample, all the above said samples were annealed at 300°C for 3h in flowing air. PTS and ZFO along with all the STZF samples show well grown planes and show 100% anatase phase till STZF-5 sample. But in STZF-10 sample 70-30 anatase-rutile phase formation is seen, which confirms that, as concentration of zinc ferrite increases, anatase to rutile transformation increases at lower temperature. In all the coupled samples ZnFe$_2$O$_4$ peaks did not appear, might be because of very low concentration of ZnFe$_2$O$_4$ in TiO$_2$. The crystallite size of TiO$_2$ in TiO$_2$-ZnFe$_2$O$_4$ composite STZF-1 sample is lower than that in TiO$_2$ (PTS) under same annealing temperature. This observation suggests that the zinc ferrite coupling protocol followed here affects the particle growth. The observed 2Θ values at 25°, 27°, 48° can be attributed to (101), (110), (200) planes of TiO$_2$ having mixed phase of anatase (JCPDS file No. 86-1157) and rutile (JCPDS file No. 86-0147). The four diffraction peaks at 2Θ values (shown in Figure 5.2f) at 30°, 35°, 42° and 56.5° can be ascribed to the reflection of (220), (311), (400) and (511) planes, and can be indexed to the spinel ZnFe$_2$O$_4$ (JCPDS file No. 22-1012).

Figure 5.2 illustrates XRD patterns of pristine sample STZF-3 and after annealing from 300-700°C for 3h in flowing air. We can observe from this figure that with increase in the annealing temperature crystallite size increases. Pristine sample shows mixed phase of TiO$_2$ which on annealing at 300 (5.2b) and 500°C (5.2c) shows 100% anatase phase. STZF-3 sample after annealing at 700°C shows 60:40 ratio of anatase rutile phases (5.2d) due to the inherent substitution of Fe$^{3+}$ ions for Ti$^{4+}$ ions, thereby creating oxygen vacancies that promote the formation of rutile throughout the bulk of the nanoparticles [420]. Comparatively low temperature anatase rutile transformation is also due to the same reason. To understand the role of zinc ferrite in the transformation, an analysis of the crystalline structure of anatase and rutile is necessary. The comparison of the two crystal structures of titania indicates that the transformation involves a collapse of the open anatase structure to a closed rutile structure, with a volume change of about 8%. This process takes place by the rupture of two of the six Ti–O bonds of
the titanium coordination octahedral in anatase to form new bonds in rutile, as indicated earlier by Shannon [421, 422].

**Figure 5.2**: Overlay of a) Pristine STZF-3 sample, after annealing b) at 300°C, c) 500°C and d) 700°C. Where A = Anatase phase and R = Rutile phase of TiO$_2$

Anatase mass fraction in sample 37STZF-3 i.e. STZF-3 sample after annealed at 700°C is calculated by the equation (1).

$$X_A = \frac{1}{1 + 1.26 \left( \frac{I_A}{I_R} \right)} \times 100$$  \hspace{1cm} (1)

Where, $X_A$ is the mass fraction of anatase,

$I_A$ and $I_R$ are the X-ray integrated intensities of the (101) reflection of anatase and rutile phases, respectively.
It should be noted that this equation only takes into consideration the percent of anatase and rutile in the formed TiO$_2$ and not of the entire nanocomposite.

The average small crystallite sizes of all samples are calculated by Debye Scherer formula. Crystallite sizes of all samples after annealing at 300°C, BET surface area and band gap energies of PTS, ZFO and anatase - rutile phases in various coupled samples are given (Table 5.1) in a tabular form.

**Table 5.1:** Textural summary of TiO$_2$, ZnFe$_2$O$_4$ and various TiO$_2$-ZnFe$_2$O$_4$ nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sample code</th>
<th>Crystallite / Particle size after annealing at 300°C for 3 hours</th>
<th>Surfact area$^a$ (m$^2$/g)</th>
<th>Band Gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>PTS</td>
<td>12 (±1)nm by XRD, 10 (±1)nm by TEM</td>
<td>230 m$^2$/g</td>
<td>3.02eV</td>
</tr>
<tr>
<td>TiO$_2$-ZnFe$_2$O$_4$-1</td>
<td>STZF-1</td>
<td>8 (±1)nm by XRD, 8 (±1)nm by TEM</td>
<td>280 m$^2$/g</td>
<td>2.81eV</td>
</tr>
<tr>
<td>TiO$_2$-ZnFe$_2$O$_4$-3</td>
<td>STZF-3</td>
<td>13 (±1)nm by XRD, 12 (±1)nm by TEM</td>
<td>117 m$^2$/g</td>
<td>2.78eV</td>
</tr>
<tr>
<td>TiO$_2$-ZnFe$_2$O$_4$-5</td>
<td>STZF-5</td>
<td>15 (±1)nm by XRD, 13 (±1)nm by TEM</td>
<td>105 m$^2$/g</td>
<td>2.58eV</td>
</tr>
<tr>
<td>TiO$_2$-ZnFe$_2$O$_4$-10</td>
<td>STZF-10</td>
<td>18 (±1)nm by XRD, 15 (±1)nm by TEM, 18 (±2)nm by TEM</td>
<td>99 m$^2$/g</td>
<td>2.38eV</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>ZFO</td>
<td>--</td>
<td>70 m$^2$/g</td>
<td>1.93 eV</td>
</tr>
</tbody>
</table>

$^a$ All the samples for BET analysis were annealed at 250°C for several hours

### 5.2.2. Surface area measurements (BET)

The BET specific surface area of various TiO$_2$-ZnFe$_2$O$_4$ nanocomposites having 1, 3, 5, 10 % v/v concentration of ZnFe$_2$O$_4$ is given in Table 5.1. The standard multipoint BET method was used to calculate the specific surface area. All the samples were treated at 250°C before surface area analysis. From the Table 5.1, it is observed that surface area of the catalyst increases and the particle size decreases with increase in the concentration of ZnFe$_2$O$_4$ till 1% ZnFe$_2$O$_4$ in TiO$_2$ matrix. STZF-1 sample
shows surface area 280 m$^2$/g. Further increase in the concentration of ZnFe$_2$O$_4$ in TiO$_2$ matrix decreases the surface area and increases the particle size. This is obviously due to progressive aggregation of small crystallites into larger particles. Therefore it is confirmed that concentration of Fe$^{3+}$ ions plays crucial role in TiO$_2$ matrix. Photocatalysts having a larger BET surface area have a higher conversion for organic compounds in the gaseous phase. [423, 424].

5.2.2.1. Nitrogen sorption isotherm and pore diameter distribution

![Figure 5.3: nitrogen sorption isotherm and corresponding pore diameter distribution obtained for sample STZF-3](image)

Figure 5.3 illustrates N$_2$ adsorption desorption isotherm and corresponding pore diameter distribution (inset) obtained for sample STZF-3. Pore size distribution was obtained from the isotherm adsorption branches based on Barrett-Joyner-Halenda (BJH) model. Nitrogen adsorption desorption isotherm of sample STZF-3 indicate the presence of mesoporous particles (average pore size of ~1.2 nm), but the pores seem to be too small to observe clearly in the TEM image [425]. The pore volume of STZF-3 sample is around 1.3 cm$^3$ g$^{-1}$. The hysteresis loop shown in the adsorption/desorption isotherms is believed to be related to the capillary condensation associated with the modulation of channel structure within the nanoparticles [426].
surface area and the total pore volume decreased with increase in annealing temperature for this sample [427]. All other samples including bare TiO$_2$ sample are not mesoporous, the mesoporous nature of this particular coupled system must be due to concentration of ZnFe$_2$O$_4$ in TiO$_2$ bulk. The decrease in surface area at high temperature is due to the collapse of the porous structure.

5.2.3. SEM Analysis

**Figure 5.4:** SEM images and EDS graphs of A) PTS and B) STZF-3 composite after annealing at 300°C

Figure 5.4 illustrates the SEM images with different magnification and EDX microanalysis spectra of TiO$_2$ (33PTS) and TiO$_2$-ZnFe$_2$O$_4$ (sample 33STZF-3) nanocomposite after annealing at 300°C for 3h in flowing air. Figure 5.4A and B indicates that the morphology of TiO$_2$-ZnFe$_2$O$_4$ composite did changed, if compared with that of TiO$_2$ sample. Wire/rod like Morphology of TiO$_2$ is well
reported [134]. Change in morphology of the catalysts after incorporation of ZF sol is observed.

The elemental composition of 33PTS and 33STZF-3 composite were confirmed by EDX analysis (shown in Figure 5.4C and 3D), which shows near agreement with the theoretical ratio of Ti : Zn as 1 : 0 and 1 : 0.028 respectively and Zn : Fe (1 : 1.98) ratio for sample 33STZF-3, predicted from the synthesis conditions.

5.2.4. TEM, HRTEM and SAED pattern Analysis

![TEM images](image1)

**Figure 5.5:** A and B) TEM images, C) HRTEM micrograph and D) SAED pattern of 3% TiO$_2$-ZnFe$_2$O$_4$ composite after annealing at 500°C

To study in detail about the morphology and size we have done TEM, HRTEM and SAED analysis for the same samples, shown in Figure 5.5A-D. The
particle sizes for all catalysts are in the range of 8-22 nm and are given in Table 5.1. The rod/wire like morphology of sample 33PTS whose size is around 4µm, is made up of aggregation of 10-12 nm sized small nanoparticles (shown in Figure 4.7A-C). Figure 5.5A to 5.5D shows TEM, HRTEM and SAED pattern of sample 33STZF-3. Particle size (12-13nm) of this sample is in well agreement with XRD analysis. From Figure 5.6C, the well developed hkl planes with d values (interplaner distance) of 3.5175 Å in 33STZF-3 NPs, which matches exactly with the primary (101) family of planes of the anatase TiO₂ matrix, The selected area electron diffraction (SAED) pattern of 33STZF-3 sample confirm the polycrystalline nature, (Figure 5.5D) match well with the anatase phase of TiO₂ (JCPDS file No. 86-1157).

5.2.5. FTIR Studies

![FTIR Spectra](image)

**Figure 5.6:** FTIR spectra of pristine a) ZFO, b) PTS and c) STZF-3 as well as STZF-3 sample after annealing at d) 300°C, e) 500°C and f) 700°C for 3h in flowing air
Figure 5.6 show FTIR spectra of pristine a) ZFO, b) PTS and c) STZF-3 as well as STZF-3 sample after annealing at d) 300°C, e) 500°C and f) 700°C for 3h in flowing air. A broad band around 3300 cm\(^{-1}\) indicates -OH stretching mode and the O-H bending mode at around 1620-1700 cm\(^{-1}\) is due to physisorbed water in pristine samples. Bands around 2935 and 2880 cm\(^{-1}\) confirms –C-H stretching vibration frequency. Sharp peaks around 1300 cm\(^{-1}\) to 1500 cm\(^{-1}\) show carbonate stretching frequencies. All these above mentioned peak intensities go on decreasing with annealing temperature. A broad peak from 769 till 400 cm\(^{-1}\) confirms formation of Ti-O bond and thereby formation of TiO\(_2\).

### 5.2.6. X-ray photoelectron Analysis (XPS)

XPS is very sensitive to chemical environment and chemical composition. The surface chemical compositions of the TiO\(_2\)- ZnFe\(_2\)O\(_4\) composite were carried out using XPS (Figure 5. 7A to F). XPS signals showed presence of Ti, Zn, Fe, O, and adventitious C in the composite. The Ti 2p peak shape is almost identical in both bare TiO\(_2\) (description given in section 4.1.4. and Figure 4.4) and TiO\(_2\) composite cases. The Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) peaks are positioned at 459.2 and 465.1 eV, respectively, with a binding energy difference (ΔE) of 5.9 eV [428] suggesting the presence of titanium in its tetravalent state. In the case of Zn species, (Figure 5.7D), a very small peak was observed at 1022.3 eV that corresponds to Zn 2p\(_{3/2}\) and a very small peak at 1045.6 eV for 2p\(_{1/2}\). These are typical values for the oxidation state of Zn\(^{2+}\) in the compound. Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) peaks appear at 710.2 and 724.1 eV, respectively, having a binding energy difference of 13.9 eV reveals the presence of iron in its trivalent state [429]. Two shake-up satellite lines at 717 eV and 727 eV, characteristic of Fe\(^{3+}\), were also observed. Deconvolution was applied to 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks and satellites. The profile shapes and peaks positions are indicative of the presence of Fe\(^{3+}\) cations as expected for ZnFe\(_2\)O\(_4\) [430-432]. The O 1s peak is centred at about 531.1 eV in agreement with the values expected for Fe–O and Ti–O bonds [428, 433].
Figure 5.7: A) The XPS survey scan, B) Ti 2p XPS spectrum, C) C 1s XPS spectrum, D) Zn 2p XPS spectrum, E) Fe 2p XPS spectrum, and F) O 1s XPS spectrum of TiO$_2$-ZnFe$_2$O$_4$ composite
5.2.7. UV-DRS Study

![Figure 5.8: UV-DRS spectra of PTS, STZF-1, STZF-3, STZF-5, STZF-10 and ZFO](image)

Before we proceed to discuss the results of photocatalysis, it is instructive to discuss the optical properties of bare TiO\textsubscript{2}, ZnFe\textsubscript{2}O\textsubscript{4} and different % coupled TiO\textsubscript{2}-ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles, because this is a reasonably transparent way to reveal the electronic state effects due to presence of other small energy band semiconductor.

Figure 5.8 shows diffused reflectance spectroscopy (DRS) data for bare TiO\textsubscript{2} and ZnFe\textsubscript{2}O\textsubscript{4} and various coupled NPs. These data reveal that as expected, the bare TiO\textsubscript{2} exhibits the fundamental absorption edge corresponding to the band gap energy of 3.2 eV in the ultraviolet region. The absorption onset of the sonochemically assisted polyol synthesized ZnFe\textsubscript{2}O\textsubscript{4} has no structure such as shoulders and shows absorption in all visible region, indicating that the absorption in the visible light region should not be due to surface states but to an intrinsic band transition [434]. It is well known that, in the normal spinel-type compound ZnFe\textsubscript{2}O\textsubscript{4}, tetrahedral and octahedral sites are occupied by Zn\textsuperscript{2+} and Fe\textsuperscript{3+} cations, respectively [435]. The band structure of ZnFe\textsubscript{2}O\textsubscript{4} is generally defined by taking the O-2p orbital as the valence band and the Fe-3d orbital as the conduction band [436]. The
absorption of ZnFe$_2$O$_4$ in the visible light region may be due to the electron excitation from the O 2p level into the Fe 3d level around 660 nm and its band gap (E_g) was calculated to be 1.9 eV. The absorption in the visible region is red shifted with increase in the concentration of ZnFe$_2$O$_4$ in TiO$_2$ as compare to absorption edge of bare TiO$_2$. The light absorption properties of the various composites have a significant effect on their photocatalytic performance.

![Graph](image.png)

**Figure 5.9:** UV-DRS spectra of a) pristine STZF-3 sample and after annealing at b) 300, c) 500 and d) 700°C

Combining TiO$_2$-ZnFe$_2$O$_4$ with different band gaps to form heterojunctions, is more flexible than doping for broadening the visible-light absorption and shows better tolerance to component heterogeneity. This is because the heterojunction has great potential in tuning the desired electronic properties of the composite photocatalysts [437]. Figure 5.9 demonstrates the red shift in absorption edge for pristine STZF-3 catalyst after annealing at different temperatures i.e. 300, 500 and 700°C. STZF-3 sample after annealing at 300°C shows maximum absorption in the visible region and shows blue shift for samples annealed at higher temperatures like 500 and 700°C.
5.2.8. PL Studies

Figure 5.10: Room temperature photoluminescence spectra of a) PTS, b) STZF-1, c) STZF-3, d) STZF-5, e) STZF-10 and f) ZFO

Photoluminescence (PL) emission mainly results from the recombination of free carriers, therefore PL spectra is a useful technique to survey the separation efficiency of the photogenerated charge carriers in a semiconductor [438, 439]. Higher the PL intensity the probability of charge carrier recombination increases [440, 441]. The comparison of PL spectra of bare TiO\textsubscript{2}, ZnFe\textsubscript{2}O\textsubscript{4} and different % coupled TiO\textsubscript{2}-ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles at room temperature are shown in Figure 5.10. The sample was excited at a wavelength of 325 nm, and this selection of the wavelength was decided from the excitation plot. The spectra show four distinct peaks at about 375-383, 415, 440 and 476 nm. The strong band edge emission peak is observed at 375-383 nm regions this peak shows red shift with increase in concentration of ZnFe\textsubscript{2}O\textsubscript{4} in TiO\textsubscript{2}, which can be attributed to lowering of effective band gap energy for the electron transfer. All the catalysts show strong and broad blue-green emission peaks. The strongest blue emitting peak is at 470 nm, which is missing in STZF-3 sample, originating from the charge transfer transition from an oxygen vacancy trapped electron [442, 443]. It was observed that with increase in concentration of ZnFe\textsubscript{2}O\textsubscript{4} from 1 to 3 to 5 the emission
intensity is dramatically weakened indicating decrease in recombination rate which clearly indicates that the recombination of photogenerated charge carriers between the hybrid orbital of Zn, Fe and O 2p (VB) to the empty Ti 3d orbital is greatly inhibited by the heterojunction nanostructure. Again with higher concentration of zinc ferrite for sample STZF-10 the emission intensity increases. The optimum coupling of TiO₂ and ZnFe₂O₄ for 3% ZnFe₂O₄ in TiO₂ is helpful to separate the photogenerated charge carriers to enhance the photocatalytic activity in visible region. Therefore though Surface area (calculated by BET measurement) of sample STZF-1 is very high as compare to STZF-3, but photocatalytic results of STZF-3 are more favorable.

5.2.9. Visible Photocatalysis

5.2.9.1. Effect of catalyst loading

![Figure 5.11: Photocatalytic Degradation Control Experiment for Catalyst Loading.](image)

The effects of catalyst loading were studied by using STZF-3 sample which shows maximum degradability. The methylene blue degradation rate
depends primarily on the number of active sites on the photocatalyst's surface. The optimal catalyst loading will therefore be a trade-off of the maximum catalyst concentration with the maximum light penetration into the aqueous solution. These two variables are inversely proportional and therefore a wide range of catalyst loadings will provide similar MB degradation rates as shown in Figure 5.11. There was negligible degradation of MB in the absence of catalyst. The loading of a catalyst is beneficial since it allows an important degree of freedom in the photocatalytic reaction which is a function of surface area and not solely the mass or volume quantities that are commonly used to determine catalyst concentrations. Based on the results from this experiment, it was determined that a minimal catalyst loading of 0.1g/L should be used for photocatalysts characterized by a large surface area.

5.2.9.2. Optimizing molar concentrations of ZnFe$_2$O$_4$ in TiO$_2$

As previously stated, the irreversible phase transition of TiO$_2$ from anatase-to-rutile occurs by a nucleation-growth process and has no definitive transition temperature since there is no phase equilibria involved [444]. Numerous studies on the anatase-to-rutile transformation of TiO$_2$ have confirmed that the transition is not only dependent upon temperature, but also highly dependent upon the impurity content, synthetic method and conditions as well. It has been suggested in literature that the anatase-to-rutile transformation involves a collapse of the open anatase structure to a closed rutile structure, instigated by the rupture of two of the six Ti-O bonds of the titanium coordination octahedral (TiO$_6^{2-}$) in anatase to form new bonds in the rutile structure [445]. In our case as we increase the amount of ZnFe$_2$O$_4$ in TiO$_2$ the catalytic activity increases i.e from STZF-1 to STZF-3 but again it decreases for STZF-5 and further for STZF-10 (Shown in figure 5.13). A perfect bell curve is observed. There is no rutile phase observed till sample STZF-5 but for STZF-10 sample 70-30 anatase - rutile phases are obtained. Such enhancement of the anatase-to-rutile crystal structure by increasing the
concentration of ZnFe$_2$O$_4$ is most probably attributed to the diffusion of Fe$^{3+}$ into surface Ti$^{4+}$ forming an oxygen vacancy that promotes nucleation. This substitutional process may occur due to the similar ionic radii for Fe$^{3+}$ (64pm) and Ti$^{4+}$ (68pm), while probably not as conveniently for Zn$^{2+}$ (88pm). Once oxygen vacancies are induced on the surface of the TiO$_2$ lattice by the diffusion of Fe$^{3+}$, it is possible for the vacancies to migrate to the bulk of the TiO$_2$ extending the anatase to rutile transformation throughout the lattice. The more Fe$^{3+}$ (and possibly Zn$^{2+}$) available to aid in the creation of oxygen vacancies, the more probable it becomes for rutile formation to occur.

5.2.9.3. Photocatalytic Activity of by TiO$_2$- ZnFe$_2$O$_4$ nanocomposites

![Graph showing photocatalytic activity](image)

**Figure 5.12:** Visible Light MB Degradation Rates by PTS, ZFO, Degussa P-25, STZF-1, STZF-3, STZF-5, STZF-10 under visible light irradiation

Figure 5.12 shows the photodegradation of methylene blue in presence of bare TiO$_2$, ZnFe$_2$O$_4$, Degussa P-25 TiO$_2$ catalyst and TiO$_2$-(X)ZnFe$_2$O$_4$ nanocomposites created for X= 1, 3, 5, and 10 in water at neutral pH. The visible light photoactivity follows a bell curve with the maximum
degradation being achieved with X equal to 3 while bare TiO$_2$, ZnFe$_2$O$_4$ and Degussa P-25 TiO$_2$ catalyst shows 75%, 9% and 72% degradation in 60 minutes irradiation. The increased photoactivity of STZF-3 can be attributed to the role of ZnFe$_2$O$_4$ in extending the photoresponse of the catalyst to visible light. It can also be concluded, from the poor visible light photocatalytic activity of nanocomposites with X equal to 1, 5 and 10, that TiO$_2$ plays a critical role in the visible light photocatalysis of TiO$_2$-ZnFe$_2$O$_4$ composites. Although increase in ZnFe$_2$O$_4$ concentration, allows more charge carriers in response to enhanced visible light absorption. Strong reasons for STZF-3 catalyst efficiency will be 100% anatase phase, small average particle size, thereby high surface area and optimum charge separation for the reaction to proceed fast. Optimum charge separation of STZF-3 catalyst was observed from PL studies (discussed in section 5.2.8.). In conclusion, 3% (v/v) TiO$_2$-ZnFe$_2$O$_4$ nanocomposite has been proved to be an efficient photocatalyst for degradation of organic compounds like phenolic or azo dyes.

5.2.9.4. Effect of annealing on Photodegradability by TiO$_2$-ZnFe$_2$O$_4$ nanocomposites

**Figure 5.13**: Visible Light MB Degradation Rates by pristine STZF-3 and after annealing at 300, 500 and 700°C under visible light irradiation
Figure 5.13 demonstrates the effect of annealing on the degradation of MB. It was found that with increase in annealing temperature degradation ability of STZF-3 sample goes on decreasing. It was observed from XRD Figure 5.1, that with increase in annealing temperature from 300 to 700°C crystallite size increases so surface area must be decreasing resulting in substantial decrease in dye degradation. With increase in annealing temperature percentage of rutile phase goes on increasing which is also one of the strong reasons to decrease the photoregradationability of the coupled system.

5.2.9.5. Mechanistic pathway for the Photocatalytic Activity

![Diagram](image)

**Figure 5.14:** Schematic representation for energy band matching and migration and separation of electron–hole pairs in the coupled TiO$_2$-ZnFe$_2$O$_4$ photocatalyst

The energy levels of ZnFe$_2$O$_4$ and TiO$_2$ are schematically shown in Figure 5.14. In the TiO$_2$-ZnFe$_2$O$_4$ coupled system, the conduction and valence
bands of TiO$_2$ are lower than those of ZnFe$_2$O$_4$. We can propose the mechanism for photodegradation of methylene blue by changing the excitation path, promoting the separation of photogenerated charge carrier, improving the surface adsorption and reactions and synergistic effects in coupled semiconductors. Under visible light irradiation, the photogenerated electrons and holes are produced in ZnFe$_2$O$_4$, by electron excitation from valence band to conduction band, thus the photo-generated electrons can migrate from CB of ZnFe$_2$O$_4$ to CB of TiO$_2$, and photo-generated holes can transfer from VB of TiO$_2$ to VB of ZnFe$_2$O$_4$. Such a coupled system improves the separation efficiency of photo-generated carriers and increases the concentration of photo-generated carriers [446]. As discussed above, the 3% (v/v) TiO$_2$- ZnFe$_2$O$_4$ (sample STZF-3) composite photocatalyst exhibited enhanced photocatalytic activity under visible irradiation. The reason should be closely attributed to the interaction between TiO$_2$ and ZnFe$_2$O$_4$, which increased the mobility of photogenerated carriers in the photocatalyst. To confirm the effect of the interaction on the photogenerated electrons and holes, photoluminescence was investigated. The high specific surface area of STZF-3 (BET = 117 ± 15 m$^2$/g) is beneficial to the acceptance of large quantities of holes. Therefore, the photogenerated electrons and holes pairs were separated efficiently and the probability of recombination was reduced accordingly. The electrons on the surface of ZnFe$_2$O$_4$ and holes on the TiO$_2$ particles, respectively, can participate in photocatalytic reactions to directly or indirectly mineralize organic pollution, and thus the photocatalytic reaction can be enhanced greatly.

5.3. Conclusion

In this chapter a new sonochemically assisted polyol method was reported for the first time to effectively couple TiO$_2$ and ZnFe$_2$O$_4$, two photocatalysts that typically require discrepant preparation procedures and conditions. Our aim was to increase the anatase content while maintaining an adequate amount of ZnFe$_2$O$_4$ to create a composite with the potential of visible light absorption. As the concentration of ZnFe$_2$O$_4$ increases, the
anatase-to-rutile transformation begins to occur. The anatase-to-rutile transformation involves a collapse of the open anatase structure to a closed rutile structure instigated by the rupture of two of the six Ti-O bonds of the titanium coordination octahedra (TiO$_6^{2-}$) in anatase to form new bonds in the rutile structure. The transformation is most probably attributed to the diffusion of Fe$^{3+}$ into surface Ti$^{4+}$ forming an oxygen vacancy that promotes nucleation. This substitutional process may occur due to the similar ionic radii for Fe$^{3+}$ (64pm) and Ti$^{4+}$ (68pm). The optimum coupling of TiO$_2$ and ZnFe$_2$O$_4$ for 3% ZnFe$_2$O$_4$ in TiO$_2$ is helpful to separate the photogenerated charge carriers to enhance the photocatalytic activity in visible region. This particular photocatalyst is mesoporous in nature, which will also enhance the photocatalytic activity. Therefore though Surface area (calculated by BET measurement) of sample STZF-1 is very high as compare to STZF-3, but photocatalytic results of STZF-3 are more favorable.

Pristine samples of 100% TiO$_2$ and ZnFe$_2$O$_4$ synthesized by same procedure, when functioned alone, were found to have negligible photoactivity in visible light. There should be no chemical reaction between TiO$_2$ and ZnFe$_2$O$_4$ nanoparticles to be called them as coupled semiconductors. We have observed XRD reflection peaks corresponding only to TiO$_2$ phases. The absence of ZnFe$_2$O$_4$ peaks in XRD analysis might be due to very low concentration of ZF in TiO$_2$ matrix. The aim was to increase the anatase content while maintaining an adequate amount of ZnFe$_2$O$_4$ to create a composite, with the potential of visible light absorption. The visible light photoactivity for a coupled system follows a bell curve with the maximum degradation being achieved with X equal to 3. The increased photoactivity of STZF-3 can be attributed to the role of ZnFe$_2$O$_4$ in extending the photoresponse of the catalyst to visible. In conclusion, TiO$_2$-ZnFe$_2$O$_4$ nanocomposite has been proved to be an efficient photocatalyst for degradation of organic compounds like phenolic or azo dyes in visible light.

This work also attempted to unveil some of the mysteries regarding the reaction mechanisms of coupled semiconductor photocatalysts that are not clearly identified as photosynthesizers, such as in the case of TiO$_2$-CdS or
TiO$_2$-WO$_3$. From the experiments outlined during our work, several conclusions can be made about the coupling of TiO$_2$- ZnFe$_2$O$_4$ nanocomposites as prepared by sonochemically assisted polyol method. First, it was determined that ZnFe$_2$O$_4$ was necessary for visible light photoactivity, although it was not the exclusive source. There is a correlation between the metastable anatase phase of TiO$_2$ and ZnFe$_2$O$_4$. Any charge transfer mechanism for this composite, however, is enigmatic, since the conduction band-edge energy level of crystalline ZnFe$_2$O$_4$ is slightly unfavorable for the reduction of O$_2$. In addition, the band-edge energy levels of TiO$_2$ and ZnFe$_2$O$_4$ suggest that the nanocomposite cannot function as a visible light synthesizer, since both the conduction and valance band edges of ZnFe$_2$O$_4$ are lower in energy than the respective band edges of TiO$_2$. Consistent results show the inactivity of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites with a rutile mass fraction greater than 15% (sample STZF-10), suggest that anatase TiO$_2$, although incapable of absorbing wavelengths longer than 380nm, serves a primary role in the photoactivity of the nanocomposites. This experimental conclusion suggests a puzzling charge transfer phenomena existing between anatase TiO$_2$, ZnFe$_2$O$_4$.

Another possible explanation, however, can be drawn from consistent results that suggest optimal visible light photoactivity is achieved with anatase particles less than approximately 15nm coupled with ZnFe$_2$O$_4$ of low-crystallinity. It may be possible that intimately coupled particles with dimensions close to quantum-sizes experience effects which promote photocatalysis at wavelengths absorbed by the near-amorphous ZnFe$_2$O$_4$ particles. If Q-effects are indeed involved, it may also be possible that ZnFe$_2$O$_4$ nanoparticles of low crystallinity prepared at low annealing temperatures may experience a band gap increase of one to several tenths of an electron volt, thereby reducing the energy level of the conduction band edge to a potential that can effectively reduce O$_2$. 