



ZnO nanoparticles via *Tragia involucrata* green synthesis: Optical property and photocatalytic application

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Abstract

In the present work, UV-DRS and PL experiments were used to investigate the optical properties of the ZnO NPs synthesized by *Tragia involucrata* leaf extract. UV-DRS analysis was carried out for various temperatures such as 400 °C, 450 °C and 500 °C. The reflectance edges for ZnO NPs were found to be 362 nm, 364 nm and 367 nm and the corresponding energy gap values were 3.38 eV, 3.36 eV and 3.34 eV. With excitation wavelength at 325 nm, the PL spectra of the biosynthesized ZnO nanoparticles revealed two distinct emission bands: one in the UV region at 394 nm and another in the visible region at 577 nm. The photocatalytic activity for Methyl Violet (MV) and Rhodamine B (RhB) indicated 98 % and 92 % degradation being accomplished in 60 minutes and 80 minutes, respectively.

Keywords: *Tragia involucrata*, ZnO NP, UV-DRS, PLS, photocatalytic activity

Introduction

Nanotechnology is one of the most exciting fields of contemporary materials science study [1, 2]. Nano materials are superior and essential in many fields of human life due to their size-dependent properties [3]. Metal oxide and semiconductor nanoparticles have got a lot of coverage lately because they have a lot of interest in the fields of optoelectronics and bio-applications [4, 6]. While chemical and physical methods can produce pure and well-defined nanoparticles, they are both costly and potentially hazardous to the environment [7]. Different synthesis methods can be used to prepare ZnO nanoparticles but the green method is an eco-friendly and cost-effective method. Biological methods may be an environmentally sustainable alternative to chemical and physical methods for generating nanoparticles. Green synthesis is primarily concerned with reducing the usage of toxic chemicals in order to minimize emissions into the atmosphere. The selection of an environmentally acceptable solvent, a reducing agent, and a non-toxic stabilizing chemical are the three most important requirements for the synthesis of nanomaterials [8].

ZnO is a major metal oxide that can be grown up, is environmentally safe, and can be used in a range of applications. It has many properties that make it ideal for medical, commercial and technological applications [9]. In this work, *Tragia involucrata* leaf extract was used to make the ZnO NPs. This plant has long been used in herbal medicine to treat a number of ailments [10]. This medicinal plant can be used to treat diaphoretic, wound healing, microbial infections, constipation, hemorrhoids, giddiness, headache, asthma, fevers, diarrhea, excessive urination, vomiting, dermatoses, cold, leg and arm pain, skin eruptions, venereal diseases and fever [11]. These plants are used in Tamilnadu's Siddha medicine. The leaves were most widely used to produce a tea that was consumed to treat intestinal worms.

Synthetic dyes contaminants are a significant source of pollution in industrial effluents, which are discharged into

the atmosphere and cause severe water contamination [12]. Since most dyes are toxic and take a long time to decompose naturally, there is a pressing need to develop methods for degradation and removal of these environmental pollutants. Nano-sized ZnO, with a band gap of 3.3 eV at 300 K and a strong exciton binding energy of 60 me V, has got a lot of attention as a promising photo catalyst for photo catalytic degradation of water contaminants [13, 14].

In this paper, we present an inexpensive and easy green method for synthesizing ZnO NPs. In this work, optical property of the bio synthesized NPs were characterized using UV-DRS and PL spectroscopy. Besides, an attempt has been made, here, to investigate the Photo catalytic activity of the ZnO NPs synthesized using *Tragia involucrata* leaves.

Materials and Methods

1. Chemicals

Zinc acetate dihydrate was acquired from Sigma Aldrich (Mumbai, India) and used as a precursor in the present work. *Tragia involucrata* leaves, found all along the roadside, have been used as a bio agent and were collected in the vicinity of Chidambaram town, Cuddalore district, Tamil Nadu, India, during the month of May, 2019.

2. Preparation of ZnO nanoparticles

The healthy leaves were washed with tap water to remove the dust that had adhered to the leaves' surface. After initial washing, the leaves were carefully washed and wiped with the filter paper. A known quantity of leaves (10 g) was added into 100 ml of distilled water. On a temperature controlled hot plate, it was heated for 45 minutes at 60 °C. Furthermore, the extract was filtered (using Whatman No.1 filter paper) before being used for further experimental research.

A temperature controlled hot plate was used to heat 50 ml of the filtrate to 60 °C. 5 g of the precursor was then added and

slowly stirred until the solution becomes paste-like. To remove organic impurities, the paste was carefully gathered in a crucible and kept in a muffle furnace for two hours. After 2 hours, the prepared ZnO NPs were used for further analyses [15].

3. Characterization techniques

UV-Visible - DRS spectra were recorded using Varian model 5000 Spectrophotometer. Luminescence behavior of the prepared samples was studied using the FLUOROLOG-3 Spectrophotometer.

4. Photocatalytic activity

The degradation of Methyl violet (MV) and Rhodamine B (RhB) in aqueous solutions using sunlight as a radiation source was used to test the photocatalytic behavior of synthesized ZnO NPs. 4-10M dye solutions were prepared by dissolving in 500 ml distilled water to achieve optimal concentrations for both dyes. For the degradation step, 50 mL of dye solution was placed in a 100 mL beaker, along with the catalyst (20 mg for MV and 30 mg for RhB). A magnetic stirrer was used to stir the whole solution. For the UV analysis, the solutions of both dyes were collected for every 10 minutes.

Results and Discussion

1. UV-DRS analysis

UV-DRS (Diffused Reflectance Spectroscopy) analysis of the biogenic ZnO NPs synthesized with *Tragia involucrata* leaf extract, calcined at 400 °C (TZ 1), 450 °C (TZ 2) and 500 °C (TZ 3), was carried out and represented as Fig 1a. Here, UV-DRS technique was adopted to analyze the Optical behavior of ZnO NPs synthesized using the *Tragia involucrata* leaf extract. As expected, the reflectance edges for ZnO NPs corresponding to different samples such as TZ 1, TZ 2 and TZ 3 rose to 362 nm, 364 nm and 367 nm. Fig. 3.1a indicates a red shift in the edge wavelength of the reflection band with corresponding increment in temperature [16, 18]. The band gap was found using the Kubelka-Munk equation [19],

$$F[R] = \frac{[1-R]^2}{2R}$$

Where R = relative diffusion reflectance.

The graph plotted between $h\nu$ and $[F(R), h\nu]^{1/2}$ (in Fig. 1b) shows the energy gap values of 3.38, 3.36 and 3.34 eV corresponding to TZ 1, TZ 2 and TZ 3, respectively [20].

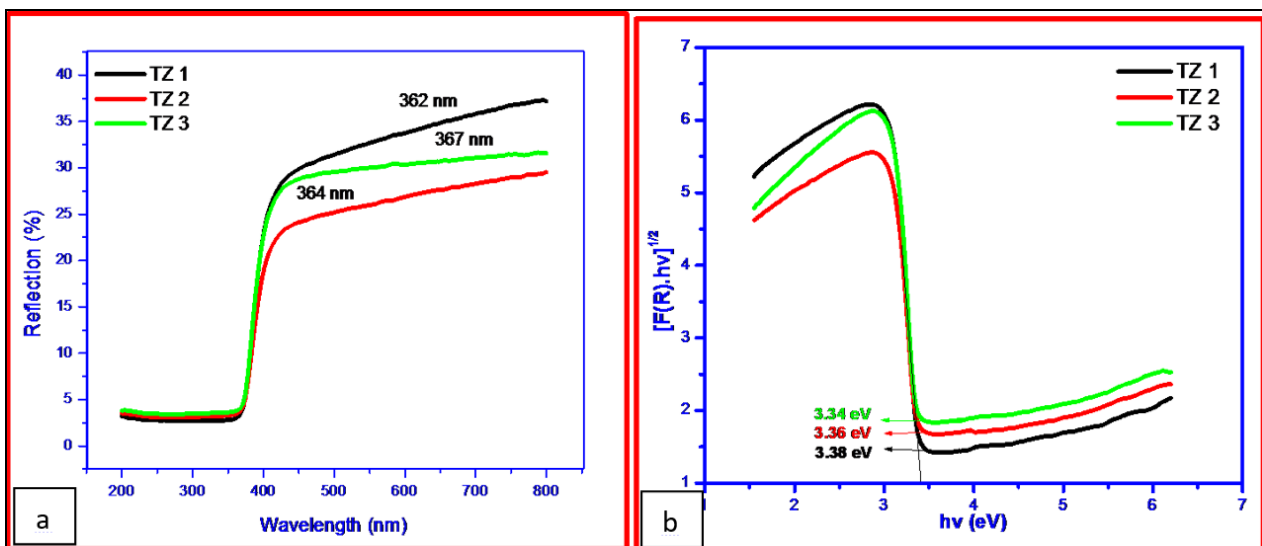


Fig 1: a) Reflectance spectra and b) K-M plot of biosynthesized ZnO NPs using *Tragia involucrata* leaf extract

The energy gap values were also calculated by using following energy equation:

$$E = h\nu = \frac{hc}{\lambda} = \frac{1240}{\lambda}$$

Where h = Planck's constant = 6.62176×10^{-34} J s,

c = speed of light = 3×10^8 m/s,

λ = absorption edge or reflectance edge

and the calculated values are 3.42 eV (TZ 1), 3.40 eV (TZ 2) and 3.37 eV (TZ 3), respectively. These band gap values are almost matching with the values found by the K-M plot (Fig. 3.1b).

2. Photoluminescence spectral (PLS) study

PLS method was used to analyze the luminescence property of the prepared ZnO NPs. The spectra were recorded with the excitation wavelength at 325 nm (Fig. 2). The excitation energy (3.8 eV) used is greater than the ZnO band gap (~3.4 eV). Thus, it is possible to directly excite an electron in the valence band to the conduction band; additionally, it was feasible to excite even the electrons present well inside the band gap [21]. These spectra exhibit two sharp emission bands: one in the UV region at 394 nm and another in the visible region at 577 nm. Earlier researchers [22, 24] propose that the PL spectrum of ZnO NPs typically consists of two emission bands: one in the UV region (about 370 nm to 400 nm) and the other in the visible region (about 400 nm to 700 nm).

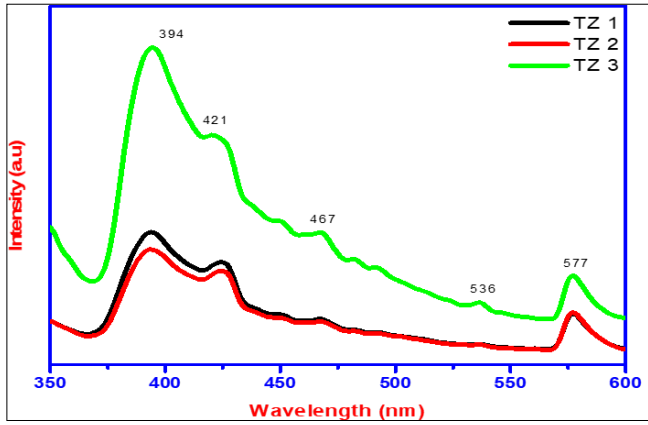


Fig 2: PL spectra of bioinspired ZnO NPs using *Tragia involucreta* leaf extract

The peak at 394 nm refers to ZnO Near-band edge (NBE) emission and is due to free exciton radiative recombination [25, 26]. The recombination of electrons with strongly locked holes at ~2.2 eV below the conductive band will trigger yellow band at 577 nm [27, 28].

The intensity of the band in UV region increased with increasing temperature, but the decrease in intensity for 450 °C, may be due to particle size reduction leading to large surface area. The large surface area will capture more atoms and thereby increases the trapping rate of photo generated holes, which in turn enhances the strength of the emissions [29].

SEM examination pointed out nano-rod shaped structures for the ZnO nanoparticles biosynthesized using *Tragia involucreta* leaves [11]. This finding is consistent with what has been recorded for the nanorods and nanotubes whose PL spectrum consists mainly of a solid, sharp UV emission band and a weak visible emission band [23, 30, 31].

3. Evaluation of photocatalytic activity

The UV-Vis spectra were recorded and peaks were found to be at 245, 299 and 575 nm (prominent peak) for MV and 260, 357 and 554 nm (prominent peak) for RhB (Fig. 3 a & b). After adding the catalyst into dyes the absorption peaks began to disappear and the spectrum were recorded for the solutions collected for every 10 minutes.

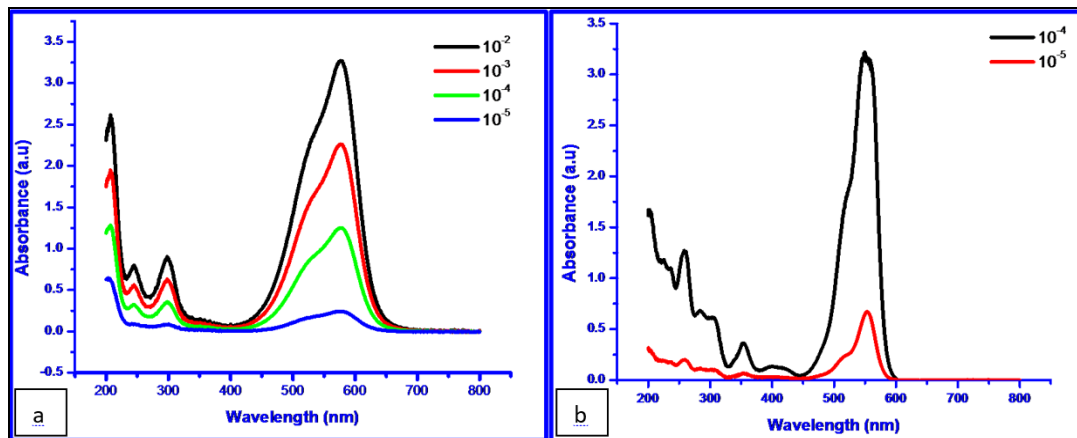


Fig 3: a & b UV-Vis spectra of MV and RhB for different molar concentrations

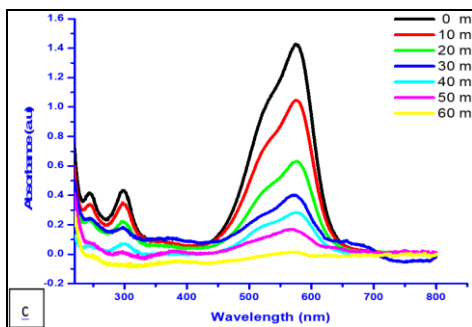


Fig 4: c Photocatalytic degradation of Methyl violet (MV)

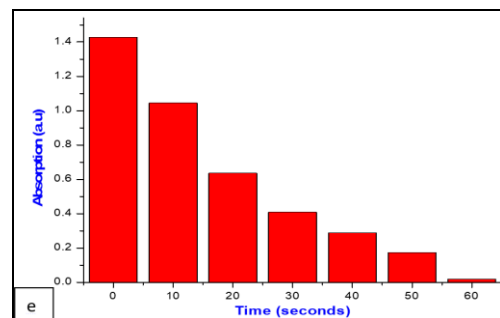


Fig 6: e Absorbance of MV for different degradation times

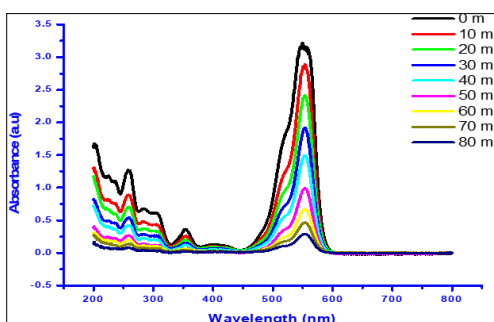


Fig 5: d Photocatalytic degradation of Rhodamine B (RhB)

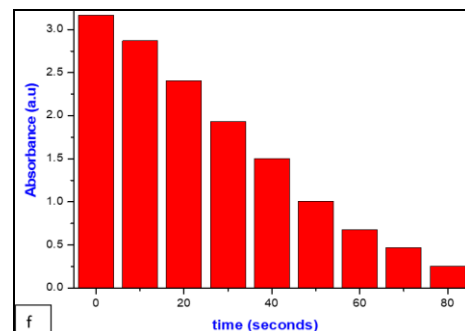


Fig 7: f Absorbance of RhB for different degradation times

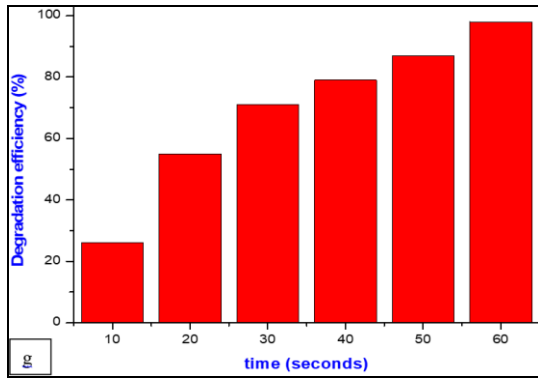


Fig 8: g Degradation efficiency of MV for different degradation times

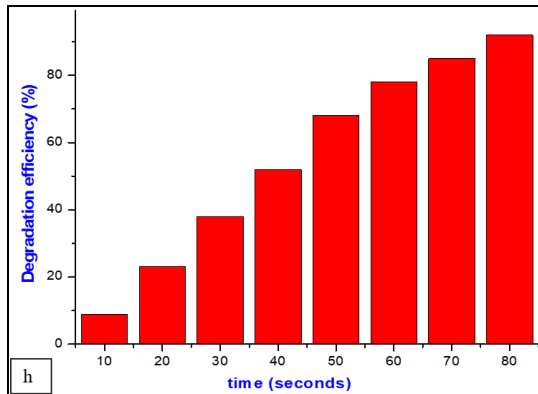


Fig 9: h Degradation efficiency of RhB for different degradation times

The peaks at 245 nm and 299 nm for MV and 260 nm and 357 nm for RhB almost disappeared in 30 and 50 minutes of time respectively. The peaks at 575 nm for MV and 554 nm for RhB were lost in 60 minutes and 80 minutes, with 98 % and 92% of degradation (Fig. 3 c & Fig. 4 d). Fig. 3.3 e & 3.3 f are the bar diagram plotted between time and absorption which clearly explains the degradation of MV and RhB. The degradation efficiency was calculated using the following equation [32, 33]:

$$\text{Photo degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 - initial absorbance of the dye and C_t - absorbance of the dye solution after irradiation with sun light.

Fig. 8 g & h are the bar diagram plotted between time and degradation efficiency which explained clearly the rate of degradation of MV and RhB. The kinetic study of ZnO NPs for degradation of MV and RhB was carried out using Langmuir – Hinshelwood Kinetic model by using equation [34],

$$\ln \left(\frac{C_0}{C_t} \right) = kt$$

where t is irradiation time and k is Pseudo first order rate constant. The rate constant (k) can be obtained from the slope of the graph drawn between $\ln (C_0/C_t)$ and time. The calculated values were found to be $4.40 \times 10^{-2} \text{ min}^{-1}$ and $2.39 \times 10^{-2} \text{ min}^{-1}$ for MV and RhB, respectively (Fig. 3.3 I & j).

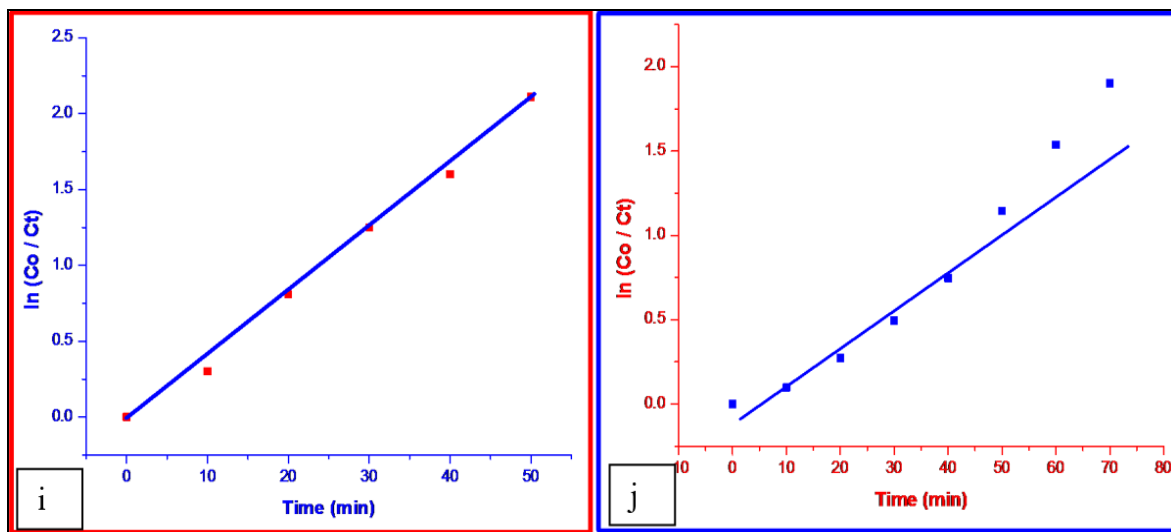
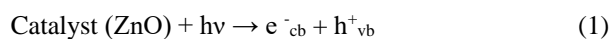


Fig 10: i & j Rate constant curve for MV and RhB

1. Mechanism of Photocatalytic activity

When a ZnO nanoparticle is exposed to sun light, electrons are advanced from the valence band to conduction band, resulting in the formation of an electron-hole pair (equation 1).



where e^{-}_{cb} and h^{+}_{vb} represent the conduction band electrons and the electron vacancies in the valence band. These two entities may move to the catalyst surface, where they may enter in to a redox process with other species presented on the surface. Generally, h^{+}_{vb} can respond effectively with

surface-bound H_2O to create OH^{\bullet} radicals, while e^{-}_{cb} can respond with O_2 to create superoxide radical anion of oxygen (equations 2 and 3) [35].



These reactions can lead to the combination of the electron and the hole which are created in the first step. The reactions of OH^{\bullet} and $O_2^{\bullet -}$ with the dye may result in the formation of other species and may thus be responsible for the degradation of the dye (equations 4 and 5) [36-39].



Fig 3.3k portrays the whole mechanism of photo catalytic degradation of the dye using biogenic ZnO nanoparticles.

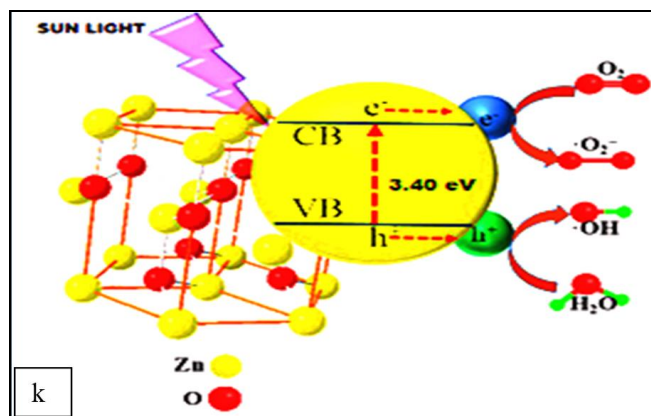


Fig 11: k Mechanism for photo catalytic degradation of dyes using ZnO photo catalyst under sun light

The current study uses ZnO NPs as catalyst to investigate photocatalytic degradation of MV and RhB dyes while exposed to sunlight for various periods of time. Thus, the bioinspired ZnO NPs, using *Tragia involucrata*, can be envisaged for handling colored industrial effluents and conserving large quantities of water, particularly in countries where clean water is scarce.

Conclusion

In the present study, the ZnO NPs have been synthesized in a simple, efficient and cost-effective biological method by using *Tragia involucrata* leaf extract. The Optical behavior of the synthesized ZnO nanoparticles was studied using UV-DRS technique and the band gap was found to be ~3.34 eV. The prominent emission band at 577 nm indicated the luminescence property of the biosynthesized nanomaterial. The prepared ZnO NPs exhibited a good Photocatalytic activity for the dyes of MV and RhB, with 98 % and 92 % of degradation, respectively.

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Declaration

The authors declare that they have no known competing financial interests in this research work.

Disclosure Statement

No potential conflict of interest was reported by the authors

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