Digest Journal of Nanomaterials and Biostructures Vol. 9, No. 4, October - December 2014, p. 1323 - 1330

EXPLORATION OF SYNTHESIS, STRUCTURAL, MORPHOLOGY AND ANTIBACTERIAL ACTIVITY OF $Zn_{1-x-y}Mg_xAl_yO$ NANO PARTICLES

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In the present investigation, ZnMgAlO nanoparticles were prepared by soft chemical method. X-ray diffraction (XRD), Scanning electron microscope (SEM), and Fourier Transformation Infrared spectroscopy (FT-IR) were used for the characterization of the prepared nanoparticles. The structure of ZnMgAlO was confirmed through powder XRD technique as hexagonal wurtzite. The surface morphology was analyzed from SEM images. The size of sample (S4) was estimated 11 nm using scherrer formula. When the concentration of Aluminum was increased, the rod like nano formation was observed. The presence of various functional groups in FT-IR spectra was established the formulation of ZnMgAlO nano particles. Antibacterial activity of all the prepared samples was tested against Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi and Klebsiella.. The ZnMgAlO (S4) was emerged as a better antibacterial agent than the other samples.

(Received August 1, 2014; Accepted October 8. 2014)

Keywords: Soft chemical method, ZnMgAlO nanoparticles, Antibacterial activity, XRD and SEM.

1. Introduction

Nano science is managing the materials at nano scale. It has the ability to produce highly ordered nano particles. Semi conductor nano materials are excellent multifunctional nano materials. Zinc oxide has a wide band gap of 3.37 eV and exciton biding energy of 60 meV [1]. Zinc oxide nano particles are chemically stable and better electronic properties [2]. The doping of impurities improves the performance of the zinc oxide nano particles. It is commonly doped with elements like Al [3], Mg [4], Ni [5] and also co-doped with Mn, Ni [6] Mg, Al [7]. Zinc oxide nano particle have been prepared by various methods like hydro thermal [8], direct precipitation [9] and pulsed LASER deposition [10].

The antibacterial agents are used to kill or prevent the growth of bacteria. Zinc oxide nano particles are better antibacterial agent. The antibacterial activity of zinc oxide nano particles were probed by many researchers [11-14].

The present work aimed to prepare ZnMgAlO nano particles by soft chemical method. The structural, morphological and antibacterial activity of the prepared nano particles was investigated.

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2. Experimental details

2.1. Materials

Analytical grade reagents namely zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, Aluminium nitrate nano hydrate $Al(NO_3)_3.9\ H_2O$, Magnesium nitrate hexahydrate $Mg\ (NO_3)_2.6H_2O$ and sodium hydroxide obtained from Merck chemicals were used without further purification. Pure de-ionized water was used for preparing solutions and purification of the prepared nano particles.

2.1.1. Synthesis

The soft chemical method was employed for the preparation of $Zn_{1-x-y}\ Mg_x\ Al_y\ O$ nano particles. The precursor solution was allowed for 24 hours reaction time at room temperature. The resulting precipitate was purified with de-ionized water several times and it was dried at air for 3 hours for the preparation of nano particles. The growth temperature was chosen as 120 °C. The different doping concentration of Magnesium and Aluminum [x = 0, 0.10, 0.05, y = 0, 0.10, 0.15] were added. Zinc nitrate was used as host precursor. Magnesium nitrate and aluminium nitrate were used as host precursors.

2.2. Characterization

Synthesized ZnMgAlO nanoparticles were characterized by X-ray diffractometer, Scanning electron microscope and Fourier-transform infrared spectrometer. The X-ray diffraction patterns of ZnO nanoparticles were recorded using X-ray diffractometer (BRUKER) with Cu Kα radiation (λ=1.54060 Å) with a step size of 0.02°. Scanning Electron Microscope with EDAX (JEOL) was used to understand the surface morphology. The FT-IR spectra were recorded using a Fourier transform infrared spectrometer SHIMADZU (FT-IR 8400).

2.3. Antibacterial Activity

Antibacterial activity of ZnMgAlO nanoparticles were tested by agar well diffusion method. The microorganisms used for this study were Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi and Klebsiella. The wells were loaded with 25, 50, 75 and 100 μg/ml of ZnMgAlO nanoparticles. The diameters of Minimum inhibition concentration zones were determined.

3. Results and discussion

3.1. XRD Analysis

XRD patterns of ZnMgAlO nano particles synthesized by soft chemical method shown in figure 1 (S1, S2, S3, S4). The XRD pattern analysis revealed that the samples were crystallized in hexagonal wurtzite structure with space group P63mc (JCPDS and number 80-0075 for S1, S2 and S4; 03-0888 for S3). All the observed reflections in the pattern matched well with the JCPDS data. The broadened diffraction peak confirmed the formation of nano particles. There was no diffraction peak associated with Mg/Al related compound. This indicates the doping of Mg/Al have not changed the structure of ZnO [7]. The lattice parameters were calculated using equation (1) and (2).

$$a = \frac{\lambda}{\sqrt{3}} Sin\ \theta_{100} \quad (1)$$

$$c = \frac{\lambda}{Sin\ \theta_{102}} \tag{2}$$

Where, λ and θ were wavelength of X-ray and Bragg angle of the diffraction peak. The parameters calculated from XRD analysis are tabulated in Table 1.

The calculated a and c values agreed well with standard values a = 3.253 A^0, c = 5.206 A^0, JCPDS card no 80-0075). The c/a ratio values revealed that the prepared nano particles were good crystalline structure. The unit cell volume values were matched well with reported value (V=47.77 A^0 for JCPDS cared number 80-0075).

The reflections 100, 002 and 101 were high intensity whereas the reflections 102, 101 and 112 were weak in intensity. These peaks from the patterns substantiated the formation of hexagonal wurizite structure of prepared nanoparticles [6].

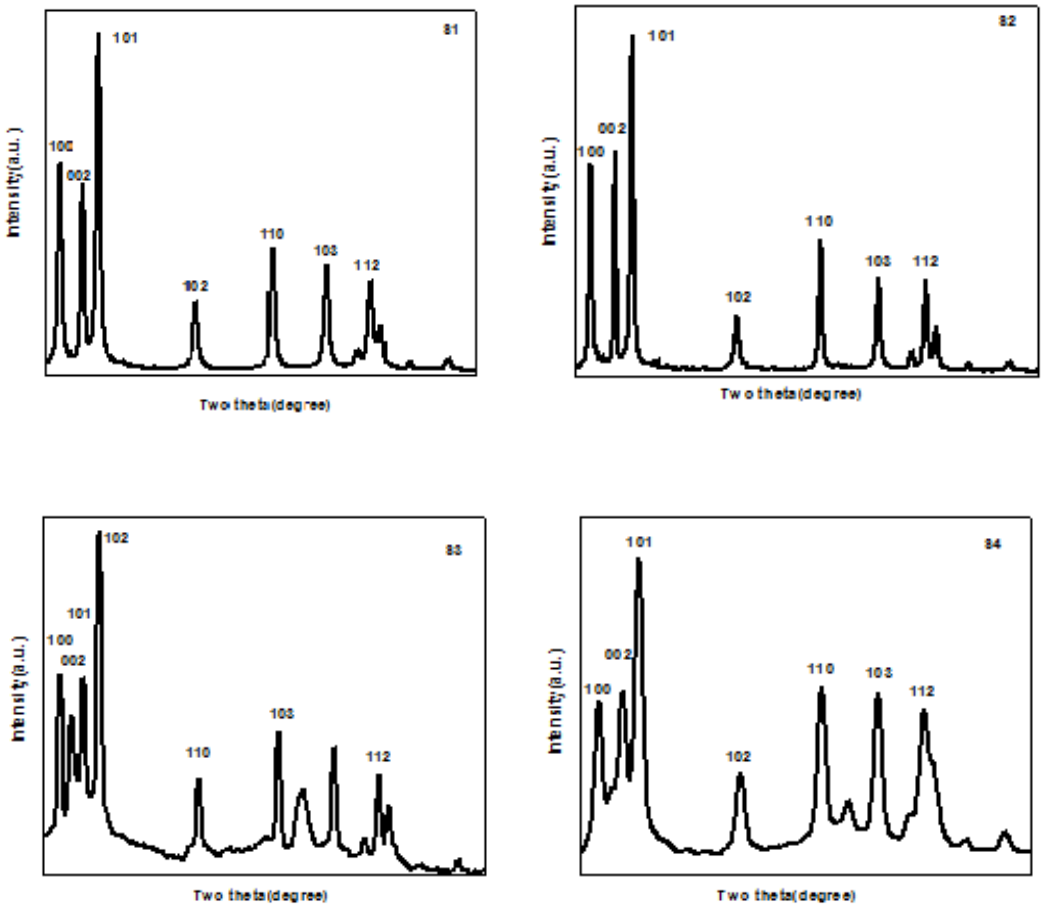


Fig. 1 XRD spectra of ZnMgAlO nanoparticles (S1) ZnO, (S2) $Zn_{0.90}Mg_{0.10}O$, (S3) $Zn_{0.85}Mg_{0.05}Al_{0.10}O$, (S4) $Zn_{0.80}Mg_{0.05}Al_{0.15}O$

Table 1 Parameters calculated from XRD analysis

Sample	a A^0	c A^0	c/a	V A^{03}	D nm
S1	3.264	5.231	1.602	48.28	22
S2	3.249	5.207	1.602	47.60	27
S3	3.247	5.408	1.665	49.37	32
S4	3.236	5.718	1.603	46.78	11

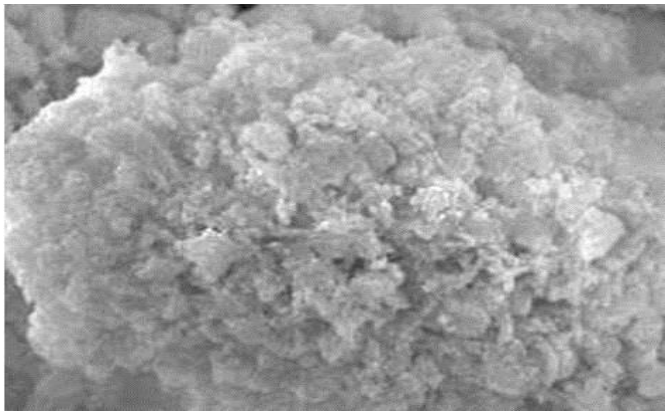
The particle size of ZnMgAlO nanoparticles were determined by scherrer equation[5].

$$D = \frac{0.9\,\lambda}{\beta\, Cos\,\theta} \tag{3}$$

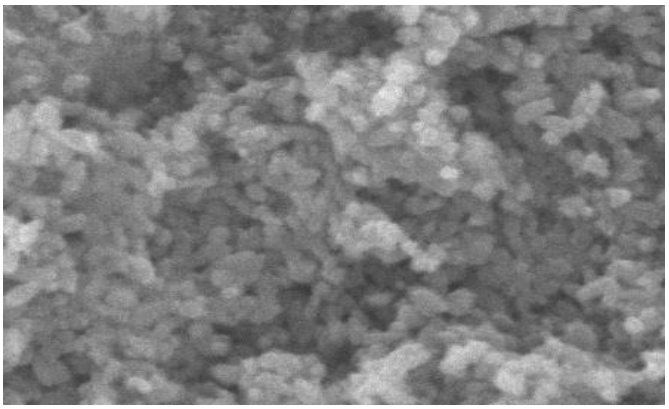
Where, D and β were particle size and full-width at half-maximum respectively. The full-width at half-maximum was measured with help of Gaussian fitting program. The calculated particles size of prepared samples found 11 – 32 nm.

3.2. SEM Analysis

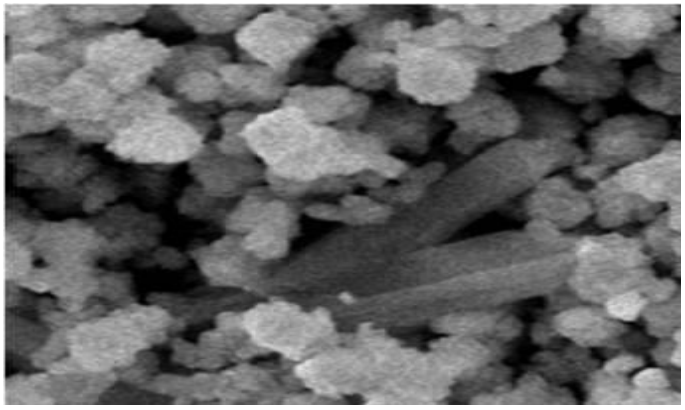
Fig. 2 shows SEM micrographs of ZnMgAlO nanoparticles. The surface morphology of the prepared nanoparticles was investigated by SEM analysis. Figure 2(a) shows the morphology of pure ZnO nanoparticles. The cauliflower shaped nanolayers were formed in pure ZnO particles. The addition of Mg improved the formation of spherical nanoparticles (Figure 2(b)). The ZnMgAlO nanorods were observed in (Figure 2(c)). The surface of nanorods was improved due to incorporation increase in Al concentration (Figure 2(c)). The SEM micrograph of ZnMgAlO nanoparticels established that the size of these prepared samples was in nanoscale.



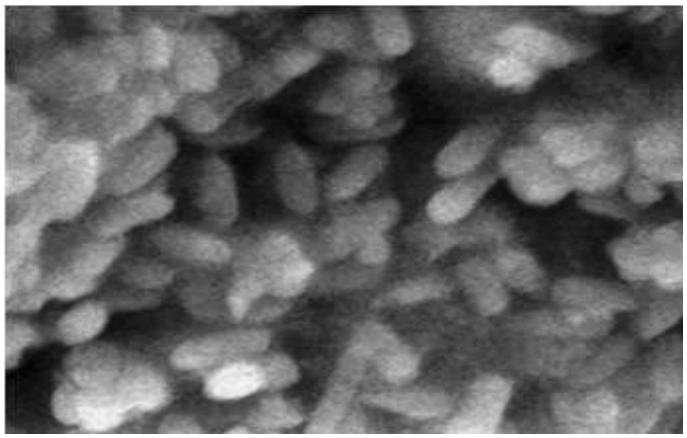
S1



S2



S3



S4

Fig. 2 SEM micrographs of ZnMgAlO nanoparticles (S1) ZnO, (S2) $Zn_{0.90}Mg_{0.10}O$, (S3) $Zn_{0.85}Mg_{0.05}Al_{0.10}O$, (S4) $Zn_{0.80}Mg_{0.05}Al_{0.15}O$

3.3. FTIR Analysis

Fig. 3 shows FTIR spectra of the ZnMgAlO nanoparticles. The formation of prepared nanoparticles was confirmed the presence of various chemical functional groups. The observed peaks were listed in the Table 2. The peaks at 452, 494, 646 and 651 cm^{-1} of the samples (S1, S2, S3 and S4) assigned for stretching modes of ZnO [1, 15]. The absorption peaks at 887, 840 and 833 cm^{-1} in the samples (S2, S3 and S4) proved the incorporation of Mg and Al in ZnO lattice [6, 16]. The peaks in the range 1600 – 1670 cm^{-1} and 3300 – 3570 cm^{-1} were assigned to OH - bending and OH – stretching modes of vibrations. A shift to lower frequency is observed in the Mg - O / Al - O stretching vibrations due to increase in Al concentration.

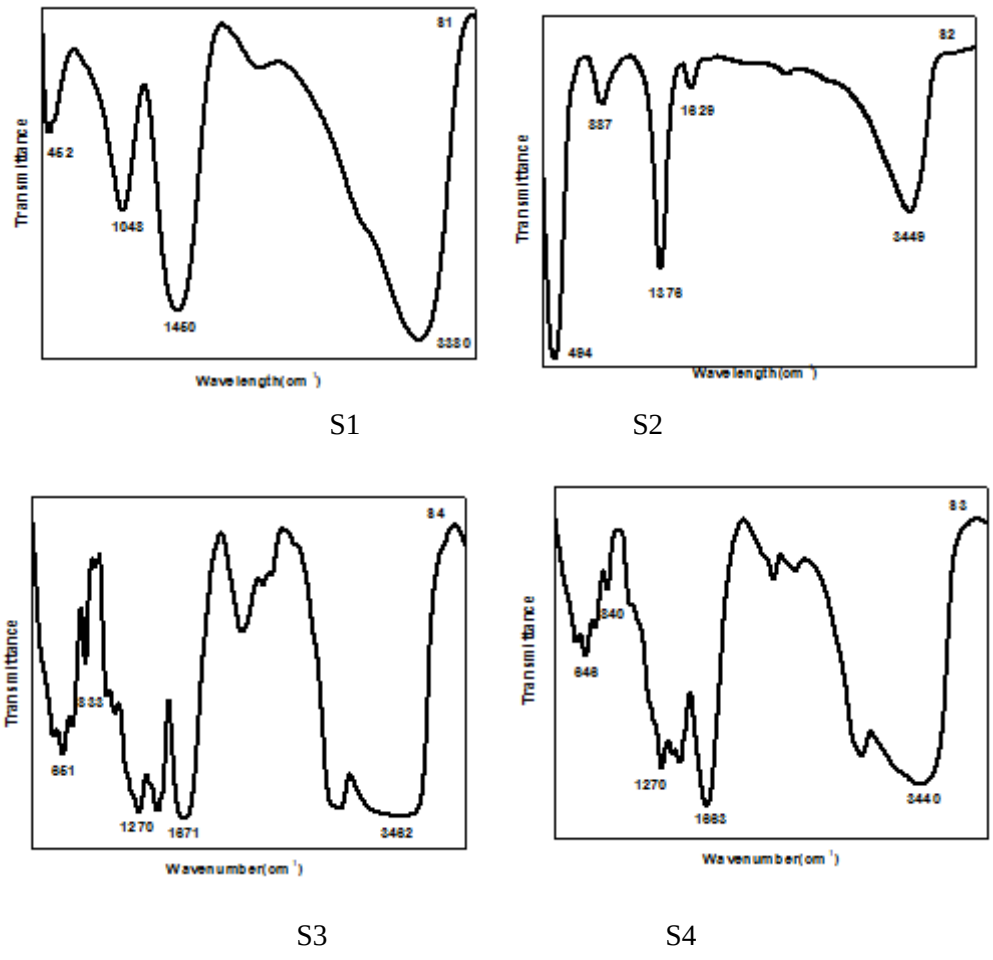


Fig. 3 FTIR Spectra of ZnMgAlO nanoparticles (S1) ZnO, (S2) $Zn_{0.90}Mg_{0.10}O$, (S3) $Zn_{0.85}Mg_{0.05}Al_{0.10}O$, (S4) $Zn_{0.80}Mg_{0.05}Al_{0.15}O$

Table 2 Functional groups assignment of FT-IR spectra

Assignment	Functional groups (cm^{-1})			
	S1	S2	S3	S4
Zn-O stretching	452	494	646	561
Mg-O/Al-O stretching	--	887	840	833
C=O	1450	1376	1270	1270
OH- bending	--	1629	1663	1671
OH- stretching	3380	3449	3440	3462

3.4. Antibacterial Studies

Antibacterial effects of ZnMgAlO nanoparticles were tested by disc diffusion method. The activity of the prepared nanoparticles was evaluated against Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi and Klebsiella. Zinc oxide nanoparticles showed good antibacterial effects against the bacterial strains. The diameter of Minimum Inhibition Concentration values of the prepared nanoparticles were listed in Table 3.

Staphylococcus aureus was a gram-positive bacterium. It was normally found in human skin. The pure ZnO (S1) was effective against Staphylococcus aureus. The diameter of Minimum Inhibition Concentration increased with increase in the concentration. The sample S4 was highly efficient (MIC = 11mm) for 100 μg/ml concentration.

Pseudomonas aeruginosa was a gram-positive bacterium. It was found in man-made environments. The prepared nanoparticles showed superior activity against pseudomonas aeruginosa. The sample (S4) is observed to be effective against pseudomonas aereiginosa. The diameter of minimum inhibition concentration values were 10, 12, 14 and 16 mm for 25, 50, 75 and 100 μg/ml concentration.

Table 3 Minimum Inhibition Concentration of ZnMgAlO nanoparticles

Strains	Minimum Inhibition Concentration															
	S1				S2				S3				S4			
	25	50	75	100	25	50	75	100	25	50	75	100	25	50	75	100
Staphylococcus aureus	4	5	6	9	0	4	6	9	0	0	4	6	0	5	9	11
Psedomonas aerelginosa	9	11	12	14	6	8	9	10	4	5	7	9	10	12	14	16
Salmonella typhi	10	14	15	17	6	9	10	13	5	7	8	9	5	6	6	15
Klebsiella	7	10	11	13	8	9	10	13	5	6	10	11	6	10	11	13

Salmonella typhi was gram-negative bacterium. The pure ZnO (S1) was found efficient in controlling the strain. The diameter of minimum inhibition concentration values were 10, 14, 15 and 17 mm for 25, 50, 75 and 100 μg/ml concentration.

Klebsiella was a gram-negative bacterium. The diameter of minimum inhibition concentration values of ZnMgO(S2) were 8,9,10 and 17 mm for 25, 50, 75 and 100 μg/ml concentration.

The ZnMgAlO nanoparticles were effective antibacterial agents. Increase in concentration of nanoparticles increased in the diameter of minimum inhibition concentration. All the samples were excellent antibacterial agents. The sample ZnMgAlO(S4) exhibited valuable antibacterial effect against the test strains.

The bacterial inactivation mechanism was discussed in different research works [11, 12, and 13]. The leakage of genetic materials due the damage in cell membrane was reported

for the reason of cell death [11]. The surface-to-volume ratio of prepared nanoparticles was high. The prepared nanoparticles were highly reactive. When the nanopartilces were placed on the surface of bacterial strains, then reactive organ species (ROS) were formed. These ROS were responsible for the increase in the permeability of the cell membrane. This confusion in the activity of cell membrane directs cell death. The prepared ZnMgAlO nanoparticles showed good growth inhibition against the bacterial strains.

4. Conclusion

ZnMgAlO nanoparticles were prepared by soft chemical method. The formation of nano particles were confirmed in XRD spectral analysis. The size of the particles were found in between 11 -32 nm. The SEM micrographs demonstrated the surface morphology of the prepared ZnMgAlO nanoparticles. FTIR spectra predicted the presence of mental-oxygen bond in all the samples. Antibacterial effect of ZnMgAlO nano particles were demonstrated against Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi and Klebsiella. The ZnMgAlO nanoparticles increased permeability of cell membrane which leads to cell death. The enhanced antibacterial effect was observed in the prepared ZnMgAlO nanoparticles.

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