Effect of microwave irradiation power for the morphological changes of ZnO nanoparticles

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Abstract. The present investigation focuses on the effect of microwave watt power for the synthesis of ZnO nanoparticles (NPs) by microwave irradiation using two different precursors. The prepared samples were confirmed by XRD, SEM and EDXA to analyse the particle size, morphology and chemical composition of ZnO NPs. SEM images were recorded for the synthesis of ZnO NPs from different watt power using different precursors to analyse the morphological changes. The particle size was calculated by Debye-Scherrer formula using XRD pattern. Apart from that, the band gap was calculated from UV spectroscopic technique. The results confirmed that by increasing the watt power ranging from 240 to 420, a wurtzite structure (flower-like) are formed. By changing the zinc acetate with zinc sulphate at various watt powers, the morphology of ZnO NPs changes from spiral to tubular shaped particles were formed.

1. Introduction

Recently, metal oxide nanomaterials have been a major potential material for various engineering applications ¹. Among the metal oxides, ZnO nanoparticles have shown the significant importance and their excellent properties in both technical and fundamental applications. These ZnO nanoparticles have semiconductor material with high band gap energy (3.2-3.60 eV), which has great attention in optoelectronics ², solar cells ³, gas sensors ⁴ and catalysis ⁵. There is a high specific surface area of ZnO NPs and their electrostatic behavior it mainly used in the field of biomedical applications ⁶. In attention to that due to the neutral hydroxyl group on the surface of ZnO nanomaterial plays a key role in the charge behavior ⁷. The ZnO NPs were synthesized by using microwave irradiation technique. In this method proved as a cost-effective ⁸, reduces the particle size with narrow particle distribution ⁹, increases the yield and purity compared to that of a conventional method. Currently, the microwave irradiation technique is often used for the rapid synthesis of micro- nanostructures of different morphologies by varying the reaction conditions. Like nanorods, flower-like, flakes, hexagonal tube, and spherical tubes. However, the effect of the microwave irradiated power and the influence of the precursor on the morphology and optical properties of ZnO NPs were rarely reported ¹⁰-¹².

In the present study focused on the synthesis of ZnO nanoparticles with zinc acetate and zinc sulphate used as a precursor by microwave irradiation of nanoparticles in an aqueous medium and the influence of microwave watt power and precursors on the structural morphology and optical properties of ZnO NPs.

2. Materials and methods:

2.1 Chemicals

Chemicals were purchased from different distributors like Sigma Aldrich, Merck etc. Analytical reagent grade chemicals were used in the experiment and were used without further purification. Milli-Q water was used throughout the analysis.
2.2 Microwave irradiation method for the synthesis of ZnO nanoparticles.
0.5 M zinc ion concentrations were dissolved in 50 ml of deionized water in a round bottom flask. Then, ammonia (NH₃) solution was added to the flask until the pH reached 9. The subsequently prepared sample was irradiated with a microwave oven for 20 minutes at different watt power i.e 240, 360 and 420 W. The obtained zinc oxide nanoparticles are centrifuged and washed with 1:1 water and ethanol. Thereafter, the sample was dried at 80 °C for about 5 hours in a hot air oven. The schematic representation of the synthesis of ZnO nanoparticles is shown in figure 1.

![Figure 1 Schematic representation of Microwave irradiation method for the synthesis of ZnO nanoparticles](image)

2.3 Characterisation of ZnO nanoparticles
Prepared ZnO NPs were confirmed by X-ray diffraction spectroscopy (RIGAKU smart lab X-ray Diffractometer operating at 40 kV), structure and composition of ZnO NPs were recorded by Scanning electron microscopy and Energy dispersive X-ray analysis was carried out by (GEMINI ULTRA 55). Absorbance were recorded by ELICO made SL-159 UV–visible spectrophotometer.

3. Results and Discussion:

3.1 Structural Characterisation
The XRD spectrum for synthesized ZnO nanoparticles with two different precursors showed in figure 2. All the obtained peaks are well matched with JCPDS card no (03-065-3411) and JCPDS card no (01-080-0075) with no impurity peak for nanoparticles synthesized from zinc acetate and zinc sulphate precursor respectively. A most intense peak is at the Bragg angles (2θ) = 31.71, 34.35, 36.20 for ZnO NPs synthesized using zinc acetate as precursor. Similarly, ZnO NPs synthesized using zinc sulphate as precursor, most intense peak located at the (2θ)= 31.75, 34.45, 36.50. all these respective peaks are of high intensity corresponds to the Miller indices (1 0 0), (0 0 2) and (1 0 1) respectively. The most intense and sharp peak indicates the synthesized ZnO NPs with high purity and crystalline nature. The obtained data confirmed that the synthesized NPs have a hexagonal wurtzite structure with the average crystallite sizes (D) of ZnO NPs were calculated as follows using the Debye – Scherrer equation. The average crystal sizes of ZnO NPs with different precursors were found to be 50 nm and 73 nm.
\[ D = \frac{K\lambda}{\beta \cos \theta} \]

Where, \( K \) - Debye constant, \( \lambda \) - wavelength of the X-ray source, \( \beta \) - full width at half maximum of the diffraction peak, and \( \theta \) - Bragg angle of an intense peak. The EDXA images for the ZnO NPs are represented in the figure 3. It is a good corresponding agreement with the XRD pattern. There is no impurity peak or trace elements are observed. It confirms the synthesized ZnO NPs with high purity.

**Figure 2** XRD spectra for ZnO NPs synthesized by zinc acetate precursor (top) and zinc sulphate precursor (bottom)
The FESEM images for ZnO NPs synthesized by using two different precursors i.e. zinc acetate and zinc sulphate are represented in figure 4. In figure 4a, represents the zinc acetate precursor used for the synthesis of ZnO NPs with different watt power. Initially, ZnO NPs irradiated with 30 minutes at 240 watt power exhibited a needle-shaped morphology. There are slight changes from the figure 4b and 4c. As the microwave watt power is increased from 240 to 420, the morphology of the ZnO NPs are completely changed into the wurtzite structure. A common trend has been observed for zinc sulphate precursors used for the synthesis of ZnO NPs are shown in figure 4d, 4e and 4f. Initially, the nanoparticles shown in the spiral morphology then get changes to tubular structure while increases the watt power. Gusatti et al. 13, phlegmatic influence of the precursor on the structural changes of ZnO NPs, the zinc acetate precursor was replaced by zinc nitrate and hydrazine hydride used as reducing agent. In figure 4, clearly indicates that the changing the morphology of nanoparticles is strongly dependent on the effect of the precursor and irradiation power.
Figure 4 FESEM images for ZnO NPs form zinc acetate precursor at different watt power a. 240 Watt power, b. 360 Watt power and c. 420 Watt power and zinc sulphate precursor at different watt power a. 240 Watt power, b. 360 Watt power and c. 420 Watt power
3.2 optical characterization

The absorption maximum of ZnO NPs was observed at 365 and 371 nm that shows the blue shift related to the electronic transitions and the quantum confinement effect along with band gap energy shown in figure 5. The band gap energy (E_g) of synthesized ZnO NPs was calculated using Tac plot by the following equation.

\[ E_g = h\nu \]

Where, h - plank constant and \(\nu\) - frequency \((\nu = c / \lambda)\). In the present study, the \(E_g\) value found in the range 3.322 -3.602 eV. As reported in the literature \(^{12}\), the \(E_g\) value for ZnO was found to be 3.37 eV.

![UV spectra and Tac plot for ZnO NPs](image)

**Figure 5** UV spectra (left) and Tac plot (right) of ZnO NPs for different precursor solution i.e. a. Zinc sulphate (red) and b. Zinc acetate (black)

4. Conclusions

ZnO NPs were successfully synthesized by microwave irradiation method with two different zinc precursors. XRD data confirms that synthesized ZnO NPs are of high purity and crystalline nature. The result obtained from EDXA analysis is good corresponding agreement with the above results. The key observation was that the nanoparticles synthesized from zinc acetate were well organized and changed the morphology into a wurtzite structure to change the watt power from 240 to 420 watts. However, the morphology of ZnO synthesized from zinc sulphate slightly changes from spiral to tubular morphology due to change in watt power. The band gap energy for ZnO NPs found to be 3.34-3.602 eV, which is higher than that of the bulk material. The main focus is to expand the study by using these nanoparticles for their efficiency in various applications such as optoelectronics and mechanical fields.

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