



Photo Catalytic Decomposition of Malachite Green in Aqueous Solutions under UV Irradiation Using Nano ZnO Rod

P. Rejani, Asha Radhakrishnan and B. Beena

Department of Chemistry, D.B. College, Sasthamcotta, Kollam, Kerala, India 690 521

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Abstract: ZnO nano rod was prepared by microwave assisted method. The crystal structure of the nano powders were confirmed by X-Ray diffraction analysis and the mean particle size was estimated by the Scherrer's formula. The surface morphology of the nano particles were analyzed by SEM and TEM. The absorption spectrum of the material in the UV-Vis range was recorded. The prepared ZnO rod was used as a photocatalyst in presence of UV light against Malachite Green dye. The ZnO nanoparticle was found to be an efficient low cost photocatalyst which degraded Malachite Green dye in presence of UV light in a relatively short period of time.

Key words: Nanoparticles • Zinc oxide rod • Malachite Green dye • Photocatalytic activity

INTRODUCTION

Water contamination becomes a serious issue due to the fact that two percentages of dyes that are produced from different industries is discharged directly in aqueous effluent [1]. Recently, there has been an increasing concern, particularly in highly developed countries, about penetration of pharmaceuticals compounds into environment and related risks [2]. Nowadays, U.V. and visible light illuminated photo catalytic reaction has attracted great deal of attention for application in waste water treatment [3]. Photo catalytic decolorization process is one of the emerging advanced technology which are considered as alternative method for the degradation of dyes in wastewater [4]. Among advanced oxidation process (AOP), semiconductor assisted photo catalysis has attracted considerable attention as an alternative treatment method and a promising technique for treating dye contaminated waste water at low cost [5].

Photo catalysis is a process by which a semiconducting material absorbs light of energy more than or equal to its band gap; thereby generating holes and electrons, which can further generate free-radicals in the system to oxidize the substrate. The resulting free radicals are very efficient oxidizers of organic matter. The degradation of organic compound is the most widely used photo catalytic application of nano crystalline

particles [6, 7]. The photo catalytic decolorization of many dyes has been extensively explored in many previous studies using various nano particles [8, 9]. Photo catalysis has been considered and proved as a cost effective alternate for the purification of dye containing wastewater [10].

Photo catalytic degradation of organic compounds by semi conducting materials such as TiO₂ [11, 12], ZnO [13], CdS [14] and SnO₂ [15] has been used for environmental cleaning. Photo catalytic degradation of organic pollutants in water using semi conductive particles such as TiO₂ and ZnO, has attracted extensive attention. ZnO is a suitable alternative to TiO₂, as it has a similar band gap energy (3.2eV), larger quantum efficiency than TiO₂ and higher photo catalytic efficiency have been reported [16-22]. ZnO is a low cost alternative photo catalyst to TiO₂ for decolorization of organics in aqueous [23, 24]. The presence of metals on semiconducting metal oxides which acts as electron-hole separation centers can enhance the degradation efficiency of photo catalytic reactions [25].

Here we are interested in the photo catalytic degradation of malachite green using ZnO photo catalyst. The dispersion and surface area of zinc oxide depends on method of synthesis; that is important factor for determination of photocatalytic activity. Zinc oxide nanoparticles can be prepared by various methods,

Corresponding Author: B. Beena, Department of Chemistry, D.B. College, Sasthamcotta, Kollam, Kerala, India 690 521.

such as, alkali precipitation [26-28]], thermal decomposition [29], hydrothermal synthesis [30], organo-zinc hydrolysis [31], spray pyrolysis [11, 32, 33] and microwave irradiation [34, 35], etc.

The ZnO photo catalyst was synthesized via micro wave assisted method and the photo catalytic degradation of the dye was carried out using UV light irradiation.

MATERIALS AND METHODS

Experimental: All chemical $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, hexamethylenetetramine $\{(\text{CH}_2)_6\text{N}_4\}$, HMT} and malachite green (MG) were purchased from Merck Company as analytical grade and were used as received.

Preparation of Nano ZnO Rod: ZnO nano rods were prepared from Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). A 0.5g zinc nitrate hexahydrate salt was dissolved in 65 mL of demineralized water. Appropriate quantity of a moderate alkali namely hexamethylene tetramine $\{(\text{CH}_2)_6\text{N}_4\}$, HMT} was mixed to reach the pH level 7. The prepared solution was then stirred well for 30min to obtain a homogeneously turbid liquid. Then the solution was microwave-heated by a 300W domestic microwave oven for 20 min to obtain a curdy white precipitate, which was cooled to room temperature, filtered, washed with water followed by drying in hot air oven.

Characterization: X-ray diffractogram ($2\theta=10-90^\circ$) was obtained on XPERT-PRO powder diffractometer with Cu-K α radiation. The FTIR spectrum was recorded using KBr wafer on the Thermo Nicolet FTIR model AVATAR 370 DTGS. In the present study, SEM of the sample was recorded using a JED-2300 system and HRTEM was taken using 300kv HRTEM (FEI-Model). The absorption spectra were recorded at room temperature using SHIMADZU UV-2550 UV Visible spectrophotometer.

Evaluation of Photo Catalysis: Photo catalytic activity of nano ZnO rod was evaluated by determining the decolourization efficiency of MG photo degradation. An aqueous solution of MG were used as model pollutant for investigation of the photo catalytic activity of ZnO. Photo degradation experiments were carried out us keeping the dye solution of concentration 25ppm prepared using distilled water. A known concentration (0.1g) of photo catalytic ZnO was added in to the beaker containing 50 mL dye solution and mixture was stirred in the dark for 30 min to obtain uniform suspension. After

that the beakers were kept in a UV-light irradiation using 40W UV tube lamp. During irradiation, agitation was maintained to keep the suspension homogeneous. The concentration of dye in each degraded sample was determined with UV-Vis spectrophotometer. The percentage of degradation was determined by using the following equation

$$\text{Removal}(R\%) = \frac{(c_o - c_t)}{c_o} \times 100 \quad (1)$$

where $R\%$ is the degradation efficiency of MG, C_o [mg L^{-1}] and C_t [mg L^{-1}] are initial and concentration of MG in aqueous solution at different reaction time, t [36].

RESULTS AND DISCUSSION

X-Ray Diffraction Patterns: The structure identity and purity of the prepared nano particles were verified by XRD. Fig. 1 show the XRD pattern for ZnO rod at different temperatures. The observed peaks of the nano crystallite match well with standard JCPDS files and no other crystalline phases were detected. The average crystallite size of the powders were determined by using Scherrer's formula,

$$D = 0.9\lambda/\beta\text{Cos}\theta \quad (2)$$

where D is the average crystallite size in nm, λ the wavelength of X-ray radiation, θ the Bragg's angle and β the full width at half maximum of the peak observed for the sample [37].

A hexagonal wurtzite crystalline structure with lattice parameters of $a=3.2498$ and $c=5.2066$ were observed. All peaks correspond to hexagonal ZnO without evidence of any other crystal phase or another material. ZnO of wurtzite crystal structure; has no center of inversion and an inherent asymmetry along the c -axis is present, which allows the anisotropic growth of the crystal along the (1000) direction [38, 39]. Here the major intensity of the peaks centered at $2\theta=31.5$ and 36.1 show a preferred growth in (1010) and (1011) directions, in agreement with the micro rods observed in SEM micrograph. The grain size of ZnO nano rod has been found to be 26nm.

FT-IR Spectra of ZnO: FT-IR spectra of ZnO is shown in Fig. 2. The room temperature spectrum shows bands in the region $\sim 3485\text{cm}^{-1}$ and $\sim 2355\text{cm}^{-1}$ due to the presence of adsorbed water molecules or surface hydroxyl groups and C=O residues, probably due to atmospheric moisture and CO_2 respectively. The spectrum also shows Zn-O absorption band near 480cm^{-1} .

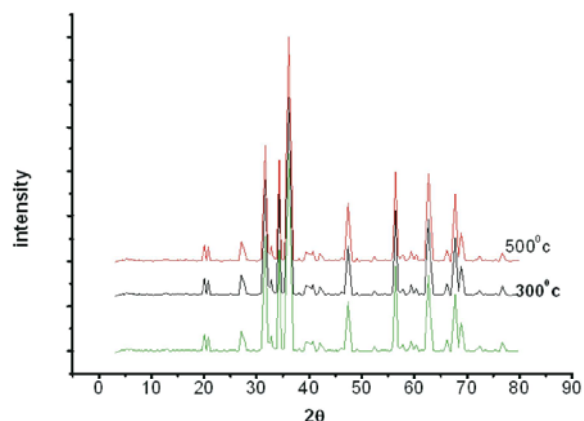


Fig. 1: XRD spectrum of ZnO rod at different annealing temperatures

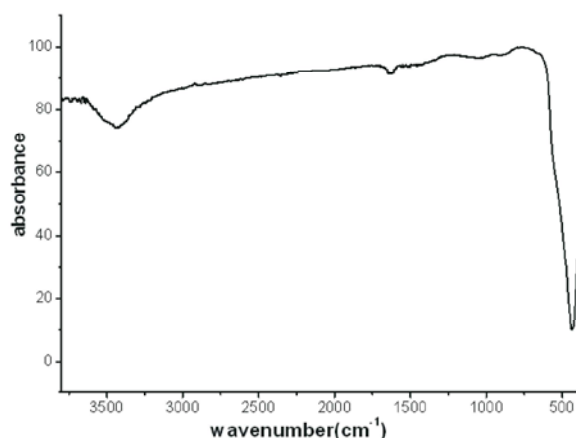


Fig. 2: FT-IR spectrum of ZnO nano rod

Surface Morphology of ZnO: The surface morphology of the as synthesized ZnO is revealed by scanning electron micrograph. Microwave irradiation might have played an important role in the fast synthesis of ZnO rods. As a polar material, ZnO may be significantly affected by microwave irradiation. The applied microwave field induces a rotation of polarized dipole of polar materials, which can generate heat due to molecular inner friction. The presence of an internal electric field also leads to orientation effects of dipolar molecules and hence reduces the action energy. The reduction in surface energy of the polar crystal may be the primary driving force for the faster nucleation, growth of the material and morphology evolution. The formation of the ZnO rods may be explained as follows. In the first stage OH^- ions are formed as a result of the reaction of H_2O with HMT and subsequently ZnO nuclei are formed. In the second stage, the formed ZnO nuclei grow preferentially along the (1000) direction, resulting in the formation of single-crystalline ZnO rods [38].

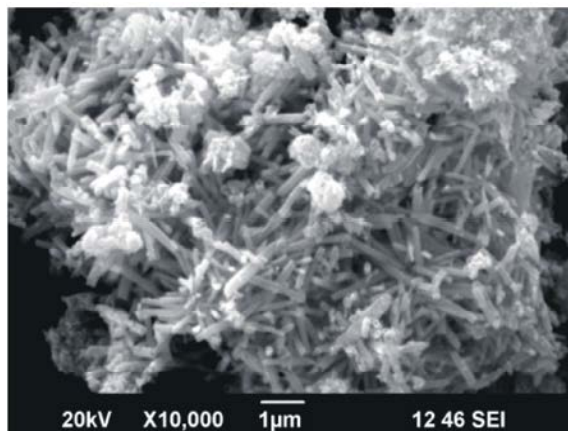


Fig. 3: SEM image of ZnO nano rod

In this study, hydroxide anions are provided by hydration of hexamethylenetetramine (HMT). When HMT is used as the hydroxide anion-generating agent, the reactions involved in the formation of ZnO crystals are believed to be as follows:

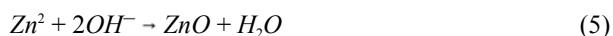


Fig. 3 clearly shows ZnO crystals with rod like structure with average length of 1-2 μm . Chemical composition by EDS indicate stoichiometry (Fig. 4). The resulting atomic-percent contents for ZnO rod was O 30.42%; Zn 69.58%. The high content of Zn indicates a high value of oxygen vacancies in their crystalline structures. The TEM micrograph, Fig. 5 of the sample revealed that the ZnO nano rod synthesized in this study have an average diameter of about 96 nm and an average length 400nm.

Evaluation of Photo Catalytic Activity: The variations in different experimental conditions affecting on photo catalytic oxidation of malachite green using the catalyst ZnO, such as, illumination time and amount of catalyst loaded were taken in to account to reach to integrated model for the photo catalytic degradation of malachite green.

Effect of Illumination Time: To investigate the effect of contact time on the decolorization efficiency of malachite green, the experiments were carried out with the contact time from 0 to 150 min. Fig. 6 shows time dependent

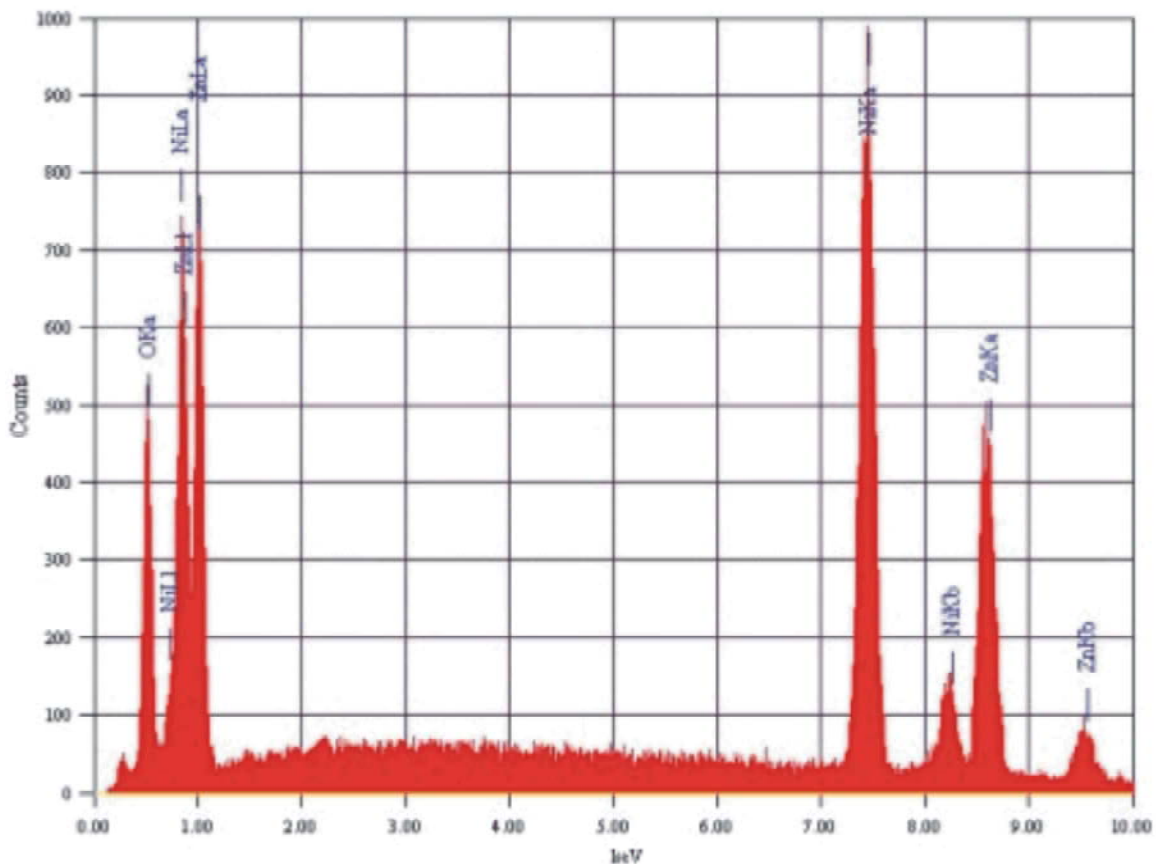


Fig. 4: EDS of ZnO nano rod

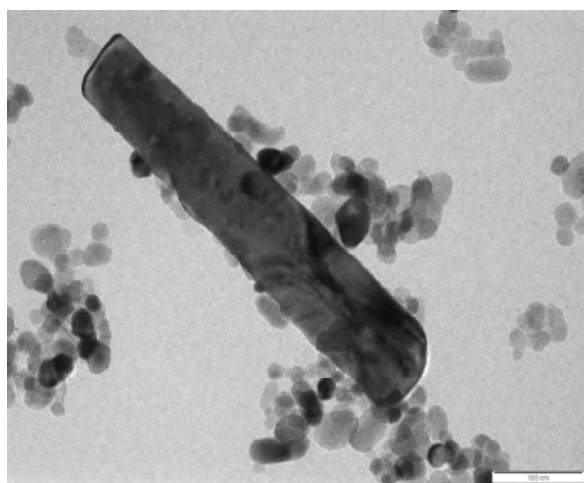


Fig. 5: TEM micrograph of ZnO nano rod

absorption spectra of the dye malachite green during the process. It can be seen that the intensity of absorption peak decreases with increases in the contact time, which indicate that the MG dye was decolorized as time prolonged.

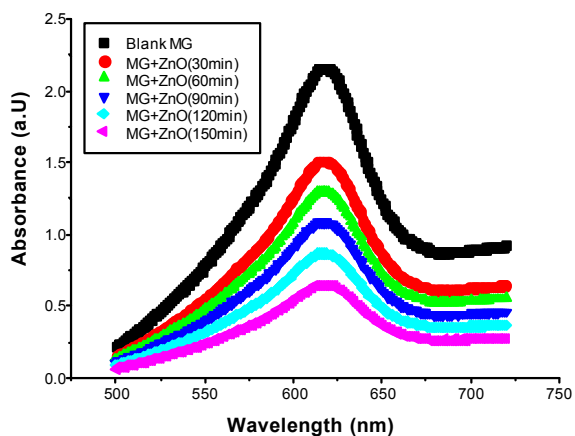


Fig. 6: Variation of absorbance of MG solution at various irradiation time

Effect of Catalytic Concentration: The amount of photo catalyst is another critical parameter to the degradation efficiency. In order to determine the effect of catalyst amount on the degradation of MG, a series of experiments were carried out by varying the catalyst amount from 0.025 to 0.125 g for 25 mg L⁻¹ of malachite green solution

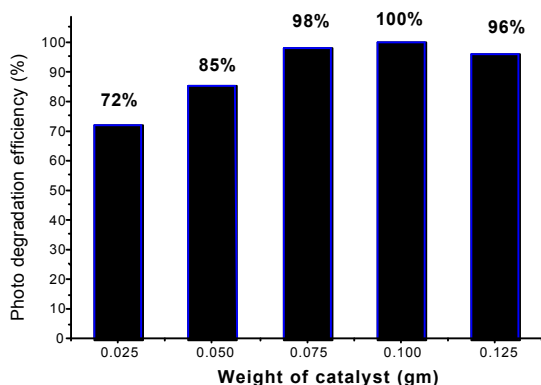
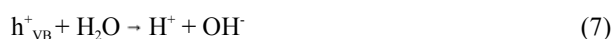


Fig. 7: Effect of catalyst dosage on the decolorization of MG using ZnO nano rod

keeping all other parameters identical and the results are presented in Fig. 7. As the photo catalytic amount increased from 0.0125 to 0.125g the degradation efficiency of MG enhanced and reached to maximum of 100% at 0.1g. The increase in amount of catalyst load increased the number of active sites on the photocatalytic surface, which in turn increased the number of hydroxyl radicals. Further increasing the loading of photocatalyst has increased the catalyst surface area and as a result increased the decolorization rate. It was assumed that further increase in photo catalyst may hindered the transmission of UV light in the reaction vessel if catalyst dosage was increased more than 0.1g and consequently decreased the decolorization rate [40].

Mechanism of photo catalytic decolorization



Upon exposure to UV – irradiation, ZnO is photo excited and an electron – hole pair is formed, where e^-_{CB} is the electron in the conduction band and h^+_{VB} is the hole in the valence band.

CONCLUSION

Pure hexagonal-phase ZnO nano rod was synthesized through fast and simple microwave irradiation method from the solution comprising Zinc nitrate and hexamethylenetetramine. The grain size of ZnO nano rod

have been found to be 26nm. The nano rods structures were found to have an average diameter of about 96 nm and an average length 400nm from HRTEM. Photo catalytic degradation activities of MG have been studied using ZnO nano rod. It is to be found that at lower catalyst concentration the catalyst surface and adsorption of light on catalyst surface are the limiting factors. Thus, an increase in catalyst concentration greatly enhanced the process efficiency. On the other hand, at higher concentration, overlapping of adsorption site and deactivation of activated catalyst reduced the process efficiency.

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Persian Abstract

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چکیده

نانولوله ZnO با استفاده از روشی بهره گیری از میکروویو تهیه شد. ساختار کریستالی نانوپودر با استفاده از آنالیز پراش اشعه ایکس تایید شد و اندازه میانگین ذرات با استفاده از فرمول شرار تخمین زده شد. مورفولوژی سطح نانوذرات با استفاده از SEM و TEM آنالیز شد. نانولوله ZnO تهیه شده بعنوان یک فوتوکاتالیست در حضور نور UV برای رنگ سبز مالاشیت استفاده شد. نانوذرات ZnO بعنوان فوتوکاتالیستی ارزان قیمت و موثر، رنگ سبز مالاشیت را در حضور نور UV و در یک بازه زمانی نسبتاً کوتاه تجزیه نمود.
