International Journal of Advanced Interdisciplinary Sciences

Vol.1, Issue.1, August 2021, 38-48

Green Synthesis of ZnO/MgO Nanocomposites and their Optical Studies

Chithra P G[a,*], Poornima Vijayan P[a], Vijayalekshmi V[a], Renjini S[a]

a. Department of Chemistry, Sree Narayana College for Women (affiliated to University of Kerala), Kollam, Kerala-691001

*Corresponding author: chithrasumej@gmail.com

Abstract

Present study highlights the synthesis of ZnO/MgO nanocomposites from *Allium Sativum* extract through green route. Here, *Allium Sativum* extract act as reducing as well as stabilizing agent. The biosynthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform Infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), Energy dispersive X-ray analysis (EDAX) and UV-Visible spectroscopy (UV-Vis). The average particle size calculated using XRD is in the range 18-22 nm. The formation of ZnO/MgO in Nanoflake morphology was confirmed from FESEM analysis. The presence of Zn, Mg and O in the prepared nanocomposite was confirmed by EDAX analysis. The band gap calculated for ZnO/MgO nanocomposite is 4.7 eV. The photoluminescence (PL) emission spectrum of ZnO/MgO is at 469 nm and 470 nm and make them promising candidate for blue light emitting devices.

Keywords: Nanomaterials, Green synthesis, Optical properties

Article History: Received 29 May 2021; Revised 1 July 2021; Accepted 7 July 2021; Published 16 July 2021.

1. Introduction

The emerging interdisciplinary science ‘Nanotechnology’ deals with materials and structures having one billionth to one hundred billionth of a meter in size. New fascinating properties, which are substantially different from their bulk counterpart, are obtained when the dimensions of matter change by a few nanometers. This would result in the creation of new usable materials and technical advancements [1-3]. The newly formed materials are called ‘nanomaterials', in which tunable nanoscale structures have a dominant effect on desired behavior of the end product [4-6].

Even though, nanotechnology offered technological advancement, there are some serious environmental concerns over the production and usage of nanomaterials [7]. The nanomaterial synthesis through various physical and chemical routs produces massive amounts of pollution and hazardous byproducts in the atmosphere. Considering this, ‘green chemistry’ for nanoparticle processing is getting much attention, which ensures safe, non-toxic and environment friendly methods [8, 9]. Recent developments of an environment friendly approach for the biological synthesis of nanomaterials are of significant importance in the different fields especially in environmental and biomedical applications [10]. Plant-mediated synthesis have been extensively reported for many metals and metal oxide nanoparticles including gold (Au NPs) [11], silver (Ag NPs) [12], copper (Cu NPs) [13], magnesium oxide (MgO NPs) [14], zinc oxide (ZnO NPs) [15] and many more.

Among the popular metal oxide nanoparticles, MgO and its composites getting much attention due to wide band gap, excellent thermal stability, low electrical conductivity, low refractive index and catalytic behavior [16, 17]. MgO nanoparticles and its nanocomposite with ZnO (ZnO/MgO nanocomposite) has been developed with superior semiconducting, optical, biological and catalytic properties. Both MgO and ZnO are safe for human being. The green synthesis of ZnO/MgO nanocomposite (ZnO/MgO) further lineup with the ecofriendly production of nanomaterials by avoiding the usage of toxic chemical sand solvents.

The current research focuses on an economical and simple green approach to synthesis ZnO/MgO nanocomposites using *Allivum sativum* (Garlic) extract for the first time. Here, the plant extract act as a reducing and stabilizing agent for the nanoparticles conversion. The phytochemical compounds present in plant extract are behind these reducing and stabilizing action. This study aims to conduct morphological and chemical characterization of the prepared ZnO/MgO nanocomposites. More importantly, the optical properties of nanocomposite will be explored.

2. Materials and Methods

2.1.Materials

The extract used for the preparation of ZnO/MgO nanocomposites was made using 25g *Allium Sativum* and 250 ml distilled water. The extract was mixed in a magnetic stirrer at 25 ^{o}C for 30 minutes. After stirring the extract was cooled and filtered using filter paper. Analytical grade Zinc Nitrate and Magnesium nitrate were purchased.

2.2.Synthesis of ZnO/MgO nanocomposite

For the synthesis of ZnO/MgO nanocomposite, the *Allium Sativum* extract was mixed with about 5g of magnesium nitrate and 5 g zinc nitrate and boiled to 70 °C using a magnetic stirrer for 1 hour. Then it is concentrated using a burner, and precipitate has been collected in a crucible. It was then heated in a muffle furnace for 2 hours at 600 °C. A white colored powder obtained was collected and grinded in mortar.

2.3.Characterization

The crystalline characteristics of the nanocomposite were determined by Powder X-ray diffraction technique using Bruker D8 ADVANCE. Atomic force microscopic images of the samples were taken using Bruker Dimension Edge. In order to take AFM images, the nanoparticles were first dispersed in alcohol, followed by placing a drop of this solution on a glass plate and dried.Fourier transform infra-red spectrum of the samples was taken in Thermoscientific Nicolet iS50. The morphology of prepared nanoparticles were analyzed using the field emission scanning electron microscope NOVA Nano SEM 450 at different magnifications. UV-Vis spectrum of the samples were recorded in Spectrophotometer (Ocean optics). Photoluminescence (PL) of the synthesized ZnO/MgO nanocomposites were recorded using FP-8500 Fluorescence spectrometer to characterize the luminescence properties of the nanoparticles.

3. Results and discussion

Figure 1 shows the XRD pattern for the synthesized ZnO/MgO nanocomposites. The crystal size of ZnO/MgO nanocomposite was obtained by Debye-Scherrer equation (**Equation.1**)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots \text{(1)}$$

Where D is the crystal size, λ is the wavelength of radiation used, K is the crystallite-shape factor usually taken as 0.9 and β full width at half maximum of the X-ray diffraction peak in radians and θ is the Bragg angle. All the peaks in the pattern could be indexed to ZnO/MgO nanocomposite. The existence of strong diffraction peaks at 2θ values located at 31.683, 34.428, 36.189, 47.514, 56.485, 62.867, 66.260, 67.879, 69.112, 72.681, 76.870, 81.468 and 89.591 corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4), (2 0 2) , (1 0 4), (2 0 3) correspond to primitive lattice with hexagonal system of ZnO (JCPDS Card No-89-0510) and peaks at 36.653, 42.717, 62.041, 74.318 and 78.327 correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) correspond to face centered lattice with cubic system of MgO. From Scherrer formula the particle size of ZnO/MgO was found to be in the range of 18-22 nm.

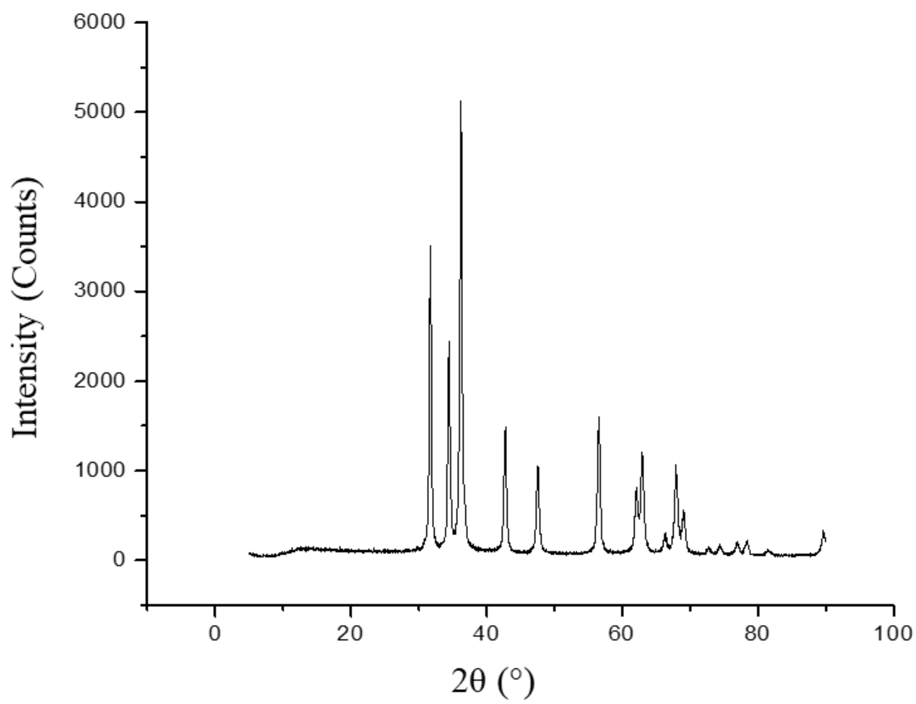

Figure 1. XRD pattern for ZnO-MgO nanocomposite.

The FTIR spectrum of ZnO/MgO nanocomposite has been studied in detail to confirm the presence of ZnO and MgO. In the FTIR spectrum of prepared ZnO/MgO sample (**Figure 2**), the peak observed at 1500 cm^{-1} is the stretching vibration of -OH group. The peaks at 1132 cm^{-1} and 873.7 cm^{-1} is assigned to the stretching vibration of Mg-O and Zn-O, which confirm the formation of ZnO/MgO nanocomposite.

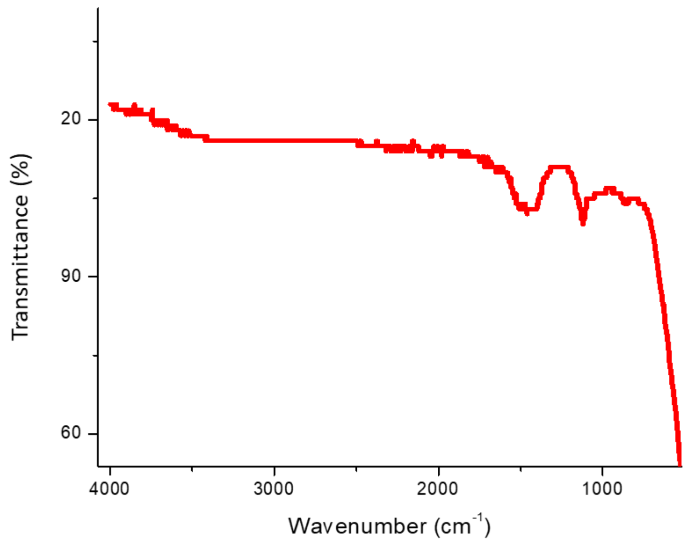

Figure 2. FTIR spectrum of synthesized ZnO/MgO nanocomposite.

The morphology of the nanocomposite was investigated using the field emission scanning electron microscopy (FE-SEM) technique. SEM analysis enable the visualization of the shape and size of nanoparticles. SEM images (**Figure 3**) indicate that the particle exist as irregularly shaped nanoflake having particle size in the range 28-81 nm. Mostly they are seen as small aggregates. Similar nanoflakes like morphology was detected for ZnO/MgO nanocomposites synthesized using *Kappaphycus alvarezii* [18]. The particle size obtained from XRD analysis is smaller than that estimated from FE-SEM. The discrepancy in the particle size may be due to nanoparticle distribution.

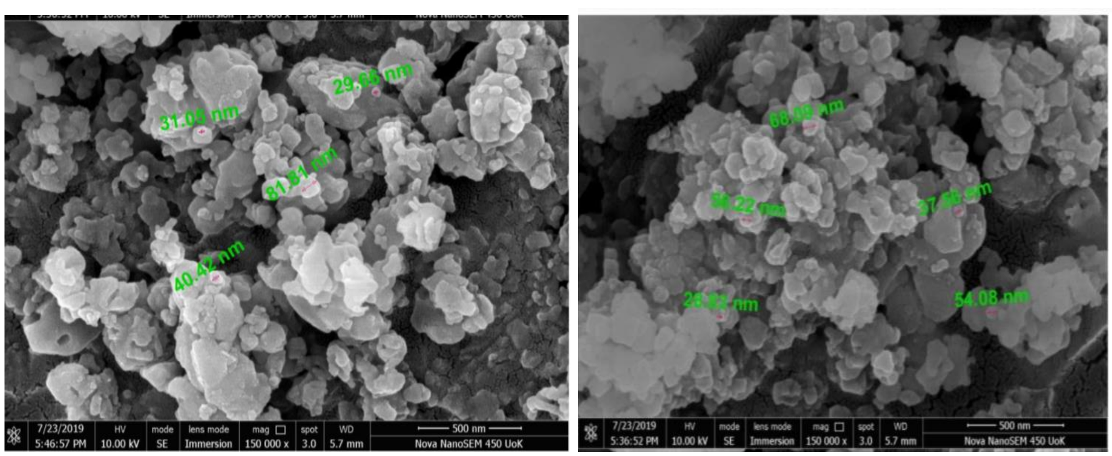

Figure 3. FESEM images of synthesized ZnO/MgO nanocomposite.

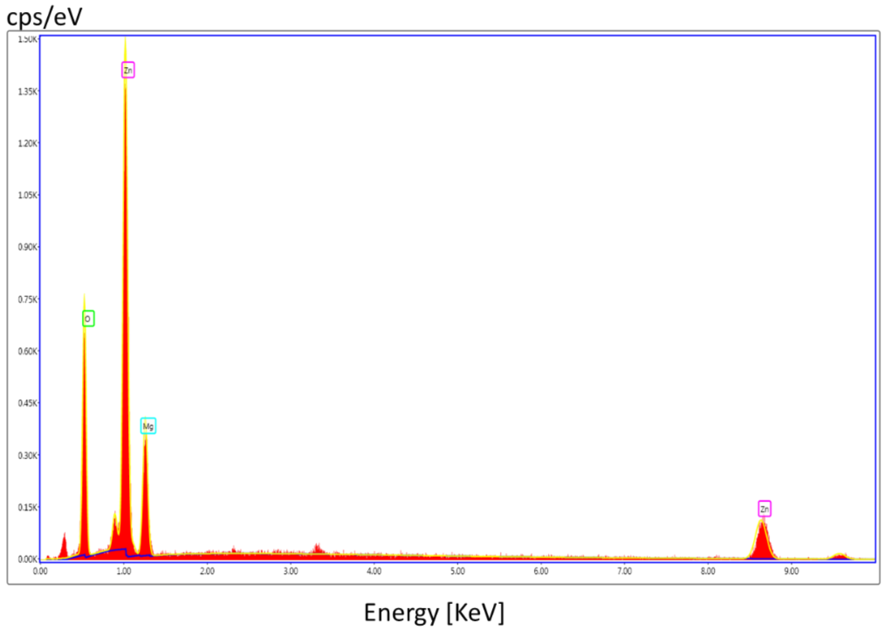

Figure 4. EDAX spectrum of ZnO/MgO nanocomposite.

Further, the elemental distributions in the prepared nanocomposite has been obtained from EDAX spectrum **(Figure 4)** and it confirms the presence of as Zn, Mg, and O. **Table 1** tabulated the individual composition of these three elements in the sample.

Table 1. Composition of Zn, Mg and O in ZnO/MgO nanocomposite.

Element	**Weight %**	**Atomic%**
O	20.74	44.83
Mg	14.82	21.08
Zn	64.44	34.09

AFM images of the nanocomposite were investiagted to confirm the morphology and roughness. **Figure 5 (a)** and **(b)** represents the 2D and 3D AFM images of dispersed ZnO/MgO nanocomposite on glass plate. The nanoparticles are appeared as uniform particles with particle size less than 50 nm. Good structural quality of the film was observed. A roughness (Rq-root mean square) value of 0.232 µm and a maximum height (R_{max}) of 1.25 µm was obtained from the high resolution images.

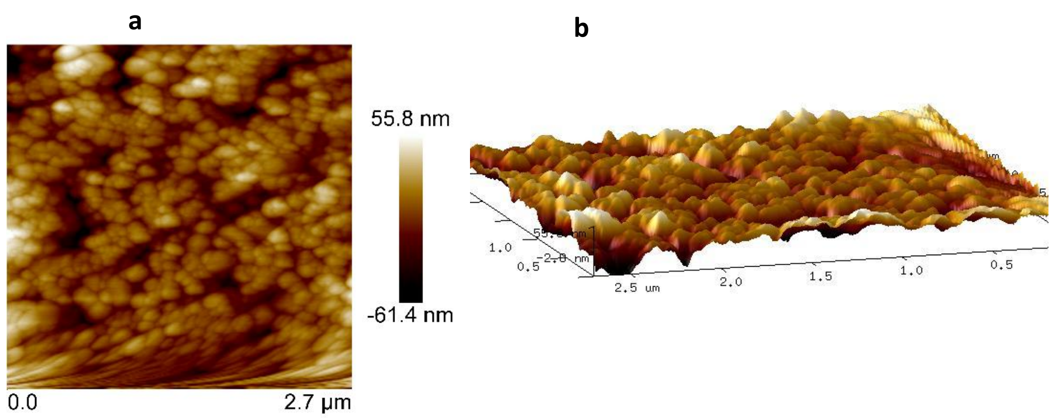

Figure 5. AFM images of synthesised ZnO/MgO nanocomposite a) flattend view at 2.7 µm and b) 3-D view at 2.5 µm

UV-Vis absorption spectroscopy is a useful technique to study the optical properties and electronic structure of nanoparticles [19]. **Figure 6a** shows the UV-Vis absorption spectra of ZnO, MgO and ZnO/MgO in the range 200-1200 nm. It can be seen from the spectra that strong absorption peaks were observed at 226.81 nm, 222.65 nm and 222.86 nm. Also, the absorption peak for ZnO/MgO nanocomposite is at 222.86 nm close to MgO. The optical band gap (Eg) of ZnO/MgO nanocomposites can be estimated by using the Tauc relation (**equation 2**)

$$\alpha h\nu = C(h\nu - Eg)^n \quad \ldots\ldots..(2)$$

The direct optical band gap for the absorption peak can be obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ versus hν curve (**Figure 6b**). In this study, the band gap energy calculated from tauc plot for MgO, ZnO and ZnO/MgO nanocomposite are 5.2, 4.9 and 4.7 eV respectively. Upon incorporating ZnO with MgO, the band gap energy decreases. In this study MgO has a cubic face centered lattice and also the percentage of Mg from EDAX measurement is found to be lower than Zn.

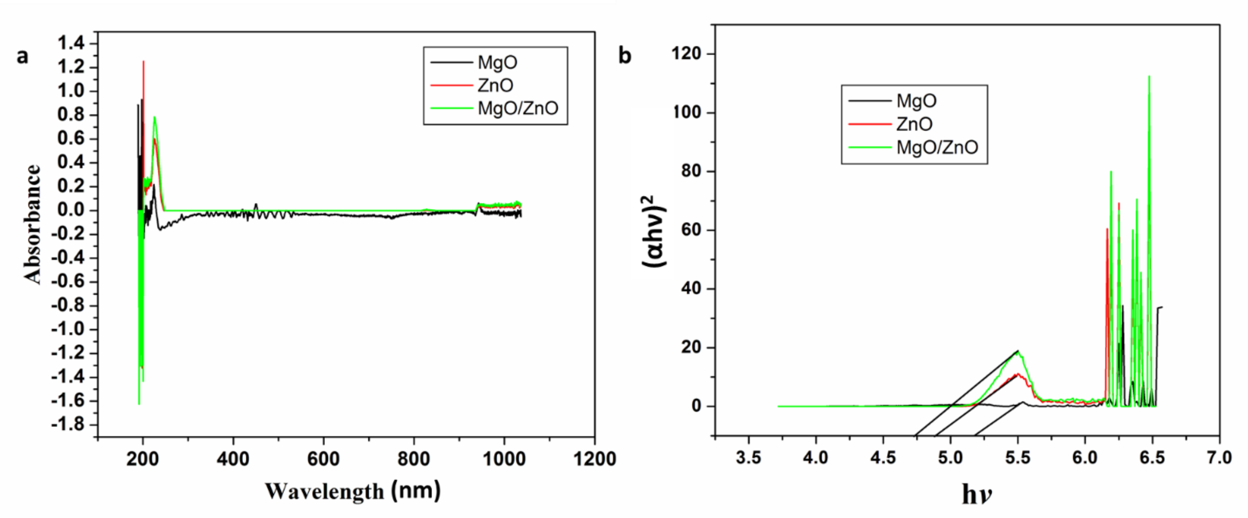

Figure 6. a) UV-Vis absorption spectra and b) tauc plot for MgO, ZnO and ZnO/MgO nanocomposite.

Figure 7 gives the photoluminescence spectra (PL) of ZnO/MgO nanocomposite at different excitation wavelength (λ_{ex}), which shows distinct PL peaks in the visible region. The PL emission spectra reveal emission peak at 469 nm and 470 nm for ZnO/MgO. The peak occurs in the visible region can be attributed to oxygen related defects. The PL emission spectra in the visible region arises due to transfer of electrons to the conduction band by leaving holes in the valence band. Thus a band to band excitation occurs and this cause migration of holes from the valence band to deep levels and recombination between electrons from either the conduction band or shallow donor levels and trapped hole on deep levels [20, 21]. Generally, ZnO/MgO nanocomposites has two kinds of defects, i.e., intrinsic defect and surface defects. The emission in the visible region termed as deep level emissions (DLE) which are usually attributed to surface defects, the origin of which is not clearly understood. The origin of the DLE band is usually attributed to optical centers associated with impurities such as native defects [22].

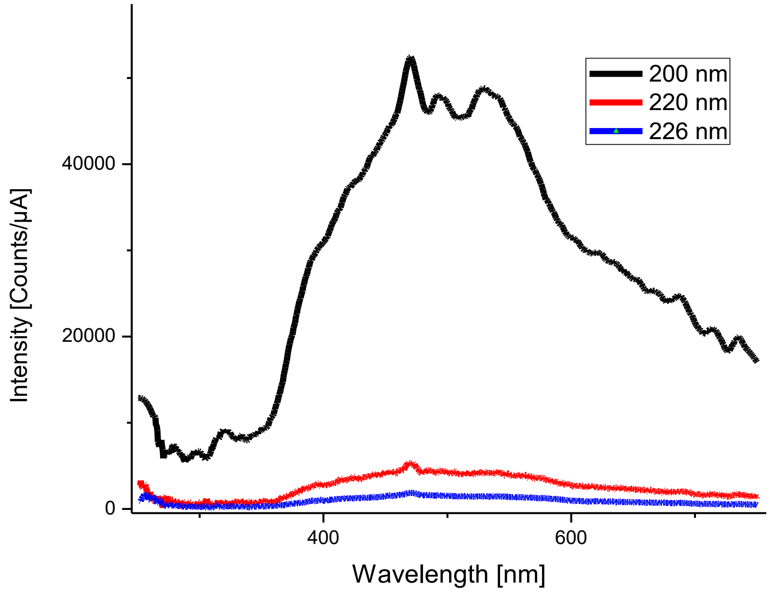

Figure 7. Photoluminescence emission spectra (λ_{ex} =200, 220 and 226 nm) for ZnO/MgO nanocomposite.

4. Conclusions

ZnO/MgO nanocomposite material was successfully synthesized by green method using Allium sativum extract. The synthesized material was characterized by using XRD, FTIR, SEM and AFM. From XRD study the particle size was found to be in the range 18-22 nm. The FTIR spectrum confirms the formation of ZnO/MgO nanocomposite. The formation of uniform sized ZnO/MgO nanoflakes were evident from morphological investigations. From the UV-Vis absorption spectrum the absorption peak for ZnO/MgO nanocomposite is at 222.86 nm close to MgO. The band gap calculated from tauc plot for ZnO/MgO nanocomposite is 4.7 eV. The PL emission spectrum of ZnO/MgO is at 469 nm and 470 nm and arises due to donation of electrons to the conduction band by making holes in the valence band. The broad and intense blue emission make the synthesized ZnO/MgO nanocomposite suitable for blue light emitting devices.

Author contributions: All the authors were equally contributed.

Funding source: No external funding for the present research work

Conflict of Interest: There is no conflict of interest.

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