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Process and Characterization of Ni Doped ZnO Nanoparticles

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ABSTRACT

Zinc oxide nanoparticles have a wide area of use because of their unique properties such as catalytic, electrical, and optical properties and low cost. Since the suitable additive materials can be changed the electrical and optical properties of zinc oxide, the demand of the industrial commercial area to the zinc oxide increased. In this study, Ni doped ZnO nanoparticles produced by using the methods of reduction thought having materials of the $Zn(SO)_4$, $Ni(SO)_4$ and NaOH. XRD, SEM and EDS used for making analyzing of structural and dimensional of particles. XRD and EDS analyses show that the Ni atoms substitute with Zn atoms succesfully. This result shows that the chemical reduction method can be use for Ni doping to ZnO nanoparticles.

Keywords: ZnO, Ni, Nanoparticles, XRD, EDS

1 INTRODUCTION

Nanostructured materials are important component of fundamental research and technological application due to their physical properties (surface and strong quantum confinement effects etc.) [1-2]. One of them is semiconductor nanoparticles which different from those of their bulk materials because of the fact that confinements make their properties unique [3]. Zinc oxide (ZnO) is one of the most important semiconductor for nanostructure applications. It has wide direct band gap (3.37 eV at 300 K) and a large exciton binding energy (60 meV) [4]. The ZnO has many uses such as varistor, gas-sensor, catalyst, pigment, light-emitting diodes, solar cells, touch panels, thin film transistor, piezoelectric devices etc. [5-6]. ZnO, in recent years, has become remarkable because of the fact that its properties can be changed with appropriate doping.

ZnO doped with different metals (Mn, Fe, Co, Ni, [3], Ga [7]) can enable the design of new applications, consequently ZnO increased the industrial and commercial use. [8-10]. The dopant Ni among the transition metal ions, are the most efficient doping element to improve ZnO materials performance. Ni^{2+} (0.69A˚) and Zn^{2+}(0.74A˚) has the same valence value and their the atomic radius are in closer to each other, therefore, it is possible to substitute of Ni^{2+} with Zn^{2+} in the ZnO lattice [8]. But, Ni is very much unstable metal in the ZnO semiconductor matrix [11].

Studies have been mainly focused on investigating their contribution to the enhancement of its properties by the metals have doped into ZnO with various techniques. For instance, Yang Liu et al. synthesized Ni-doped zinc oxide nanoparticles by the using a sol–gel method showed good high-Tc (Curie temperature) ferromagnetism [12] and F. Giovannelli et al. reported that the influence of temperature, hydrolysis duration, reagent concentration and time on the precipitation of Al-doped ZnO synthesized with a simple precipitation process.[13].

Many techniques used to synthesize ZnO nanoparticles can be categorized into either dry or wet process[13]. Dry processes are, for instance, RF-plazma [14], pulsed laser energy [15] and dc thermal plasma technology [16] while wet processes are coprecipitation method [17], electrodeposition [18], hydrothermal method [19], sol–gel method [12], photoreduction method [20]. Among these techniques, precipitation from colloidal solutions is a usual method for progress in synthesis of metal doped nanoparticles. The precipitation process are described with hydrolysis and water condensation reactions. The former consists in the formation of an insoluble hydroxide. This hydroxide converts into the oxide compound by heat assisted dehydratation. The latter could also appear directly in the solution. [13]

In this study, Ni-ZnO nanoparticles were synthesized by using precipitation process because of its simplicity, less temperature, inexpensive equipments, excellent and control over stoichiometry, larger degree of solubility of dopants and ability to obtain good quality nanoparticles.[17-21]. However, preparation of Ni-doped zinc oxide nanoparticles is particularly challenging due to the large driving force for phase segregation into NiO and ZnO [11] as well as in the case of using nanoparticle material it is important to control the nanoparticle structure, morphology, the size or problems related to the contained residues [22-14]. Structural and morphological properties of ZnO nanoparticles containing 4 wt.% Ni were investigated by using XRD, EDS and SEM.

2 EXPERIMENTAL PROCEDURE

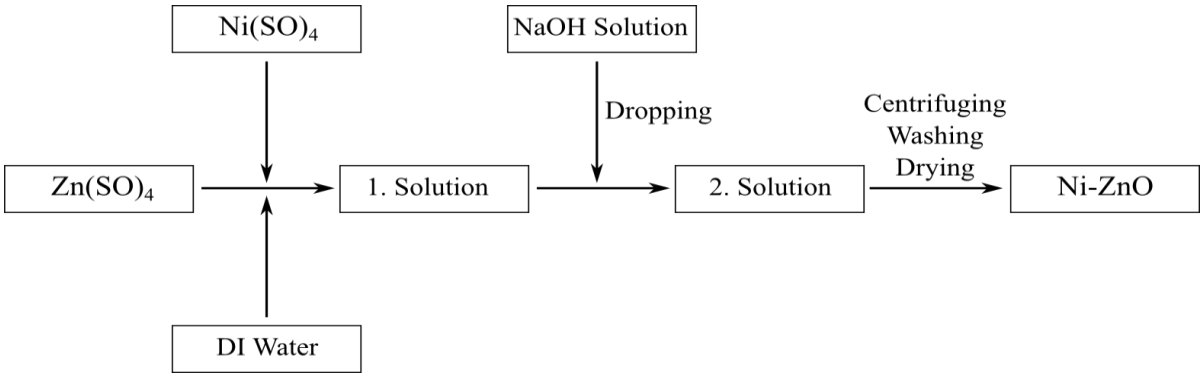
Ni doped ZnO nanoparticles was manufactured by the chemical reduction method. The synthetic procedures for the Ni-ZnO nanoparticles are briefly summarized in Scheme 1. In this study, $Zn(SO)_4$, $Ni(SO)_4$ and NaOH materials (Sigma Aldrich %99) were used without any further purification. Firstly, 0.1 M $ZnSO_4$ and appropriate amount of $Ni(SO)_4$ were dissolved in 100 mL deionized water. The concentration of Zn is 0.1 M and Ni concentration corresponds to 4 wt.% of Ni-ZnO. This solution was stirred at 40^0C

for 30 minutes. Aqueous solution of 1 M 150 ml NaOH was added dropwise to the solution under continuous stirring about for 1 h. at 60°C on a magnetic stirrer. Then the precipitates were collected at 4000 rpm for 5 min by centrifugation,washed with deionized water for five times to remove the impurities. Finally, the synthesized Ni-ZnO nanoparticles were dried in a horizontal tube oven at 80 ^{0}C for 4 hours ,and then the Ni–ZnO nanoparticles were obtained. During the reduction process, the mechanism for Ni-ZnO formation can be considered as follows:

$Zn(SO)_4 + OH^- \rightarrow Zn(OH)_2 \quad K_{aa} = 1{,}3.\ 10^{-16}$

$Ni(SO)_4 + OH^- \rightarrow Ni(OH)_2 \quad K_{aa} = 6.\ 10^{-16}$

$Zn(OH)_2 + Ni(OH)_2 + NaOH \rightarrow (Ni)ZnO + \text{other products}$



Scheme 1

The crystal structure of the samples was analyzed using RIGAKU Part D/Max 2200 x-ray diffraction (XRD)(Rigaku/Smartlab) system with Cu Kα irradiation (λ=1.5418 Å) operated at 40 kV and 30 mA at the room temperature. The surface morphology of Ni doped ZnO nanoparticles was investigated with a scanning electron microscope (SEM) (FEI İnspect 550). Furthermore, the ratio of Ni as weighting in the Ni-ZnO nanoparticles was investigated by Energy Dispersive X- ray spectrometer (EDS) analyzer.

3 RESULTS AND DISCUSSION

3.1 X-ray Diffraction Results

The structural properties of Ni-ZnO nanoparticles have been investigated by XRD. Figure 1 shows that the XRD patterns Ni doped ZnO nanoparticles. While red tringulars in the figure show the main peaks of Ni-ZnO nanoparticles, other peaks show the main peaks of ZnO nanoparticles.

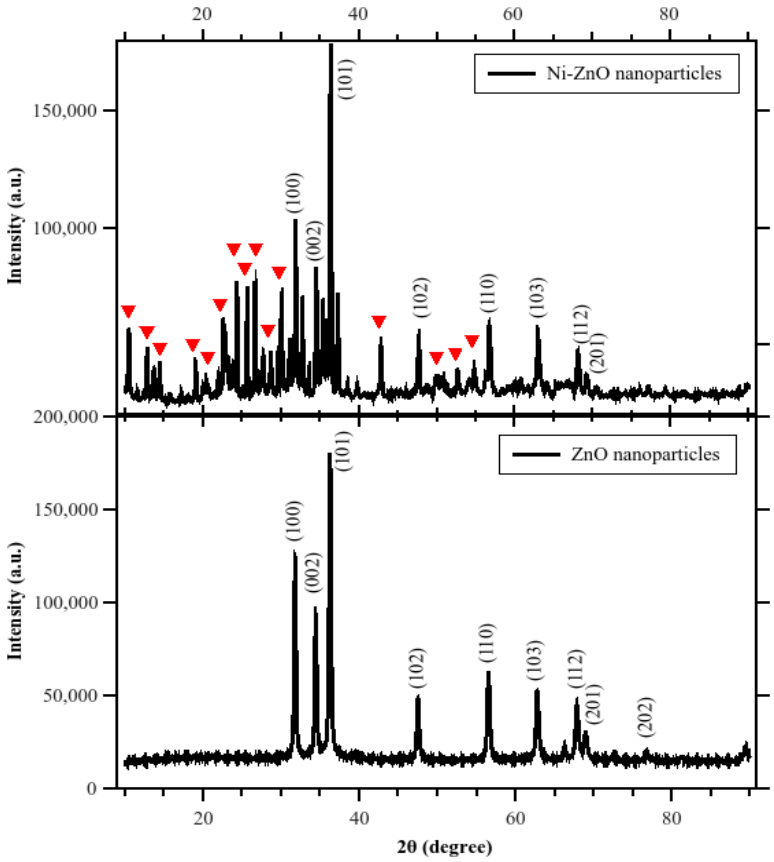


Figure 1. XRD patterns of the Ni-ZnO nanoparticles.

XRD pattern of Ni doped ZnO sample belongs to that crystal structure of pure and Ni doped ZnO nanoparticles are polycrystalline hegzagonal wurtzite structure with (101) orientation at 36.35 degree. The a, b, and c parameter of the pure and Ni-doped ZnO nanoparticles are refined by Cohen's Method of Least Squares using XRD data. The a, b, and c parameters of pure ZnO are found 3.253 Å, 3.253 Å, and 5.213 Å respectively. These values consistent with the literature [23]. On the other hand a, b, and c parameters of Ni doped ZnO nanoparticles are found 3.243 Å, 3.243 Å, and 5.198 Å respectively. Changing of a, b, and c paremeter of Ni-doped ZnO shows that the doping process is successful. Otherwise, c/a parameters of pure and Ni doped ZnO nanoparticles are 1.602 and 1.602 respectively. The c/a parameters of samples are unchanged. This result can interpret as a unchanged of wurtzite structure of nanoparticles. Preferred orientation of Ni-doped ZNO is (101). The size of particles of crystal in the form of powder (D) and microstrain (ε) values over all peaks are determined by the Scherrer equations (1) – (2) [24] as shown below.

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

$$\varepsilon = \frac{\beta}{4tan\theta} \quad (2)$$

In these equations, β is full width at half of the peak maximum (FWHM) and calculated by Analysis of Variance (ANOVA), λ is the wavelength of the using X-ray and θ is the peak position which known as Bragg's angle. Calculated size of particles of nanocrystals and microstrain values of nanoparticles are given in Table 1.

Table 1 Structural parameters which calculated XRD patterns of pure and Ni-doped ZnO nanoparticles.

Pure ZnO nanoparticle					**Ni-doped ZnO nanoparticles**				
a,b (Å)	c (Å)	c/a	D (nm)	ε (x10^{-3})	a,b (Å)	c (Å)	c/a	D (nm)	ε (x10^{-3})
3.253	5.213	1.602	30.21	1.95	3.243	5.198	1.602	47.68	1.23

Unit cell dimensions are little changed because of the fact that the Ni and Zn atoms have almost same atom and bonding size. But, the crystallite size of ZnO is increased with doping of Ni atoms. This result shows that the doping process is successful.

3.2 SEM and EDS results

The scanning electron microscopy (SEM) images of Ni-ZnO nanoparticles given in Figure 2. The composition of the Ni doped ZnO nanoparticles was determined by energy dispersive X-ray spectroscopy (EDX). EDX spectra of Ni doped ZnO nanoparticles and the composition of elements in ZnO structure which viewing area are given in Figure 3. EDS spectra clearly confirm the existence of Zn, Ni and O elements in the Ni doped ZnO nanoparticles. While weighting ratio of Ni/(Ni + ZnO) (wt.%) in the starting solution is 4%, EDX analysis shows that the ratio is 1.9% in the Ni doped ZnO nanoparticles. This value is half of starting solution ratio. This is evidence of that the some of Ni atoms did not enter the ZnO nanostructure. But, that EDS measurement is taken from only the displayed area and experimental errors may be cause the low weighting ratio of Ni. XRD results, however, confirm the reliability of the reduction method used in experiments.

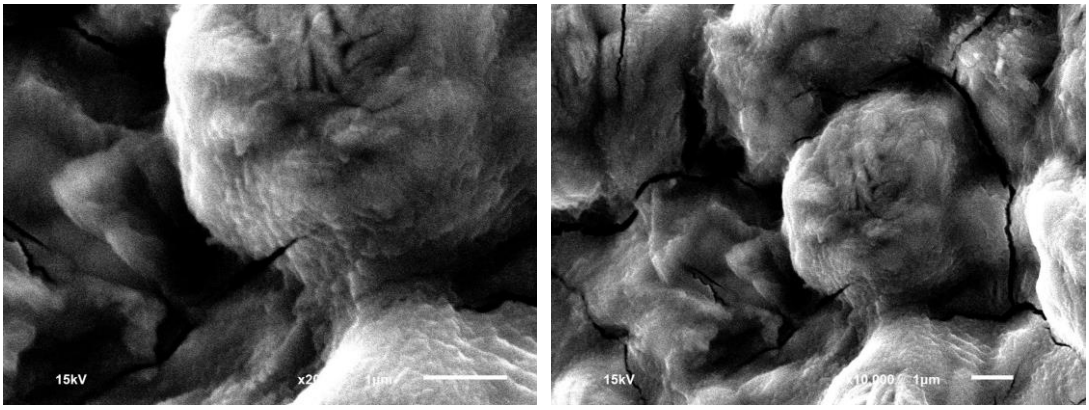


Figure 2. SEM micrographs of the nanoparticles with 4 wt.% Ni-ZnO

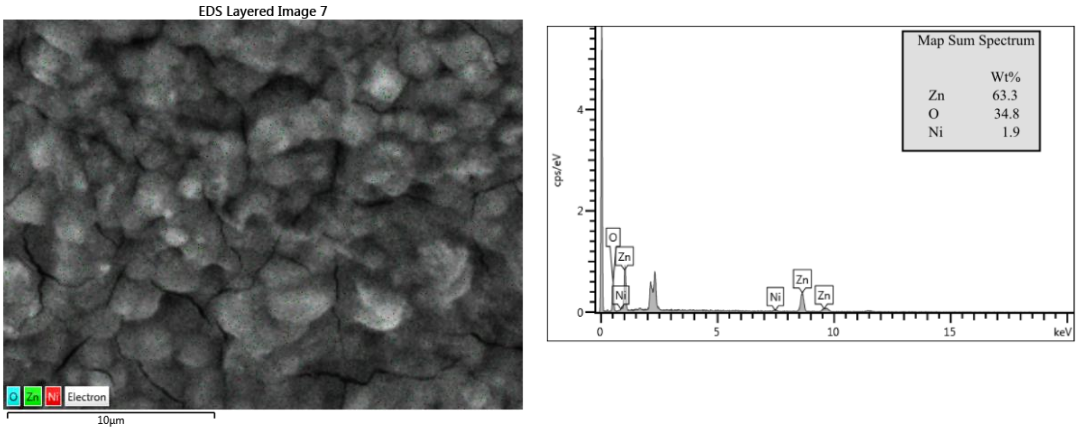


Figure 3. SEM images and EDS results on the nanoparticles with 4 wt.% Ni-ZnO

4 CONCLUSION

In this study, Ni doped ZnO nanoparticles were successfully synthesized by using precipitation process and the structural morphological properties of the nanoparticles are investigated. XRD measurements showed that doping ZnO with Ni increased the particle size significantly. The powder structure, shape and composition of weight of atoms were investigated by SEM/EDS. It was found that Ni doped ZnO nanocrystals have spherical shape. EDS analysis shows that the half of amount of the Ni atoms substitute with Zn atoms succesfully. This result shows that the chemical reduction method can be use for Ni doping to ZnO nanoparticles.

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