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# Synthesis and Characterization of Ni Doped ZnO Nanoparticles

M.R.A. Bhuiyan<sup>a,\*</sup>, M.K. Rahman<sup>a</sup>

<sup>a</sup>*Department of Applied Physics, Electronics and Communication Engineering, Islamic University, Kusthia-7003, Bangladesh*

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## Abstract

This paper discerns key ideas and themes of the possibility of growing Ni doped ZnO nanoparticles by electrochemical method. The purpose is to study the growth mechanism and to optimize the parameters of this method. Upon successful synthesizing the samples, they were characterized using various techniques. XRD, SEM, FTIR, photoluminescence spectroscopy together with the measured optical parameters obtained from UV-VIS absorption testing were analyzed. The X-ray diffraction (XRD) was measured by using a Bruker D8 Advance X-ray diffractometer with CuK<sub>α</sub> radiation. The surface morphology was investigated using an 'EVO LS 15' scanning electron microscope. The FTIR absorption spectra were recorded on a Perkin-Elmer GX FTIR system. The PL spectra were collected on a Jobin Yvon-Horiba Triax 190 spectrometer with a spectral resolution of 0.3 nm. UV-VIS absorption spectrum was recorded by using a UV-VIS spectrophotometer in the photon wavelength range between 300 and 600 nm. XRD pattern reveals that the polycrystalline of hexagonal wurtzite structure and the average size of the particles were estimated to be approximately 61 nm, which conform the nanoparticle. The FTIR result shows the stretching vibration of the Zn-O bond in Ni doped ZnO nanoparticles. There is a green emission peak centered at about 384 nm in the PL behavior. The band edge is shifted to the lower energy side of the Ni doped ZnO nanoparticle. Analyzing the results of various types of characterizations, it has been assessed that Ni doped ZnO nanoparticles was successfully synthesized.

**Index Terms:** Ni doped ZnO, Compositional uniformity, Structural parameter, Optical parameter.

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## 1. Introduction

Nanometer-sized particles (1–100 nm) have attracted considerable interest for a wide variety of applications, ranging from electronics via ceramics to catalysts due to their unique or improved properties, which are primarily determined by size, composition, and structure [1]. These properties are strongly related to the synthesis processes. Numerous solution techniques, for example, sol–gel, emulsion, colloidal, and

\* Corresponding author. Tel.: +88 01711 443079; fax: +88 071 62399  
E-mail address: [mrab\\_iu@yahoo.com](mailto:mrab_iu@yahoo.com)

aerosol processes, have been used to synthesize a variety of nanoparticles [2–6]. As an alternative approach, the electrochemical route is of considerable interest because of a possibly precise particle size control achieved by adjusting current density or applied potential. For electrochemical synthesis, extensive investigations have been focused on the metal particles, especially on noble metal particles. This method, in fact, skillfully combines an electrochemical process with plasma at ambient pressure and temperature. Compared with other methods of synthesizing Ni doped ZnO powder, this access has some advantages. Firstly, the whole process, with a simple experimental set-up and electrolyte system is performed under mild conditions. Secondly, particles can be obtained within a few minutes. Finally, changing the volume ratio of the electrolyte can effectively control the size of the obtained particles. The earlier study of the magnetic nature of Ni doped ZnO shows different results. Some authors [7, 8] reported that, ZnO doped with 5 to 25at.% Ni did not show room temperature ferromagnetic (RT-FM) behavior and the FM characteristics disappeared for temperatures higher than 30K. Wakano et al. [9] observed and measured FM properties in 3 to 25 at.% Ni doped ZnO at temperatures less than 30K, however, super paramagnetic behavior was observed at least up to 300K. i.e. absent of RT-FM. Liu et al. [10] have noticed that the preparation details of the prepared Ni doped ZnO has great influence on their magnetic properties, so that annealing at 800oC in Ar gas atmosphere significantly increases the magnetization, however, RT-FM was not detected. Recently, the RT-FM was observed in ~12at.% Ni doped ZnO prepared by sputtering method [11] and in 5at.% Ni doped ZnO prepared by laser ablation method on sapphire substrate [12]. Thus, the experimental evidence for the existence of RT-FM phase in Ni doped ZnO at room temperature is still questionable and needs more investigations. Generally, experiments show that the magnetization properties of ZnO:Ni depend strongly on the preparation method and procedure and seems to be sensitive to the crystalline structure and concentration of intrinsic (like oxygen vacancies) and extrinsic defects. A clear understanding of the RT-FM ordering can provide us with new experimental approaches to an opportunity to develop spintronic devices based on Ni doped ZnO.

## 2. Experimental Details

### 2.1. Synthesis of Ni doped ZnO Nanoparticles

The synthesis method has been employed a modified version of the originally used by Reetz and Helbig [13] for metal particles (in a one-phase electrochemical system). Ni doped ZnO particles were synthesized at room temperature by an electrochemical route. The electrolytic bath consisted of acetonitrile and tetrahydrofuran (THF) mixed in the ratio 4:1, in which high purity Ni doped Zn metal sheet (1cm × 1cm) and laboratory grade platinum sheet (1cm × 1cm) served as anode and cathode respectively. The capping agent tetra-trimethyle ammonium-bromide (TTAB) also served as the electrolyte. Electrolysis was carried out in nitrogen atmosphere for a few hours in constant current mode (GPS-30D, 0-30V, 0-5A). Current density was maintained to obtain different sized of particles. The molarity of TTAB in the chemical bath was varied from 0.1 mM to 0.9 mM. The white Ni doped ZnO particles remain suspended in the solvent and separated by using centrifugation. On drying, a free flowing powder of Ni doped ZnO particles are obtained.

### 2.2. Measurements

The structural properties of the Ni doped ZnO particles were measured by using a Bruker D8 Advance X-ray diffractometer with  $\text{CuK}\alpha$  radiation of wavelength  $\lambda = 1.54056 \text{ \AA}$ . The X-ray diffraction (XRD) measurements were carried out in the locked coupled mode in the  $2\theta$  range of 20 to 60o. The surface morphology and composition of Ni doped ZnO particles were investigated by using an ‘EVO LS 15’ scanning electron microscope developed by Carl Zeiss. An accelerating voltage of 15 to 19 keV and probe current of ~800 pA. UV-VIS absorption spectrum of Ni doped ZnO particles were recorded by using a UV-VIS

spectrophotometer in the photon wavelength range between 300 and 600 nm. The FTIR absorption spectra were recorded on a Perkin-Elmer GX FTIR system used to obtain 16 cm<sup>-1</sup> resolution spectra in the range 500 to 4000 cm<sup>-1</sup> region, scanned 30 times (absorbance mode), in order to exploit the instrumental built-up noise reduction algorithm. The Photoluminescence (PL) measurements were carried out from room temperature by employing a 488 nm line of an argon ion laser. The PL spectra were collected on a Jobin Yvon-Horiba Triax 190 spectrometer with a spectral resolution of 0.3 nm, coupled with a liquid nitrogen-cooled CCD detector.

### 3. Results and Discussion

#### 3.1. Structural and Compositional

X-ray diffraction (XRD) is mainly used for phase identification. Fig.1 shows the XRD pattern of the prepared Ni-doped ZnO sample. The grown sample shows the peaks of (100) and (101). No signals of the metallic Zn are detected by XRD. Also, there is no peak corresponding with the Ni, suggesting that the Ni element may be doped into ZnO. This pattern reveals that the polycrystalline of hexagonal wurtzite structure that is known ZnO structure. The Bragg angle of the intense (101) reflection is observed as light shift towards higher values relative to that of pure ZnO which has been indicated that Ni-doped ZnO was formed along with NiO phase. Of course, this happens relating to the limit of the solids solubility of Ni in ZnO. This is an evidence for creation of internal compressive micro stress. Such case was also observed in ZnO annealed in hydrogen atom sphere [14]. It is known that more oxygen content is introduced into the sample. It is clear that the (101) peak is sharper and stronger.

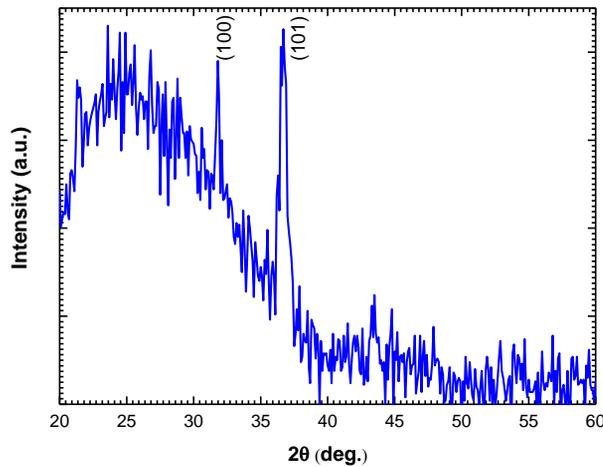


Fig. 1. XRD spectrum of Ni doped ZnO particles

The size of the Ni doped ZnO particles was estimated by applying the Scherrer equation [15] to the half intensity width of the (101) peak:

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $k$  is the particle shape factor and taken as 0.827 because of the hexagonal Ni doped ZnO particles,  $\lambda$  is the wavelength of  $\text{CuK}\alpha$  radiation (0.154nm),  $\beta$  is the calibrated half intensity width of the selected diffraction peak (degrees), and  $\theta$  is the Bragg angle (half of the peak position angle). From this equation, the average size of the Ni doped ZnO particles was estimated to be approximately 61 nm, which conforms reasonably well to the literature value [16]. This implies that the samples are successfully synthesized.

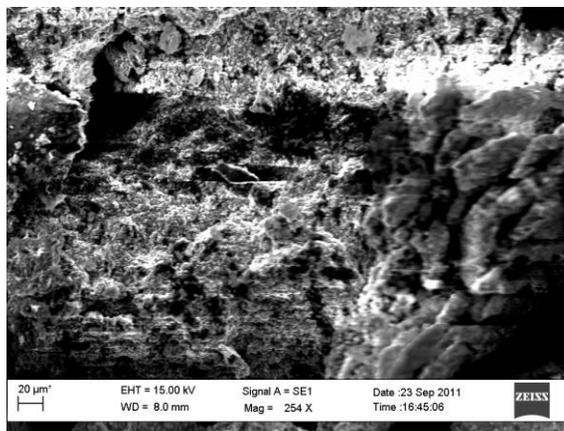


Fig. 2. SEM image of Ni doped ZnO particles

SEM image in fig. 2 shows the morphology of Ni doped ZnO particles. It is observed that there is a rough surface in the particles.

### 3.2. Optical absorption

Substitution of Ni cations in tetrahedral sites of the wurtzite structure was further conformed by UV–vis optical spectroscopy. The room temperature spectra of the Ni doped ZnO particles are reported in fig. 3 and compared to the spectrum recorded for the other researcher report [17].

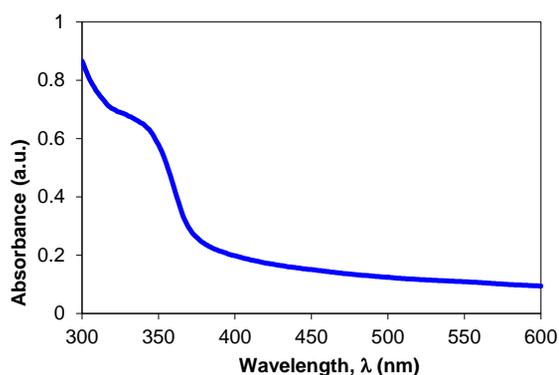


Fig. 3. Optical absorption spectrum of Ni doped ZnO particles

From this figure, the band edge is shifted to the lower energy side of the Ni doped ZnO samples. The decrease in the band edge is a clear indication for the incorporation of Ni inside the ZnO lattice [18].

### 3.3. FTIR absorption

To make the clear interactions with the particles, FTIR absorption spectrum of the particles was performed. Fig. 4 shows the FTIR spectrum of Ni doped ZnO particles. The peak at 3180  $\text{cm}^{-1}$  is the stretching vibration of the H-O bond. The peaks at 1620 and 1400  $\text{cm}^{-1}$  are assigned to the vibrations of amide I and amide II, respectively. The peaks are similar to other worker [19]. A peak at 530  $\text{cm}^{-1}$  is the stretching vibration of the Zn-O bond in doped ZnO particles.

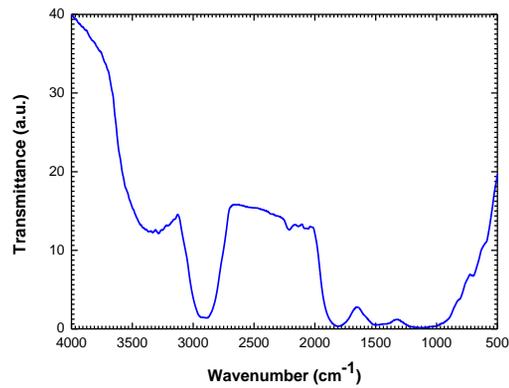


Fig. 4. FTIR spectrum of Ni doped ZnO particles

### 3.4. Photoluminescence spectroscopy

The room-temperature PL spectrum on the Ni doped ZnO sample is shown in fig. 5. Only a UV emission

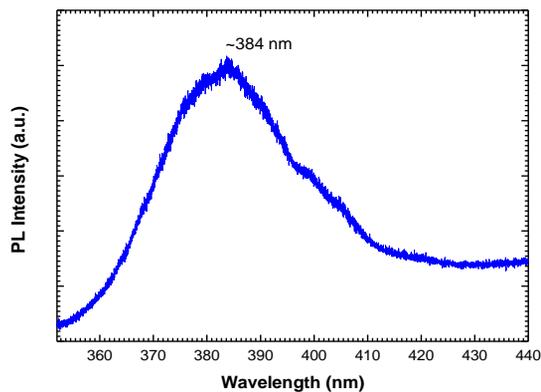


Fig. 5. Photoluminescence spectrum of Ni doped ZnO particles

peak can be observed on the pure ZnO cone arrays without any significant emission in visible region, though the green emission is often observed in many reports [20-23]. The UV emission is attributed to the near-band-edge emission from the recombination of free excitons through an exciton-exciton collision process [24]. Vanheusden et al. [22] proved that the individually ionized oxygen vacancy is responsible for the green emission in ZnO. To observe the green emission that indicates its good crystallization with little oxygen vacancy. After the Ni ion incorporation, the UV emission peak shifts to a little longer wavelength, consistent with the result of the UV-visible absorption. Besides, the intensity of UV peaks of Ni doped ZnO decreases. There is a green emission peak centered at about 384 nm. As more oxygen ions would be pulled out from lattices by Ni ions to form NiO in interstices of lattices.

#### 4 Conclusions

In summary, Ni doped ZnO particles have been synthesized by a simple electrochemical route at room temperature. Structure analysis indicated that the Ni doped ZnO particles are polycrystalline of hexagonal wurtzite structure and the average size of the particles was estimated to be approximately 61 nm, which conforms the nanoparticles in form. The band edge is shifted to the lower energy side of the nanoparticles. The FTIR result shows that the stretching vibration of the H-O and Zn-O bond. Photoluminescence spectrum measurement demonstrated that the nanoparticles exhibit a strong near band edge UV emission peak centred at 384 nm.

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### Author(s) Profile



**Prof. M. Ruhul Amin Bhiyyan** was born on Dec.10, 1972 in Comilla, Bangladesh. He received the M.Sc degree in Applied Physics and Electronics from Rajshahi University, Bangladesh in 1995, and Ph.D. degree from Islamic University, Kushtia, Bangladesh in 2008. He is currently a Professor in the Department of APE & Com. Engineering, Islamic University, Bangladesh. His current interest is thin-film solar cell and nanoparticle materials characterization. His work has produced nearly 30 peer-reviewed scientific International and National papers.



**Md. Khalilur Rahman** was born on July 1, 1971 in Madaripur, Bangladesh. He received the M.Sc. degree in Applied Physics, Electronics & Communication Engineering from University of Dhaka, Bangladesh in 1992. He is currently an Associate Professor in the Department of Applied Physics, Electronics & Communication Engineering, Faculty of Applied Science & Technology, Islamic University, Kushtia-7003, Bangladesh. His interest is in Optoelectronics and Wireless Communication. His work has produced nearly 20 National and International papers.

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