Surfactant-less Sol-Gel Technique for the Synthesis of Mg-ZnO Nanoparticle

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Abstract. In this study, sol–gel technique has been used to prepare nanoparticle Mg doped ZnO with 2 wt. % at low pH without using any capping or surfactant agent. The Mg-ZnO nanostructure, surface area and porosity, surface morphology and element analysis was analyzed by X-Ray Diffraction (XRD), Fourier Transforms Infra-Red (FTIR), N2 Physisorption and Field Emission Scanning Electron Microscopy with energy dispersive X-ray spectroscopy (FESEM-EDX). The characterizations confirmed that the surfactant is not necessary for sol-gel synthesis technique, whereby highly crystalline material with smaller crystallite size (30nm) and high surface area (21.7) was obtained. Besides, the synthesis approach is useful for accurately immobilized the required amount of Mg as doping element on ZnO material with the accuracy up to 99.5% confirmed through EDX analysis.

1 Introduction

The important properties of nanostructured materials have started motivation among scientists to explore the possibilities of using them in various technological applications. In particular, the electronic and optical properties of nanostructured materials have been of interest because of their potential applications in the fabrication of microelectronic and optoelectronic devices [1-3]. Materials in nanoscale in size will typically having higher surface area compared to their bulk counterpart of similar mass. One benefit of greater surface area can dramatically improve the reactivity of surface dependent chemical processes especially in catalysis application. Nano engineered catalysts have benefited the oil and chemical production industries. Besides, energy technology sectors such as batteries, fuel cells, etc can potentially enhanced by incorporating nanomaterials. Indeed, the physico-chemicals characteristics of nanoscale materials are size dependent and this offers the possibility for researchers either in academic or industry to fine-tune a material property of interest to suite their niche application[4].

ZnO for example, is considered to be one of suitable metal oxides[5] that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is well-known as an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciting binding energy of 60 meV [6]. From this point of view nanostructured ZnO powders display an excellent potential in many applications such as gas sensors [7], solar cells [8], and photocatalyst with high chemical activity [9]. On the other hand, the ZnO characteristics can be enhanced by incorporating other element on its. For instance, addition of magnesium (Mg^{2+}) with ionic radius of 0.66 Å, which is very close to ionic radius of Zn^{2+} (0.74 Å). Therefore, substitution of Zn by Mg does not give rise to significant changes in lattice constants. It is possible to obtain a wide band gap ZnO-Mg NPs by doping ZnO with a suitable concentration of Mg as reported by several research groups [10-12]

Recently, several chemical techniques, such as co-precipitation, sol–gel[13], hydrothermal [14], wet chemical [15], precipitation [1] and combustion method [16] have been used to prepare nanocrystalline materials. Among them, sol-gel technique gives us excellent thermal stability with controllable material purity. However, most of them utilised surfactant in the synthesis route [17]

Thus, this study aims to synthesize ZnO and Mg-ZnO through modification of existing sol-gel techniques. The simplicity with less starting material will open up the possibility in the production of targeted material in large scale.

2 Materials and method

ZnO and Mg-ZnO materials were prepared by using zinc acetate dehydrate $Zn(CH_3COO)_2{\cdot}2H_2O$ (99.5%), Magnesium (II) nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ (99.5%) and oxalic acid $C_2H_2O_4{\cdot}2H_2O$ (99.5%) from (R&M chemicals), ethanol (99.99%) from (Fisher chemical) and acetone CH_3OCH_3 (99.5%) from (Friendemann Schmidt chemical). As calculated percentages of Mg and Zn precursor was prepared by dissolved it in ethanol. Then, oxalic acid solution was

added slowly with continuous stirring until the gel is formed. Next, the gel are filtered and washed with acetone prior to drying step for 4 h in 100 ºC. As dried powder then subjected to calcination process for 2 h at 400 ºC under static air environment.

X-ray diffractometer (RIGAKU, MINIFLEX II), FTIR spectrometry (Perkin-Elmer, Spectrum 100), BET (MICROM ERETICS, ASAP 2020) and FESEM (JEOLEVO-50, Japan) are used in powder characterizations.

3 Results and discussion

The XRD spectrum of the 2% Mg on ZnO nanoparticle is shown in Figure 1. However, only diffraction peaks correspond to ZnO were observed. This finding might due to high dispersion of Mg into the lattice of the ZnO crystal or due to the small amount of Mg used in doping.

The peak positions of each sample exhibit the hexagonal wurtzite (a=3.24 Å, c=5.188 Å) structure of ZnO which were confirmed from the ZnO (ICDD - 10800075). It is important to note that the availability of Mg was confirmed through EDX analysis.

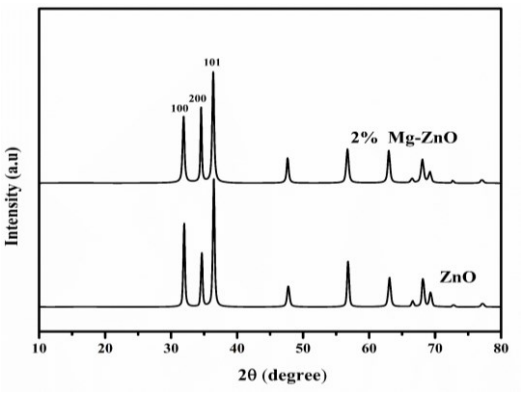

Fig. 1. XRD diffractogram of ZnO and 2wt%.Mg-ZnO.

The crystallite size calculated using Scherrer's equation (equation 1) [18] demonstrated around 36nm for ZnO and 30nm for 2% Mg-ZnO (Table 1). The reduction in the crystalline size was due to the cations segregation at the boundaries of the grain and that will prevent the growth of the grain by restricting the grain direct contact.

$$D = \frac{K\lambda}{\beta COS\theta} \quad (1)$$

λ is the x-ray wavelength,
K is shape factor (0.89),
β is the peak broadening at half maximum for Cu kα
θ is the Bragg angle.

In addition to XRD analysis, FTIR spectroscopy was used to study the structure of Mg-ZnO sample and the KBr technique has been used to prepare the sample.

Table 1. Crystal properties of ZnO and Mg-ZnO.

Catalyst	Diffraction angle (2θ)	Lattice parameter			*Crystallite size (nm)
		a (Å)	c (Å)	c/a	
ZnO	36.41	3.240	5.188	1.601	36
2% Mg-ZnO	36.46	3.227	5.232	1.621	30

Figure 2 shows the FTIR spectrum for ZnO and Mg-ZnO where the band in range (400- 600) cm^{-1} can be attributed to the Zn-O stretching mode. The bands in range (1400-1650) cm^{-1} correspond to stretching of C–O and C=O at while the stretching vibration at the range (3200 to 3600) cm^{-1} corresponds to the stretching of OH bond the water molecule bound on the surface of sample.

In case of Mg-ZnO doping there are changes in the positions and sizes of FTIR peaks, which is a clear indication of Mg incorporation with in ZnO host lattice. The shifted peak from 593cm^{-1} to 598cm^{-1} for (Zn–O) also favors the amalgamation of Mg doping in the lattice.

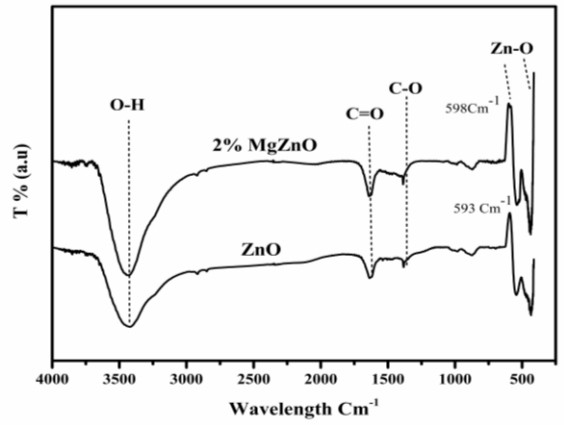

Fig. 2. FTIR spectra of 2wt. %Mg-ZnO

The surface area and porosity of prepared powders were analysed with N_2-physisorption technique. The surface area of Mg-ZnO sample was found to be bigger than ZnO (Table 2). The adsorption-desorption isotherms (Figure 3) of the Mg-ZnO to be of type IV in nature and exhibited a H1 hysteresis loop, which is typical of mesopores solids [18, 19].

Table 2. BET surface area and pore volume data of ZnO and Mg-ZnO.

Catalyst	BET Surface area (m^2/g)	Pore Volume (cm^3/g)
ZnO	17.5	0.079
2%Mg-ZnO	21.7	0.098

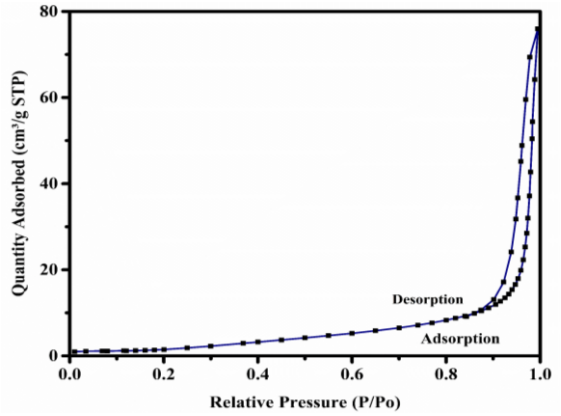

Fig. 3. Nitrogen adsorption-desorption isotherms of 2wt% Mg-ZnO

Surface morphology of Mg-ZnO with 2 % loading is illustrated in Figure 4. It can be seen from the micrographs that Mg-ZnO show sphere in-shape, the sphere particle for doped samples is closely connected as straight line-structure. The average crystallite size calculated from micrographs is slightly higher than XRD. The sizes observed from FESEM were ~ 40nm. However, it is important to note that the modified sol-gel technique used in this study able to accurately use to immobilize Mg with the accuracy up to 99.5% with the calculated and required Mg doping.

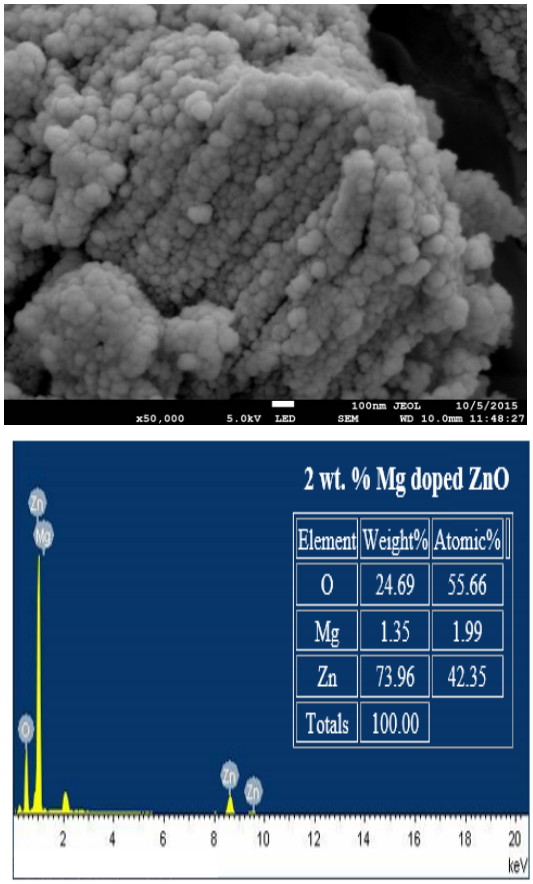

Fig. 4. FESEM and EDX of 2wt% Mg/ZnO

4 Conclusions

In concise, Mg-ZnO material with controlled size, uniform distribution and good structural have been successfully synthesized using simple, inexpensive sol-gel method without using capping agent. The synthesis approach produced highly crystalline material with high purity and structurally developed in ordered morphology.

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