
Synthesis, Characterization and Photocatalytic Degradation of Crystal Violet Dye by ZnO Nanoparticles

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ABSTRACT

ZnO nanoparticles were synthesized by using soft chemical route via ultrasonication directly from an aqueous solution of zinc acetate dihydrate and ethanol. Synthesized ZnO nanoparticles have been characterized by XRD, SEM and FT-IR techniques. X-ray diffraction pattern shows a wurtzite structure (hexagonal phase) with high crystallinity. The photocatalytic activity was evaluated by using the Crystal Violet (CV) dye. The CV dye degradation was done over the surface of ZnO under dark and UV light illumination to elucidate the photo-catalytic activity. A series of experiments were carried out to study the influences of irradiation time, catalyst concentration, and initial concentration of Crystal violet solution on the photocatalytic degradation percentage (PDP) of Crystal violet on ZnO nanoparticles. A tentative mechanism for the photocatalytic degradation of CV is proposed.

Keywords: Semiconductors, Sol-gel, Crystal violet, Photo catalytic degradation.

INTRODUCTION

ZnO is an important semiconductor material which has a direct band gap of 3.3 eV at room temperature; it has also large exciton binding energy [1], which could lead to lasing action based on exciton recombination even above room temperature. The uniqueness of ZnO powder is based on its size and methods of preparation. ZnO nanoparticles can be prepared on a large scale low cost by simple solution-based synthesis methods, such as chemical precipitation [2–4], sol-gel synthesis [5, 6] and solvothermal/hydrothermal reaction [7–10]. ZnO finds applications in photo catalysis have received a great deal of interest because of its good catalytic activity and quantum efficiency [11].

We present here, a simple procedure for the synthesis of ZnO through sol-gel process via ultrasonication in a surfactant-free system. Besides their structural properties, the interesting photocatalytic properties of synthesized ZnO nanoparticles were also investigated, which demonstrated that ZnO nanoparticles would provide another useful system for environmental applications.

EXPERIMENTAL SECTION

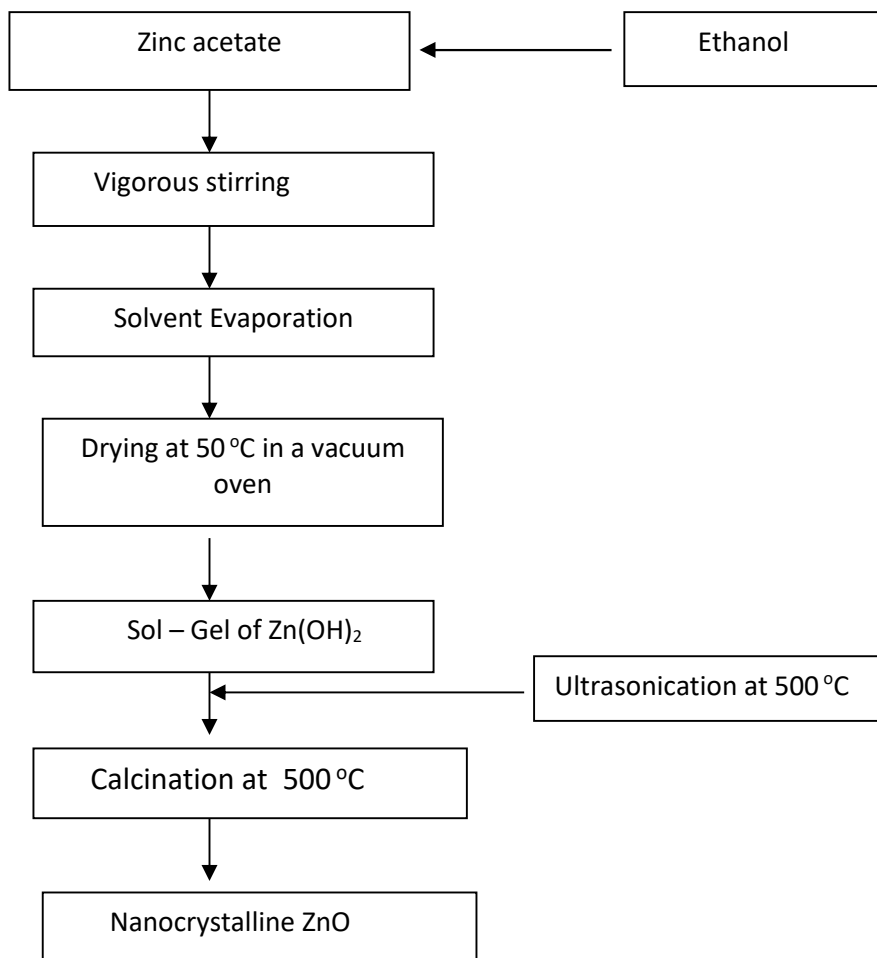
MATERIALS AND METHOD

Zinc acetate supplied by E Merck and Analar grade ethanol obtained from Sd's Fine Chemicals and were used as such without further purification. The dye, Crystal Violet (CV) was procured from Sd's Fine Chemicals and used as received.

SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Zinc acetate (2.0 g) in ethanol is added to 10 ml of double distilled water in a 250ml round bottom flask and subjected to constant stirring. The contents are stirred vigorously for 6-8 hours. The excess solvent is evaporated by drying in a vacuum air oven at 50°C for 1 h. The ZnO sol obtained was ultrasonically treated for 15 min. The derived gel obtained is subjected to calcination at 500°C for 15 min. The final product is ground to get fine particles (Figure 1).

FIGURE 1 FLOW CHART FOR THE SYNTHESIS OF ZnO



CHARACTERIZATION TECHNIQUES

The phase composition and nature of the product was determined by X-ray diffraction (XRD) pattern using a Shimadzu model XRD 6000 X-ray diffractometer equipped with high intensity Cu K α radiation ($\lambda=1.54 \text{ \AA}$). The scanning rate was 0.06°S^{-1} in the 2 ranges of 10-70°. Scanning Electron Microscope has been widely used for characterization of surface topography, bulk chemical composition and structure of thin specimens. Morphology of the synthesized nano ZnO was studied by using JEOL model JSM 6360 Scanning Electron Microscope. Infrared spectra were recorded using Shimadzu FT – IR with the use of transparent pellets of compounds in KBr (Aldrich FT-IR grade) matrix.

PHOTO REACTOR

Experiments were performed in a quartz reactor of 150 ml capacity, provided with water circulation in order to maintain constant temperature. The UV irradiation was carried out using 125 W (311 nm) medium pressure Hg arc lamp (SAIC, INDIA).

PHOTO DEGRADATION OF CRYSTAL VIOLET USING NANO ZnO PHOTOCATALYST DEGRADATION OF CRYSTAL VIOLET – DARK STUDIES

In a photo Reactor, 150ml of desired initial concentration (10, 15, 20 & 25 ppm) of dye solution is mixed with a fixed amount nano ZnO (50 mg) at natural pH(6.2). This mixture is magnetically stirred in absence of light. The sample from the photo reactor is withdrawn after one hour and centrifuged. The supernatants are analyzed at its absorption maximum using UV-VIS spectrophotometer (Shimadzu, UV 1601).

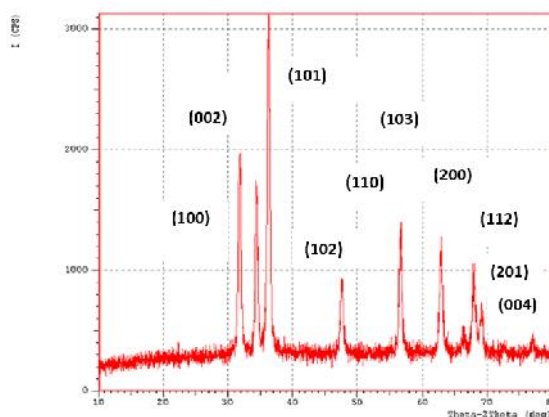
DEGRADATION OF CRYSTAL VIOLET – PHOTO STUDIES

In a photo Reactor, 150ml of desired initial concentration (10, 15, 20 & 25 ppm) of dye solution is mixed with a fixed amount nano ZnO (50 mg) at natural pH(6.2). This mixture is magnetically stirred and subjected to UV illumination as shown in Fig.6b. The sample from the photo reactor are withdrawn at different time intervals and centrifuged. The supernatants are analyzed at its absorption maximum (585 nm) using UV-VIS Spectrophotometer (Shimadzu, UV 1601).

RESULTS AND DISCUSSION

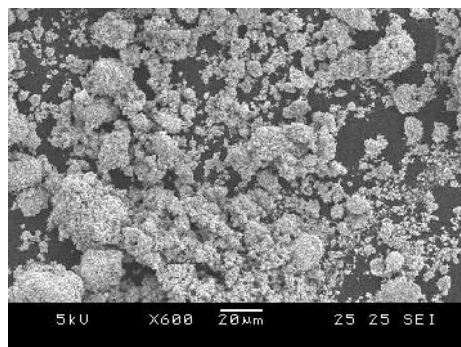
The phase identification and structure analysis of the as-synthesized zinc oxide nano particles were done by X-ray powder diffraction. Figure 2 shows the XRD patterns of the ZnO nano particles obtained after annealing at 500°C for 1 h. The pattern is simulated for Cu K radiation ($\lambda = 1.5406 \text{ \AA}$). The nano ZnO particles have three strong reflection at (100), (002) and (101) and moderate reflections at (102), (110), (103), (112) and weak reflections at (200), (201), (004) and (202). The preferential orientation of the crystallites is not lost with annealing. All diffraction peaks in the patterns of the ZnO nano particles can be indexed to the hexagonal Wurtzite structure of the ZnO crystal (JCPDS No.36 –1451). The diffraction peaks are sharper and stronger which suggests that the crystal quality of the resultant nano particles and the particle size is larger. There are no new peaks observed in the XRD pattern, suggesting the absence of any impurities. Usually a large broadening of XRD peaks and lowering of intensity are observed for nano materials. This can be attributed to the effect of crystallite size. The particle size of very small crystallites can be estimated from the width of their diffraction peak using the Scherrer formula [12]. The crystallite size and surface area calculated from XRD patterns were found to be 20 nm and 53 m²/g, respectively.

FIGURE 2 X-RAY DIFFRACTION PATTERN OF NANO ZnO



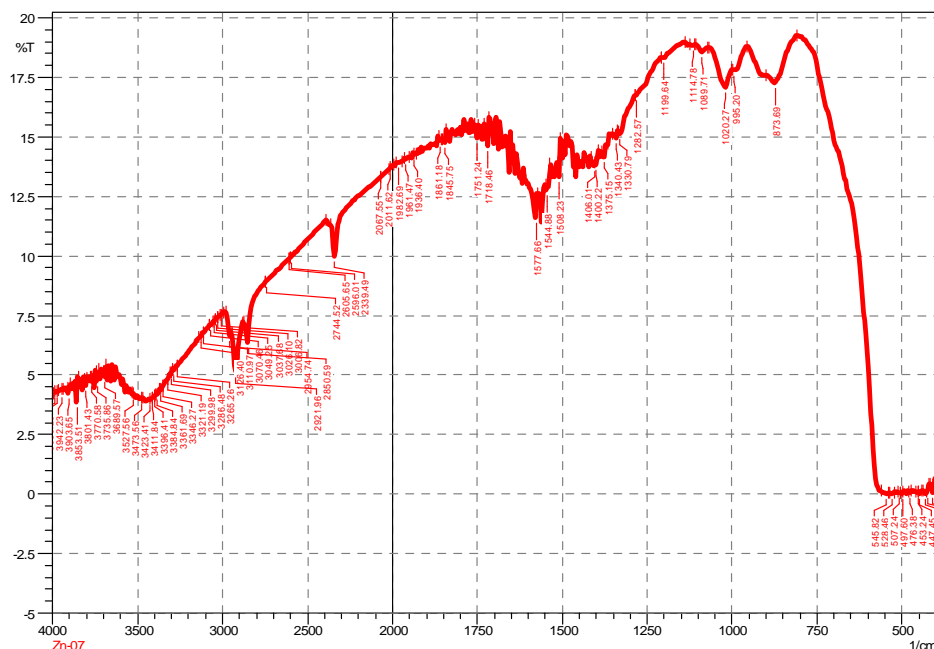
The Scanning Electron Microscope clearly indicates the morphology of the particles is roughly angular and homogenous (**Figure 3**). Some of the particles are agglomerates.

FIGURE 3 SCANNING ELECTRON MICROSCOPE IMAGES OF NANO ZnO



The IR absorption spectrum was recorded in the range of 4000-400 cm^{-1} using Infrared spectrometer. The resultant IR spectrum is shown in Figure 4. The IR spectral analysis of the nano ZnO clusters confirms the product formation, in addition to substantiate the absence of any unreacted precursors. The absorption region from 650-1500 cm^{-1} generally represents the fingerprint of the materials. As reported in the literature the Zn-H vibrations, both symmetric and antisymmetric are indexed around 1500 cm^{-1} and O-H stretching is observed around 3500 cm^{-1} [13].

FIGURE 4 . FT-IR OF NANO ZnO

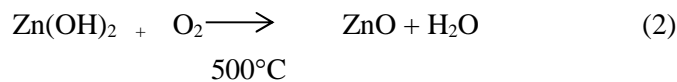


Based on the XRD and FTIR results we can prove a reaction mechanism for the formation of ZnO by the sol-gel technique via ultrasonication using zinc acetate. Here the precursor material zinc acetate is an ester and the hydrolysis of esters leads to the production of acetic acid and alcohol. We note that the hydrolysis of the precursor is a fundamental step in the production of materials by the sol-gel process. Zinc acetate, $\text{ZnO} (\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ transforms to mono acetate in ethanol, besides, water molecules are incorporated whether from the solution or from the air to hydrolyze the solution. It is then heated over 100°C, ethanol totally evaporates. The components $\text{CH}_3 \text{COO}^-$ and H^+ describes the second and third terms of the composition that

react to give acetic acid which evaporates on heating. Further, the hydrolysis of zinc mono acetate, the first component in composition in this equation undergoes saponification.



XRD is unable to identify the zinc hydroxide phase, probably because it is an amorphous phase. Finally, temperature, over 500°, ZnO will be formed in presence of oxygen through the chemical reaction.



ADSORPTION OF CRYSTAL VIOLET ONTO ZnO SURFACE

In order to evaluate the equilibrium constant of the adsorption of CV on ZnO surface at different concentration dark experiment were carried out. The dye adsorbs strongly onto ZnO particles from aqueous solution with a visible decrease in the concentration of the dye solution subsequent to equilibration for 60 min with ZnO in the dark. The number of CV molecules (n^{CV}) adsorbed per gram of ZnO as a function of the equilibrium solute concentration C_{eq} can be expressed by the equation.

$$n = \frac{\Delta C V}{W} \quad (3)$$

Where ΔC is the difference in concentration of initial and equilibrated solution, V is the volume (0.150L) and W is the weight of ZnO (0.05 g). It is believed that due to competition with solvent molecules it is unrealistic to expect for all the available sites of ZnO surface to be occupied by the organic molecules. In this case, n can be expressed as n_{max} giving the limited number of dye molecules that can be adsorbed on to a gram of ZnO. Thus, the adsorption data have linearised by using the following equation

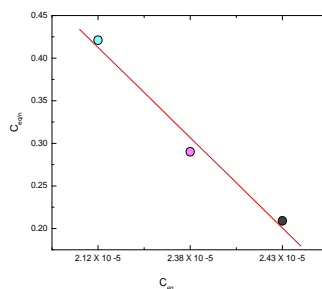
$$\frac{C_{\text{eq}}}{N} = \frac{1}{K n_{\text{max}}} + \frac{C_{\text{eq}}}{n_{\text{max}}} \quad (4)$$

where K is the equilibrium constant for CV adsorption, C_{eq} is the equilibrium concentration of the dye. The plots of C_{eq}/n vs C_{eq} are shown in Figure 5. The value of n_{max} is calculated from the slope of the straight line and are presented in Table 1.

TABLE 1. LANGMUIR ISOTHERM (DARK STUDY)

C_0 mol/L	3.8×10^{-5}	5.1×10^{-5}	6.3×10^{-5}
C_{eq} mol/L	2.12×10^{-5}	2.38×10^{-5}	2.43×10^{-5}
C	1.68×10^{-5}	2.72×10^{-5}	3.87×10^{-5}
n	5.04×10^{-5}	8.16×10^{-5}	11.61×10^{-5}
C_{eq}/n	0.421	0.29	0.209

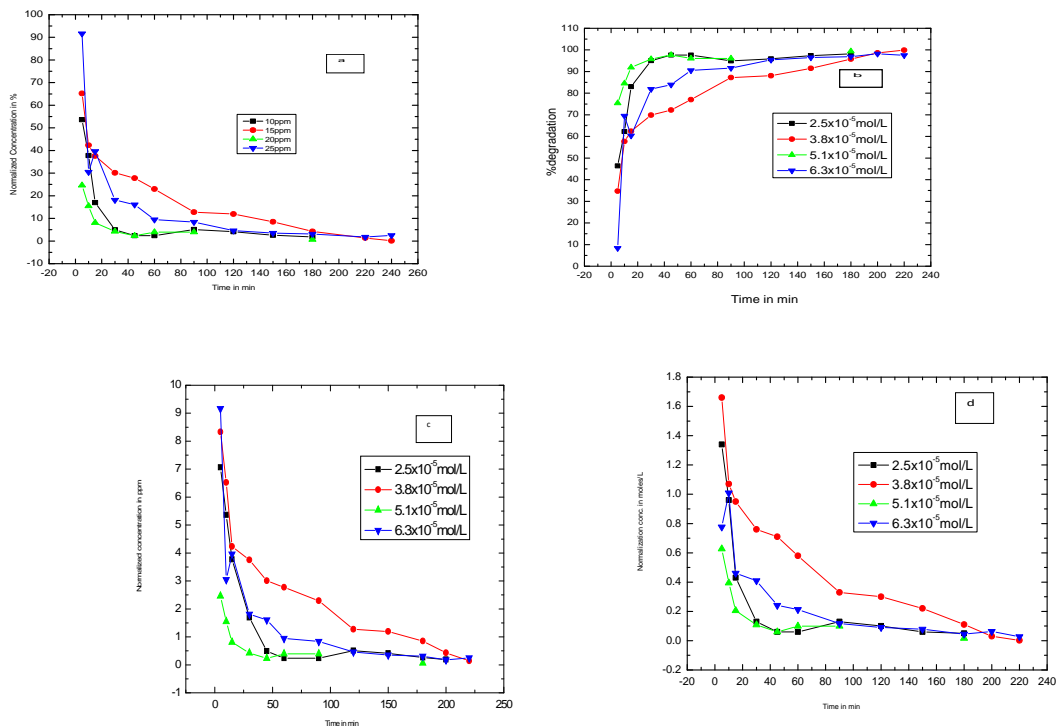
FIGURE 5. THE PLOTS OF C_{eq}/n VS C_{eq}



EFFECT OF INITIAL CONCENTRATION OF DYE ON PHOTO DEGRADATION

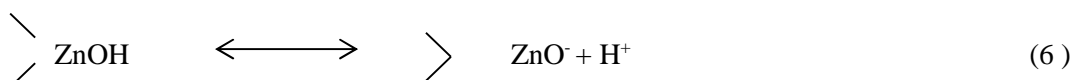
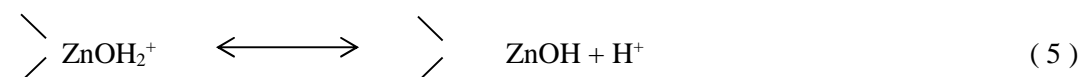
Figure 6 shows the normalized concentration versus irradiation time for different initial Crystal Violet concentration at fixed ZnO concentration. The photodecomposition kinetics of different initial concentration of Crystal Violet ($2.5 - 6.3 \times 10^{-5}$ mol/L) in the presence of fixed amount of ZnO (0.05g) at pH 6.2, is illustrated in (Figure 6 a-d) which depicts the distinct equilibrium between the dark adsorption equilibrium and in addition decrease in Crystal Violet concentration caused by UV illumination. From Figure 6, it's clear that Crystal Violet is adsorbed strongly on ZnO surface. The percentage degradation decreases with increase in initial concentration of Crystal Violet. This suggests that the path length of the photon entering the solutions decreases and in low concentration, the reverse effect was observed, thereby increasing the number of photons absorption by the catalyst in low dye concentration. It follows Pseudo first order kinetics.

FIGURE 6 EFFECT OF INITIAL DYE CONCENTRATION



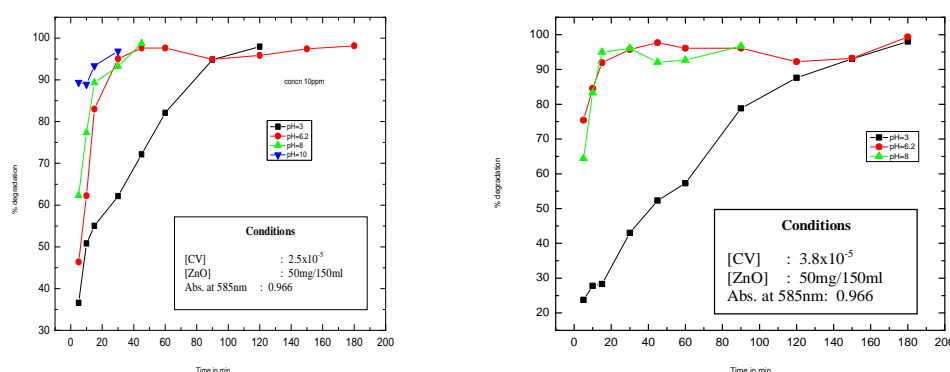
EFFECT OF pH

The influence of pH on the decolorization CV of is shown in Figure 7 & 8. The results showed that there was a strong dependence of pH of the solution on the heterogeneous photo process. It is known that the metal oxide particles suspended in water behave similar to diprotic acids. For ZnO hydroxyl groups undergo two acids base equilibrium.



Generally, for charged substrates, a significant dependency of the photo catalytic degradation efficiency on pH value had been observed, since the overall surface charge and hence adsorptive properties of semiconductor particles depend strongly on the solution pH [14]. In our experiments, any changes in initial degradation rate with varying pH values must be ascribed to variations of the acid / base properties of the ZnO particle surface. Since the photo oxidation of dyes is accompanied by the release of protons [15], its efficiency may then change because of the reversible protonation of the ZnO surface. The CV is a cationic dye in aqueous solution

FIGURE 7 & 8 SHOWS THE INFLUENCE OF pH ON THE DECOLORIZATION OF CV.



In acidic pH range ($\text{pH} < 4.2$) ZnO acquire positive charge and hence electrostatic repulsion between ZnO and dye cation retards the degradation rate. On the other hand, pH ($\text{pH} > 4.2$) electrostatic interaction between the negative ZnO and dye cation leads to strong adsorption with the corresponding high rate of degradation and reached a maximum at pH 10. This behavior is characteristics for many photo catalytic systems and similar results have been reported by the photo degradation of other dyes [15].

CONCLUSION

Nano crystalline pure Wurtzite Zinc oxide was prepared by a simple sol-gel process via ultrasonication. The sol-gel coupled with ultrasonic technique is fast and gives uniform distribution of nano crystalline ZnO particles. Ultrasonication reduces the crystalline size but also enhances the hydrolysis of ZnO for better crystallization ZnO particles. From XRD pattern, the average crystallite size and surface area were calculated to be 20 nm and $53 \text{ m}^2/\text{g}$, respectively. SEM pictures confirmed the angular shaped ZnO nano structures, which were uniform and homogeneous. Experimental results suggest that the synthesized nano ZnO was efficient for the photo degradation of a basic dye, Crystal Violet from aqueous solutions. The photo degradation of Crystal violet follows first order kinetics. Total mineralization of CV dye was achieved at pH 10.0 for 15 min of irradiation.

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