Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Research

Elixir Crystal Res. 85 (2015) 34563-34565

ISSN: 2229-712X

# Visible light photocatalytic activity of vanadium doped zinc oxide nanoparticles

Kakuli A. Maiti[1], R. Jaiswal[2], Abhijit Bhogale[2], N. Patel[2], Rajlakshmi Neogi[3] and D.C.Kothari[2]

[1]Datta Meghe College of Engineering, Airoli, Navi-Mumbai-400708.

[2]Department of Physics, University of Mumbai, Vidyanagari, Mumbai-400098.

[3]S.P. Mandali's Ramnarian Ruia College, Matunga, Mumbai.

**ARTICLE INFO**

**Article history:**

Received: 19 July 2015;

Received in revised form: 10 August 2015;

Accepted: 22 August 2015;

**Keywords**

Zinc-Oxide nanoparticles,

Sol-gel method,

Photocatalytic dye degradation,

Rhodamine-B.

**ABSTRACT**

Zinc oxide nanoparticles doped with Vanadium of varying concentrations were synthesised by Sol-gel method. Samples prepared after annealing for 2 hrs at 600 $^{o}$C are characterised by XRD,UV-Vis Spectroscopy, SEM and EDS. The hexagonal wurtzite structure is maintained in ZnO after vanadium doping at high concentration (15 at.%) as confirmed by X-ray analysis. The absorption edge of ZnO is red shifted by increasing the vanadium concentration. SEM shows the nanoparticle nature of the ZnO particle, molar concentration of dopants is confirmed by EDS analysis. The photo catalytic activity of Rhodamine-B dye solution under visible light is better for V-doped ZnO as compared to pure ZnO.



## Introduction

The industrial waste water when released untreated in the natural water resources is of concern for the ecological balance of the environment. This waste water contains toxic dyes along with other pollutants. Various techniques have been employed to detoxify the water but they produce secondary pollutants which again require steps of treatments. Photo catalysis is one of the harmless routes for degradation of dyes into minerals using abundant solar energy [1]. It is reported that some metal oxide like Titanium dioxide ($TiO_2$), Tungsten oxide ($WO_3$), Strontium titanate ($SrTiO_3$) and hematite are proven to be dynamic photocatalyst for degradation of organic pollutants in water and air under UV radiation. $TiO_2$ is highly studied as it showed relatively high activity and chemical stability. ZnO, having a band gap of 3.23 ev and high chemical stability, acquires the energy band edges matching with re dox potential of water to produce hydroxyl radicals for degradation of pollutants. Band gap engineering has proved to be an efficient method to improve its photocatalytic activity in the visible region. Transition metal such as Mn [5], Co [6], Ag [9], has been used for doping. Studies have revealed that ZnO doped with Vanadium showed improved optical properties [1]. It has also been found to increase carrier life time [3]. Vanadium is having energy level below the conduction band of Zinc oxide. Some reported the absorption of V-doped ZnO shifted in the visible region [3], while others reported the absorption starts in the ultraviolet region. In addition V-doped ZnO is easy to form intrinsic oxygen vacancy during preparation process [4].The applications of V-doped ZnO are in new optical devices such as lasers, optical detectors, transparent conductive oxide, solar cells, photo catalysis and photo electrochemistry [7].

In the present work, V-doped ZnO photo catalyst powder was synthesized by sol–gel method. The photo catalytic activities of un doped and V-doped ZnO with varied vanadium doping levels are systematically studied for the degradation of Rhodamine-B (Rh-B) dye solution. Experimental Zinc Acetate dehydrate and ammonium metavandate were used aprecursors purchased from SDFCL. Ethanol and double distilled water were used as solvent. All chemical compounds were used as received without any further purification.

### Preparation

Vanadium doped Zinc oxide was prepared by adding 5.485 gm of Zinc acetate in 100 ml ethanol and stirring it for 30 mins at 65$^{o}$C. Another solution was prepared by adding appropriate amount of ammonium metavanadate in 6.3035 gm oxalic acid and 50 ml ethanol. The later solution was added dropwise with continuous stirring in the zinc precursor solution and the resulting solution was further stirred for 1 hr. The resulting solution was kept overnight for the gelation. ZnO gel was later washed several times with ethanol followed by drying at 125 $^{o}$C for 2 hrs to remove the excess solvent. The obtained powder was further annealed for 2 hrs at 600$^{o}$C in air.

### Catalyst Characterisation

The structural characterization of the samples were carried out by conventional X-ray diffraction (XRD), Cu k α radiation (λ= 1.5414A˚), in Bragg–Brentano (θ-2θ) configuration. The band gap of the doped ZnO was determined by measuring the UV–vis absorption spectra (taken in diffuse reflectance mode), using Cary 500 UV–vis–NIR spectrophotometer, in the range of 200–800 nm. The surface morphology of all the samples was studied by Scanning Electron Microscope (SEM-FEG, JSM 7001F, JEOL) equipped with Energy-Dispersive Spectroscopy analysis (EDS, INCA PentaFET-x3) to determine the composition of the samples.

### Photo reactor and experimental procedure

The photo catalytic activity of ZnO and doped ZnO were tested by using Rhodamine blue (Rh-B) dye degradation. The experiment was performed by dispersing 25 mg of catalyst in 50 ml of dye solution (0.01 mM). 150 watt xenon lamp having spectral match to the solar spectrum was used as light source. The distance between the beaker and the light source was kept 75 cm. The photocatalytic activity was determined by measuring the normalized intensity of the absorption band of Rh-B at 500

**Tele:**

**E-mail addresses: kakulimaiti@yahoo.in**

nm using UV-Vis nano-photometer and plotting it as function of time of irradiation.

## Result and discussion

### Structural analysis of the catalyst

The XRD patterns of V-doped ZnO were shown in Fig.1. The peaks attributed to the hexagonal wurtzite structure of ZnO are observed in all un doped and V-doped ZnO samples. At lower concentration of vanadium (5%V), no characteristic peaks of vanadium or vanadium oxide was found but as the concentration increases (for 10%V and 15 %V) the additional phase of $Zn_3(VO_4)$ (JCPDS Card 37–1485) was obtained. This shows that the V ions have been incorporated into ZnO lattices. The broad nature of the peak signifies the nanocrystalline nature of the ZnO which was confirmed by calculating the particle size (table 1) using Debye Scherrer formula.

**Table 1. Band gap and crystallite size of samples with different atomic percentages of vanadium doped zinc oxide.**

| Sample | Eg(ev) | D(nm) |
|---|---|---|
| ZnO | 3.21 | 33.84 |
| 5%V-ZnO | 3.20 | 87.80 |
| 10%V-ZnO | 3.19 | 42.99 |
| 15%V-ZnO | 3.17 | 53 |

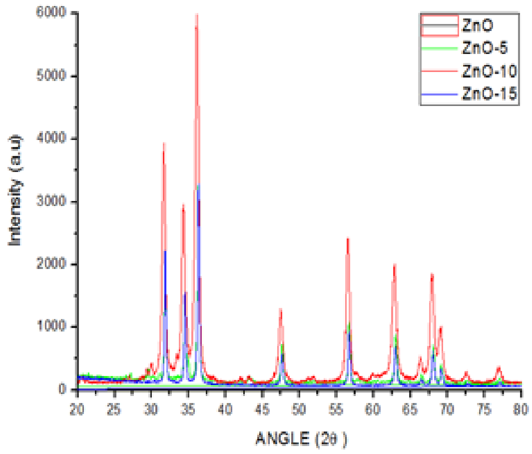


**Figure 1. XRD patterns of pure and V-doped ZnO samples.**

### Morphological analysis of ZnO

SEM images in Fig 2 shows the particle like morphology of all ZnO samples. The particle size of ZnO nanoparticle is in a good agreement with the results of crystallite size obtained by Debye–Scherrer formula. However, the nanoparticles are assembled in form of clusters with narrow particle size distribution. The atomic concentration of vanadium was confirmed by energy dispersive spectroscopy analysis present in Fig. 3.

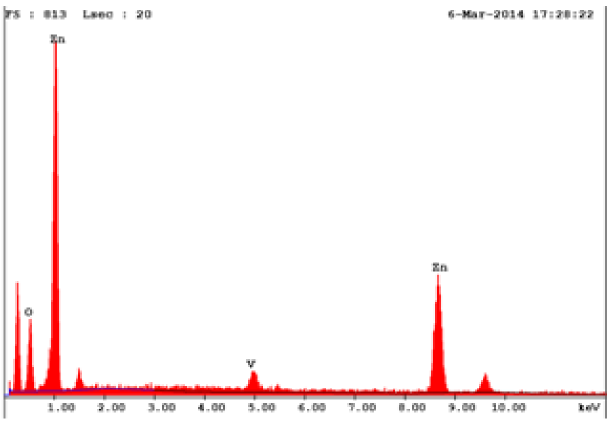


**Figure 3. EDS of sample V-doped ZnO**

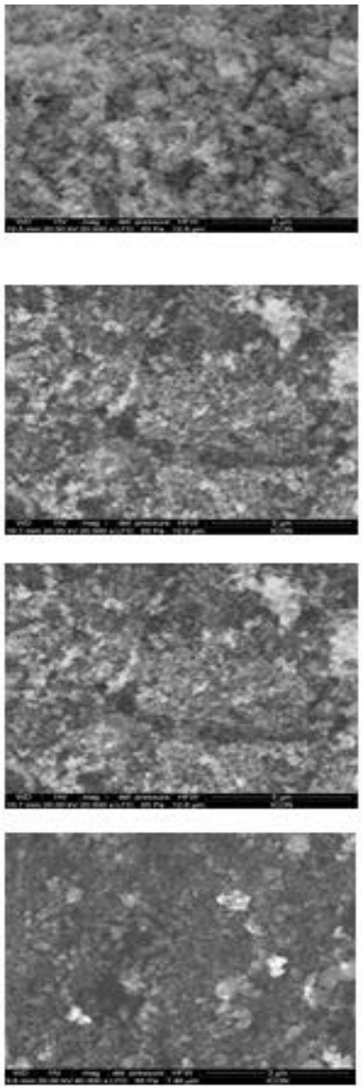

**Figure 2. SEM of ZnO, ZnO-5% V, ZnO-10% V, and ZnO-15%**

### Optical Study of ZnO

The Tauc plot obtained from the UV-Vis spectra of ZnO and doped ZnO are shown in figure 4. In comparison to un doped ZnO higher absorption of doped ZnO is established with a red shift of absorption edge towards the visible region was observed with increase in vanadium concentration. The band gap energies were calculated using the kubelka Munck function and summarised in table 1. V-doped ZnO showed lower band gap as compared to pure ZnO. The narrowing of the band gap is due to energy state created by vanadium in the ZnO which is located 0.7 eV below the conduction band of ZnO

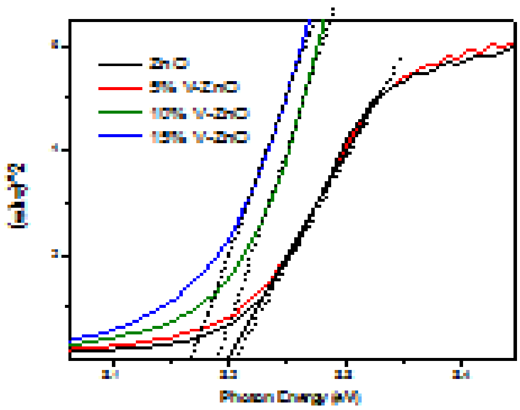


**Figure 4. Tauc plot of un doped ZnO and V-doped ZnO**

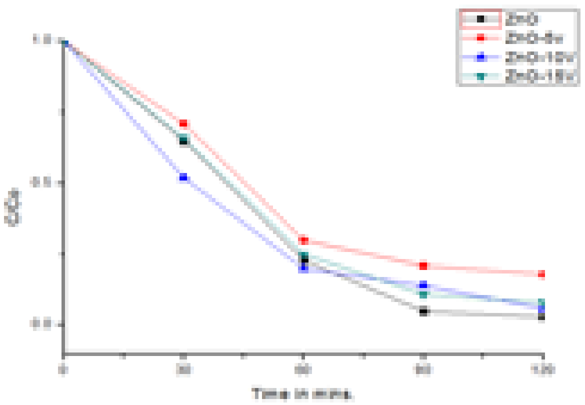


**Figure 5. Photo catalytic degradation of Rh-B using undoped ZnO and V-doped ZnO with different concentration of V under light irradiation**

**Photo catalytic degradation**

The photo catalytic activities of pure and V-doped ZnO catalysts were examined by the photo degradation of Rhodamine-B under light irradiation (Fig. 5). ZnO doped with 10 at. % of V shows better photo catalytic activity than un doped ZnO. While the concentration above and lower this value shows the decrease in the rate of degradation of dye. Ability to absorb higher amount of light for V-doped ZnO is the main reason for the enhance photocatalytic activity. However, at highest doping concentration of 15 at. % the vanadium atoms might cover active sites of ZnO which lead to decrease in activity as compared to 10%V-ZnO. This highest photocatalytic efficiency may also be attributed to surface area provided by ZnO due to its nanoparticle form which provides high surface to volume ratio to increase the contact area between the active sites and the reactants.

**Conclusion**

Zinc oxide and V-doped ZnO were prepared by Sol-gel method. A study of structural, optical and photo catalytic properties of ZnO doped with different concentrations of V was investigated. Among all the samples 10%V-ZnO exhibits the good photocatalytic performance. The enhancement of photoactivity is mainly due increased in visible light absorption and high surface area of catalyst.

**Acknowledgements:**

We are grateful to Department of Physics, Mumbai Univesity, Mumbai, Ramnarian Ruia college,Matunga, Mumbai for their laboratory assistance and also to DattaMeghe College of Engineering, Airoli, Navi Mumbai for the support.

**References**

[1] X.Yang, F.Y. Ma, K.X.LI,Y.N.Gua, journal of hazardous materials, vol. 175, pp.420-438, 2010.

[2]R.Jaiswal, N.Patel, D.C.Kothari, A.Miotello.Applied catalysis B;Environmental, vol. 120, pp. 47-54,2012.

[3] R. Salma, F.Ghribi, A Houas,C. Barthou, L.Ei Mir.Thin solid Films, vol. 510, pp. 5792-5795, 2011.

[4]Qing-bo Wang,Cui Zhou, juan Wu, Tao Lu,Optics communication, vol. 297, pp.79-84, 2013.

[5] U.G.Akpan, B.H.Hameed. Journal of Hazardous Materials vol. 170, pp. 520-525, 2009.

[6] D.G.Huang, S.J.Liao, W.B.Zhou, S.Q Quan, L. Liu, Z.J.He, j.B Wan, journal of physics chemistry of Solids vol. 70, pp. 853-859, 2009.

[7] Y.Nakano, T. Morikawa, T. Ohwaki, Y. Tagaq, Applied Physics Letters vol. 86, pp. 132104-132113, 2005.

[8] I.K. Konstantinou, T. A. Albanis, Applied Catalysais B. Environmental vol. 49, pp. 1-14, 2004.

[9] S. Liu, T. Xie, Z.XChan, J. Wu, Applied Surface Sciences vol. 255, pp. 8587-8592, 2009.

[10] X.Yang, F.Y. Ma, K.X.Li, Y.N.Guo, J.I.Hu, M.X.W.Huo, H.J.Guo, Journal of Hazardous materials vol. 175,pp.429-438, 2010.

[11] X.Ma, L.Miao, S.Bie, J.Jang. Solid State Communications vol. 150, pp. 689-692, 2010.

[12] K.Yanagisawa,J.Ovenstone, Journal of physical chemistry B, vol. 103, pp. 7781-7787, 1999.

[13] J.Zhang,Y.Wu, M.Xing, S.A.K.Laleghari, S.Sajjad, Energy and Environmental Science vol. 3, pp.715-726,2010.

[14] Q.Xio, J.Zhang, C.Xiao, X.Tan, Matter.Sci.Eng. B vol. 142, 121, 2007.

[15]J.Xu,Y.Chang,Y.Zhang,S.Ma,Y.Qu,C.Xu,Appl.Surf.Sci.vol. 225, 1996,2008.

[16] K.A.Jeon, J.H.Kin, W.Y.Shim, W.Y.Lee,M.H.Jung, S.Y.Lee, Journal of crystal Growth vol. 287, 66, 2006.

[17] L.Li, W.Wang, H.Liu, X.Liu, Q.Song, S.Ren, Journal of physical chemistry C vol. 113, 8460, 2009.

[18] T.Chihi, J.C.Parlevas, M.Guemmaz Physica status Solidi B Basic Solid State physics vol. 248, 2787, 2011.

[19] R.Elilarassi, G.Chandrasekaran, Journal of Material Science vol. 22, 75, 2011.