

## Visible light photocatalytic degradation of Textile Azo dyes using Sn doped ZnO nanorods

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The surface and ground water bodies are grossly polluted as a result of uncontrolled discharges from industries. The effluents from textiles, tanning, pesticides, petrochemical, pharmaceutical, distilleries etc. are highly coloured and contains vast amount of toxic and non-biodegradable pollutants, which are difficult to treat. Particularly, the wastewaters from textile industries are highly coloured and with organics which are difficult to mineralize. Hence, attempt has been made to treat them by using cost effective ZnO nanorods. Here, Sn doped ZnO nanorods were prepared by hydrothermal method. The XRD results revealed that the sample showed a hexagonal wurtzite structure. The result of EDAX revealed that Sn was doped in to ZnO lattices. FESEM image shows that the sample possesses hexagonal rod morphology with an average of 1µm in length and 50 to 100nm in diameter. Optical transmittance of the sample was recorded in the wavelength range of 300–800 nm, and the band gap of the samples was determined. The photocatalytic activity of Sn doped ZnO nanorods were tested with different azo dyes using visible light (365nm) in an annular photoreactor. The results reveal that the decolourisation was complete in 45 minutes whereas the organics were removed at 180 min. Complete mineralisation of organics could be achieved by further optimizing the reactor parameters depending on the industrial requirement.

**Key words:** Sn doped ZnO, Nanorod, Photocatalytic activity, AZO dyes.

### 1. Introduction

Wastewater sources are generally categorized as municipal, agricultural, or industrial. One of the most challenging issues that Indian industries face is the treatment of these wastewaters with wide range of both synthetic organic chemicals and naturally occurring substances which are recalcitrant and toxic. Different treatment technologies have been practiced to treat these polluted waters. Semiconductor photocatalysis technology is a rapidly developing field of research with a wide range of applications in water disinfection, hazardous waste remediation and water purification. Zinc Oxide (ZnO) is one of the most promising semiconductors in this field due to its unique properties, such as high chemical stability, high catalytic activity, low cost and non-toxicity. However, the rapid recombination rate of the photo induced charge carriers in ZnO results in reduction of its photocatalytic activity which is unfavourable for commercial application [1]. One of the important strategies to reduce the recombination of charge carriers in ZnO is doping where doping generates more defects and vacancies which traps the charge carriers and enhances photocatalytic activity of ZnO [2 - 4]. Recent studies demonstrated that transition metal doping into ZnO lattices can tune various properties of

ZnO and enhance its visible light photocatalytic activity [5 - 8]. Among them, Sn is considered as an important dopant material for ZnO, because of the different structure of the electronic shell and the similar ionic radii of Sn<sup>4+</sup> (0.071nm) and Zn<sup>2+</sup> (0.074nm) [9]. The incorporation of Sn in ZnO lattice generates ROS, when it is illuminated by UV or visible light that in turn enhances the photocatalytic activity of the sample. Furthermore, one dimensional (1D) nanostructures such as nanorods, nanofibers and nanowires can also improve the photocatalytic activities of ZnO since electrons are confined in one direction. The present work reports the synthesis of Sn doped ZnO nanorods by a simple hydrothermal method, as well as the characterization of the resultant sample by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and UV–vis spectroscopy. The Visible photocatalytic activity of different azo dyes such as Reactive Red 122, Reactive Yellow 145 and Amaranth has been studied for Sn doped ZnO photocatalyst.

### 2. Experimental detail

Sn doped ZnO powder was prepared by hydrothermal method. All the reagents were of analytical grade purity. Aqueous solutions of 0.1 M ZnCl<sub>2</sub> and 0.01 M SnCl<sub>4</sub> were mixed under continuous stirring for 45 min at room temperature. After stirring, aqueous solution of 0.1 M hexamethylenetetramine (HMTA) was added in the previous solution and the resultant solution was again stirred for 30 min. The pH of the solution was maintained to 8.0 by adding few drops of ammonium hydroxide. The final solution was again vigorously stirred for 30 min and consequently

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transferred to Teflon lined autoclave which was then sealed and heated up to 120°C for 5 h. and the same procedure was repeated without tin chloride for pure ZnO. After terminating the reaction, the autoclave was allowed to cool at room-temperature and the obtained products were washed several times with deionised water and ethanol. Finally the prepared products were dried at 60°C. The catalyst thus prepared is used for the degradation of different azo dyes in a annular photoreactor.

### 3. Characterization

The pure and Sn doped ZnO samples were investigated by XRD using Rigaku Miniflex-IIC model diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) in the scan range ( $2\theta$ ) from 20° to 80° at room temperature. The surface morphology and elemental confirmation of the Sn doped ZnO sample was studied using FEI Quanta FEG 200 model FESEM operated at 30 kV equipped with an energy-dispersive X-ray (EDAX) detector. The optical transmission spectra were recorded using LABINDIA T90+ UV-Vis spectrophotometer in the wavelength range of 300-800 nm.

#### 3.1 Photocatalytic activity

The photocatalytic activities of the synthesized Sn-doped ZnO nanorods were evaluated by the degradation of different dyes in aqueous solution. The experiments were carried out in a annular reactor with 365 nm UV lamp. 0.2 g/L Sn doped ZnO photocatalyst was added to 500 mL of the dye solution (20 mg/L). Prior to illumination, these suspensions were thoroughly stirred in the dark to ensure the establishment of absorption equilibrium. The suspension is then exposed to visible light in the annular photoreactor. The reaction parameters such as pH, catalyst dosage and dye concentration were optimized and final degradation experiment was performed in the annular reactor in the optimized reaction conditions. Optimization studies preferred acidic pH of 2 for the photocatalytic reaction and dye concentration was chosen as 20mg/L. Samples were withdrawn at regular intervals and analysed for the percentage of decolourisation and degradation. Decolourisation was monitored by decrease in absorbance at 418nm, 522nm and 530 nm respectively for Reactive Yellow 145, Amaranth and Reactive Red 120 in the UV-visible spectrophotometer. Chemical Oxygen Demand measured by open reflux potassium dichromate titrimetric method [10] showed the decrease in degradation.

### 4. Result and discussion

#### 4.1 Structural studies

The powder XRD patterns of the pure and Sn doped ZnO samples are depicted in Fig. 1. The XRD results reveal that the samples are in single crystalline with hexagonal wurtzite structure. Within the XRD detection limit, no extra diffraction peak from Sn-related second phases was observed. This indicates that  $\text{Sn}^{4+}$  substituted for  $\text{Zn}^{2+}$  of ZnO host without changing the wurtzite structure. The

intensity of the (1 0 1) plane in the pure ZnO is much stronger than that of Sn doped ZnO and a slight shift of peaks positions related to the change of lattice spacing was observed due to the substitution of relatively less ionic radii (0.071 nm)  $\text{Sn}^{4+}$  at the  $\text{Zn}^{2+}$  (0.074 nm) sites. The weak intensity peaks and the slight shift of peaks positions may imply that  $\text{Sn}^{4+}$  incorporates into the ZnO lattices and substitutes the  $\text{Zn}^{2+}$  site.

#### 4.2 Morphological studies:

The surface morphology and compositional analysis of samples was determined using field emission scanning electron microscopy (FESEM) equipped with EDAX analysis. FESEM image reveals that the sample consists of

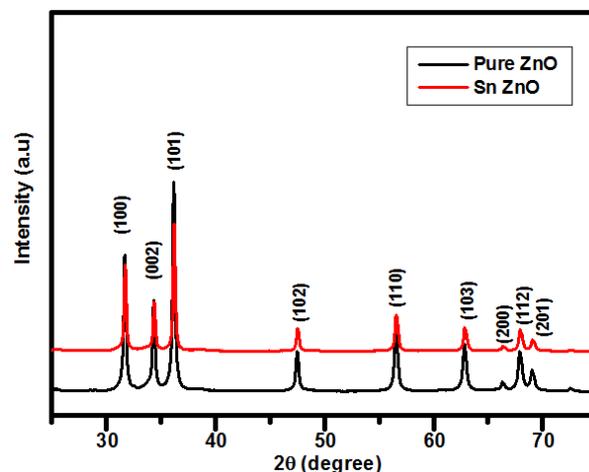


Fig.1 Powder XRD patterns of Pure and Sn doped ZnO samples

nanorods with length and diameter in the order of 1  $\mu\text{m}$  and 50-90 nm. Figures 2(a) indicate the uniform distribution of hexagonal nanorods without any cracks and exhibit good crystalline quality. The EDAX analysis was performed to confirm the presence of Sn in ZnO thin films. Figures 2(b) show the EDAX spectra of Sn doped ZnO sample. The results reveal that the sample consists of Zn, Sn and O which confirms the substitution of tin in ZnO.

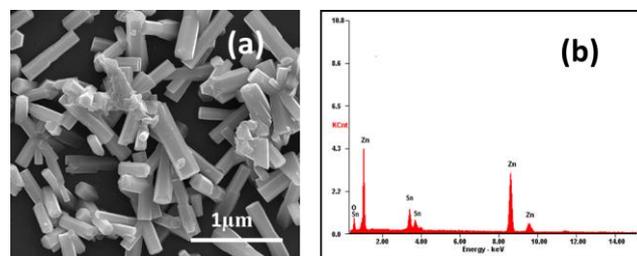


Fig. 2. (a) FESEM image of Sn doped ZnO and (b) EDAX spectrum of Sn doped ZnO sample

#### 4.3 Optical Studies

The optical transmission spectra of pure and Sn doped ZnO samples are shown in Fig. 3(a). The samples are

transparent in the visible optical region, and the transmittance maxima decrease with the increase in Sn doping. The optical band gap ( $E_g$ ) was estimated from the Tauc's relation [11],

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$

Where A is an energy dependent constant,  $E_g$  is the optical band gap of the sample. The optical band gap energy was calculated by extrapolation of the linear part of plot between  $(\alpha h\nu)^2$  and  $h\nu$  as shown in Fig.3(b) and the estimated band gap values are 3.22eV and 3.05eV for pure and Sn ZnO respectively. There are two primary reasons behind the band gap energy change, one is quantum size effect and another is electronic structure modification. In the present study the band gap reduction is not due to the quantum confinement since the size of the nanorods are around 50-90nm. The decrease of band gap value of ZnO with Sn doping has been attributed to the band shrinkage effect due to increase in carrier concentration as reported earlier [12].

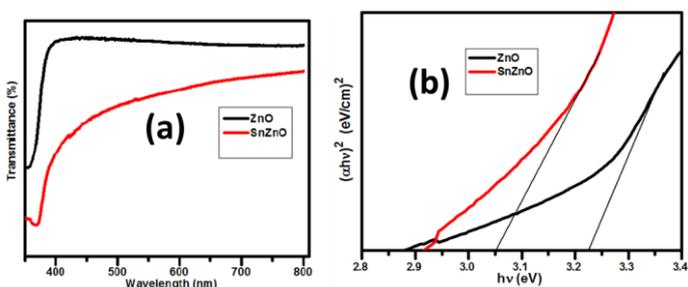


Fig.3. (a)Optical transmission spectra of Pure and Sn doped ZnO and (b) plot of  $(\alpha h\nu)^2$  versus Photon energy

**4.4 Photocatalytic activity**

The photocatalytic activity of pure and Sn doped ZnO sample was investigated using various azo dyes degradation under visible light irradiation. The degradation efficiency was calculated using the relation,

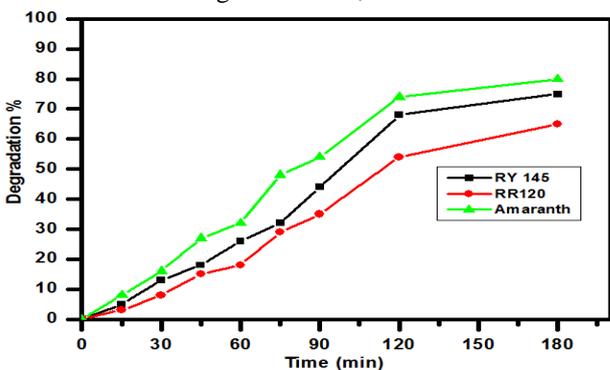


Fig.4. Degradation of different azo dyes by Sn doped ZnO nanorods

$$\text{Degradation (\%)} = (C_0 - C_t)/C_0 \times 100$$

where  $C_0$  is the initial COD,  $C_t$  is the COD after 't' min. In 180 minutes, 75%, 65%, and 80% degradation was achieved with RY145, RR 120 and Amaranth respectively as shown in figure 4.

decolourisation was studied using the equation,  

$$\text{Decolourisation} = (A_0 - A_t)/A_0 \times 100$$

$A_0$  is the initial absorbance and  $A_t$  is the absorbance after 't' min.

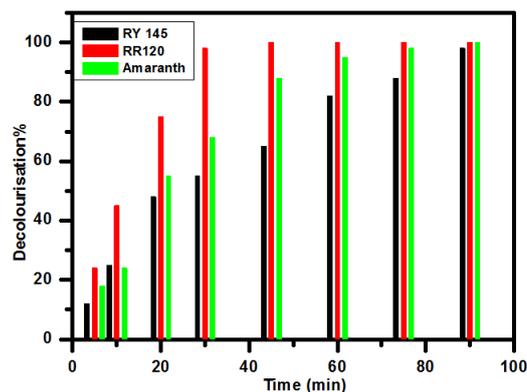


Fig.5. Decolourisation of azo dyes by Sn doped ZnO nanorods

But decolourisation studies do not imply the organic content removal in the wastewater and hence complete mineralization of the dye is required for the discharge of the effluent by the industries. The reaction time taken for complete degradation could be minimized by further optimisation of the influencing reactor parameters.

**5. Conclusion**

Nanorod structured pure and tin (Sn) doped ZnO powder samples prepared by hydrothermal method. The XRD results indicate that the Sn doping does not change the wurtzite structure of ZnO in the sample. The presence of tin in ZnO was showed by EDAX. FESEM images showed that the sample consist of hexagonal nanorod morphology without any crack. The band gap determined from optical transmittance spectra shows a reduction in band gap for Sn doped ZnO. The influence of Sn in ZnO exhibited a better photocatalytic activity under visible light irradiation than pure ZnO. The enhancement in photocatalytic efficiency of Sn doped ZnO sample is due to 1D nanorod morphology, band gap reduction, increase in defects or oxygen vacancies and ROS generation. The efficiency of this catalyst is evaluated with the degradation of different azo dyes which proved that this could be a cost effective simple method for the industries to adopt for the treatment of their complex structured recalcitrant pollutants.

**References**

- [1] I. Udo, M.K. Ram, E.K. Stefanakos, A.F. Hepp, D. YogiGoswami, *Mater. Sci. Semicond. Process* 16 (2013) 2070-2083.
- [2] W. Xie, Y. Li, W. Sun, J. Huang, H. Xie, X. Zhao, *J. Photochem. Photobiol.A* 216 (2010) 149-155.
- [3] P. Jongnavakit, P. Amornpitoksuk, S. Suwanboon, N. Ndiege, , *Appl.Surf. Sci.* 258 (2012) 8192–8198.
- [4] J. Zhao, L. Wang, X.Q. Yan, Y. Yang, Y. Lei, J. Zhou, Y.H. Huang, Y.S. Gu, Y. Zhang, *Mater. Res. Bull.* 46 (2011) 1207–1210.
- [5] Manjula G. Nair, M. Nirmala, K. Rekha, A. Anukaliani, *Mater. Lett.* 65 (2011) 1797–1800.
- [6] P. Madahi, N. Shahtahmasebi, A. Kompany, M. Mashreghi, M. M. Bagheri-Mohagheghi, A. Hosseini, *Phys. Scr.*, 84 (2011) 035801-5.
- [7] S. Suwanboon, P. Amornpitoksuk, P. Bangrak, N.Muensit, *Mater.Sci. Semicond.Process* 16 (2013) 504–512.
- [8] R. Ullah, J. Dutta, *Journal of Hazardous Materials* 156 (2008) 194–200.
- [9] J.H. Sun, S.Y. Dong, J.L. Feng, X.J. Yin, X.C. Zhao, *J. Mol. Catal. A: Chem.* 335 (2011) 145–150.
- [10] APHA (1998). *Standard methods for the examination of water and wastewater*, 20<sup>th</sup> edn., American Public Health Association, Washington DC, USA.
- [11] J. Tauc, R. Grigorovici, A.Vancu, *Phys. Stat. Sol.* 15 (1966) 627-637.
- [12] C. Zegadi, K.Abdelkebir, D.Chaumont, M. Adnane, S.Hamzaoui, *Adv. Mater. Phys. Chem.*4 (2014)93–104