Biological and Photocatalytic Activities of ZnO NPs Over Neutral Red: Hydrothermal Method

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Abstract. In this report, it has been proved that the synthesized Zinc oxide NPs (ZnO NPs) are the competent photocatalyst and it has potent antibacterial activity. Herein, we have synthesized the hydrothermal ZnO NPs using zinc sulphate as precursor. The synthesized ZnO NPs subjected for various characteristics such as UV-Visible spectrophotometer. Fourier transforms infrared spectroscopy (FT-IR), Atomic force microscopy (AFM). The absorption maxima (λ_{max}) were observed at 265 nm & energy band of ZnO NPs was estimated at 3.69 eV. The organic and inorganic compounds confirmed by FT-IR. Morphological study was done using AFM. Further, using Neutral red we have subjected the synthesized NPs for the photocatalytic test and it has been performed well with good degradation of dye as we illuminate the solution to UV light with respect to time. Finally we concluded that synthesized ZnO NPs are good antibacterial activity against two pathogenic bacteria showing the good zone of inhibition. So the synthesized ZnO NPs are excellent in photocatalytic and biological activities.

INTRODUCTION

ZnO NPs has wide applications in animal feed, agricultural spray, fertilizers, electrolytes for zinc plating, skins and leather preservatives, catalyst, gas sensors, active filters in rubber and plastics, cosmetics and antiviral agent [1-4]. ZnO NPs are synthesized in many ways. Some of the methods are sol-gel, co-precipitation, hydrothermal, mechanical and high energy ball milling [5]. The importance of ZnO NPs is it has high surface to volume ratio and its energy band gap [6, 7] which leads ZnO NPs for the best application in biological, agricultural and medical fields too. Now a day's ZnO NPs has extended its potential results photocatalyst in dye degradation and antibacterial activities.

Herein, we have synthesized the ZnO NPs using simple hydrothermal method. The synthesized NPs were confirmed by the study of UV-Vis spectroscopy and FT-IR analysis. For the topological structure we preferred AFM. The applications of the synthesized NPs were shown by the antibacterial studies with two bacteria and also potentials results were obtained in photocatalytic studies.

EXPERIMENTAL SECTION

Chemicals

For the synthesis of ZnO NPs, Zinc sulphate ($ZnSO_47H_2O$) and sodium hydroxide (NaOH) are purchased from Himedia Laboratories Pvt. Ltd. Mumbai, India. For the purification of obtained precipitation ethanol is purchased from CHF Chemical co. Ltd, China city, China. Using the distilled water precursor and reacting agent is prepared. Neutral red indicator ($C_{15}H_{17}CIN_4$) is purchased from SRL Pvt. Ltd, Maharashtra, India. All the chemicals were of AR grade.

Synthesis of Zinc oxide nanoparticles

Zinc oxide nanoparticles were synthesized using hydrothermal method. Here we have used zinc sulphate ($ZnSO_47H_2O$) as a precursor and sodium hydroxide (NaOH) as a reacting agent. Initially 1.14 gm of $ZnSO_47H_2O$ with 0.4 M is dissolved in 15 ml of distilled water to prepare $ZnSO_47H_2O$ solution and 0.08 gm of NaOH with 0.2 M is dissolved in 10 ml of distilled water. Further, NaOH solution is added to $ZnSO_47H_2O$ solution drop wise to prepare aqueous mixer. The solution was stirred vigorously for 20 minute. After that the solution is poured to Teflon lined stainless steel autoclave (Hydrothermal kit) and heated for 3 hour with constant temperature of 180°c. Further, it is allowed to cool with room temperature. The obtained solution subjected to centrifugation using distilled water several times and finally once with an ethanol. The obtained residual is heated in oven for 90 min with 60°c. Finally the zinc oxide nanoparticles are collected and used for further characterization.

Characterization of prepared ZnO NPs

Optical properties of ZnO NPs were studied using UV-Visible spectrometer of model V-670 Jasco at the wavelength range of 200 nm – 800 nm at USIC, K.U. Dharwad, Karnataka, India. The functional groups were confirmed using the Fourier transform infrared spectroscopy (FT-IR) spectroscopy model Nicolet 6700 at the range of 4000 cm^{-1} to 400 cm^{-1} at USIC, K.U. Dharwad, Karnataka, India. The surface morphology and topological structure was studied using Atomic force microscopy (AFM) model Nanosurf, AG-easy scan 2 at USIC, K.U. Dharwad, Karnataka, India. Photocatalytic activity of synthesized ZnO NPs was studied by UV-Visible spectrometer of model V-670 Jasco at USIC, K.U. Dharwad, Karnataka, India.

RESULTS AND DISCUSSION

Optical studies

The synthesized ZnO NPs were primarily subjected for the UV-Visible spectrometry for the confirmation of a ZnO sample and to calculate the energy band gap (E_g). The ZnO is confirmed by showing the absorption maxima (λ_{max}) 265 nm and by the absorption data we calculated the E_g. As our previous studies using Kubelka-Munk transformation equation [8] we have used the obtained data and the graph of $(\alpha hv)^{1/2}$ Vs hv was plotted. The tangent has been elongated to the x-axis to get the E_g. The obtained E_g for synthesized ZnO NPs is 3.69 eV. FIGURE 1 (a) & (b) shows the absorption peak and E_g of ZnO NPs respectively. Kubelka-Munk transformation equation [9],

$$\alpha = \frac{A(hv-E_g)^{1/2}}{hv} \text{ --} \quad (1)$$

Where α is optical absorption coefficient, h is energy of the photon, E_g is band gap energy, A is constant depends on the transition probability.

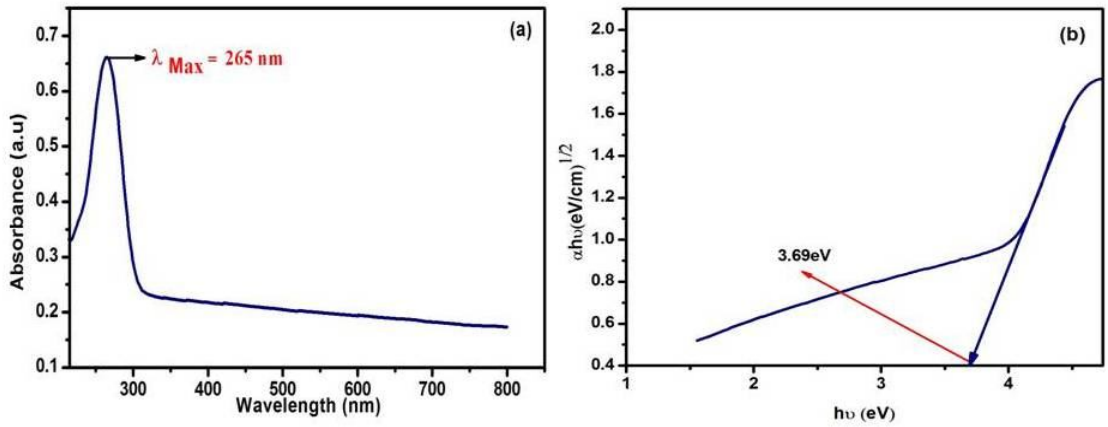

FIGURE 1. (a) UV-Vis spectrum of ZnO NPs and (b) Tauc's plot of ZnO NPs.

Determination of functional groups

The hydrothermally synthesized ZnO NPs were subjected to FT-IR spectroscopy with making the pellet of KBr powder. The spectra were obtained in the range of 4000 – 400 cm^{-1}. The organic, inorganic compounds presented in the sample, their stretching, bending and vibrations of bonds are analyzed and listed in the **TABLE 1** and shown in FIGURE 2.

TABLE 1. FT-IR analysis of synthesized ZnO NPs.

Functional group	Transmittance (cm^{-1})	Intensity	References
O-H (Alcohol Stretching)	3605,3524,3370,3299	Strong	[10]
C-H (Alkane Stretching)	2855,2923,1385	Low	[5, 10]
H-O-H Bending	1632,1460	Moderate	[10]
C-N Bond vibration	1184,1114,1047	Strong	[10]
Zn-O	508,438	Strong	[5]

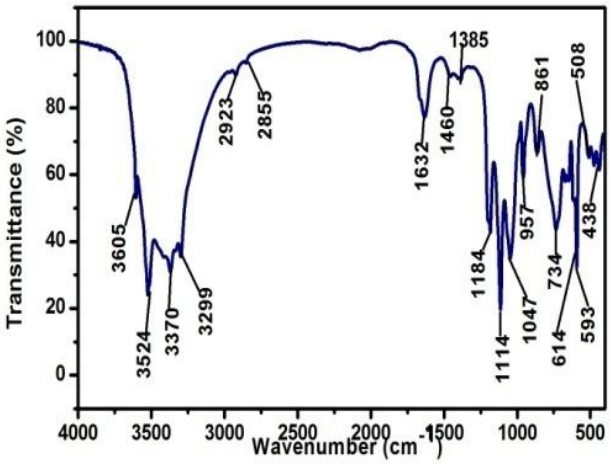

FIGURE 2. FT-IR spectra of ZnO NPs.

Surface topological studies

The **FIGURE 3** (a) and (b) shows the two and three dimension AFM images of ZnO NPs respectively. The AFM images indicate the average grain size and surface roughness of the samples. The below images shows the grain in x and y directions. With that we can conclude the particles are uniform and similar and the particles are having the size around 20 nm.

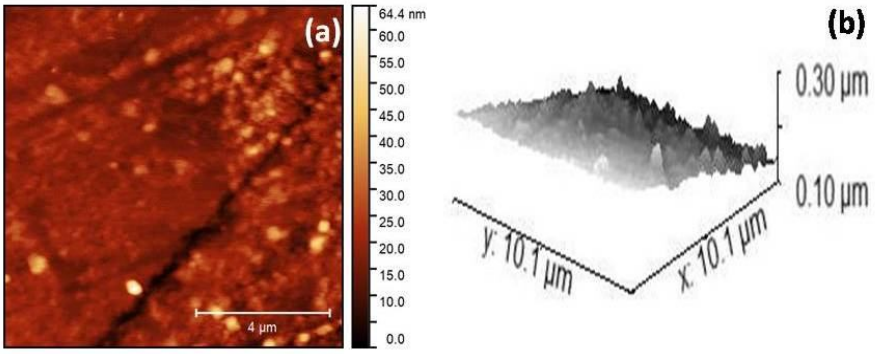

FIGURE 3. (a) 2-D morphological structure of ZnO NPs (b) 3-D morphological structure of ZnO NPs

Degradation of Neutral red with synthesized ZnO NPs

The catalytic activity is dependent on structure of catalyst that is nano size and high surface area. Here we tested the catalytic activity of ZnO over the dye neutral red under the illumination of UV light in an aqueous solution of ZnO dispersion. The photocatalytic behavior was studied using UV-Vis absorbance spectra for different illumination time as shown in FIGURE 4 (a). The irradiation of UV light significantly showed the degradation of dye by decreasing the maximum absorption peak from 3.44 a.u to 2.44 a.u with respect to time.

The effect of ZnO NPs as a catalyst is also studied using relation of concentration and absorbance. The decrease in the absorbance means the decrease in the dye concentration. The photocatalytic efficiency (η) of synthesized ZnO NPs was estimated using the below equation [11, 12],

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100 = \left(1 - \frac{A}{A_0}\right) \times 100$$

C_0 is the Initial concentration of dye, C is the residual concentration of the dye with respect to time, A is the intensity of absorption band with respect to time, A_0 is the intensity of absorption band.

The rate of degradation $\frac{c}{c_0}$ is shown in FIGURE 3 (b) which reveals that the synthesized ZnO NPs are the efficient photocatalyst for the dye degradation.

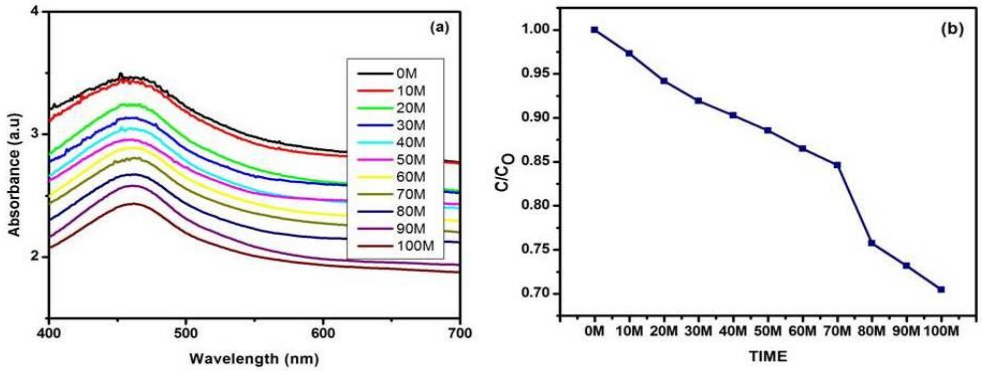

FIGURE 4. (a) Photo degradation of dye by ZnO NPs (b) Photo catalytic activity of ZnO NPs under UV light, plotted as a function of time.

Antibacterial effect of ZnO NPs

The antibacterial performance of synthesized ZnO NPs was studied using two gram-positive and gram-negative microorganisms Escherichia coli and Staphyllococcus aureus respectively. Herein, we took S. aureus because it is effecting widely on human skin to endocarditis and toxic shock syndrome [12, 13]. The antibacterial activity was studied using the agar well diffusion method. Here the bacterial suspension was applied uniformly in culture plate and synthesized ZnO NPs was applied on it with four different concentrations (25, 50, 75 and 100 µg ML^{-1}). After sometime it has observed that ZnO NPs exhibit excellent antibacterial activity with the zone of inhibition on the culture plates (shown in **TABLE 2)**. It revealed that ZnO NPs show comparatively higher antibacterial activity for S. aureus as compared to E.coli. The antibacterial activity of S. aureus and E.coli is shown in FFIGURE 5

TABLE 2. Antibacterial activities of ZnO NPs

	Staphylococcus aureus (Gram-positive)	Escherichia coli (Gram-negative)
	ZnO NPs	ZnO NPs
Concentration (µg mL^{-1})	Zone of inhibition in mm	Zone of inhibition in mm
25	18	16
50	21	18
75	25	23
100	30	28

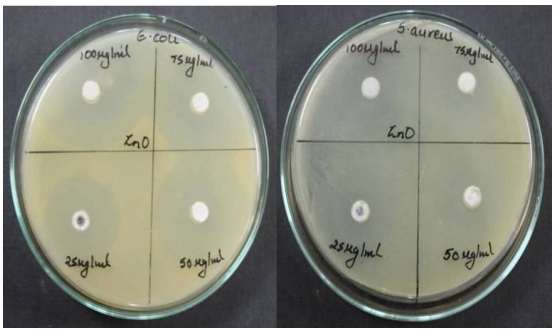

FIGURE 5. Antibacterial activity of E.coli and S. aureus.

CONCLUSION

The ZnO NPs are successfully synthesized using hydrothermal method and by spectral characterization we have noted that ZnO NPs exhibited good optical properties, the chemical functional were analyzed and structural studies by AFM. Based on these characteristics of NPs it has been studied for their photocatalytic activity over neutral red by irradiation of UV light and antibacterials studies. Finally, it has been suggested that ZnO NPs are suitable for the industrial scale production as a photocatalyst and biological active NPs.

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