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Effect of Annealing Temperature on ZnO Nanoparticles and its Applications for Photocatalytic Degradation of DR- 31 dye

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***Abstract*— This paper reports the effect of annealing temperature on ZnO nanoparticles prepared by simple combustion method. The synthesized nanoparticles were characterized in term of structural, morphological, optical and kinetic properties. The detailed characterization confirms that the prepared nanoparticles are well crystalline. It is observed that annealing temperature greatly influence the morphology, band gap and photodegradation of organic dye and suggests an ideal annealing temperature is 600^{0}C. FESEM shows the grain size is of the order of 40-60 nm. Further the prepared nanoparticles annealed at different temperatures were used as photocatalyst for photodegradation of DR-31 dye. Kinetics study reveals the photodegradation of direct red - 31 (DR-31) dye follows first order rate constant. It was observed that the samples annealed at 500^{0}C, 600^{0}C, 700^{0}C and 800^{0}C, the percentage photodegradation were 89.62%, 96.78%, 94.77% and 92.56%, respectively. It exhibits the complete degradation of dye only in 60 min under UV illumination.**

***Index Terms*—Annealing temperature, DR-31 dye, Nanoparticles, simple combustion method, ZnO**

I. Introduction

IN the present scenario, advanced industrialization is growing the demand of synthetic dyes. These dyes are mostly used in various fields such as food, leather industries, and textiles [1, 2]. Researchers around the globe are doing their best effort to protect the environment from non biodegradable dyes [3]. These dyes are main cause of serious fulmination to aquatic life. Recently nanotechnology plays an important role to protect the environmental contamination caused by dye pollutants. Advanced oxidation process has potential application in environmental remediation. Intervening these processes, ZnO as photocatalysts plays a vital role for the degradation of hazardous chemicals by using UV light. ZnO is II-VI semiconductor has wide band gap (3.37 eV and large exciton binding energy (60meV). These properties make this material promising for potential applications such as solar cell, sensor and photocatalyst [4-6].

Direct red 31 (DR 31) dye is organic dye having IUPAC name Bis (4-hydroxy-2-sulfonapthalen-7-yl) amine with molecular formula $C_{32}H_{21}N_5Na_2O_8S_2$. DR - 31 is of red brown powder and this yield to red when dissolved in water. This dye is soluble in ethanol and slightly soluble in alcohol and insoluble in organic solvents. This dye can be used for cotton, printing. It can also be used for dyeing silk, wool and silk fabric printing. However, DR-31 dye has unfavourable effects on human health. Therefore, it is mandatory to find the effective methods to control these human related issues. Due to its soluble nature, various types of methods are used for degradation of dye such as sedimation, filtration, adsorption and photocatalytic degradation [7]. Among these, photocatalytic degradradtion is one of the advanced and original methods in the presence of photocatalyst.

ZnO is inorganic semiconductor photocatalysts for degradation of dyes. In comparison with other metal oxides ZnO has better photocatalytic properties. According to Bora et al. [8] the presence of neutral (VO) singly charged (V_O^+), doubly charged (V_O^{2+}) oxygen vacancies on the surface of ZnO nanoparticles are responsible for the adsorption of various gases. During photocatalytic degradation process, O_2 adsorbed on the surface of the ZnO nanostructures generates hydroxyl radicals ($HO^\bullet$) responsible for highly efficient and non selective degradation of the harmful, toxic and non biodegradable dyes on the surface as well as in the solution. Adsorption followed by reduction of harmful gases by the conduction band electrons makes ZnO nanoparticles as a potential candidate for sensing applications also. The photodegradation of methyl orange dye by cobalt photocatalyst under UV light is reported [9].

In the present study, ZnO nanoparticles were synthesized by simple combustion method. Further the effect of annealing temperature on structural, morphological and photocatalytic efficiencies of ZnO nanoparticles were studied.

II. Materials and Methods

Synthesis of ZnO Nanoparticles

Synthesis of ZnO nanoparticles has been prepared by

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simple combustion method. In this synthesis process 0.27M of Zn nitrate hexahydrate ($Zn(NO_3).6H_2O$) (10 ml) was mixed well with equi molar concentration of sucrose (10 ml) at room temperature under continuous stirring. After proper mixing prepared solution was filtered and transferred to a crucible which was then placed into the furnace at 400^{0}C. The content results the formation of spongy like material which was further annealed at different temperatures such as 500^{0}C, 600^{0}C, 700^{0}C and 800^{0}C for an hour was named as AT1, AT2, AT3 and AT4 respectively. The obtained samples were characterized in detail by using various analytical techniques.

Photocatalytic degradation of DR - 31 dye

A specially designed photo-reactor with a water-circulating unit for photocatalytic experiment against model DR - 31 was used. A 125 W low pressure mercury lamp was used as a source of UV radiations. 0.056 g of ZnO nanomaterials was suspended into the dye solution as photocatalyst. Prior to the UV irradiation, the resulting suspensions were ultra-sonicated for 25 minutes in dark for proper homogeneity of the photocatalyst. A 5.0 ml sample of the solution was taken out from the photo-reactor at regular interval of time followed by centrifugation at 2000 rpm for 15 min in order to remove the ZnO suspensions from the solution. Each sample was finally analyzed to record UV-Vis spectrum through UV-Vis 2600/2700 (Shimadzu). For DR - 31 dye, the λmax corresponds to 595 nm wavelength. The percentage photocatalytic degradation was calculated using the equation

$$\text{Percentage photodegradation} = \frac{Ao - A}{Ao} \; X \; 100 \qquad \textbf{(1)}$$

where, Ao = initial absorbance of dye and A = absorbance of dye solution after UV light irradiation.

The various properties of ZnO nanoparticles were prepared by simple combustion method. Crystallinity of these samples were analyzed by X Ray Diffractometer, by use of analytical, Xpert Pro with CuKα, nickel metal is used asbeta filter, radiation source in the range 20-800. Surface morphology was observed from field emission Scanning Electron Microscope (FESEM- JSM6100 (Jeol)). Fourier Transformation Infrared Spectra (FTIR) was obtained from the KBr pellets using FTIR spectrometer (FTIR 8400S, IR Prestiage 21) obtained from Shimadzu, it gives the information about organic, inorganic compound and vibrational modes. For the optical measurements (absorbance and optical band gap) a double beam spectrophotometer (UV-Vis 2600/2700) Shimadzu with the wavelength range 200-700 nm was employed.

III RESULTS AND DISCUSSIONS

Structural, morphological and optical Properties of ZnO Nanoparticles

The crystallinity of ZnO nanoparticles was analyzed by the X- Ray Diffraction (XRD) method. "Fig 1" shows the typical XRD pattern of prepared nanoparticles for AT1-AT4. Observed XRD pattern exhibits well reflections at 2θ = 31.76^0, 34.42^0, 36.23^0, 47.57^0, 56.62^0, 62.93^0, 66.48^0, 68.28^0, 69.18^0 corresponding to the wurtzite hexagonal phase of (100), (002), (101), (102), (110), (103), (112) and (004) respectively. In all the pattern of nanoparticles high diffraction intensity was observed for (101) phase. These observed diffraction peaks well matched with standard card number (JCPDS 36-1451). Crystal size can be found from scherrer's formula

$$D=K\lambda/(\beta \cos\Theta)$$

Where D is the crystalline size, K is constant i.e 0.92, λ = 0.154 nm, mean wavelength of CuKα1 radiation, β is full width half maxima and θ is Bragg's angle in radians. Lattice parameters are observed in Table 1.

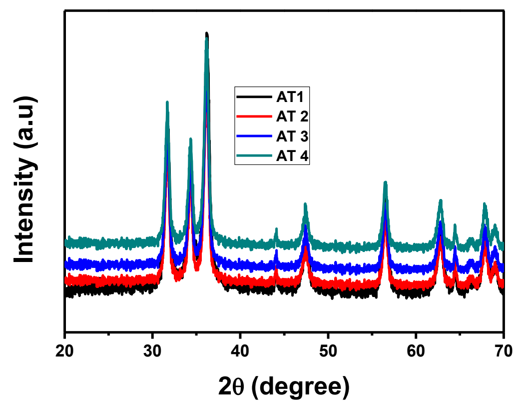

Fig. 1. Typical XRD patterns for ZnO nanoparticles annealed at 500-800^0 C temperature.

"Fig 2" shows FESEM images of ZnO nanoparticles annealed at 500-8000C. Average size of synthesized nanoparticles is found to increase with increasing annealing temperatures. ZnO nanoparticles with 42-49 nm, 52-72 nm, 80-95 nm and 100-120 nm were formed at 500^{0}C, 600^{0}C, 700^{0}C and 800^{0}C respectively.

Sample	Lattice Parameter (A^0)	Volume $(A^0)^3$	Density (g/cm^3)
AT-1	a= b= 3.251 c = 5.2060	47.649	11.34
AT-2	**a = b = 3.258** **c = 5.2064**	**47.858**	**11.29**
AT-3	a = b = 3.247 c = 5.2049	47.522	11.38
AT-4	a= b= 3.242 c = 5.2035	47.363	11.41

Table 1 lattice parameter for ZnO nanoparticles.

The result of increase in particle size can be explained on the basis of increased extent of agglomeration with increasing

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annealing temperature [9]. It is clearly observed from "Fig 2" that synthesized ZnO nanoparticles produces Spherical, hexagonal, pentagonal and other morphologies. But mostly spherical shaped morphology was observed [10]. The average width and length of ZnO nanoparticles are found in the range of 18.7 - 20.1 nm [11].

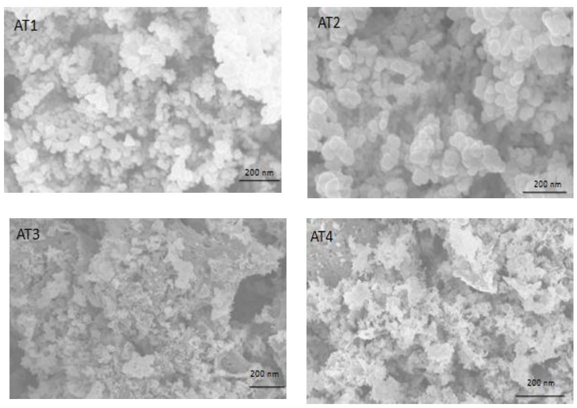

Fig. 2 Typical FESEM images for ZnO nanoparticles annealed at different temperatures AT1- AT4 respectively.

To evaluate the chemical composition of annealed ZnO nanoparticles Fourier Transformation Infrared spectroscopy (FTIR) was used at room temperature in the range 400-4000 cm^1. "Fig 3(a)" shows the typical FTIR spectra of annealed ZnO nanoparticles (AT1-AT4). The band was near the region 3000-3470 cm^{-1} is only because of OH group. The absorption bands at 900-1000 cm^{-1} appearing in IR spectrum can be ascribed to stretching and bending vibrations of C=O species. The band near 1250-1750 cm^{-1} indicates COO^- group. The band located near 400-500 cm^{-1} indicating the formation of stretching mode of ZnO. This shows the presence of ZnO [12].

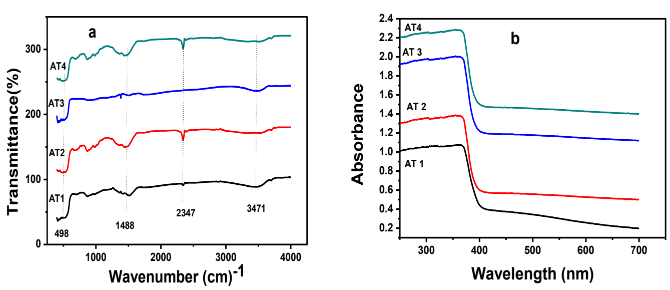

Fig.3 (a) FTIR spectra (b) UV Vis spectra of ZnO nanoparticles for AT1-AT4 respectively.

The absorbance spectra of annealed nanoparticles were observed from UV Vis spectrophotometer at room temperature. "Fig 3(b)" shows typical UV Vis spectra of ZnO nanoparticles annealed at different temperature (AT1-AT4). This gives information about excitonic and inter transition of nanomaterials [13]. The UV absorption peak shift from 380 nm to 415 nm is due to size difference [14]. The shifting in peak attributed to the formation of oxygen vacancies at higher temperature. These oxygen vacancies are responsible for photocatalytic degradation of dye.

Based upon the absorbance spectra from optical band gap of the prepared nanoparticles can be calculated from energy and wavelength relation. The decrease in band gap may be due to the influence of various factors such as grain size, structural parameter, carrier concentration, or may be due to presence of impurity [15]. Calculated band gap lies in the range of 3.10 -3.30 eV [16].

Photocatalytic applications

"Fig 4" shows the variation of absorbance as function of wavelength for photocatalytic degradation of DR-31 dye in the presence of annealed ZnO as photocatalyst. A continuous decrease in the absorbance intensity clearly confirms the fact that synthesized ZnO nanoparticles are acting as photocatalyst for the degradation of the dye under UV irradiations [17,18]. A/A_o value almost approaches to zero after 60 min of UV irradiation of the aqueous suspensions of DR-31 dye and ZnO photocatalyst (Fig.5 (a)).

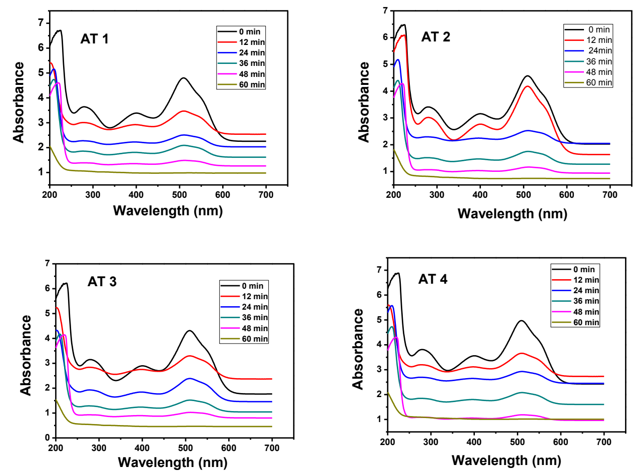

Fig. 4 Absorption spectra Vs wavelength for photocatalytic degradation of DR-31 dye in the presence of In-doped ZnO nanoparticles (IZ1-IZ4) respectively.

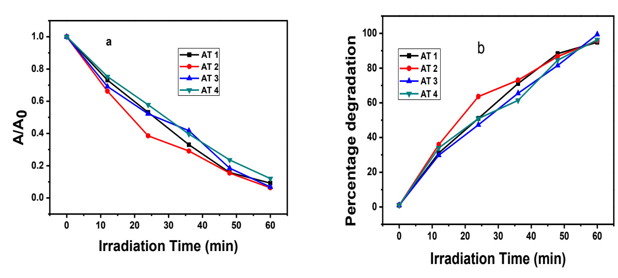

Fig. 5. Variations of (a) Percentage photodegradation and (b) A/Ao for DR-31 dye with ZnO nanoparticles annealed at different temperatures (AT1-AT4) respectively.

The corresponding percentage photocatalytic degradation of DR-31 dye as a function of UV irradiation time is shown in "Fig 5(b)" Complete degradation (100%) of the said dye was observed within 60 min of UV irradiations in the presence of ZnO nanoparticles.

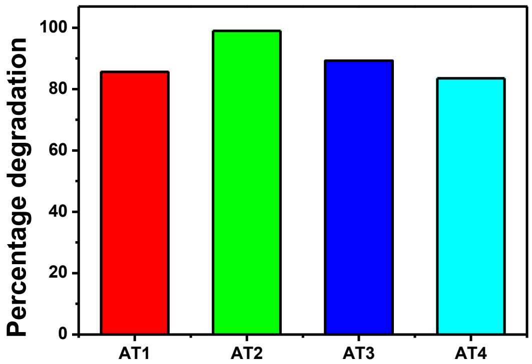

Fig. 6. Comparison of percentage photodegradation for DR-31 dye for AT1-AT4 respectively.

Mechanism under UV light

It has been proposed that DR-31 dye molecules are physiosorbed or chemisorbed onto the surface of ZnO nanoparticles where a series of photo induced redox reactions are initiated through the formation of electron/hole pairs (excitones)[19]. The optimized band gap of ZnO nanoparticles prevents the formation of electron/hole recombinants. As a result the conduction band electrons generates various oxygenated free radicals such as $O_2^{-\bullet}, HO_2^{\bullet}, H_2O_2$ and •OH through the reduction of chemisorbed O_2 on the surface of the ZnO nanoparticles (Eq. 2-5). Positively charged holes in the valance band are also involved in the formation of •OH free radicals by the ionization and oxidation of water molecules (Eq. 6). The generated •OH radicals are non selective and strong oxidant which oxidize the aromatic dyes by attacking their aromatic rings and converting them to non toxic chemical species.

$$O_2 + e_{CB}^- \rightarrow O_2^{\bullet -} \quad (2)$$

$$O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + HO^- \quad (3)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^{\bullet} + HO^- + O_2 \quad (5)$$

$$H_2O + ZnO(h_{VB}^+) \rightarrow ZnO + HO^{\bullet} \quad (6)$$

Figure 6 shows a comparative study of degradation percentage under different experimental conditions. It clearly shows the role of annealing temperature for degradation of DR-31 under UV illumination and maximum photodegradation percentage has been found for AT2. These studies confirmed that different annealing temperature is responsible for the photodegradation of dye.

IV Conclusion

To conclude, well crystalline ZnO nanoparticles annealed at different temperatures were synthesized through simple combustion method and were used for photodegradation of DR-31 dye. The detailed characterization of annealed nanoparticles was well crystalline and good optical properties. Surface morphology reported with increase in annealing temperature, grain size increases and band gap decreases. Application of these nanoparticles as photocatalyst exhibited maximum percentage degradation for ZnO nanoparticles annealed at 600^0C. For all the samples complete degradation of dye was observed within 60 min under UV irradiation. Percentage degradation was found to increase upto 600^0C. Thus synthesized nanoparticles shows an ideal temperature is 600^0C for photodegradation of DR-31 dye. Decrease in percentage degradation was attributed to there is reduction of surface area.

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