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Synthesis and Characterization of Undoped and Magnesium Doped Zinc Oxide Nanoparticles

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ABSTRACT

Undoped and Mg-doped ZnO nanoparticles were synthesized by co-precipitation method. The synthesized nanoparticles are successfully characterized by XRD, SEM, and UV-visible analysis. The Structure, Morphology, and Optical activity of the synthesized nanoparticle were studied with respect to $ZnxMg_{1-x}O$ (where x= 0, 2.5%M and 7.5%M). The XRD patterns revealed the wurtzite structure for all the nano samples. XRD studies confirmed that the crystalline size increased with increase in Mg content. The surface morphology of the prepared pure and Mg doped ZnO nanoparticles are investigated by SEM analysis. Optical characterization reveals that band gap energy decreases from 3.24 to 3.13 eV with Mg doping. UV-Visible results revealed that absorption underwent a red shift with Mg into ZnO as compared to pure ZnO.

Keywords: ZnO nano particles, Co-precipitation, Nano particles, UV-Visible analysis

I. INTRODUCTION

Among nanomaterials, ZnO is the most noteworthy metal oxides to the extent that its application perceptions are concerned. So, their synthesis procedures and the rules governing their combination are also important. The various parameters used play an authoritative function in the progress of different types of fabrication procedures. A large number of varied methods were reported globally for the synthesis of ZnO nano-powder, nano-composites, nanofilms, etc., These varied methods up to some extent either evolved or pre-decided to give some sort of useful applications viz. photo-catalytic activities of different dyes, drugs, pesticides, etc., anti-microbial activities against harmful bacteria, protozoans, etc., polymer nanocomposites with characteristic optical, mechanical behaviors, etc.; growth on different substrates like thin films finds their uses in devices, solar cells, sensors, electronics/ photonics, semi-conductors, etc. in anti-oxidant studies and so on [1,2]. Zinc is an essential element whose significance to health is increasingly appreciated[3].

Recent literature reported that Mg doping in nanoparticles was found to be a good method for tuning of band gap and photoluminescence of ZnO nanoparticles[4, 5]. Magnesium doping of ZnO can be achieved in several ways including sol-gel, solid-state doping, calcination at different temperatures, vapor

phase transport and pulsed laser deposition [6,7-10]. In this work, we have synthesized undoped and Mg-doped ZnO nanoparticles by co-precipitation method. Structural, morphological and optical properties of the prepared nanoparticles have been studied in detail.

II. METHODS AND MATERIAL

2.1 Preparation of pure ZnO nanoparticles

The zinc oxide nanoparticles were prepared by co-precipitation method using zinc chloride and sodium hydroxide as precursors. Zinc chloride of equivalent weight 34.0715g (1M) was added in water. Then the solution was kept under constant stirring for 30 minutes using magnetic stirrer to completely dissolve the zinc chloride. 1 M, 250 ml Sodium hydroxide solution is prepared. After the complete dissolution of Zinc chloride, 1 M of sodium hydroxide solution was added under constant stirring, drop by drop touching the walls of the vessel. The reaction was allowed to proceed under constant stirring for 5 hours after the complete addition of sodium hydroxide. The solution was allowed to settle down and the supernatant solution was then discarded carefully. The remaining solution was centrifuged at 5000 rpm for 10 minutes and the supernatant was discarded. The obtained nanoparticles were washed using distilled water and acetone for many times. After washing, the nanoparticles were dried at 100ºC for 6 hours. The nanoparticle is taken out and grind into powder. After grinding the particles, the powder is calcined at 400ºC for 4 hours. During calcination the complete conversion of zinc hydroxide into zinc oxide takes place.

2.2 Preparation of Mg dopped ZnO nanoparticles

Mg doped zinc oxide nanoparticles were prepared by co precipitation method using zinc chloride, anhydrous $MgCl_2$ and sodium hydroxide as precursors. Here 0.1M ,300 ml zinc chloride solution is prepared and is stirred for 30 minutes. To it 2.5% Mg is doped such that the solution contains 292.5 ml of $ZnCl_2$ and 7.5 ml of Mg. This solution is again stirred for 30 minutes. After stirring, 0.1 M 150 ml of NaOH is added drop by drop through the walls of the beaker. The solution mixture is stirred for 5 hours at room temperature. The precipitate is centrifuged and washed in distilled water and acetone for several times. Then the samples are dried at 100ºC for 6 hours. The nanoparticle is taken out and grind into powder. After grinding the particles, the powder is calcined at 400ºC for 4 hours. To synthesize 7.5% Mg-doped ZnO, molar ratios of $ZnCl_2$and $MgCl_2$ were measured as $Zn_{1-x}Mg_xO$ (where x= 0.075) and the above procedure is repeated.

III.RESULTS AND DISCUSSION

3.1 Powder XRD analysis of ZnO nanoparticles

Fig.1 illustrates the X-ray diffraction (XRD) patterns for the pure ZnO samples. The X-ray powder diffraction patterns of the ZnO nanoparticles were recorded using X-ray Diffractometer equipped with nickel filtered Cu-Kα1 radiation (λ=1.5406 A°). The data have been collected in the scan range (2θ) from 20-80°. In the figure, major peaks are seen at XRD spectra show peaks at (2θ) positions 31.750, 34.450, 36.20, 47.50, 56.550, 62.80, 66.30, 67.900, 69.10, 72.40, and 76.850 which can be consigned to diffraction from (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes respectively. The XRD pattern shows the presence of the hexagonal wurtzite phase crystal structure for pure ZnO nanoparticles.

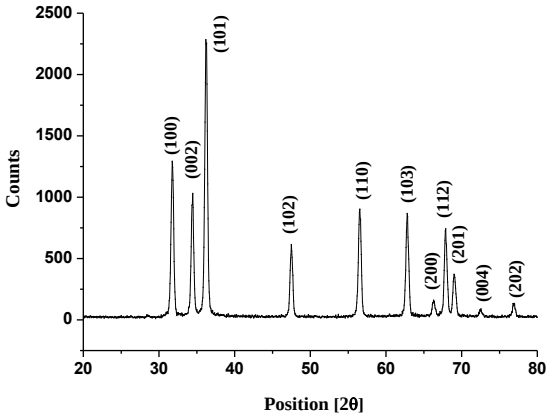

Figure 1: The powder X-ray diffraction pattern (XRD) patterns of the synthesized ZnO NPs

The mean crystallite size is obtained as 16.3821 nm by using Scherrer formula (5)

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (5)$$

where, D is average crystallite size, λ is wavelength of incident beam (1.5406 A0), β is full width at half-maximum (FWHM) in radians and θ is scattering angle in degrees. The FWHM values were estimated using Microcal Origin Version 8.5.

For a wurtzite phase, the lattice parameters are calculated by using the Eq. (6-8) where, a = b, and c are the lattice parameters, dhkl is the interplanar distance corresponding to its Miller indices (hkl).

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + k^2 + hk}{a^2}\right] + \frac{l^2}{c^2} \quad (6)$$

$$a = \frac{1}{\sqrt{3}}\frac{\lambda}{sin\theta(100)} \quad (7)$$

$$c = \frac{\lambda}{sin\theta(002)} \quad (8)$$

The calculated lattice constants (a= 3.2521Å and c= 5.2028Å) also indicate the hexagonal structure of ZnO. The standard value of the c/a ratio for the wurtzite structure is about 1.63. There is a good agreement between obtained value 1.5998, and the standard one.

3.2 Powder XRD analysis of Mg doped ZnO nanoparticles

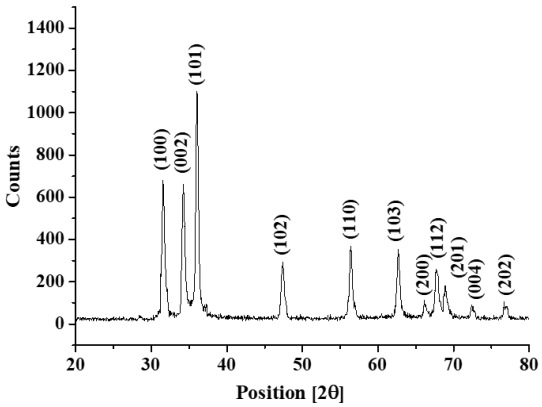

Figure 2: (a) The powder X-ray diffraction pattern (XRD) patterns of the synthesized Mg doped ZnO ($Mg_xZn_{1-x}O$, where x = 0.025%) nanoparticles

The pattern of Mg doped ZnO ($Mg_xZn_{1-x}O$, where x = 0.025%) nanoparticles has been revealed that no secondary phases are formed with Mg dopant into ZnO crystal lattice and no significant changes are observed in the XRD pattern of the Mg-doped ZnO nanoparticles. The intensity of the XRD peak is found to be decreases with increase in Mg doping concentration (Fig.2 a and b). The calculated average crystalline sizes using Debye Scherer formula are 24.91 nm and 38.28 nm for the concentrations 0.025 and 0.075% of Mg doped ZnO. From the calculated values, it is observed that the mean crystallite size increases with an increase in Mg doping concentration.

The distortion of lattice causes a small loss in their crystallinity. The Mg ions doping inside the crystal lattice of ZnO has been produced a little amount of strain in it and this results in change the regularity of crystal. The dopant materials can make changes in the lattice characteristics of the host materials. Since the ionic radius of the substituted Mg^{2+} (RMg^{2+} = 0.057 nm is 0.57 Å) is smaller than that of Zn^{2+} (RZn^{2+} = 0.06 nm is 0.60 Å) the Mg ions may replace the Zn

ions in the host lattice [11]. The basic structure of ZnO nanoparticles is found to be as their original wurtzite structure which reveals that most of the Mg^{2+} ions replace the Zn^{2+} ions.

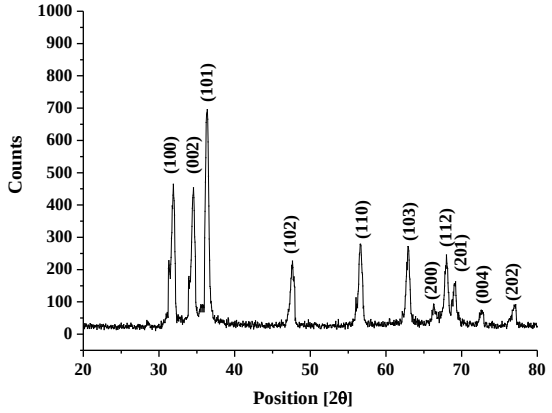

Figure 2(b): The powder X-ray diffraction pattern (XRD) patterns of the synthesized Mg doped ZnO ($Mg_xZn_{1-x}O$, where x = 0.075%) nanoparticles

3.3 Scanning Electron Microscopy of pure ZnO and Mg doped ZnO nanoparticles

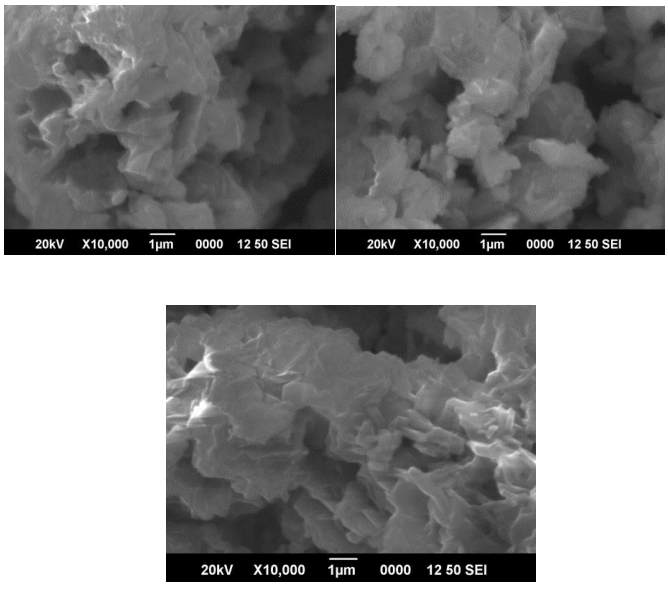

Figure 3: SEM images of ZnO and MgxZn1-xO (x= 0.25%, and 0.075%) nanoparticles

The surface morphology of the prepared pure and Mg doped ZnO nanoparticles are investigated by SEM analysis shown in the figure 3. It is observed that the particles get aggregated on their surface. Aggregation of particles on the surface has been originated from the high surface energy of the synthesized nanoparticles [12].

3.4 UV-Visible Spectroscopy of pure ZnO and Mg doped ZnO nanoparticles

The UV-Visible absorption spectra of pure and Mg-doped ZnO NPs as a function of wavelength for the range of 200 to 800 nm are illustrated by figure 4. From the UV- Visible spectra it is observed that the absorption peak increases with the increase in doping concentration. The increase in absorbance may be due to various factors like particle size, oxygen deficiency, and defects in grain structure [13].

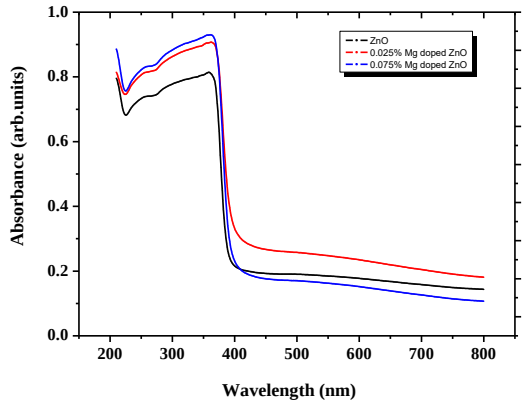

Figure 4 : UV-Visible absorbance spectra of the pure and MgxZn1-xO, (x = 0.025, 0.075%) nanoparticles

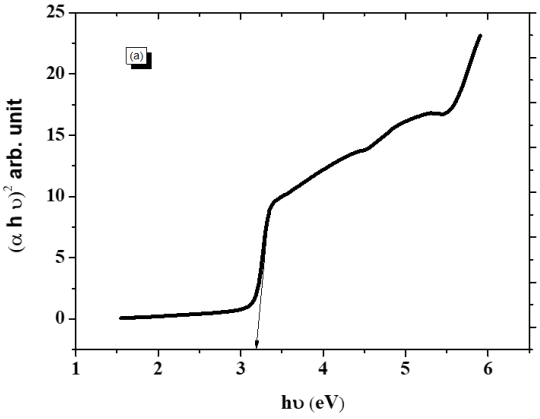

Figure 5 (a): Determination of band gap of ZnO nanoparticles from the plot of (αhν) 2 versus photon energy (hν) in eV

It is to be noted that for Mg-doped ZnO nanoparticles the absorption edge is shifted to the longer wavelength as increase in Mg content. This shifting behavior can cause a decrease in its band gap (Eg) value. The optical band gap (Eg) is determined from a Tauc-plot from the following relation (9).

$$\alpha h\nu = B(h\nu - E_g)^n \quad (9)$$

where α is absorption coefficient, h is Plank's constant, ν is the frequency of light radiation, and E_g is the band gap energy, where "n" takes the value of ½ for allowed direct transition [14]. Plots of $(\alpha h\nu)^2$ versus (hν) are made for pure and Mg-doped ZnO nanoparticles. The band gap energy (E_g) is obtained from the extrapolation of the linear portions of the plots onto the x-axis.

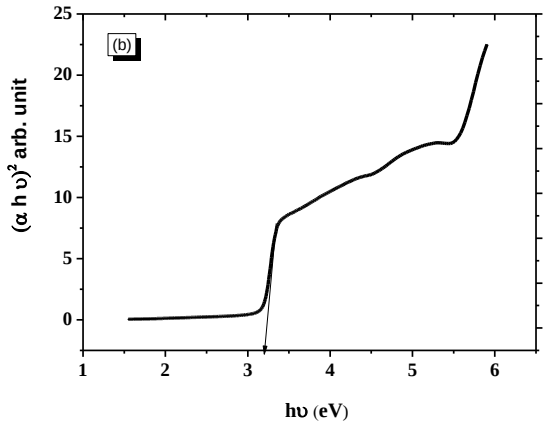

Figure 5(b): Determination of band gap of $Zn_{1-x}Mg_xO$ (where x=0.25%and 0.075%) nanoparticles from the plot of $(\alpha h\nu)^2$ versus photon energy (hν) in eV

From Fig.5 (a) and (b), it is found that the band gap energy (E_g) for pure ZnO nanoparticles is around 3.24 eV and decreases with increase in Mg dopant (3.24 to 3.13 eV). The band gap is decreased due to strong quantum confinements and enhancement in their surface area to volume ratio [15]. The shifting behaviour in UV spectrum (redshift) and decrease in band gap energy (E_g) confirm the presence of Mg^{2+} inside the Zn^{2+} site of the ZnO lattice.

IV.CONCLUSION

Pure and Mg-doped ZnO structures were successfully synthesized by co-precipitation method using Zinc Chloride and Sodium Hydroxide. The synthesized nanoparticles are successfully characterized by XRD, SEM, and UV-visible analysis. The XRD patterns revealed the wurtzite structure for all the nano samples. No other impurity phases were observed. The crystallite size obtained from XRD for all samples were less than 100 nm. XRD studies confirmed that the crystallite size increases with increase in Mg content. Average Crystalline size of the sample calculated from Debye- Scherrer formula are 24.91 nm and 38.28 nm for the concentrations 0.025 and 0.075% of Mg doped ZnO and 16.3821nm for undoped ZnO. It is also noted that the intensity of the XRD peak decreases with increase in Mg doping concentration which confirms the slender loss in their crystallinity due to distortion of lattice. The surface morphology of the prepared pure and Mg doped ZnO nanoparticles are investigated by SEM analysis. The UV-Visible results revealed that the Mg-doped ZnO nanoparticles the absorption edge is shifted to the longer wavelength as increase in Mg content. Optical band gap energy was found to decrease from 3.24 to 3.13 eV with Mg doping.

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