

Structural and Photocatalytic Behaviour of TiO₂ and α -Fe₂O₃-TiO₂ Nanorods

Shanmugapriya P¹, Pandiyarasan V¹, Sanju Rani², Rajalakshmi N²

Department of Physics and Nanotechnology,

SRM University, Kattankulathur, Kanchipuram, Tamilnadu-603203.

Centre for Fuel Cell and Technology, International Advanced Research Centre for Powder Metallurgy and New Materials(ARCI), IITM-Research Park, 6, Kanagam Road, Taramani, Chennai, Tamilnadu- 600113.

ABSTRACT

We report the effect of α -Fe₂O₃ doping (varied weight%) on the photocatalytic activity of TiO₂. Synthesis of TiO₂ and α -Fe₂O₃-TiO₂(N1 [0.34wt%], N2 [0.68wt%]) were done using single step hydrothermal technique. The structural, morphological and optical characteristics of TiO₂ and doped samples were analyzed by X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Diffuse Reflectance UV-Vis Spectroscopy (DRS) and Fourier Transform InfraRed Spectroscopy (FTIR). The photocatalytic property of the samples were studied by the dye degradation experiment, which was carried out under natural sunlight. The experiments were carried out for 150 mins and aliquot samples were collected for each of them at the interval of 15 mins. The absorption spectrum of aliquot samples were obtained using UV-Visible Spectrophotometer to study the rate of degradation. Irradiation time Vs C/C₀ graph revealed the rate of degradation for each sample. The order of reaction, rate constants and half lives were analysed using ln[C] Vs time graph which exhibited a linear fit for all samples, it shows they follow first order reaction kinetics. It showed that lower doped nanorods (N1) had greater rate constant and improved efficiency as compared to others.

Keywords: Photocatalytic activity, TiO₂, α -Fe₂O₃-TiO₂, Natural sunlight, nanorods.

1. INTRODUCTION

Waste water has become an alarming problem around the world, which has been resulted through the discharge of sewage water, industrial wastes, agricultural wastes, ingress of seawater, river water, manmade liquids, rainfall runoff. This includes discharge of industrial wastes like toxic wastes, emulsions, industrial process waters, release of dyes from textile industries. The ingress of excessive dyes into the natural water is often serious concern. The dyes could react with environmental conditions which will make it more toxic and carcinogenic for aquatic and human life. The dyes are quiet stable even under sunlight and its difficult to detect their individual presence for the study of toxicity[1].There are a variety of conventional methods like physical,

chemical and biological methods to treat the waste water. These methods were found to be not paving the way for complete remediation from this issue.

Nanomaterials are highly known for their excellent optical, electronics, chemical properties which greatly helps in addressing various issues that are not met with bulk materials[2]. One dimensional nanostructures are of greater interest for a photocatalyst due to its unique optical, structural and electronic properties. Metal oxide semiconductors are widely used as a photocatalyst due to their stability, non-toxicity, low cost and tunable properties, possibility of noble metal loading, doping and sensitization[3]. Among them TiO₂, ZnO, WO₃, SnO₂ are widely studied, where ZnO, WO₃ and SnO₂ are performing inferior when compared to TiO₂. TiO₂ is found to be the most dominating material as a photocatalyst in dye degradation process owing to its higher photocatalytic efficiency[4].

The requirements of a good photocatalyst for photodegradation includes maximum utilization of visible region, higher efficiency, mineralization of the dye molecules, separation and reusability of the photocatalyst. TiO₂ was being widely studied, which is considered to be the dominating material in photodegradation. But it has a disadvantage of wide bandgap (3.2eV) due to which it is not able to absorb visible light. Here, we have reported TiO₂ and α -Fe₂O₃-TiO₂ nanorods, of which α -Fe₂O₃-TiO₂ has shown enhanced photocatalytic activity under sunlight.

2. EXPERIMENTAL METHODS

All the chemical reagents were analytically pure and were used without any further purification. The synthesis of TiO₂ and α -Fe₂O₃-TiO₂ samples was carried out using a single step hydrothermal technique. 10 M aqueous solution of Sodium Hydroxide (NaOH) was prepared by stirring for 15mins at room temperature. 2gms of TiO₂ powder was added to the NaOH solution under stirring. α -Fe₂O₃-TiO₂ was also prepared using the aforementioned procedure with the addition of 0.34wt% (N1) and 0.68wt% (N2) of FeCl₃ to the precursor. The precursor was transferred to the 100ml Teflon lined autoclave. It was sealed, kept in furnace and the temperature is maintained at 160^o. After 24hours, the autoclave was removed and allowed to cool down at room temperature. The resulted solid mass in the autoclave was washed with distilled water several times and separated by centrifugation, dried in hot air oven at 60^o for about 8hrs. The dried powder was crushed and stored for further characterizations and studies.

3. SAMPLE CHARACTERIZATIONS

The crystallinity and phase analysis of the samples were done using PANalytical X Ray Diffractometer using Cu K α radiation (λ =1.54056Å) with 2 θ ranging from 20^o to 80^o. Fourier Transform InfraRed Spectroscopy (Alpha-T FT-IR Spectrometer) was used to study the functional

groups formed in the samples. The diffuse reflectance spectrum were obtained using Diffuse Reflectance UV-Vis Spectroscopy (JASCO V-650) in the wavelength range of 200 to 800nm in order to calculate the bandgaps of the material. The surface morphology of the samples were seen using Scanning Electron Microscope (FEI Quanta™ 100). The photocatalytic activity of all the samples were studied by dye degradation experiment using Methylene Blue(MB) dye. The initial concentration was 6.25 μ M (200 μ l in 100ml distilled water) and 1gm of the sample was loaded to the MB solution. The photocatalytic study was done under natural sunlight for about 150mins and the aliquot samples were collected at the time interval of 15mins. The absorption spectrum of aliquot samples were obtained by UV-Visible Spectrophotometer (UV 3000+) in the wavelength range of 200-800nm.

4. RESULTS AND DISCUSSIONS

4.1 XRD

The XRD pattern of TiO₂ and α -Fe₂O₃-TiO₂ (N1 and N2) were shown in Fig1. All the peaks in each diffraction pattern correspond to anatase phase of TiO₂[5,6,7] however in case of doped samples there were traces of α -Fe₂O₃[(104),(110)]. It was observed that the peak intensity of the planes (104),(110) corresponding to α -Fe₂O₃ was increased with increase in doping concentration. It was also observed that the peak corresponding to anatase TiO₂ was decreasing and FWHM was broadening with increase in α -Fe₂O₃ doping. It shows that there was reduction in crystallite size and increase in surface area with α -Fe₂O₃ doping as compared to

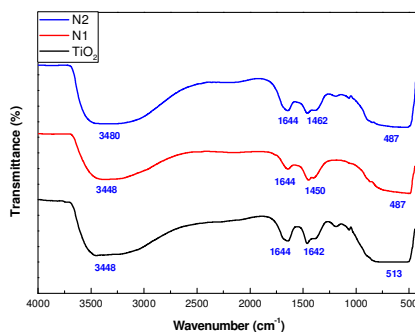
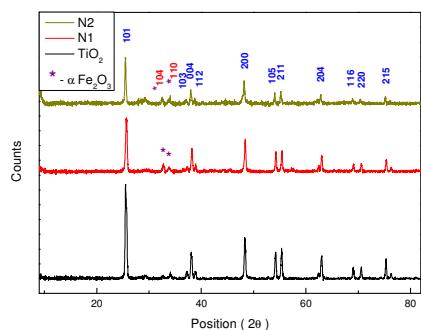


Fig 1 showing XRD pattern of TiO₂, N1 and N2 **Fig 2** showing FTIR spectrum of TiO₂, N1 and N2

4.2 FTIR

Fig2. Shows the FTIR spectrum of all the samples in the range of 400-4000cm⁻¹. The patterns were found to have peaks around the region of 3400cm⁻¹, 1640cm⁻¹, 1450cm⁻¹ and 480/500cm⁻¹. There

was reduction in the intensity of all the peaks with the incorporation of α -Fe₂O₃. The broad peaks found in the region of 3450 cm⁻¹ and 1650 cm⁻¹ corresponds to the stretching and bending vibrations of -OH group[8]. These groups play a major role in the phase formation as well as in phase stabilization of all the samples[9]. In the photocatalytic dye degradation experiments -OH group plays a vital role. During the reaction, it prompts to react with photogenerated holes in order to degrade the dye into intermediate products leading to mineralisation[10]. The peak observed in the region of 513cm⁻¹ for TiO₂ correspond to Ti-O bond, were observed to be shifted to 487cm⁻¹ with doping, which associates with Fe-O stretching mode.

4.3 DRS

The absorption spectrum of TiO₂ and α -Fe₂O₃ doped samples were depicted in Fig3a. The spectra of TiO₂ revealed an absorption edge at 380nm. The spectrum of α -Fe₂O₃ doped samples exhibited broad absorption in the visible region (450-600nm) as compared to TiO₂. This shows there is a bathochromic (red) shift in the absorption region which leads to reduction in the bandgap of the material[11,12].

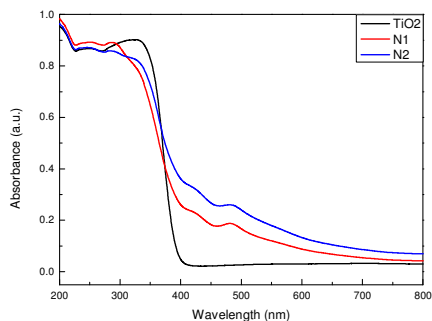


Fig3 showing DRS UV-Vis spectrum

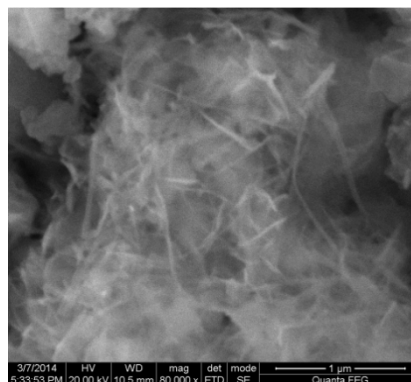


Fig4 showing SEM image of N1

4.4 SEM

The SEM images are shown in Fig4. The images clearly depict the formation of uniformly distributed nanorods. The morphology of the samples were not affected due to doping. There was formation of one dimensional nanostructures, an important concern for the photocatalytic activity.

4.5 Degradation Studies

Fig6(a, b, c) shows the UV visible absorption spectrum of gradual degradation in Methylene Blue(MB) dye in the presence of the photocatalysts(TiO₂, N1, N2 respectively). All the graphs show a gradual degradation had taken place. In case of α -Fe₂O₃ doped samples, there was the hypsochromic (blue) shift in the spectrum (Fig 6b, 6c). This might be due to the demethylation of

the MB and formation of other intermediate products under sunlight[13]. The degradation rate for all the samples were analysed using irradiation time Vs C/C₀ curve (Fig 6d). It shows that rate of degradation is increased with that of doped samples (N1,N2) than in TiO₂. Rate constants and Half Lives had been calculated which is listed in Table1. All the samples were following first order reaction kinetics and the rate constant was highest for N1 among them. The table shows that higher the rate constant, lesser the half life. The degradation efficiency[14] have been calculated using the formula $(1-(C_t/C_0))*100$ which showed greater efficiency with lower doped sample(N1). The efficiencies were found to be 92%, 95.07% and 94.08% for TiO₂, N1, and N2 respectively.

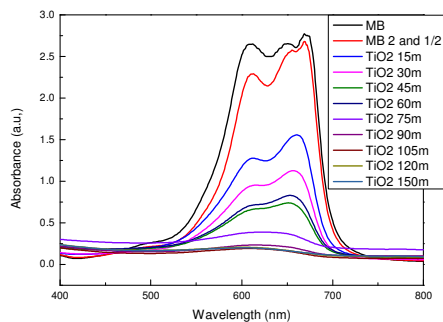


Fig 6a

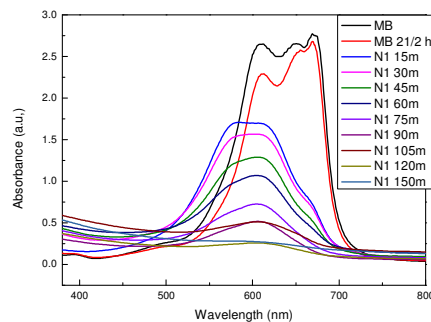


Fig6b

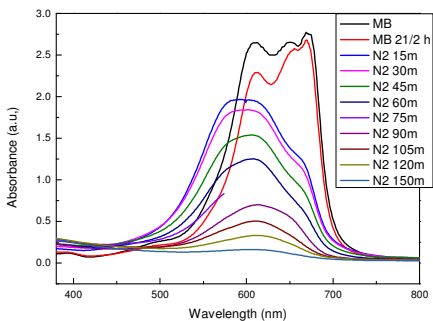


Fig 6c

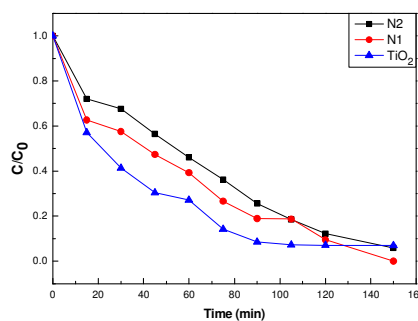


Fig6d

Table1 showing the rate constants, Half lives and Efficiencies of all samples

Sample name	Order of the reaction	Rate constant (10^{-2}min^{-1})	Half Life ($t_{1/2}$)	Efficiency (%)
TiO ₂	First	4.46	15.54	92
N1	First	7.45	9.35	95.08
N2	First	4.19	16.54	94.07

5. CONCLUSION

TiO₂ and α -Fe₂O₃-TiO₂ (N1,N2) nanorods had been prepared using a simple one step hydrothermal technique. It was observed that there was reduction in the bandgap on α -Fe₂O₃ doping. The degradation studies have revealed that doping with lower concentration of α -Fe₂O₃ could enhance the photocatalytic activity to an extent which further reduces the enhancement on increase in doping concentration.

REFERENCES

- [1] Ratna, Padhi. B.S, Pollution due to synthetic dyes toxicity & carcinogenicity studies and Remediation, International Journal of Environmental Sciences Volume 3, No 3, 2012, ISSN 0976 – 4402, 940-955.
- [2] Emil Roduner, Size matters: why nanomaterials are different, Royal Society of Chemistry, Chem. Soc. Rev., 2006, 35, 583–592.
- [3] Zaharia Carmen and Suteu Daniela, Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview, Organic Pollutants Ten Years After the Stockholm Convention – Environmental and Analytical Update, ISBN 978-953-307-917-2, 55-86.
- [4] Samuel Hong Shen Chan, Ta Yeong Wu, Joon Ching Juan and Chee Yang The, Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water, DOI 10.1002/jctb.2636, J Chem Technol Biotechnol2011, Society of Chemical Industry, 86: 1130–1158.
- [5] GUPTA Shipra Mital and TRIPATHI Manoj, A review of TiO₂nanoparticles, Chinese Science Bulletin, Physical Chemistry - Review, doi: 10.1007/s11434-011-4476-1, June 2011 Vol.56 No.16: 1639–1657.
- [6] Hakan Ceylan,Cagla Ozgit-Akgun,Turan S. Erkal,Inci Donmez,Ruslan Garifullin,Ayse B. Tekinay,Hakan Usta,Necmi Biyikli & Mustafa O. Guler, Size-controlled conformal nanofabrication of biotemplated three-dimensional TiO₂and ZnO nanonetworks, SCIENTIFIC REPORTS| 3 : 2306 | DOI: 10.1038/srep02306.
- [7] Chin-Jung Lin, Wen-Yueh Yu, Yen-Tien Lu and Shu-Hua Chien, Fabrication of opened-end high-aspect-ratio anodic TiO₂ nanotube film for photocatalytic and photoelectrocatalytic applications, Electronic Supplementary Material (ESI) for Chemical Communications, The Royal Society of Chemistry 2008.
- [8] M.A. Ahmeda, Emad E. El-Katori, Zarha H. Gharni, Photocatalytic degradation of methylene blue dye using Fe₂O₃/TiO₂ nanoparticles prepared by sol–gel method, Journal of Alloys and Compounds 553 (2013) 19–29.
- [9] Xian-Ming Liu, Shao-Yun Fu, Hong-Mei Xiao, Chuan-Jun Huang, Preparation and characterization of shuttle-like α -Fe₂O₃ nanoparticles by supermolecular template, Journal of Solid State Chemistry 178 (2005) 2798–2803.
- [10] S. K. Apte, S. D. Naik, R. S. Sonawane, and B. B. Kale, Synthesis of Nanosize-Necked Structure α -Fe₂O₃ and its Photocatalytic Activity, J. Am. Ceram. Soc.,90[2] (2007) 412–414.
- [11] Biswajit Choudhury, Munmun Dey and Amarjyoti Choudhury, Defect generation, d-d transition, and band gap reduction in Cu-doped TiO₂ nanoparticles, International Nano Letters 2013 3:25 1-8.
- [12] Mohammad Mansoob Khan, Sajid A. Ansari, D. Pradhan, M. Omaish Ansari, Do Hung Han, Jintae Lee and Moo Hwan Cho, Band gap engineered TiO₂ nanoparticles for visible light induced

photoelectrochemical and photocatalytic studies, Royal Society of Chemistry, J. Mater. Chem. A, 2014, 2, 637–644.

- [13] Damian Marcinkowski, Monika Wałęsa-Chorab, Violetta Patroniak, Maciej Kubicki, Grzegorz Kaździołka and Beata Michalkiewicz, A new polymeric complex of silver(I) with a hybrid pyrazine–bipyridine ligand – synthesis, crystal structure and its photocatalytic activity, Royal Society of Chemistry, New J. Chem., 38 (2014) 604-610.
- [14] N.P. Mohabansi, V. B. Patil and N. Yenkie, A Comparative Study on Photodegradation of Methylene Blue dye effluent by Advanced Oxidation Process by using TiO₂/ZnO Photocatalyst, Rasayan Journal of Chemistry, Vol.4, No.4 (2011) 814-819, ISSN: 0974-1496.