

Synthesis and characterization of Fe-doped TiO₂ Nanoparticles by modified sol-gel method

Aware Dinkar V

Department of Chemistry, Shri Dnyaneshwar Mahavidyalaya,, Newasa, Dist. Ahmednagar, Affiliated to S.P. Pune University, India

*Corresponding author, E-mail address : awaredinkar@gmail.com

Manuscript Details

Available online on <http://www.irjse.in>
ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:

Aware Dinkar V. Synthesis and characterization of Fe-doped TiO₂ nanoparticles by modified sol-gel method, *Int. Res. Journal of Science & Engineering*, January 2018; Special Issue A3: 80-84.

© The Author(s). 2018 Open Access

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License

(<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

ABSTRACT

Undoped and iron-doped TiO₂ nanoparticles (Ti_{1-x}Fe_xO₂ where x = 0.00 – 0.05) were synthesized by acid catalyzed sol-gel method. The synthesized products were characterized by sophisticated instrumental techniques like X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet –visible spectroscopy (UV-Vis-DRS) XRD pattern confirmed the tetragonal structure of synthesized materials. Average grain size was determined from X-ray line broadening using the Debye-Scherer relation. The crystallite size was found to be in the range 5.6 to 17.9 nm when calcined at 500 °C temperature. The doping of 1–5 mole% Fe into TiO₂ proved a great decrease in the size of nanocrystals as compared to undoped TiO₂. The TEM micrographs revealed the spherical-like morphology with average diameter of about 8 to 10 nm which is in agreement with XRD results. UV-Vis-DRS clearly showed the shift in the absorption towards visible region of the spectrum.

Keywords: Sol-gel, XRD, TEM, UV-DRS.

INTRODUCTION

TiO₂ is well known for its widespread applications in paints, pigments, cosmetics, food stuffs, environmental treatment and purification purposes [1-5]. There is a particular current interest in the application of titanium dioxide (Titania) in the photocatalytic degradation of organic pollutants and in the photochemical water splitting,

Which are becoming vital importance due to environmental concerns and future energy need. Due to its wide energy band-gap (3.0-3.2 eV) effective utilization of solar energy is limited to about 3-5% of the total solar spectrum [6-10]. Doping of the semiconducting metal oxides [6-8] like CuO, NiO and Fe₂O₃ with low band gap energy is one of the most widely used way to reduce band gap energy (Red Shift) and to lower the recombination of photogenerated e⁻/h⁺ pairs. Among the various semiconducting metal oxides Fe³⁺ is suitable for doping with Titania because both of them have nearly same ionic radii [8] (Fe³⁺ = 0.690 Å and Ti⁴⁺ = 0.745 Å). Also iron is among ten most abundantly occurring chief elements from the earth crust. In its (+III) oxidation state it is having half filled d⁵ orbital acts as a charge carrier trap and inhibits the recombination of photogenerated e⁻/h⁺ pairs. Owing to this it enhances the photocatalytic activity of doped Titania. Efficient photocatalytic activity of Fe³⁺-doped Titania is reported by many researchers[9-11] while according to some reports, photocatalytic activity of Titania doped with Fe³⁺ decreases as the dopant acts as a center for electron-hole recombination.[12] It very interesting to study the effect of concentration of Fe as a dopant on photocatalytic activity of Titania.²⁴ Different methodology are employed for synthesis of nanocrystalline, photocatalytic active Titania including hydrothermal, solvothermal, co-precipitation and sol-gel method.[11] Out of these hydrothermal/solvothermal methods are energy and time consuming, while sol-gel method is very simple, rapid, reproducible, fabricates nanoparticles with precise morphology and particle size[13].

In this article iron doped Titania nanoparticles were synthesized very simple surfactant free acid catalyzed modified sol-gel method and were characterized by various sophisticated instrumental techniques like XRD, TEM, EDX and UV-DRS.

METHODOLOGY

1. Chemicals

For the synthesis of undoped and iron-doped TiO₂ nanoparticles, the materials used were titanium (IV) butoxide [M = 340.76, Ti (OC₄H₉)₄], ferric nitrate

nonahydrate [Fe (NO₃)₃ 9H₂O], obtained from Sigma-Aldrich. Isopropyl Alcohol [M =60, (CH₃)₂CHOH] and acetic acid were obtain from S.D Fine Chemicals and Ethyl alcohol [M=46, C₂H₅OH] from local distillery. The deionized water was used as a solvent.

2. Synthesis

Synthesis of TiO₂ nanoparticles

The bare Titania powder was synthesized by modified sol-gel method. In a typical experimental procedure 20 gram of titanium (IV) butoxide was slowly added to the solution containing 15 ml isopropanol and 10 ml glacial acetic acid. It was ultrasonically dispersed in ultrasonic bath for 30 minutes and was added to 50 ml solution containing acetic acid-water (1:3) mixture under constant magnetic stirring. The vigorous magnetic stirring was continued for next four hours. It was then dried in hot air oven at 80°C for 12 hours, calcined at 500°C in high temperature muffle furnace for 4 hours in static air atmosphere and it was labeled as PT.

Synthesis of Fe-doped TiO₂ nanoparticles

Fe-doped TiO₂ nanoparticles were synthesized by using sol-gel method in presence acetic acid as solvent. Calculated quantity (1.0, 3.0 and 5.0 mole %) of ferric nitrate hexahydrate were ultrasonically dispersed and dissolved in 50 ml glacial acetic acid - water (1:3) solution (Solution A). The required quantity of titanium (IV) butoxide was slowly added to a mixture of 15 ml isopropyl alcohol and 10 ml glacial acetic acid (Solution B). Then the solution A was slowly added into the solution B with vigorous magnetic stirring and ultrasonically dispersed for 60 min. The resultant solution was continuously stirred for next 4 hours, and then it was dried in oven at 80°C for 12 hours and then it was calcined at 500°C in high temperature muffle furnace for 4 hours. Resultant powders were labeled as x % FeT, where x % is the mole % Fe in TiO₂.

3. Characterization

The synthesized samples were characterized by various sophisticated Techniques. X-ray diffraction (XRD) patterns were carried out by using Philips X-ray diffractometer with diffraction angle 2θ in between 20 to 80° using Cu-Kα radiation of wavelength 1.54058 Å. The microscopic nanostructure and particle size was determined by using a CM-200

PHILIPS transmission electron microscope (TEM) at 200 kV ($L = 600$, $\lambda = 0.0025$ nm). The elemental analysis was carried out using X Flash 6130 Bruker instrument. The absorption spectra were recorded using a double beam UV-Visible spectrophotometer, Shimadzu -2450, Japan.

RESULTS AND DISCUSSION

After calcination at 500°C , the resultant powders were analyzed to study their surface morphology and composition with the help of sophisticated analytical instrumental techniques.

X-Ray Diffraction

The XRD pattern of undoped and Fe-doped TiO_2 nanoparticles calcined at 500°C is shown in Fig.1. The XRD peaks of all the synthesized samples were wide confirming nanocrystalline nature of the photocatalyst. The peak values located at 2θ ($^\circ$) 25.2, 37.6, 48.0, 53.8, 54.9, 62.6, 68.7, 70.2 and 74.9 correspond to the Miller indices (101), (004), (200), (105), (210), (204), (214), (220) and (107) respectively, confirming formation of highly photoactive tetragonal anatase Titania. All the diffraction peaks obtained from XRD agreed with the reported JCPDS card no. 21-1272 for tetragonal anatase Titania. No distinct peaks corresponding to rutile phase or dopant were seen in the X-ray diffractograms, which may be due to the proper incorporation of Fe^{3+} ions into the TiO_2 lattice. The crystallite sizes were estimated with the help of Scherer's equation, by using the most intense reflection ($2\theta = 25.2$) and were found to be in the range of 5.6 to 17.9 nm (Table 1).

Table 1: Physical parameters of iron doped and undoped Titania nanoparticles obtained from X-Ray Diffraction and Diffuse Reflectance Spectroscopy.

Sr. No.	Catalyst	Crystallite size, (nm)	Band gap energy, (eV)
1.	PT	17.9	3.12
2.	1% FeT	7.0	2.7

3.	3% FeT	5.9	2.5
4.	5% FeT	5.6	2.4

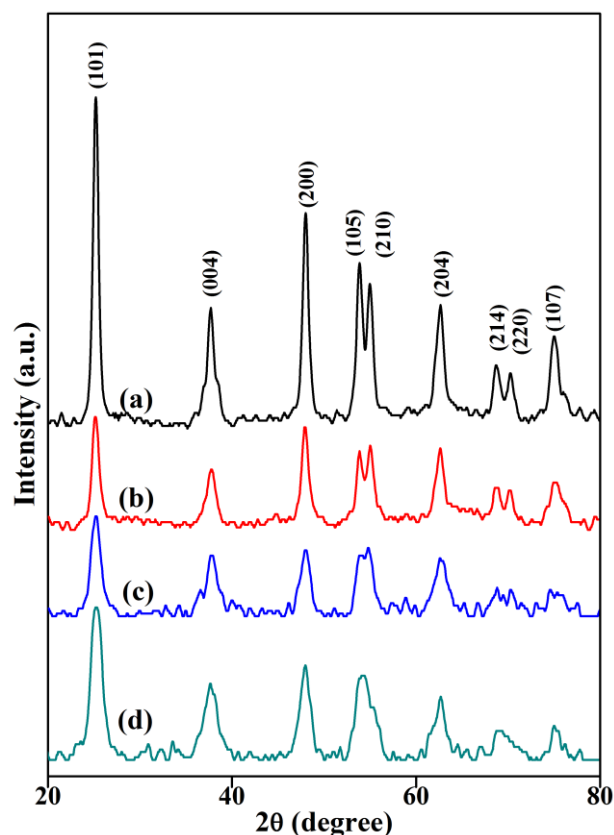


Fig.1. XRD patterns of (a) PT, (b) 1% FeT, (c) 3% FeT, and (d) 5% FeT calcined at 500°C .

Transmission Electron Microscopy (TEM)

The surface morphology of synthesized nanomaterial was studied by TEM analysis, Fig.2 show the TEM image of 1% FeT nanomaterials calcined at 500°C . From TEM analysis, it is clear that the synthesized nanoparticles are having spherical like morphology (Fig. 2 (a-b)) with excellent crystalline nature (Fig.2(c)). The SAED pattern confirms the presence of pure anatase phase (Fig. 2 (d)) which clearly supported XRD analysis. The d-spacing was indexed with the JCPDS card No 21-1272 corresponding to the anatase phase. The grain sizes were calculated from TEM analysis and were found in the range between 8 to 10 nm; thus, results obtained from TEM are in good agreements with XRD analysis.

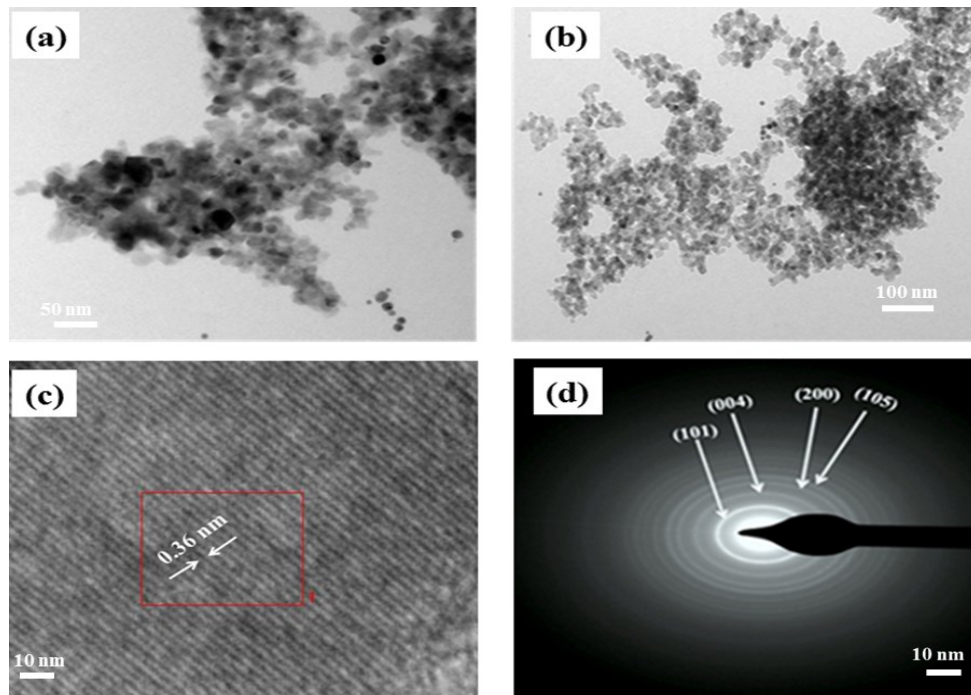


Fig.2. Typical TEM and HRTEM micrographs of synthesized nanoparticles, (a, b) TEM images at different magnifications; (c) HR-TEM image, and (d) SAED pattern of 1 % FeT calcined at 500°C.

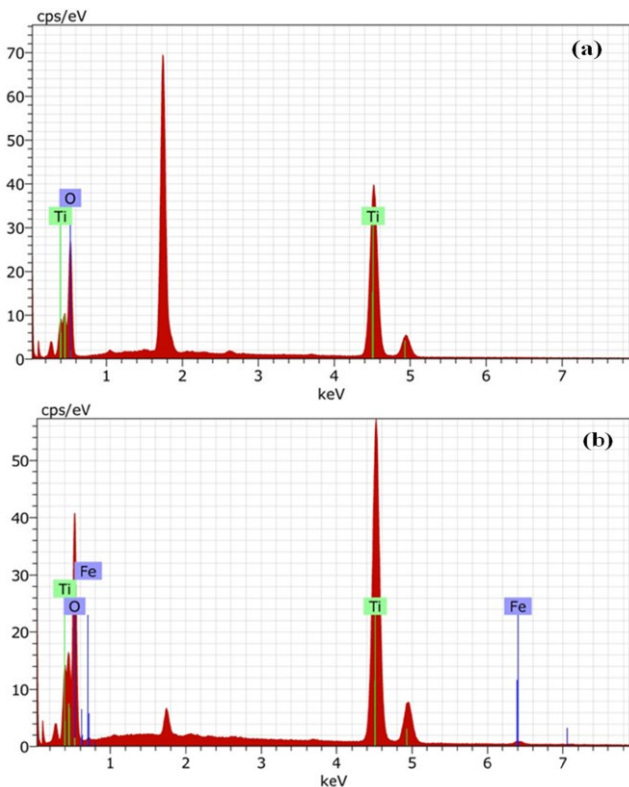


Fig. 3: EDX patterns of (a) PT, and (b) 1% FeT.

Ultra-Violet Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

In order to study optical absorption properties, all the synthesized nanomaterials were analyzed by **UV-Energy Dispersive X-Ray Spectroscopy (EDX)** Elemental analysis of Fe³⁺-doped and bare Titania was carried out using EDX technique. The EDX patterns for PT and 1% FeT (Fig. 3) confirms the presence of proper proportion of Fe with respective Ti in doped samples and iron doping leads the oxygen deficiencies in the samples

Visible DRS technique in the absorption range of 200 nm to 800 nm and the results are shown in the Fig.4. The bare Titania shows the absorption at 404 nm with band gap energy 3.1 eV, which is near the band gap energy of the anatase Titania (~3.2 eV). While significant enhancement in the absorption edge was observed for all doped samples indicating red shift in the absorption of wavelength in between 400–520 nm. The colour of the doped samples changed from white to yellowish brown with increase in the dopant concentration. The doping of transition metal ions like Fe³⁺ ions does no modify the position of valance band edge of Titania but it introduces new energy levels into the band gap of Titania. Thus, the dopant energy levels in between valance band and conduction band shifts the absorption edge towards longer wavelength

resulting in the decrease of band gap energy. The band gap energy values were calculated by extrapolation of the absorption band to the x-axis using the following equation,

$$E_{bg} = 1240/\lambda$$

Where, λ is the wavelength in nanometer and E_{bg} is the band gap energy. The calculated band gap energy values were, in the range of 2.4 to 3.1 eV (Table 1).

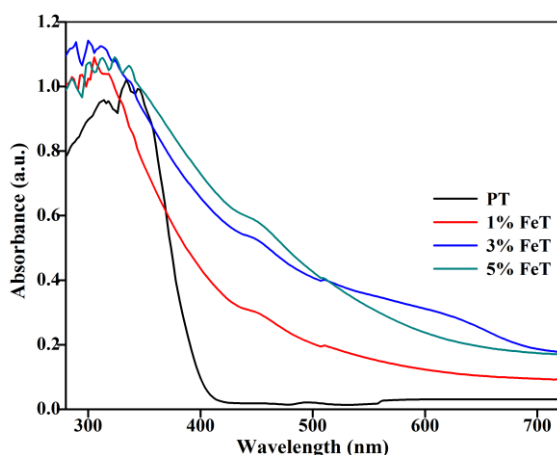


Fig.4. UV-vis DRS spectra of bare TiO₂ and Fe³⁺-doped TiO₂ nanoparticles.

The enhanced visible light absorptions may be explained by the charge transfer transition between the d electrons of the Fe dopant and the conduction band of TiO₂. These results suggest that iron was incorporated into the crystalline network of TiO₂. The ionic radius of Fe³⁺(0.69Å) and Ti⁴⁺(0.745Å) are similar, and Fe³⁺ ions potentially substitute Ti⁴⁺ in the structure of TiO₂, which would in turn introduce a new impurity level into the band gap of TiO₂ and reduce the forbidden energy gap of TiO₂.

CONCLUSION

Modified sol-gel synthetic route results the formation nanocrystalline anatase TiO₂ polymorphs with decreased in grain size (17.9 to 5.6 nm) upon iron doping was confirmed by powder XRD. TEM and HRTEM confirm the formation of nanocrystalline Titania with spherical like morphology. The SAED pattern depicts diffraction peaks corresponding to pure anatase polymorphic phase of Titania. The results of TEM and XRD strongly supports to each other. Doping of iron in the Titania lattice was

confirmed from EDX. The red shift in the absorption maxima due the iron doping was observed from UV-Vis DRS results.

Above results clearly confirms that synthesized nanomaterials may further used for environmental remedies.

Acknowledgement:

The author is grateful to the Principal, Shri Dnyaneshwar Mahavidyalaya, Newasa for providing the all required facilities to carry out the work.

Conflicts of interest: The authors stated that no conflicts of interest.

REFERENCES

1. Matthews Peter D, King Timothy C and Wright Dominic S.. *Chem. Commun.*, 2014,**50**: 12815.
2. Auvinen J and Wirtanen L. *Atmos. Environ.*, 2008, **42**: 4101.
3. Maria Eugenia Carlotti, Elena Ugazio, Lucia Gastaldi, Simona Sapino, Davide Vione, Ivana Fenoglio and Bice Fubini. *J. Photochem. Photobiol.*, 2009, B **96**:130.
4. Y.Liao and W.Que *J. Alloys Compd.*, 2010,**505**: 243.
5. Mohamed RM and Mkhaliid IA. *J. Alloys Compd.*, 2010,**501**:143.
6. Molea A, Popescu V, Rowson NA, Cojocaru I, Dinescu A, Dehelean A, and Lazar M. *Ind. Eng. Chem. Res.*, 2015, **54**: 7346.
7. Tayade RJ, Kulkarni RG, Jasra RV. *Ind. Eng. Chem. Res.*, 2006,**45**: 5231.
8. Barakat MA, Kumar R. P. A. Enhancement, "Photocatalytic Activity Enhancement of Titanium Dioxide Nanoparticles," *Springer International Publishing*, 2016, pp. 1-29.
9. Sood S, Umar A, Mehta SK, Kansal SK. *J. Colloid Interface Sci.*, 2015, **450**: 213
10. Liu W, Zhao X, Borthwick AGL, Wang Y. *J. Ni, ACS Appl. Mater. Interfaces.*, 2015,**7**: 19726.
11. Mohsen M , Yousef M. *J. Mater. Sci. Mater. Electron.*, 2015, **26**: 5509.
12. Wang W, Serp P, Kalck P, Faria JL, *Appl. Catal. B Environ.*, 2005, **56**: 305.
13. Serpone N, Lawless D, Disdier J, Herrmann JM, *Langmuir*, 1994,**10**:643.