

# Photocatalytic degradation of methelene blue dye using hydrothermally synthesized ZnO nanorods

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This study involves the photo catalytic degradation of methelene blue dye, employing photo catalytic process using hydrothermally grown zinc oxide (ZnO) nanorods. ZnO nano rods were grown by hydrothermal method from aqueous solution of Zinc Nitrate and hexamethylenetetramine with seed layer of Zinc acetate dehydrate at low temperature of 90 °C. The prepared ZnO nano rods were annealed at three different temperatures of 300 °C, 400 °C and 500 °C in air atmosphere. These nano rods were used as catalyst in to methelene blue dye. The properties of ZnO nano rods and their growth mechanisms were studied using x-ray diffraction, scanning electron microscopy, UV-Visible spectroscopy and photoluminescence measurements. Catalytic activity of ZnO nanorods has been investigated. An attempt has been made to study the effect of process parameter through irradiation time on photo catalytic degradation of methelene blue. The experiments were carried out by varying irradiation time (1 hour, 2 hour and 3 hour) and area of the catalyst (1 cm<sup>2</sup> to 2 cm<sup>2</sup>). The photo degradation of methelene blue with ZnO nano rods were studied using optical measurements. The optimum irradiation time and area of catalyst was found to be 3 hours and 2 cm<sup>2</sup> respectively for methelene blue.

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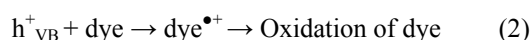
*Keywords:* Degradation, Azo dye, Methelene blue, Photo catalysis, ZnO nanorods

## 1. Introduction

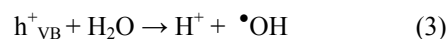
Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable [1]. Among the different types of dyes used in textile industries, 60–70% is azo compounds. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Reactive dyes are extensively used in many textile-based industries because of their favorable characteristics, such as bright color, water-fastness, and simple application [2]. However, up to 50% of reactive dyes are lost through hydrolysis during the dyeing process and therefore a large quantity of the dyes appears in wastewater [3]. These dyestuffs are designed to resist biodegradation and are barely removed from effluents using conventional wastewater treatments, such as activated sludge [4]. Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively [5, 6]. AOPs include photo catalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Photo catalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes [7,8].

The photo catalyzed decolorization of a dye in solution is initiated by the photo excitation of the

semiconductor, followed by the formation of electron–hole pair on the surface of catalyst (Eq. 1). The high oxidative potential of the hole  $h^+_{VB}$  in the catalyst permits the direct oxidation of the dye to reactive intermediates (Eq. 2).



Another reactive intermediate which is responsible for degradation is hydroxyl radical (OH•). It is either formed by the decomposition of water (Eq.3) or by reaction of the hole with OH<sup>-</sup>(Eq. 4).



The hydroxyl radical is an extremely strong, non-selective oxidant ( $E^0 = +3.06$  V), which leads to the partial or complete mineralization of several organic chemicals [9].

In this work we have used glass slides as a support for ZnO nanorod photo catalysts. When affixed on to the support, ZnO nanorods offer higher surface to volume ratio compared to nano particulate films, allowing higher adsorption of the target molecules [10]. The ZnO nano rods were fabricated by dip coating method and the

variation in annealing temperatures for controlling the growth rate of ZnO nano rod was made. ZnO nano rods were grown by a hydrothermal process at low growth temperature of 90 °C and were annealed at different temperatures of 300 °C, 400 °C and 500 °C for 1 hour. The structural and optical properties of ZnO nano rods were systematically investigated. Hydrothermal growth of high quality ZnO nano rods perpendicularly oriented on glass substrates was reported. These high quality ZnO nano rods can be applied as catalyst for removal of reactive dyes in the industry effluents.

## 2. Experimental

The ZnO nano rods were prepared from zinc nitrate in a neutral aqueous solution under hydrothermal conditions. The procedure consists of two steps: (i) Deposition of glass substrates with dense and uniform ZnO films by dip coating method. (ii) Hydrothermal growth of ZnO nano rods in aqueous solution. In detail, the seed layer solution was prepared by mixing 0.1 mol of Zinc acetate in 10 ml of ethanol and stirred continuously for 2 hours and 0.25 ml of de-ionized water was added in droplets to form a clear and homogeneous solution. Well cleaned glass substrates were immersed in the seed ZnO solution for 1min by dip coating method and taken out. The process was repeated 5 times to get desired film thickness. The above seed coated film was annealed in muffle furnace at 200 °C for 1 hour in room temperature. The growth layer solution was prepared by mixing aqueous solutions of 0.02 mol of Zinc nitrate and 0.2 mol of Hexamethylenetetramine in 1:10 concentration which is the best growth layer concentration reported in our work [11] and stirred continuously for 2 hours. The hydrothermal growth was carried out at low temperature of 90 °C in a sealed beaker by immersing the seed coated substrates in the aqueous solution for 4 hours. The nano rod grown films were taken out from the hot air oven and immediately rinsed with de-ionized water to remove the impurities. Finally the films were annealed at three different temperatures of 300 °C, 400 °C and 500 °C for each 1 hour. The X-ray diffraction pattern of the prepared ZnO was recorded using a XPERT-PRO with Cu K $\alpha$  radiation at the Bragg angle ranging from 20° to 80°. The surface morphology of the prepared samples has been studied using scanning electron microscope SEM JEOL-6390. The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The photoluminescence spectra of the prepared ZnO nanorods have been recorded using a HORIBA JOBIN YVON-Fluorolog at an excitation wavelength of 350 nm.

Photo catalytic activity was carried out in a specially designed reactor in which the light source was 8W UV lamp (Philips TUV-08). The hydrothermally grown ZnO nanorods were used as catalyst. 0.5 mol of methylene blue dye was taken in a beaker and ZnO nanorods were

suspended into the beaker and treated with UV lamp by varying irradiation time and area of catalyst. The absorption spectra were recorded using UV-Vis spectrophotometer and rate of decolorization was observed.

## 3. Results and discussions

The crystal structure of samples annealed at different temperatures of 300 °C, 400 °C, 500 °C and as prepared sample was analyzed by XRD. All diffraction peaks are well indexed to the standard diffraction pattern of hexagonal ZnO phase. The detected (h k l) peaks were at 2 $\theta$  values of 31.7647°, 34.4227° and 36.2520° corresponding to the lattice planes (100), (002) and (101) respectively.

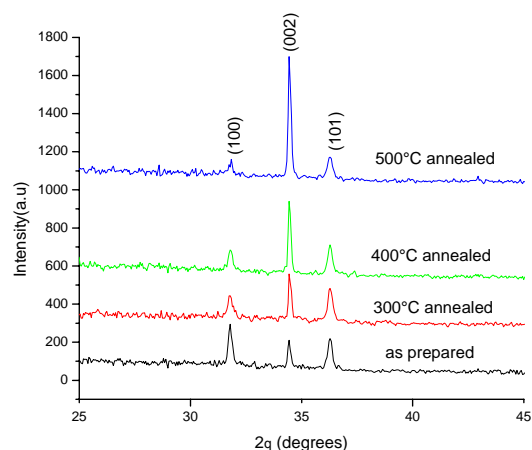


Fig. 1. X-ray diffraction patterns of ZnO nanorods annealed at different temperatures.

The (h k l) peaks are in good agreement with the standard JCPDS 036-1451 card for hexagonal wurtzite ZnO. Fig. 1 shows the XRD patterns of nano rods grown at growth temperature of 90 °C and annealed at three different temperatures of 300 °C, 400 °C and 500 °C for 1 hour. At the temperature of 300 °C & 400°C very weak (100) and (101) peaks and strong (002) peaks are observed, indicating that the ZnO nanorods were oriented in all directions. When compared to 300 °C, at 400 °C the (002) peak is stronger. At 500 °C very weak (100) and (101) peak and very strong (002) peak are observed, showing that the ZnO nanorods grown are of high c-axis orientation. In as prepared ZnO film all three peaks are found and (002) peak is weak compared to other two peaks. The strongest (002) peak of diffraction pattern appears while the annealing temperature is equal to 500 °C. The strongest peak corresponds to the (002) plane is more prevalent for the nanorods [12].

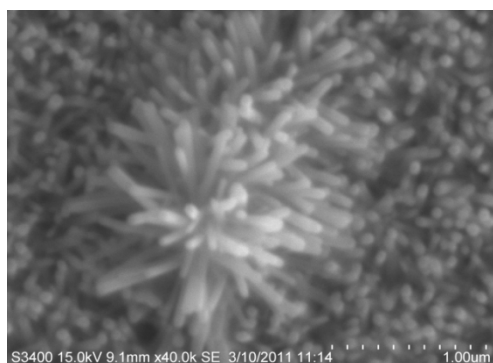


Fig. 2(a) as prepared ZnO nano rod

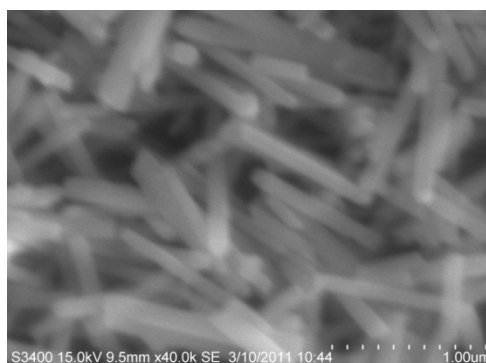


Fig. 2(b) ZnO nano rod annealed at 300 °C

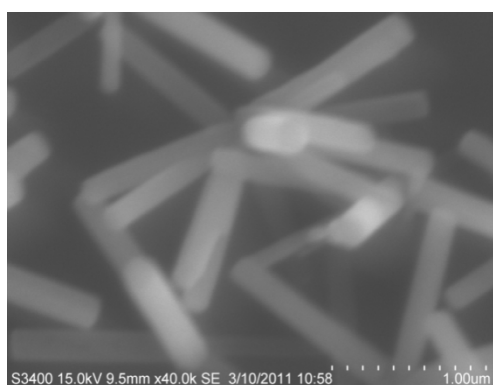


Fig. 2(c) ZnO nano rod annealed at 400 °C

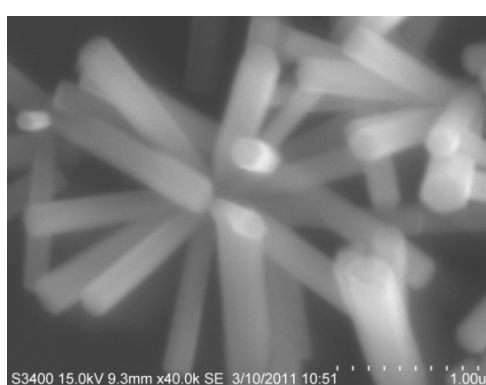


Fig. 2(d) ZnO nano rod annealed at 500 °C

The average size of the ZnO particle is calculated using Debye scherer formula,  $d_{avg} = 0.9\lambda / \beta \cos\theta$ . where  $d_{avg}$  = average crystal size,  $\lambda$  = Wavelength of incident beam (1.5406 Å),  $\beta$  = FWHM in radians and  $\theta$  = scattering angle in degree. The grain size of the nano particles are found to be 0.89 nm, 2.66 nm, 2.88 nm and 2.79 nm for as prepared film and films annealed at of 300 °C, 400 °C and 500 °C respectively.

Fig. 2 (a-d) shows the SEM images of films as prepared and annealed at 300 °C, 400 °C and 500 °C. They show the dense arrays of hexagonal ZnO nanorods having different diameters that are formed under different annealing temperatures. In Fig. 2a, the as prepared film shows that rods grown in all directions are in flower like pattern. It is clearly seen that from Fig. 2b to 2d as annealing temperature increases, the ZnO nanorods are oriented towards the vertical direction, which resembles the XRD pattern. The densities of the rods grown are decreased and diameter of rod size is increased as the annealing temperature increases. The effective surface area available for photo catalytic dye adsorption is a function of thickness, length and density of the nanarods covering the substrate [13].

The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods for photo catalytic activities [14]. Fig. 3 shows the absorption spectra of ZnO nanorods. The optical absorption edge has a tendency to shift to an upper

wavelength with increase in annealing temperature. It is well identified that the optical absorption determines the optical band gap of ZnO films which has a direct band gap. The optical band gap of ZnO films at growth temperature of 90 °C for as prepared, 300 °C, 400 °C and 500 °C annealed temperature was found to be 3.88 eV, 3.65 eV, 3.45 eV and 3.10 eV, respectively. With the increase of annealing temperature from 300 °C to 500 °C, the band gap decreases from 3.65 eV to 3.10 eV.

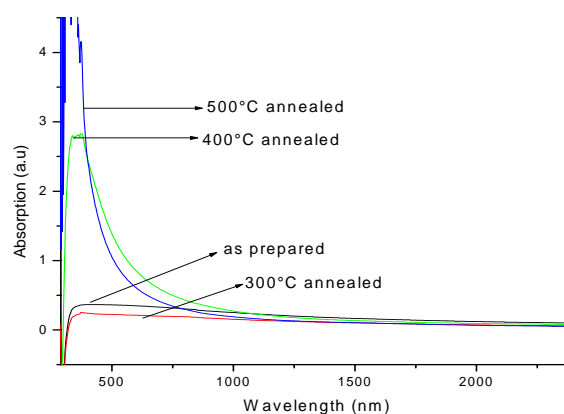


Fig. 3. UV-Vis absorption spectra of ZnO nanorods grown at different annealing temperatures.

Considering the results, it is clearly indicated that as annealing temperature increases, the band gap decreases. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size.

The Room temperature Photoluminescence spectra of ZnO samples obtained with an excitation wavelength of 350 nm for three different annealing temperatures of 300 °C, 400 °C, 500 °C and as-prepared is shown in the Fig. 4. The Ultraviolet (UV) emission peak in the range of 380-410 nm dominates all the PL spectra, the only difference being the relative intensity of peaks. The UV emission also called the near band edge emission (NBE) may originate from free excitonic emission in the ZnO materials as ZnO has a high exciton binding energy of 60meV at room temperature. Besides the strong UV emission peak, PL spectrum covers the surface related visible PL emission in the wavelength range of 550-650 nm. The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nano particles [15].

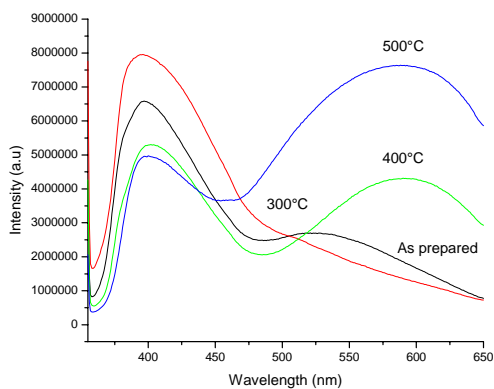


Fig. 4. Room temperature Photoluminescence spectra of ZnO nanorods.

The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as annealing temperature increases and particularly at 500 °C, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials [16].

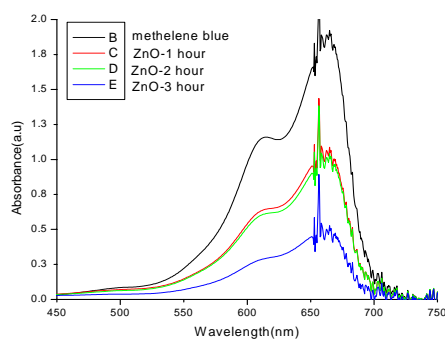


Fig. 5. Time-dependent UV-Vis absorption spectra of methelene blue and ZnO nanorods.

The emission spectra of products synthesized under different annealing temperatures are different from each other, confirming that optical properties of ZnO are very sensitive to the annealing temperatures.

Fig. 5 and 6 shows typical time and area dependent UV-Vis spectrum of methelene blue dye during photo irradiation with ZnO nanorods. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region.

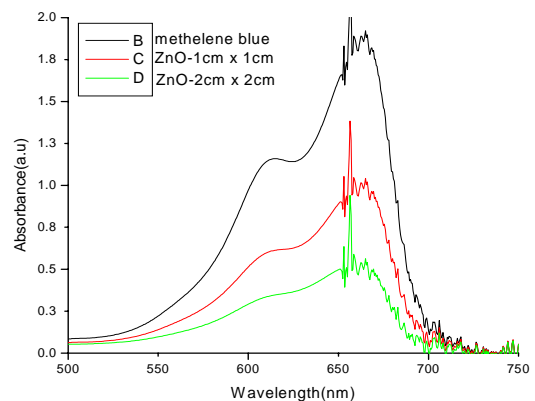


Fig. 6. Area-dependent UV-Vis absorption spectra of methelene blue and ZnO nanorods.

The prominent peak was observed at  $\lambda_{max}$  of 655 nm which decreased gradually with increase in irradiation time from 1 hour, 2 hour to 3 hour and area of the catalyst from 1 cm<sup>2</sup> to 2 cm<sup>2</sup>, indicating that the dye had been degraded. The percentage degradation (% D) was calculated using Equation (6).

$$\text{Percentage of degradation} = \frac{A_0 - A_t}{A_0} \times 100 \quad (6)$$

Where  $A_0$  = absorbance at  $t = 0$  minute

$A_t$  = absorbance at  $t$  minute

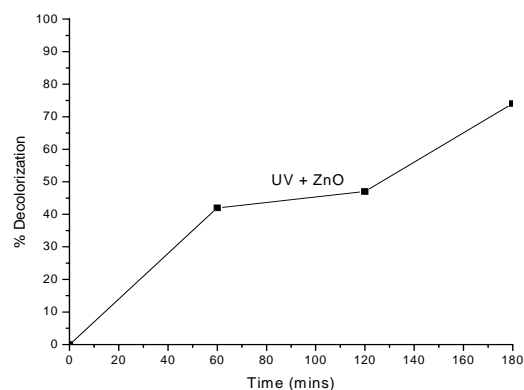


Fig. 7. Photo catalytic decolorization of methelene blue as a function of irradiation time.

For the degradation experiments, fixed amount (0.5 mol/L) of methelene blue dye was taken in a beaker and ZnO nanorods were suspended inside the beaker. The

beaker was subjected to irradiation under UV light (8W Philips bulb TUV-08) kept at a distance of 15 cm for fixed interval of time. Figs. 7 and 8 show the effect of irradiation time and area of the catalyst on the decolorization of methelene blue, respectively, at natural pH. It can be seen that initial slopes of the curves representing rate of decolorization, increase greatly by increasing irradiation time from 1 hour, 2 hour and 3 hour and area of the catalyst from 1cm<sup>2</sup> to 2cm<sup>2</sup> for methelene blue. The photo catalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose [17]. This can be explained on the basis of catalyst loading which is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases. Hence availability of more active sites on catalyst surface increases [18].

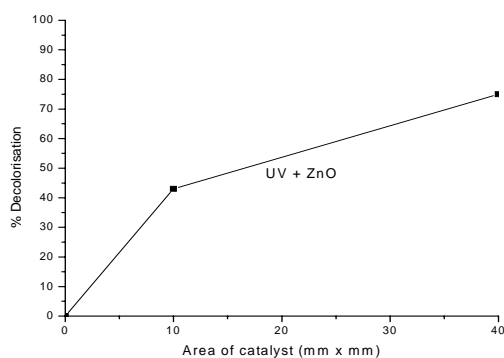


Fig. 8. Photo catalytic decolorization of methelene blue as a function of area of catalyst.

The decolorization of dye was achieved as 42%, 47% and 74% for the irradiation time of 1 hour, 2 hour and 3 hour and 43%, 75% for the variation in area of the catalyst from 1 cm<sup>2</sup> to 2 cm<sup>2</sup> respectively. It indicates that ZnO exhibits higher photo catalytic activity when irradiation time and area of catalyst are increased for the decolorization of methelene blue. The above degradation efficiencies were the result of 8W- UV irradiation. The 75% efficiency obtained with 8W-UV source is an encouraging result and it can be taken for future research.

#### 4. Conclusion

ZnO nano rods were synthesized by hydrothermal method at low growth temperature of 90 °C and their structural, morphological and optical properties were studied. From the results, it is clearly observed that, at 1:10 growth concentration and at 500 °C annealing temperature, ZnO nanorods with good optical properties can be grown. The photo catalytic activity of ZnO nanorods were carried out on methelene blue dye by varying irradiation time and area of photo catalyst. 75% degradation efficiency was reported with very low 8W-UV source.

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