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Research Article

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Synthesis, Size Characterisation and Photo Catalytic Studies on Titania Doped and Undoped Zinc Oxide Nanoparticles for Eosin Yellow Degradation

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ABSTRACT

Zinc oxide nanoparticles and Titania doped Zinc oxide nanoparticles are synthesized and size characterized using UV-DRS, PXRD, FESEM and EDAX methods. One pot batch type reactor fitted with top view vertical irradiation source was used for dye degradation studies. The irradiation sources used are UV, UV Blue and Solar. The catalyst loading was maintained as 1mg/20mL of 1mM Eosin yellow dye aqueous solution. The same was studied by incorporating H₂O₂. The progress of dye degradation is studied by measuring absorbance versus time intervals at constant wavelength maxima of the dye. Pseudo first order conditions are maintained. Based on the absorbance versus time measurements, the rate coefficient values are determined. The photo catalytic activity of the catalysts in the degrading process of the dye is found more efficient in solar irradiations. The salient features and results are put forth and discussed.

Keywords: ZnO nanoparticles, Titania doped ZnO nanoparticles, dye degradation

ARTICLE INFO

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1. Introduction

Heterogenous solution phase photocatalysis using nano crystalline semiconductors has emerged as a potential and Asian Journal of Chemical and Pharmaceutical Research

developing advanced oxidation processes used in the remediation of intensely coloured industrial dyes polluted

water effluents [1-3]. It is important that in chemical advanced treatment processes involving nanocrystalline photoactive catalysts for the treatment of waters containing such polluting dyes, green methods should be implemented. In the present work, nanocrystalline Zinc oxide (ZnO) particles are prepared using a combination method of precipitation, sol-gel and hydrothermal techniques. A literature survey exposes that nano ZnO (nanoflowers) catalyses the degradation of crystal violet under UV irradiation effectively [4-7]. Here degradation of Eosin Yellow (EY) dye is studied. EY has been used preferably as biomarker in many biological applications and thus causes water source pollution too. Another counterpart, titania (TiO₂) in the nanocrystalline form has been exploited tremendously for the photocatalytic degradation of dyes, drugs, hazardous chemicals. Here, nanocrystalline titania has been used as the dopant in to the nano crystalline ZnO using the sol gel method [8-15]. The catalytic materials are size characterized using UV-DRS, PXRD and FESEM-EDAX methods. Tuning up of band gap, size and catalytic activity are observed. Vertical one pot batch reactor with vertical type irradiation of aqueous dye solution under aerobic conditions with TiO₂ doped and pure nano ZnO photocatalysts are investigated. Irradiations with UV and solar sources are studied. Adopting pseudo first order conditions, the kinetics of photo degradation of Eosin Yellow under various conditions of irradiations, catalyst with dopant and catalyst compositions are studied. The implications of the results are discussed.

2. Materials and Methods

Eosin Yellow was purchased from Qualigens and used without further purification. Zinc acetate and Ethylene Glycol were purchased from Merck. Titanium isopropanoxide was purchased from SRL and Ethanol from Haymann. Double distilled water was used all through the experiments. UV-Vis spectrometer, double beam, Techcom instrument with 1 cm path length quartz cuvettes was used. Bruker D8 advance diffractometer was used for XRD data. FESEM of the nanoparticles were measured using SU6600, HITACHI model operating at an accelerating voltage of 100 kV.

Stoichiometric ratios of Titanium isopropanoxide and Zinc acetate were dissolved in ethanol and water respectively. The two solutions were mixed under constant stirring and ethylene glycol was added in drops. The mixture was stirred for 1hour at about 80°C and centrifuged. The centrifugate was calcined initially at 45°C - 80°C for 1hour and finally at 600°C - 650°C for 4 hours. The powder samples are collected and subjected to size characterizations. 1mM Eosin Yellow dye solution was prepared using water. Catalyst loading was 1mg/20ml for all photocatalytic studies. The kinetics of the degradation of dye was studied by measuring the absorbance at wavelength (520nm) maximum at various intervals of time. Pseudo-first order conditions were maintained. Absorbance variation plots were made. The kinetic plots for the rate constant determination were drawn from $\log (OD_0/OD_t)$ versus time data. The pseudo-first order rate coefficient values were

determined by multiplying 2.303 with the slopes of the linear kinetic plots.

3. Results and discussion

The PXRD patterns of the nanoparticles are given in Fig 2. Applying Scherrer formula for FWHM, the mean nanocrystallite sizes are found and listed in table 1. There is a slight increase in the nanocrystallite sizes in the presence of dopant. Regarding the band gap energy calculated from UV-DRS spectrum shown in Fig.1, there is a slight decrease in the doped ZnO compared to the undoped one. The FESEM images in Fig 3 shows that presence of dopant creates modified surface with more surface area than that of the undoped one.

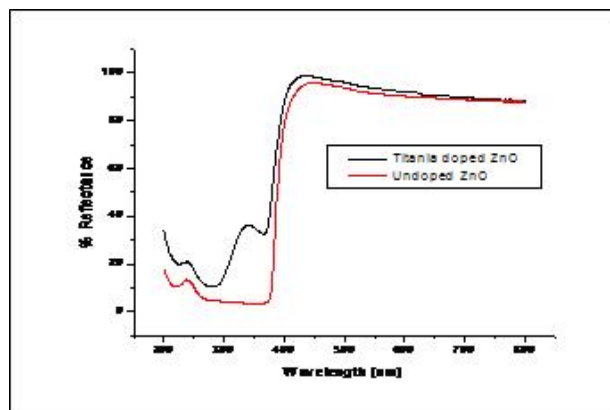


Figure 1: UV DRS of Undoped Zinc oxide and Titania doped Zinc oxide nanoparticles

It was found that the dye degradation when carried out in the absence of H₂O₂ under similar conditions, the extent of the degradation was lesser than 5 % even after 8 hours of irradiations. Therefore, the degradation results reported in this work pertains to H₂O₂ inclusion.

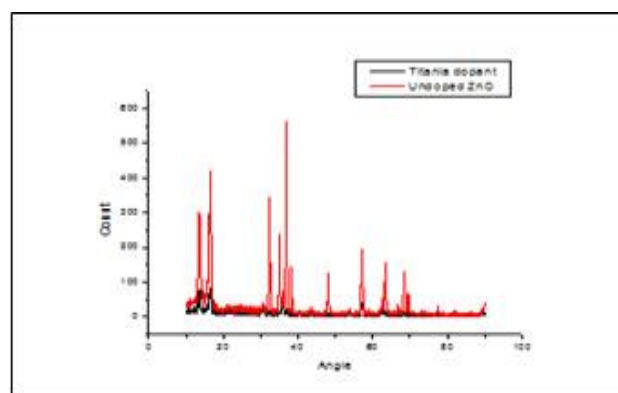


Figure 2: PXRD images of Undoped Zinc oxide nanoparticles and Titania doped Zinc oxide nanoparticles

In table 1, the overall pseudo first order rate constant values for dye degradation determined for undoped ZnO and 10% by weight titania doped ZnO are given. Adopting similar procedure for dye irradiation, various irradiation procedures are adopted with UV and solar irradiations. The rate coefficient values observed for different types of irradiation are listed in table 1. It is found that doped ZnO

nanoparticles exhibited higher photocatalytic behaviour in solar irradiation compared to UV irradiations. The trend in the rate coefficient values observed are solar > UV. Regarding the dopant effect on photocatalytic behaviour, doped ZnO nanoparticles produced higher rate coefficient

values for solar irradiation. This effect may be attributed to the band gap energy values which are lower than the undoped one. The least value of rate coefficient is observed for UV irradiation among all other rate constant values.

Table 1: Band gap energy, nanosize of the catalysts, and the pseudo first order rate coefficient values of ZnO and Titania doped nano ZnO catalyzed Eosin Y degradation with H₂O₂ under Solar and UV irradiations.

Sample description	Band Gap Energy (eV)	Crystal Size (nm)	Rate Coefficient (s ⁻¹)	
			Solar	UV
Pure nano ZnO	3.2	26.17	5.34 x 10 ⁻⁴	2.03 x 10 ⁻⁵
Titania doped ZnO	3.0	26.19	8.91 x 10 ⁻⁴	2.30 x 10 ⁻⁵

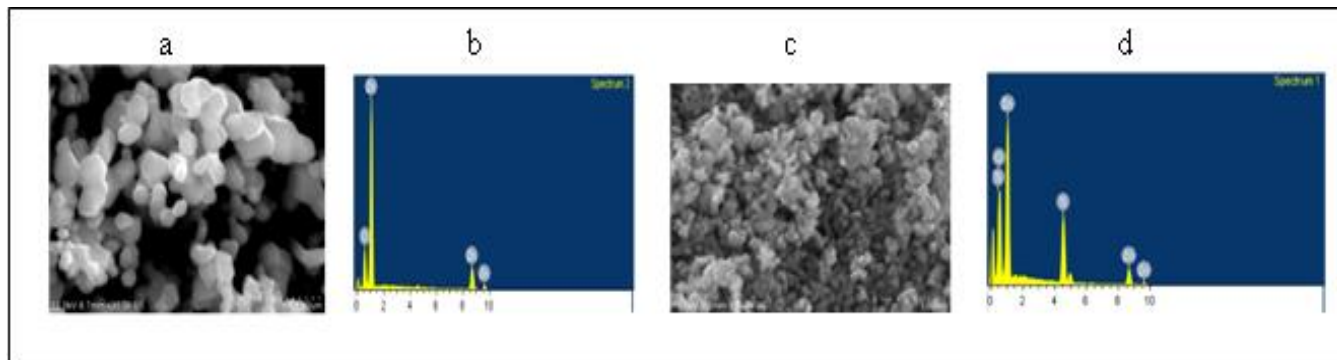


Figure 3: a) and b) FESEM and Edax images of Undoped Zinc oxide nanoparticles c) and d) FESEM and Edax images of Titania doped Zinc oxide nanoparticles

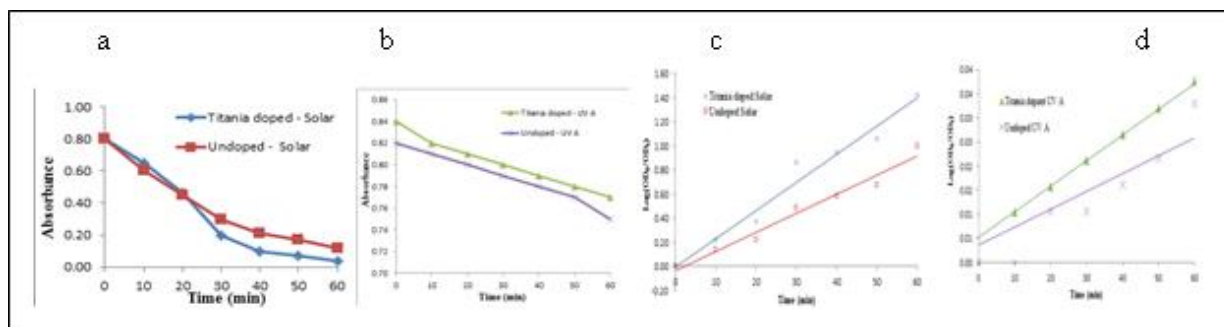


Figure 4: a) and b) Plots of Absorbance Vs time of Undoped ZnO and Titania doped ZnO nanoparticles in Solar and UV irradiations c) and d) Kinetic plots of Undoped ZnO and Titania doped ZnO nanoparticles in Solar and UV irradiations respectively

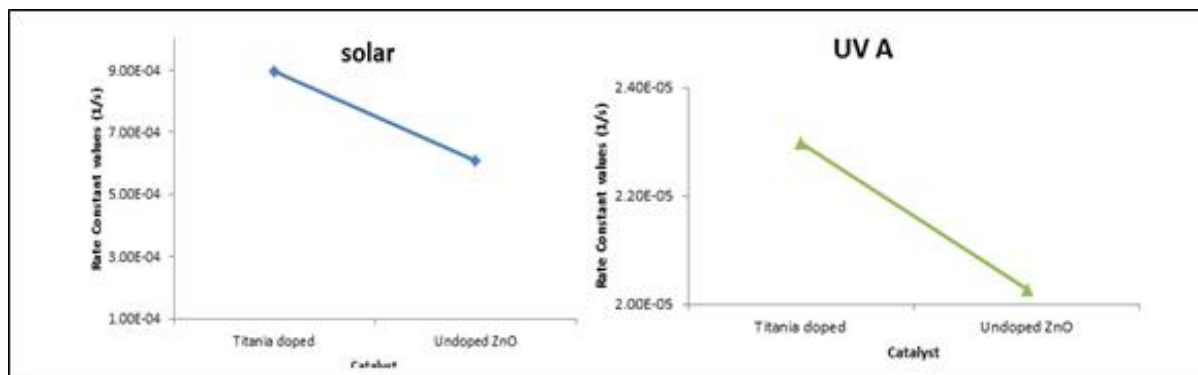


Figure 5: Effect of Dopant presence in Solar and UV irradiations for dye degradation

4. Conclusion

The pure ZnO and Titania doped ZnO nanoparticles are synthesized, size characterized and tested for the photocatalytic activity. The titania dopant lowered the band gap energy such that under solar irradiations

photocatalytic activity. The titania dopant lowered the band gap energy such that under solar irradiations

higher rate coefficient values are obtained for dye degradation. These results inform that solar irradiations can be chosen for Eosin Yellow dye degradation in presence of titania doped ZnO crystals.

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