



## SYNTHESIS, CHARACTERIZATION AND EFFECT ON PHOTOCATALYTIC PROPERTY OF Fe<sup>3+</sup>-TiO<sub>2</sub> NANOPARTICLES UNDER U.V. LIGHT IRRADIATION

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### Abstract:

Phase pure anatase nanospherical Fe<sup>3+</sup>-TiO<sub>2</sub> has been obtained by sol dissolution method using titanium chloride and ferric chloride precursor. Obtained samples were annealed at 600 °C and its structural, morphological and optical properties were determined using XRD, UV-Visible, EDX and SEM analysis. The shift in absorption towards the visible region and increase in band gap is observed with increase in Fe<sup>3+</sup> concentration. In this work about 3 weight percent of titanium atoms were successfully replaced by the iron atoms. The crystallite size was found in the range of 11-15 nm. The effect of iron doping on the catalytic activity of titania was studied and discussed.

**Keywords:** Fe<sup>3+</sup>-TiO<sub>2</sub>, Chemical synthesis, X-ray diffraction, Optical properties, Photocatalyst

### Introduction:

Titanium dioxide has attracted significant attention due to their broad spectrum and effective application particularly in photocatalysis, catalyst support, antibacterial, environmental remediation, air purification and water disinfection. This is owing to its low cost, nontoxicity and ecofriendly nature (Yadav, et al.). Many methods have been reported to synthesize TiO<sub>2</sub> nanoparticles such as solvent extraction, solvent evaporation, crystallization, self-assembly, layer by layer deposition, microbial synthesis, biomass reaction, sol-gel method, micelle and inverse micelle method, hydrothermal method, solvothermal method, chemical vapour deposition, physical vapour deposition, electrode position etc [Chen, et al.]. Extensive work has been done by many authors on TiO<sub>2</sub> photocatalyst for removal of organic pollutants. In our recent work we have reported the reflux method and direct method for the synthesis of TiO<sub>2</sub> nanoparticles from peroxo-titanium complex and synthesized nanoparticles were explored for the degradation of organic dyes under UV light (Bandgar et al., Sabale et al., Jadhav et al.). TiO<sub>2</sub> can only activate under UV light due to its wide band gap of 3.2eV. But by doping with metals and non metals this band gap energy can be decreased. The doping with small amount of metal impurities like Iron, Copper, Nickel, Silver, Gold, Zirconium, etc. used to tune the absorption in visible region so as to decrease the band gap energy and to visible light active photocatalyst [Quiroz et al.]. In present study the change in characteristics properties by doping with iron and its effect on photocatalytic properties has been studied. The Fe doped titania nanoparticles were synthesized

by direct dissolution of peroxo-titanium complex. The obtained samples were characterized using X-ray diffractometer for its structural properties, UV-Visible for its optical properties, Scanning electron microscope for its morphological properties and EDX for its compositional confirmation. Degradation of methyl orange was studied under UV light using obtained sample to evaluate effect of Fe<sup>3+</sup> doping on TiO<sub>2</sub> photocatalyst.

### Material and Methods:

The Fe<sup>3+</sup>-TiO<sub>2</sub> was synthesized with reference to sol dissolution method [6]. Titanium(III) chloride (20 mL), 15% in HCl; (Sigma-Aldrich) and 0.086 M (1 mL, 5 mL, 10 mL and 15 mL) Iron chloride (Loba Chemie, India) solution was mixed and precipitated into its hydroxide by addition of aqueous ammonia (Thomas Baker). The precipitate was thoroughly mixed by constant stirring to obtain dispersion in water. The orange colored transparent sol was obtained from this dispersion by adding hydrogen peroxide (Loba Chemie). Continuous stirring of the sol resulted in a vigorous reaction resulted into precipitate of Fe-TiO<sub>2</sub> with different concentration of iron within 15 min and settled down immediately. This powder was filtered and washed with water followed by acetone to remove water. The powder was dried at room temperature and annealed at 600 °C for 2 hr. All the samples of Fe<sup>3+</sup>-TiO<sub>2</sub> (TF1, TF2, TF3 and TF4) powder were analyzed using XRD, SEM, UV-Visible and EDX. The study was extended to investigate the effect on photocatalytic property of the TiO<sub>2</sub> in dye degradation using methyl orange as model dye. All the chemicals and reagents used during the experiment were of

analytical grade and used without further purification. Double distilled deionized water was used throughout the experiment.

The structural properties of Fe<sup>3+</sup>-TiO<sub>2</sub> powder were determined by X-ray diffractometer, BRUKER AXS using monochromatic copper radiation (Cu K $\alpha$ ) at 40 kV, 25 mA over the  $2\theta$  range 20-80°. The surface morphology of Fe<sup>3+</sup>-TiO<sub>2</sub> samples were observed by scanning electron microscopy (SEM) using JEOL JSM 6360 while optical properties (UV-Vis absorbance) and photocatalytic properties of nano TiO<sub>2</sub> for dye degradation were carried out using JASCO V-670

The photocatalytic degradation of methyl orange dye in the Fe<sup>3+</sup>-TiO<sub>2</sub> suspension under UV illumination was investigated in order to evaluate its photocatalytic activity. Methyl orange is used as a model dye in this study. A reaction system was set up by adding 50 mg of Fe<sup>3+</sup>-TiO<sub>2</sub> samples into 50 ppm, 500 ml of methyl orange solution in a photocatalytic multilamp reactor. The reactant aqueous suspension was irradiated for 1-2 hr with UV light (125 W, Hg vapor lamp with maximum emission at about 254 nm) at room temperature with continuous and constant stirring speed to form a homogeneous suspension. The suspension was withdrawn and centrifuged at 1 and 2 hr time interval to remove the Fe<sup>3+</sup>-TiO<sub>2</sub> particles. The absorption of each dye solution was measured using a UV-Visible spectrophotometer at maximum wavelength. The percentage of degradation at irradiated time intervals was calculated according to the equation

$$\text{Degradation Percentage} = [1 - A_t/A_0] \times 100$$

where, A<sub>t</sub> is absorbance after time 't' and A<sub>0</sub> is absorbance of dye solution before degradation.

### Results and Discussion:

The structural properties were determined from XRD patterns. Figure 1 shows the XRD patterns of TF1, TF2, TF3 and TF4 samples annealed at 600 °C. The diffraction peaks at  $2\theta = 25.07, 37.59, 47.98, 53.72, 54.86, 62.58, 68.54, 70.05, 75.05$  corresponds to the (101), (004), (200), (105), (211), (204), (116), (220), (215) respectively for plane of tetragonal anatase TiO<sub>2</sub> (JCPDS 21-1272). The lattice parameters of samples were determined and are matched with reported values (Table 1). No extra peaks corresponding to rutile phase was observed and the crystallite size was calculated using Debye-Scherrer formula [Cullity et al].

The calculated crystallite sizes are 11.00 nm, 15.10 nm, 13.02 nm, 11.04 nm for TF1,

TF2, TF3 and TF4 respectively. It is observed that, the crystallite size increases for TF2 and further increase in concentration of dopant the crystallite size decreases for sample TF3 and TF4. The decrease in crystallite size can be correlated to increase in structural defects that prevent particle growth [Choudhury et al]. In this work, the iron dopant is incorporated by replacing few Ti<sup>4+</sup> ions in TiO<sub>2</sub> crystal lattice. These results clearly confirm the successful substitution of few Ti<sup>4+</sup> ions by Fe<sup>3+</sup> ions.

Figure 2 shows the UV-visible absorption spectra in the range of 200-700 nm for samples TF1, TF2, TF3 and TF4 respectively. The absorption spectra of these doped samples show a stronger visible light absorption indicating the band gap was decreased upon doping Fe<sup>3+</sup>.

Band gap values were calculated using  $E = \frac{hc}{\lambda}$  [6]. The reported band gap energy for TiO<sub>2</sub> is 3.2 eV. This band gap value decreases with increase in Fe<sup>3+</sup> concentration and values of band gap are given in table 2.

The morphology of the samples TF1, TF2, TF3 and TF4 is studied using scanning electron microscope. Figure 3 shows the SEM micrographs of all the four, TF1, TF2, TF3 and TF4 samples. This surface morphological studies show that, all the obtained Fe<sup>3+</sup>-TiO<sub>2</sub> samples are with spherical morphology. The composition of the samples is determined using EDX (Figure 4) and composition is reported in the table 1. The table shows that the addition Fe<sup>3+</sup> was successfully done upto 3 wt % which attributes to the decrease in band gap and visible light active photocatalyst. Furthermore these samples were explored for the degradation of methyl orange dye as model reagent. Figure 5 shows the degradation study of methyl orange at 1 hr and 2 hr time of irradiation under UV light. From figure it is observed that the time of irradiation increases the percentage degradation but due to increase in the Fe<sup>3+</sup> concentration the percentage of dye degradation decreases. This reveals that, increasing of dopant concentration decreases the catalytic activity of the TiO<sub>2</sub> under UV light due to shifting of absorption band in the visible region and decrease in the band gap.

### Conclusion:

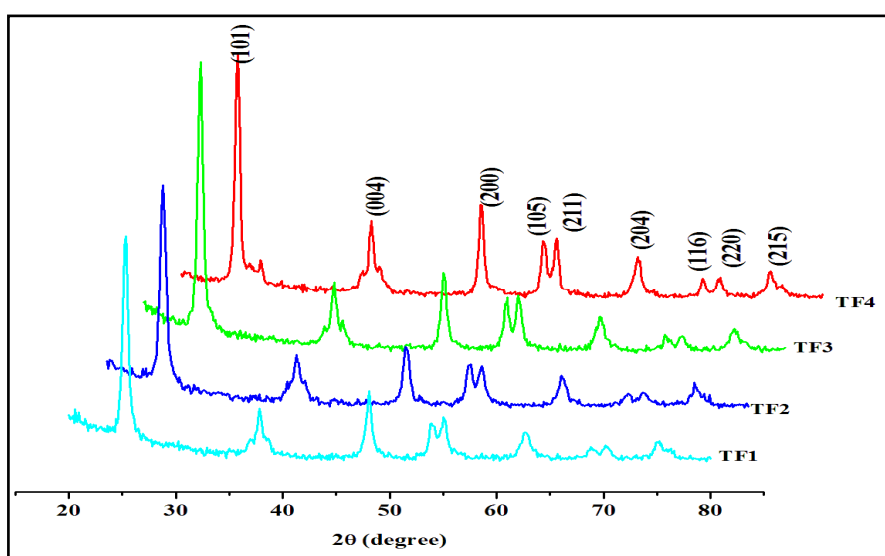
Simple, fast and direct synthesis method of Fe<sup>3+</sup>-doped TiO<sub>2</sub> is developed. Pure anatase and spherical titania nanoparticles are obtained by this method. The crystallite size was found to be in the range of 11 to 15 nm. With increase in the concentration of Fe<sup>3+</sup> the increase in size was obtained at weight percent 1.4 and further increase in concentration of Fe<sup>3+</sup>

decreases the size of titania nanoparticles. The band gap values were also decreases with decrease in  $\text{Fe}^{3+}$  concentration due to absorption band shifting in the visible region. The catalytic property for the degradation of dye is decreases

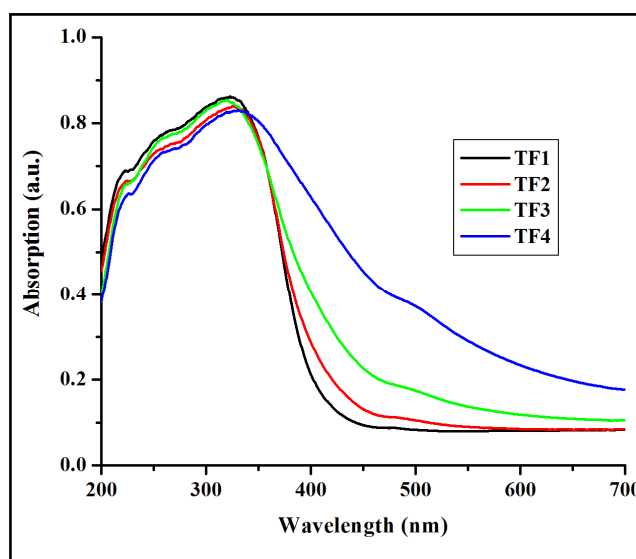
with increase in the dopant concentration under UV light irradiation. The dye degradation study will be explored in the sun light so as to develop visible light active photocatalyst.

**Table 1:** Obtained crystallite size, Lattice constant, band gap values and composition of TF1, TF2, TF3 and TF4 samples

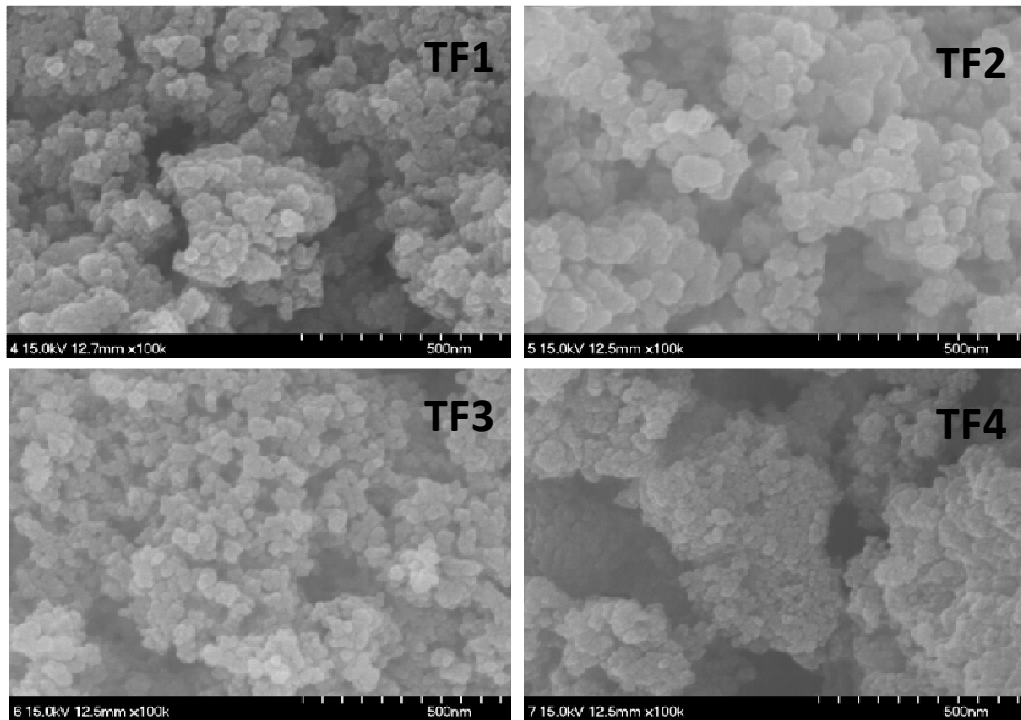
Sample	Crystallite size, D (nm)	d-spacing	Lattice const.		Band Gap (eV)	Composition (Wt. %)		
			a=b	c		O	Ti	Fe
TF1	11	3.5183	3.787	9.497	2.96	17.67	81.3	1.0
TF2	15.10	3.5176	3.782	9.515	2.84	24.17	74.4	1.4
TF3	13.02	3.5175	3.785	9.514	2.72	21.28	76.6	2.2
TF4	11.04	3.5178	3.783	9.504	2.38	21.13	75.9	3.0



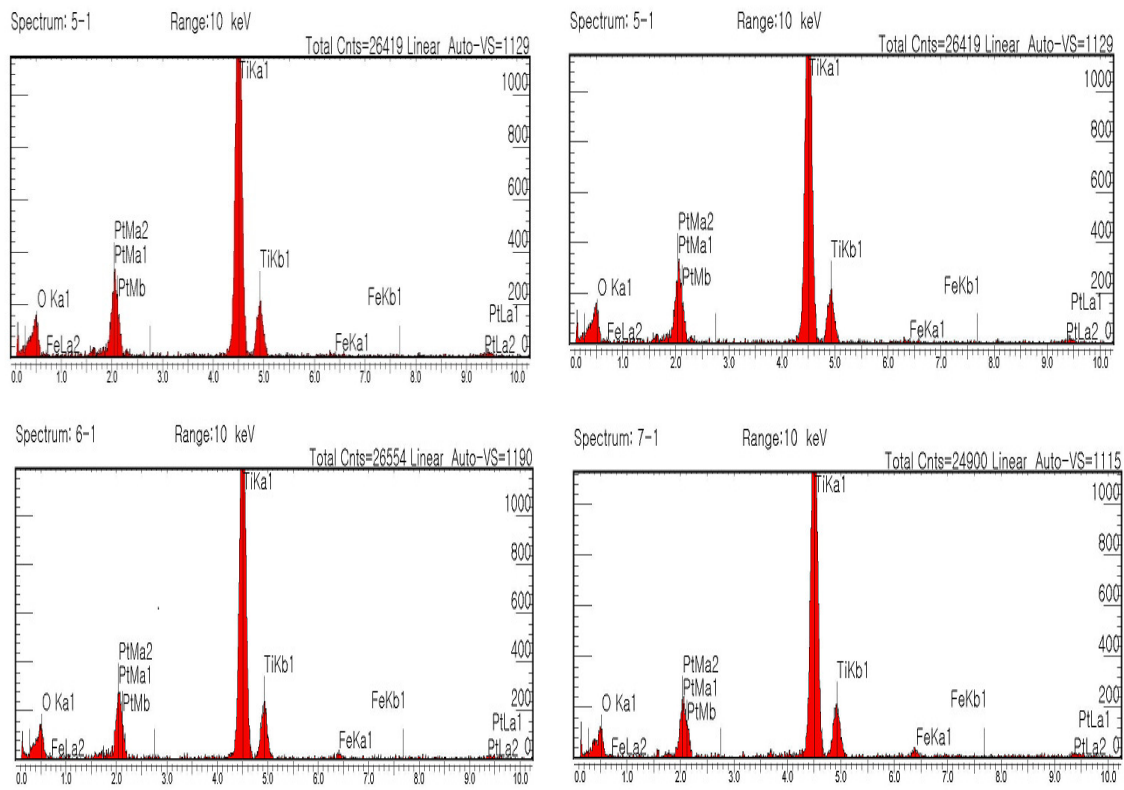
**Figure 1:** X-ray diffraction patterns of obtained titania samples



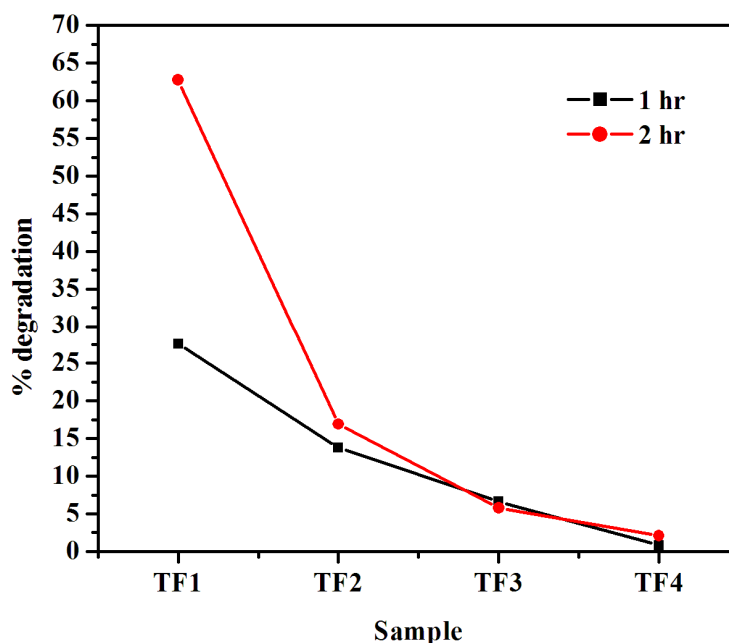
**Figure 2:** UV-Vis. Absorption spectra for obtained titania samples



**Figure 3:** Scanning electron micrographs of obtained titania samples



**Figure 4:** EDX micrographs of obtained titania samples



**Figure 5:** Percentage degradation of methyl orange dye under UV light

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