

Synthesis, Size Characterization and Photocatalytic Studies on Nanoparticles of ZnO and Titania Doped ZnO for the Oxidative Degradation of Crystal Violet Dye in Aqueous Medium

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Abstract—Nanoparticles of metal oxide show unique and enhanced properties in optical, magnetic, catalytic and electrical fields. The potentiality of nanoparticles is due to the high surface area to volume per particle. In the present work nanoparticles of pure ZnO and in doped conditions are synthesized adopting sol-gel technique. ZnO nanoparticles exhibit enhanced photocatalytic sensitivity. Titania (TiO₂) was used as the dopant and from 10% to 40% are incorporated in ZnO nanoparticles and sol-gel synthetic route was adopted. Dry samples are activated thermally in each measurement. Size characterizations are carried out using UV-DRS, PXRD, FESEM, EDAX and HRTEM measurements. Using JCPDS files card, pure Zincite structure was found out in ZnO nanoparticles. Nanoparticle photocatalysts in advance oxidation processes for remediation of polluted aqueous sources was adopted. Pure ZnO nanoparticles and Titania doped samples are loaded as catalysts separately into intensely colored 1mM solution of crystal violet under UV, UV actinide blue, IR and solar irradiations. Absorbance variations with time are noted at constant wave length (570nm), and the pseudo first order rate constant values are determined. It was found that the trend in the nature of the irradiation for the dye degradation is, solar >IR>UV>UV actinide blue, under constant catalyst loading and dye concentration. In solar irradiation, the catalytic activity of doped ZnO nanoparticles was found higher than the undoped ZnO nanoparticles. This is because, Titania dopant penetrates into the zincite lattice and also increases the band gap energy of pure ZnO nanoparticles. Therefore, instead of photocatalytic activity, sunscreen potentialities exist in Titania doped ZnO nanoparticles. The salient features of the results are discussed.

Keywords- ZnO nanoparticles; Titania doped ZnO; Dye Degradation

I. INTRODUCTION

Heterogenous photocatalysis using nano crystalline semiconductors has emerged as a potential and developing advanced oxidation processes used in the remediation of intensely coloured industrial dyes polluted water effluents [1-3]. Especially triphenyl methylene dyes are proven to be hazardous and toxic to aquatic and human life forms. Crystal violet belongs to such class of dyes which has been widely used in various domestic, industrial, cosmetic, paper, ink, paint and textile products. 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 (CV) under UV irradiation effectively [4-7].

Another counterpart, titania (TiO₂) in the nano crystalline form has been exploited tremendously for the photocatalytic degradation of dyes, drugs, hazardous chemicals etc., Here, nanocrystalline titania has been used as the dopant in various weight percentages in to the nano crystalline ZnO using the sol gel method [8-15]. Likewise, four different weights constituted, (such as 10%, 20%, 30% and 40% titania) doped ZnO nanocatalyst are prepared for the purpose of photocatalytic utility. The catalytic materials are size characterized using UV-DRS, PXRD, FESEM-EDAX and HRTEM methods. Tuning up of band gap, size and catalytic activity are observed. Vertical one pot batch reactor type irradiation of aqueous dye solution under aerobic conditions with TiO₂ doped and pure nano ZnO photocatalyst has been investigated. Irradiations with UV, UV Actinide blue, IR and solar sources are studied. Adopting pseudo first order conditions, the kinetics of photo degradation of CV under various conditions of irradiations, catalyst with dopants and catalyst compositions are studied. The implications of the results are discussed.

II. EXPERIMENTAL

A. Reagents Used

Crystal violet was purchased from Aldrich 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 and HR-TEM of the nanoparticles were measured using SU6600, HITACHI model operating at an accelerating voltage of 100 kV and FEI-TECNAI G2 model-T-30-S-twin operating at an accelerating voltage of 300 kV instrument respectively.

B. Synthesis of Nanoparticles

Various 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.

C. Photocatalytic Studies

1mM Crystal violet 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 (570nm) maximum at various intervals of time. The same experiment was repeated without the catalyst. 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.

III. RESULTS AND DISCUSSIONS

A. Band Gap Energy And Nanosizes Of Undoped And Doped ZnO

In Fig.1(ii), the UV DRS of undoped and titania doped various zinc oxide nano sized powders are given. The band gap energy values of the materials are found out. The values are listed in table1.

TABLE 1 BAND GAP ENERGY, CRYSTAL SIZE AND RATE COEFFICIENT VALUES OF ZnO AND DOPED ZnO NANO CATALYSTS

Sample description	Band Gap Energy (eV)	Crystal Size (nm)	Rate Coefficient (moles s ⁻¹)			
			Solar	IR	UV	UV-Actinide Blue
Pure nano ZnO	3.15	26.17	7.05×10^{-5}	6.74×10^{-5}	2.54×10^{-5}	6.26×10^{-5}
10% titania doped	3.76	26.19	1.17×10^{-4}	6.57×10^{-5}	3.95×10^{-5}	3.31×10^{-5}
20% titania doped	2.2	26.17	8.25×10^{-5}	8.39×10^{-5}	2.55×10^{-5}	4.93×10^{-5}
30% titania doped	2.97	26.27	1.2×10^{-4}	7.32×10^{-5}	3.04×10^{-5}	3.33×10^{-5}
40% titania doped	6.53	26.47	8.58×10^{-5}	8.37×10^{-5}	6.01×10^{-6}	1.33×10^{-5}

The PXRD patterns of pure nano ZnO and Ti doped nano ZnO powders are given in Fig. 1(v). Applying Scherrer formula for FWHM, the mean nano crystallite sizes are found out and listed in table 1. It may be seen that the nanocrystallite sizes increased in the doped condition compared to the pure ZnO nano sized. However, all the values lie within 26 ± 1 nm range. These values are the diameter of the spherical cross sectional of the nanoparticles. Regarding the band gap energy for pure ZnO nanocrystal 3.15eV was observed. When doped with various weight % titania, the band gap energy shows an initial decrease from 3.76 to 2.2 from 10% to 20% dopant and with further increase in dopant amount, the bad gap energy increases to 6.53eV. Also, when 10% titania was doped, the band gap energy of pure nano ZnO suddenly increased from 3.15eV to 3.76eV. Such significant variations in the band gap energy values are made possible by the various weight percent of dopant titania. Hence, drastic changes in the photocatalytic behavior can be envisaged.

As the degradation of the dye proceeds, the absorbance values decrease with time and the plots of absorbance dependence with time are shown in Fig.2 (i-iv). These measurements are used to generate the kinetic plots of $\log [OD_0/OD_t]$ versus time for determination of rate coefficient values. In Fig.2 (v-viii), the best fit kinetic plots are observed for pseudo first order experiment conditions. The slopes of the plots are multiplied with the constant 2.303 and the rate constant values are determined.

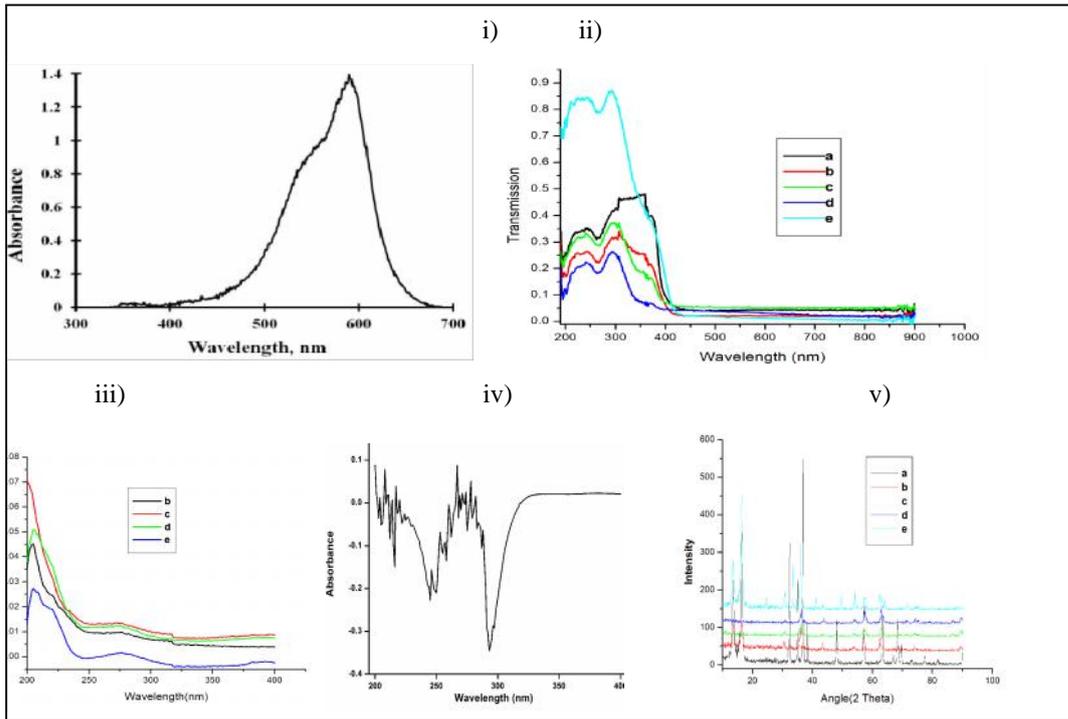


Figure 1. i. UV-VIS Spectrum of Crystal violet dye in aqueous solution. ii. UV-DRS of ZnO and titania doped ZnO. iii. UV-VIS Spectra of titania doped ZnO. iv. UV-VIS Spectra ZnO. v. PXRD pattern of undoped and titania doped ZnO, 'a' is undoped pure nano ZnO, 'b - e' are 10%, 20%, 30% and 40% % titania doped nano ZnO respectively

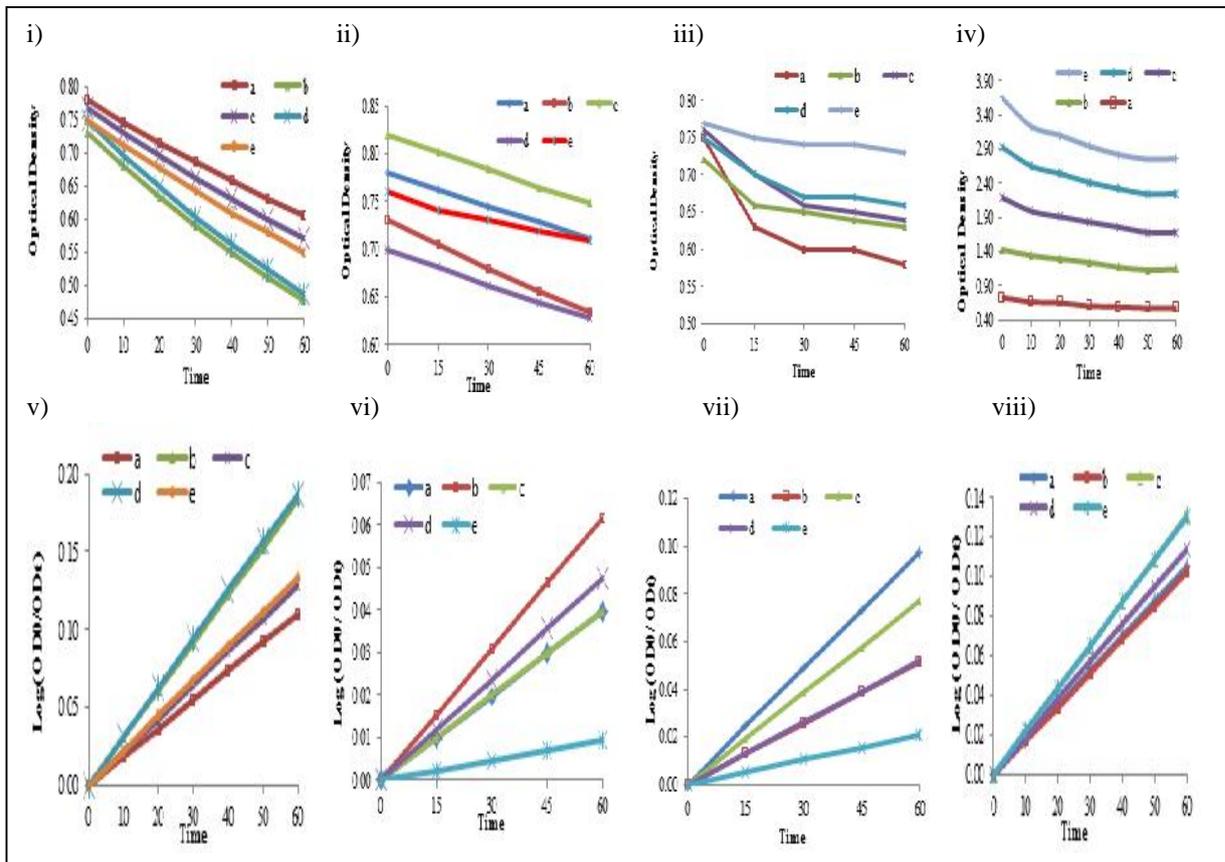


Figure 2. i – iv Optical density versus time plots of the catalysts in solar, UV, UV Actinide blue and IR irradiations respectively. v –viii kinetic plots of $\log(OD_0 / OD_t)$ versus time for the catalyst in solar, UV, UV actinide blue and IR irradiations respectively. 'a' is degradation of CV dye in aqueous medium in presence of undoped pure nano ZnO, b – e are the same dye solution in presence of 10%, 20%, 30% and 40% titania doped nano ZnO respectively.

In table 1, the overall pseudo first order rate constant values for dye degradation determined for undoped ZnO and various weight % titania doped ZnO are given. Adopting similar procedure for dye irradiation, various irradiation procedures are adopted such as UV actinide blue, UV, IR and solar irradiation. Here also, various titania doped ZnO nano crystals are used for photocatalytic purpose. The rate coefficient values observed for different types of irradiation are listed in table 1. It is found that pure ZnO nano crystals exhibited higher photocatalytic behavior in solar irradiation compared to the other irradiations. The trend in the rate coefficient values observed are solar > IR > UV actinide blue > UV. Regarding the dopant effect on photocatalytic behavior, when IR irradiation is employed all the weight % doped ZnO nano crystals produced higher rate coefficient values. For solar irradiation significantly higher rate coefficient values are obtained for 20 % and 30 % weight doped ZnO samples because the band gap energy values are lower than for the other samples. The least value of rate coefficient is observed for UV irradiation among all other rate constant values. Due to the high weight % of titania, formation of Zinc titanate may be inducing such effect in 40% doped ZnO nanoparticles.

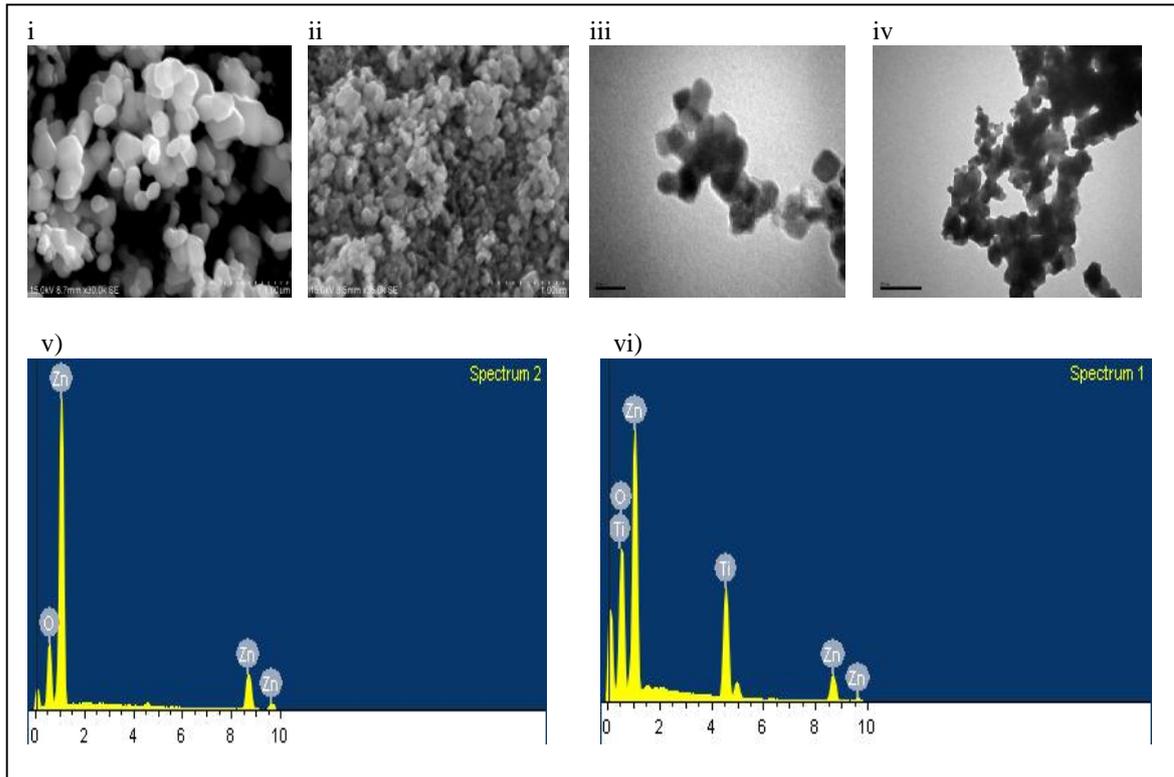


Figure 3. i-ii FESEM images of pure nano ZnO and titania doped nano ZnO, iii – iv TEM images of pure nano ZnO and titania doped nano ZnO, v – vi Edax images of pure nano and titania doped nano ZnO respectively.

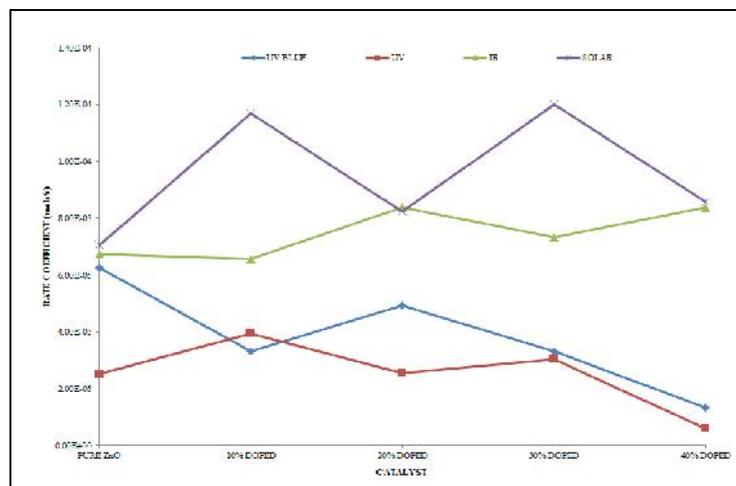


Figure 4. Plot of rate coefficient values versus catalysts under various irradiations

IV. CONCLUSIONS

The pure ZnO and titania doped ZnO nanoparticles are synthesized, size characterized and tested for the photocatalytic activity. The sizes of the nano crystals of the undoped and the doped seemed to be controlled by weight % titania doped in ZnO. 20% and 30% by weight titania dopants 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 CV dye degradation in presence of 20% and 30 % by weight titania doped ZnO crystals.

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