

Green synthesis of ZnO Nanoparticles using Amla Extract and its Degradation of Methylene Blue Dye

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Received: 6th Feb 2023, Revised and Accepted: 12th Feb 2022

ABSTRACT

ZnO nanoparticles have been synthesized by a very simple, cost effective and environmental friendly route by using powdered ZnSO₄ and Amla extracted solution as a precursor. The synthesized nanoparticles have been characterized in detail using UV-visible spectroscopy, X-ray diffraction (XRD), Thermo gravimetric analysis (TGA) and Scanning electron microscopy (SEM). The synthesized ZnO nanoparticles have been further used as a catalyst for the photocatalytic degradation of methylene blue dye.

Keywords: ZnO nanoparticles, Uv-Visible, SEM, Methylene blue.

1. INTRODUCTION

Zinc Oxide (ZnO) is one of the most promising semiconductor materials since it has numerous applications. It has excellent optical, ultra-violet properties, good thermal and chemical stability [1]. It has exclusive applications in anti-reflection coating, used in solar cells [2] as transparent electrodes and as a photocatalytic material in degradation of complex organic compounds. The contamination of water by organic pollutants has been a major environmental problem worldwide. In textile industries, the process of dyeing results in the production of wastewater with intense coloration [3,4]. The various conventional technologies used for purification of dye wastewater amount to high operation and maintenance cost along with energy consumption. [5,6] In the past few years advanced oxidation processes such as ozonation, photocatalysis and Fenton process have been widely developed for the elimination of organic dyes. [7] In the present work, ZnO nanoparticles have been synthesized by using a simple, cost effective and environmental friendly method by using ZnSO₄·7H₂O and Amla extracted solution.

2. EXPERIMENTAL

In this study, Amla extracts at the concentration (90%) were prepared with distilled water, the volume was made up to 100 ml. Subsequently, zinc sulphate (9.40 g) was dissolved in the Amla extract solution under constant magnetic stirring (120 min.) and left at rest for 12 h. The suspension

was calcined in a muffle furnace at temperatures (250 °C) for 1 h and dried. The dried precursor was crushed into powder using mortar and pestle. The precursor was characterized by thermogravimetric –differential thermal analysis (TG-DTA), Perkin Elmer Instrument to determine the thermal decomposition and crystallization temperature which was found to be above 370^o C. The dried precursors and calcined samples of ZnO were characterized by powder X-Ray Diffraction (XRD) using X-Ray diffractometer. The particle size and morphology of the calcined powders were characterized by Scanning Electron Microscopy (SEM, Zeiss). The elemental analysis of the powdered ZnO was done by Energy Dispersive X-Ray spectroscopy (EDAX). The optical absorption spectra were measured in the range 200-800 nm using UV-VIS spectrophotometer (Shimadzu, Japan).

3. RESULTS AND DISCUSSION

The UV-Visible absorption spectra of ZnO sample (Figure 1) exhibit a strong absorption spectra with a well-defined absorption peak at around 380 nm. The band gap energy of the synthesized ZnO nanoparticles at 250^o C is determined by using Tauc plot and found to be in the range 3.132 eV. This value is lower than that of 3.321 eV for Er-doped ZnO nanoparticles in the literature. [8]

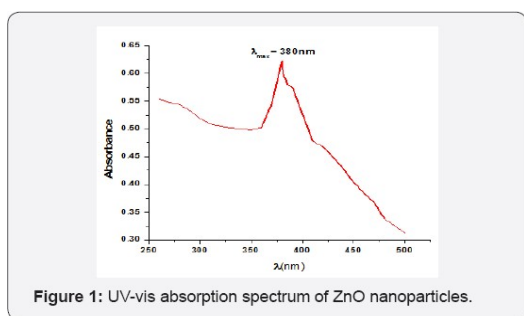


Figure 1: UV-vis absorption spectrum of ZnO nanoparticles.

Thermo gravimetric-differential thermal analysis (TG-DTA) curves of ZnO precursor are shown in Figure 2. The TG curve in Figure 2 shows slight weight loss from 150°C to 222°C with a major weight loss step from 245°C to 320°C and no further weight loss above 320°C. On the DTA curve (Figure 2) a main exothermic effect was observed between 40°C and 140°C with a maximum at about 95°C indicating that the thermal events can be associated with the burnout of organic species involved in the precursor powders (organic mass remained from Amla extract) of the residual carbon or due to direct crystallization of Nano crystalline ZnO from the amorphous component.

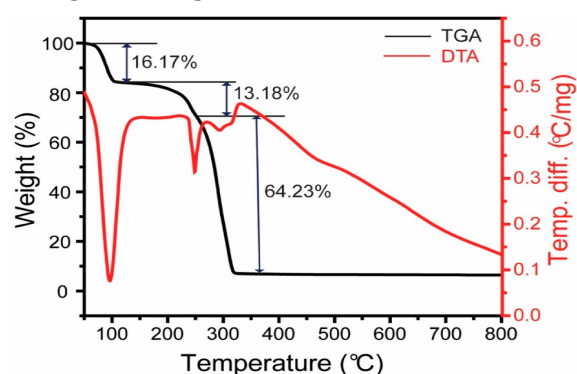


Figure - 2: TG-DTA curves of thermal decomposition of ZnO precursor at 10°C / min in static air.

The XRD patterns of ZnO sample is shown in the Figure 3. All of the detectable peaks (Figure 3) can be indexed as the ZnO hexagonal crystal structure in the standard data (JCPDS File Number - 800075). The ZnO nanoparticles have grown in polycrystalline nature, which is exhibited in the appearance of a number of XRD peaks attributed to different crystalline orientations. The average crystalline size of the products was estimated from XRD peaks by using the following Scherer equation

$$t = 0.9\lambda / B \cos \theta$$

Where t = particle size, λ is the wavelength of the incident x-ray beam, θ = the Bragg's diffraction angle, B = Full width at half maxima of the ZnO peak. The calculate size of nanocrystallites was in the range of 18-38 nm.

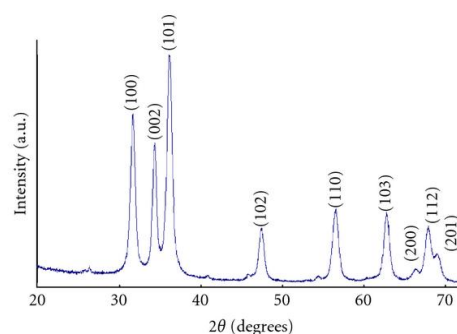


Figure - 3: XRD Patterns of Nano crystalline ZnO samples calcined in air for 1 hr.

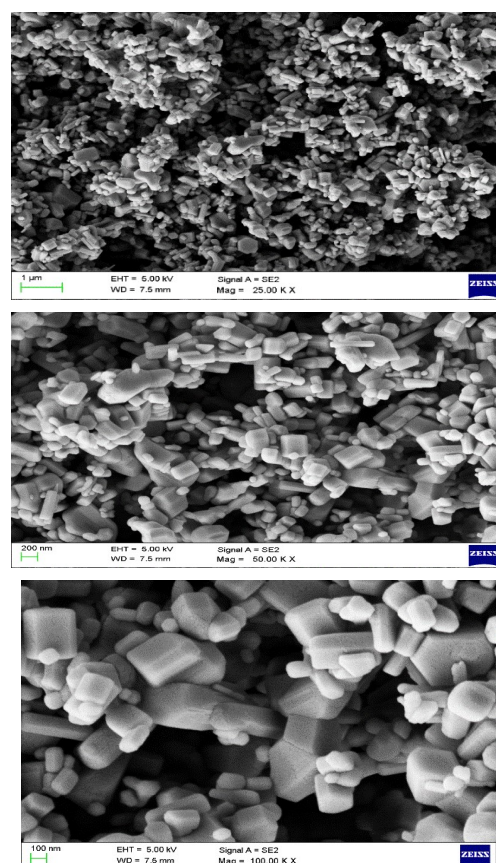


Figure 4(a).SEM images corresponding to selected area patterns of Nano crystalline ZnO

Figure 4(b).TEM images with corresponding to selected area electron diffraction of Nano crystalline ZnO.

The morphology and structure of the ZnO Nano crystallites were investigated by Scanning Electron Microscopy (SEM) Figure 4 (a) showing ellipsoids, rods and flake-like structures. It is clear from the TEM Figure 4(b) that the ZnO nanoparticles have been synthesized successfully lying in the range of particle size 5-50 nm in diameter.

Figure 5 depicts the EDS spectra of ZnO sample. The EDS analysis display the optical absorption peaks of ZnO nanoparticles and the absorption peaks of Zn and O have been observed , which substantiate the presence of Zn & O element in the synthesized sample.

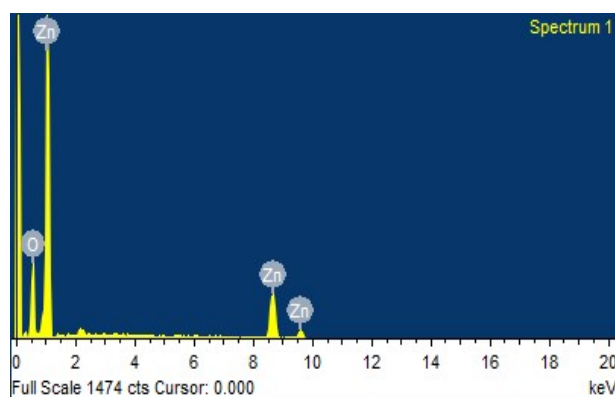


Figure - 5: Energy Dispersive X-Ray Spectrum exhibiting characteristic X-ray peaks of Zn and O corresponding to the composition of ZnO Nanoparticles.

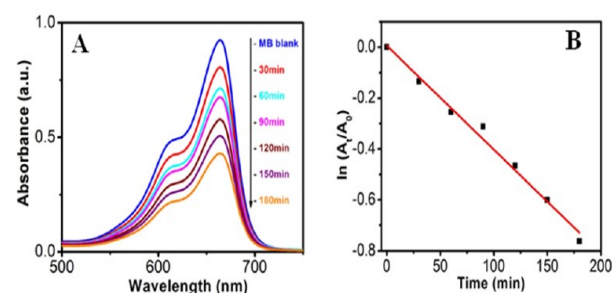


Figure - 6: Degradation of Methylene Blue Dye with 1 mM dye solution with 0.01 gm. ZnO nanoparticles with time.

Degradation of dye: The addition of ZnO nanoparticles to methylene blue dye resulted in its photo catalytic degradation in the presence of UV-light. The complete photo degradation of 2.5 ppm methylene blue in the UV light occurred in 30-180 minutes. The experiment was conducted to understand the mechanism for the degradation of the MB dye using ZnO nanoparticles. The dye solutions were stirred in dark for 30 minutes prior to ultra-sonication to ensure that the equilibrium adsorption/desorption of the substrate on the catalyst has been attained. The suspensions afterwards were placed in a ultrasonic bath apparatus producing 50 kHz ultrasonic waves for

definite time interval of 5 minutes. After ultrasonic irradiation samples were withdrawn from the reservoir, centrifuged and changes in absorbance were measured by UV-Vis spectrophotometer. The experimental conditions adopted throughout the whole investigation were initial concentration of 1mM dye added to 10 mg of catalyst under ultrasonic irradiation of 50 kHz frequency.

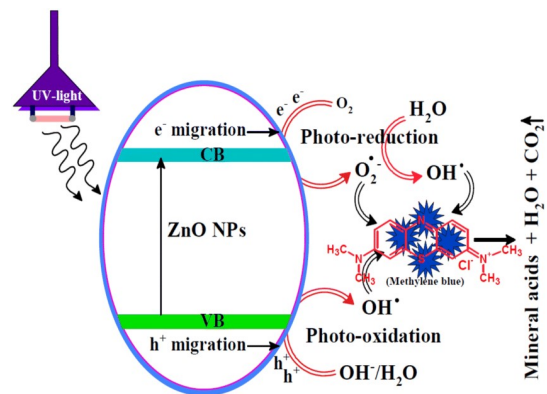


Figure - 7: Schematic diagram showing the mechanism of degradation of MB dye with ZnO nanoparticles.

Mechanism of degradation: On addition of semi-conducting catalyst, formation of hotspots caused by ultrasonic surface cavitation not only induces sonolysis of water but also couples with the catalyst to produce electron-hole pairs.(Figure7). During ultra-sonication, electron in the valence band of ZnO nanoparticles transit to respective conduction band. The electron transfer rate can be driven by thermal radiation generated from the collapse of cavitations bubbles. The trapped electron gets readily transferred to oxygen molecules to produce superoxide radical ion and trapped hole gets readily transferred to hydroxyl ion [9] which acts as radical scavengers in the degradation of MB dye.

4. CONCLUSIONS

In the reported work, a simple green approach for obtaining ZnO nanoparticles by using hydrothermal method has been used. The physico-chemical characterizations have revealed the morphology and particle size of these nanoparticles. The synthesized ZnO nanoparticles have been effectively utilized for the photo catalytic degradation of MB dye in ultraviolet radiations by ultra sonication.

5. REFERENCES

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