Indian Journal of Engineering & Materials Sciences
Vol. 30, October 2023, pp. 724-728
DOI: 10.56042/ijems.v30i5.6877

Experimental Study of the Photocatalytic Behaviour of Zinc Oxide Nanostructure for Cationic Dye (Malachite Green)

Anju, Ranjana Jha*, & Sukhvir Singh

Research Lab for Energy Systems, Department of Physics, Netaji Subhas University of Technology, New Delhi 110 078, India

Received: 9 August 2023; Accepted: 26 September 2023

In the present study, ZnO nanostructures formed by co-precipitation have been investigated for their photocatalytic behaviour against the cationic dye (Malachite Green). X-ray diffraction (XRD) technique has been used to identify the structure, crystallite size, and phase of the as-synthesized material. Surface morphology and elemental compositional analysis of the ZnO have been carried out using a scanning electron microscope (SEM) attached with an energy-dispersive spectrometer (EDS). The SEM study has revealed the formation of round-shaped pebble-like particles having sizes between 50 to 150 nm and found to be uniformly distributed. XRD analysis has shown well-resolved peaks of ZnO, indicating a polycrystalline nature with a hexagonal structure. The crystallite size has been calculated and found to be about 18 nm. Absorbance spectra have been recorded using a UV-Vis spectrometer and the optical band gap energy has been found to be 3.29 eV. Band-gap excitonic emission displays emission peaks in the photoluminescence spectrum at 390 nm. The results have shown the degradation of Malachite Green dye using ZnO nanoparticles in 3 hours, with 95% efficiency. The decomposition of the dye with ZnO nanoparticles can be utilized in industrial wastewater treatment for the benefit of mankind and the aquatic ecosystem, including their habitats.

Keywords: ZnO, Cationic dye, Degradation, Nanoparticles

1 Introduction

In recent years, the expanding population has resulted in a rise in surface and groundwater pollution. Dyes, extensively used in the textile, paper, plastics, and rubber industries, have caused serious environmental pollution by releasing poisonous and coloured effluent into water bodies. They have a significant impact on the water bodies. Wastes discarded by textile industries have been extremely dangerous to aquatic life and humans[1-3].

Recent research has revealed that heterogeneous semiconductors (ZnO, TiO_2, Fe_2O_3, Cu_2O, and WO_3) photocatalysis may have been used to replace traditional approaches for removing dye contaminants from water. Among these photocatalyst materials, ZnO has been the most prominent semiconductor due to the existence of free electrons. When the semiconductor has been exposed to a light source, electron-hole pairs (e^-- h^+) have been created, which have been adsorbed on the semiconductor surface. ZnO nanoparticles (NPs) have been more effective photocatalysts than other metal oxides because of their strong surface reactivity, large surface area, which has caused the development of many defects from non-stoichiometric oxygen. Recently, there has been a lot of focus on the photocatalytic properties of nanoparticles, particularly ZnO nanoparticles[4].

Zinc oxide has been an inorganic compound, a semiconductor presents in nature, usually in crystalline form. In naturally occurring zinc oxide, manganese impurities have been found. Due to the manganese impurity, ZnO has been a classic red or orange in colour. Zinc oxide has been a crystalline powder that has been white and insoluble in water. It has had a wide direct band gap range of 3.29eV to 3.37eV at ambient temperature and a significant exciton binding energy of 60meV [5]. For fast photo degradation, the absorbance of ZnO has to be in the entire spectrum of electromagnetic waves since the band gap has lain in the UV region. As a result of this, ZnO has absorbed UV light only, not visible light. Thus, the pure phase of ZnO has not been able to degrade the dye efficiently, as shown in the present investigation results also. To degrade the dyes efficiently, further modifications are needed, such as making binary, ternary composites with other materials so that the desired result can be achieved. In this report, the prepared ZnO NPs have been characterized to investigate their formation, morphology, band gap, and photocatalytic activity.

---

*Corresponding author (E-mail: drranjanajha@gmail.com)

2 Materials and Methods

Zinc acetate dihydrate and Sodium hydroxide (Pellets) [NaOH] were used as precursors, each of them was dissolved separately in 30 and 20 ml of deionized (DI) water. The ratio of the concentration of above precursors was kept 1:1. After stirring continuously for 30-40 minutes at normal temperature, [NaOH] solution was added drop-by-drop to zinc acetate dihydrate solution to form transparent white solution. The prepared solution was washed with DI water and ethanol three times and after that it was allowed to dry at room temperature. The powder was annealed for two hours at 600°C in order to obtain ZnO nanoparticles[6]. Synthesis steps of the ZnO nanoparticles are illustrated in Fig. 1.

2.1 Characterization techniques

Rigaku Ultima IV powder X-ray diffractometer (λ = 0.154nm) was used to identify the phase and structure of the prepared sample. Surface morphology of as synthesized sample was carried out by using SEM and EDS which is an attachment to SEM was used to analyse elemental composition. UV- visible technique was used for the measurement of the absorbance of the prepared sample. For this we have used UV-visible spectrometer (Shimadzu UV-2600i) in the wavelength range (200-800 nm). Photoluminescence study of the material was done by using PerkinElmer Fluorescence Spectrometer (FL 8500).

3 Results and Discussion

3.1 X-Ray diffraction analysis

X-ray diffraction (XRD) pattern of ZnO NPs, is recorded in 2-theta range of 10° to 80° with the Cu Kα radiation (λ= 0.154nm). The as synthesized ZnO NPs exhibit the diffraction peaks as shown in Fig. 2. XRD pattern identified that the well resolved peaks along the (hkl) planes (010), (002), (011), (012), (110), (013), (020), (112), (021), (004), and (022) which is in good agreement with JCPDS (file no. 98-005-7450). XRD analysis revealed that as synthesized ZnO has polycrystalline nature with hexagonal structure. From the XRD pattern, crystallite size was calculated and found to be around 18nm, using Debye Scherrer equation.

3.2 Surface morphology analysis

The morphological study of synthesized material was done by using SEM technique. Figure 3(a). revealed the pebble like spherical shape particles. The SEM micrograph showed that the synthesized ZnO nanoparticles have particle size between 50 to 150nm found to be uniformly distributed. In combination with SEM, EDS was used to find the elemental composition of ZnO nanoparticles. Figure 3(b) depicts

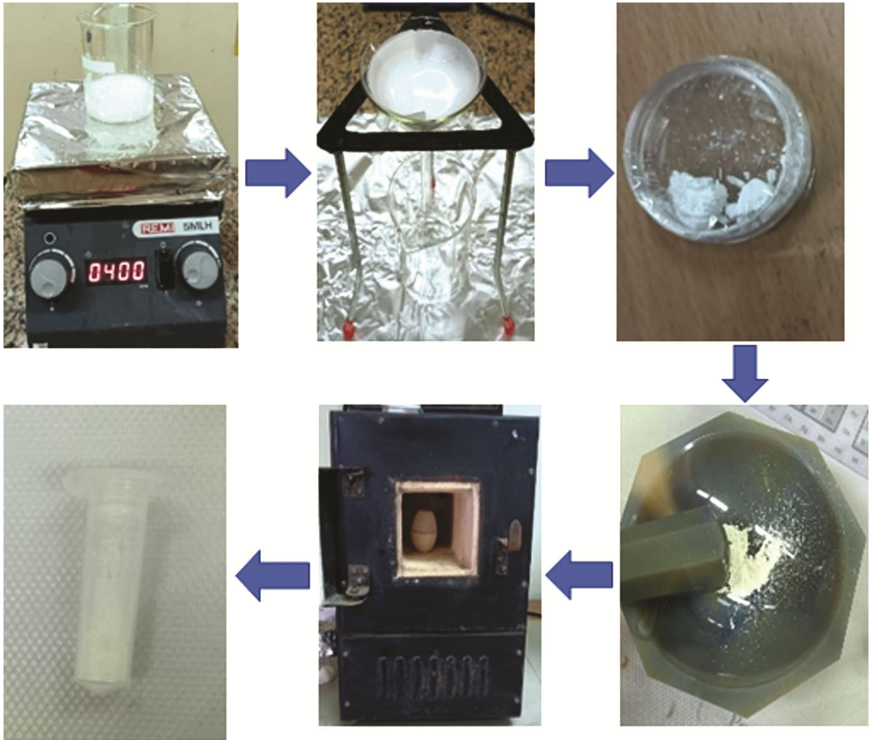

Fig. 1 — Schematic illustration for the Co-precipitation method used for the synthesis of ZnO nanoparticles.

the peaks of Zn and O elements only. Since no other elements were found in the spectra of EDS hence it indicated that the synthesized material is pure.

3.3 UV-Vis and photoluminescence spectroscopy

UV visible spectroscopy and photoluminescence (PL) spectroscopy were used to measure absorption, emission and optical spectra. A tauc plot was created using beer lambert's law to determine optical energy band gap. The Fig. 4(a) showed that the absorbance peak at 372nm which lies in UV region and optical energy band gap was found to be 3.29 eV from the slop of the Tauc plot as shown in the inset of Fig. 4(a). The tauc relation is written as:

$$\alpha h\nu = \mathrm{K}\,(h\nu - E_{\mathrm{g}})^{\mathrm{n}}$$

where α refers absorption coefficient, $h\nu$ is energy of photon, E_g is band gap energy, h is Planck's constant, ν is the frequency of wave, and K is proportionality constants and n depend on the electronic transition. Here n = ½ for direct band gap.

The Photoluminescence Spectroscopy (Fig. 4(b)) showed a sharp and strong emission peak at 390nm. It confirms the high recombination rate of e^--h^+ pairs and hence decreases the rate of photodegradation.

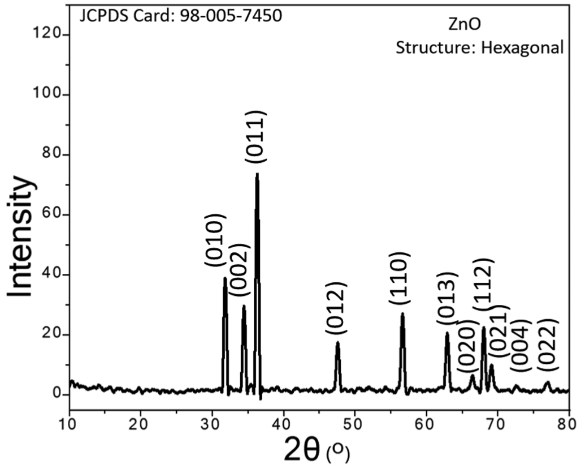

Fig. 2 — XRD pattern of ZnO nanoparticles.

3.4 Photocatalytic activity

3.4.1 Dye degradation

The photocatalytic activity of synthesized powder was looked into for photodegradation of Malachite Green (Cationic) dye aqueous solution (100ml, 10mg/L) under Solar Simulator (Xenon lamp source with power 68% = 100mW/cm^2) and the schematic illustration of dye degradation shown in Fig. 5. The degradation phenomenon was observed using UV-Vis Spectroscopy. In this experiment, dye solution (100ml, 10mgL^{-1}) was introduced along with 40mg ZnO nanoparticles as a photocatalyst.

To obtain equilibrium in adsorption- desorption, the entire system was left in dark for fifteen minutes. Here, "C_0" is the equilibrium dye concentration[7]. The UV data was taken upto 3 hours at various time interval as shown in Fig. 6. During the process centrifugation was done to extract the ZnO sample.

The following relation was used to calculate the degradation efficiency (%):

$$\%\ \text{Degradation} = [(C_0\text{-}C)\,/C_0]\cdot 100\%$$

Where 'C_0' and 'C' are the 'starting' and 'after different time interval' concentrations of dye respectively. The dye degradation peak which can be seen in the visible spectrum at 617nm, (in Fig.6) was used to quantify the degradation efficiency.

3.4.2 Mechanism

ZnO produce electron-hole pairs after absorbing UV light. The electron- hole pairs generated by UV light have the potential to go onto the catalyst surface where they will react with the surface adsorbed O_2 to produce $O_2^{\bullet -}$, as shown in Fig. 7 Which further help in degradation process. Additionally, h^+ interacts with surface-adsorbed H_2O to produce an •OH radical, it can also interact with OH to produce an •OH radical[8].

3.4.3 kinetics study

Dye degradation kinetic analysis was done and plotted as shown in the Fig. 8. It revealed the pseudo-

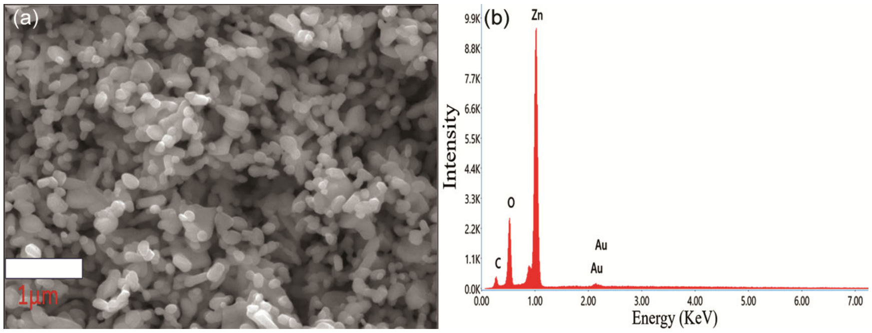

Fig. 3 — (a) SEM image of as prepared ZnO material and (b) EDS spectra shows the presence of elements.

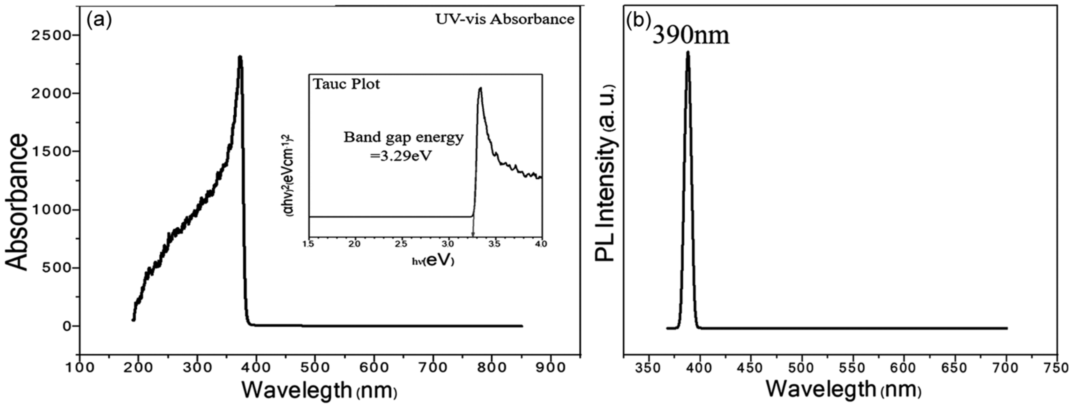

Fig. 4 — (a) The absorption spectrum of ZnO nanoparticles and its tauc plot, and (b) Photoluminescence Spectrum of ZnO.

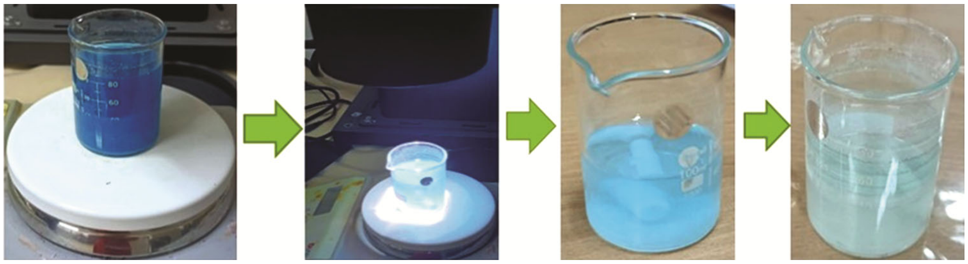

Fig. 5 — The schematic illustration of Dye degradation.

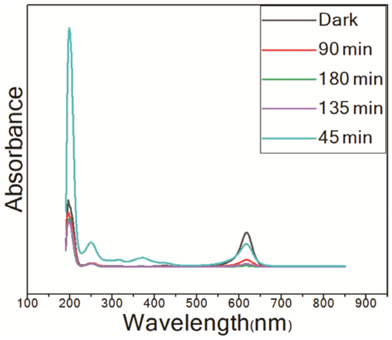

Fig. 6 — The absorption spectra of dye degradation.

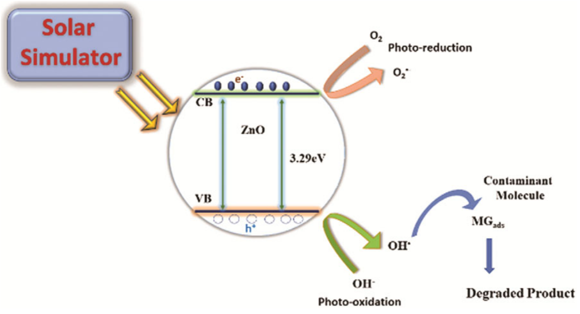

Fig. 7 — Schematic diagram for mechanism of photo- degradation in the presence of ZnO NPs under Solar Simulator.

first-order kinetics for degradation as depicted in Fig. 8. Langmuir-Hinshelwood equation as given below is used to investigate degradation kinetics.

$-\ln(C/C_0) = k_{app}t$

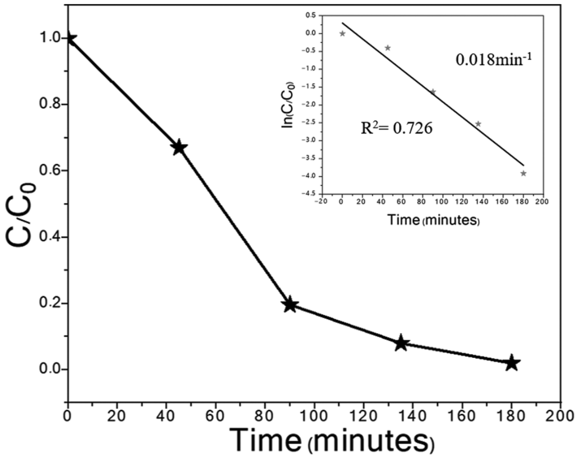

Fig. 8 — The plot showing concentration ratio (C/C_0) and pseudo-first-order reaction rate constant (k) with the function of time

Where k_{app} refers the apparent rate constant (min^{-1}), t refers the irradiation period (min), C_0 is the starting concentration of MG (mgL^{-1}) before irradiation, and C denote the concentration at a particular time concentration (mgL^{-1}). From the experimental results as shown in (Fig. 8), the apparent rate constants (k_{app}) were calculated using linear regression[9].

4 Conclusion

The preparation of ZnO NPs has been successfully carried out by the coprecipitation method. These NPs have been used as a photocatalyst to photodegrade

MG dye under Solar Simulator (Xenon lamp source with power (68% = 100mW/cm^2) light illumination. The Xenon lamp has been used to increase the degradation rate significantly, but the catalyst (40mg) has still taken 3 hours to degrade 95% of the dye (100ml, 10mg/L), indicating that the as prepared catalyst has a poor rate of degradation for the cationic dye.

The decomposition of dye with ZnO nanoparticles can be utilized in industrial wastewater treatment for the existence of mankind as well as the aquatic ecosystem with their habitats.

Acknowledgement

The authors would like to thank to the Vice-chancellor NSUT Delhi, India for providing us the opportunity to carry out research work. One of the author Anju would also like to thank Mr. Ajay Kumar (Ph.D. Scholar) for his help during the research work. Gratefully acknowledge Netaji Subhas University of Technology (NSUT) Delhi for financial support.

References

1 Sadiq H, Sher F, Saba S, Sehar S, Lima E C, Zhang S, Iqbal H M N, Zafar F, Nuhanovic M, *J Mol Liq*, 335(2021).

2 Rahman Q I, Ahmad M, Misra S K, and Lohani M, *Mater Lett*, 91 (2013)170.

3] Yang L Y, Dong S Y, Sun J H, Feng J L, Wu Q H, and Sun S P, *J Hazard Mater*, 179 (2010) 438.

4 Yarahmadi M, Ghaleh H M, Mehr M E, Dargahi Z, Rasouli F, and Siadati M H, *J Alloys Compd*, 853 (2021) 157000.

5 Chaudhari A A, Tupe U J, Patil A V, and Dighavkar C G, *IJCRT*, 10 (2022) 302.

6 Devi P G and Velu A S, *J Theor Appl Phys*,10 (2016)233.

7 Saikia L, Bhuyan D, Saikia M, Malakar B, Dutta D K, and Sengupta P, *Appl Catal A Gen*, 490 (2015) 42.

8 Yong L, Zhanqi G, Yuefei J, Xiaobin H, Cheng S, Shaugui Y, Lianhong W, Quineng W,Die F, *J Hazard Mater*, 285 (2015)127.

9 Siong V L E, Lee K M, Juan J C, Lai C W, Tai X H, and Khe C S, *RSC Adv*, 9 (2019) 37686.