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## SYNTHESIS, STRUCTURAL, OPTICAL, MAGNETIC AND PHOTOCATALYTIC ACTIVITY OF NICKEL DOPED ZnO NANOPARTICLES

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## ABSTRACT

In the current research, we have synthesized Ni doped zinc oxide nanoparticles by solvothermal method at four different ratios (X = 2%, 4%, 6% and 8%). The samples were characterized for structural analysis by X-ray diffraction, morphological analysis by Field Emission Scanning Electron Microscope, elemental composition by Energy Dispersive Spectral Analysis, optical properties by UV Visible absorption studies, photoluminescence studies, Fourier Transform Infrared Analysis, Magnetic properties by Vibrating Sample Magnetometer of (x=2%). As a application of this work all the samples were subjected to test for the degradation of Rhodamine 6G dye under visible light and exhibited a better photocatalytic activity.

Keywords: Photocatalysis, Microwave synthesis, Nickel doped Zinc oxide, Rhodamine 6G, Visible light.

## 1. INTRODUCTION

A Slovakian proverb says "Pure water is the world's first and foremost medicine". As we all well know about the contamination of pure drinking water by the industrial products, that are released as a waste product into rivers, wells and lakes, which are mostly used as a drinking water by the people. Because of this polluted water, people and also the living organism in the freshwater too get affected. The most revolutionary technology known as Nanotechnology helps alleviate water problems by solving the technical challenges that removing water contaminants including toxic metals, textile dyes, pesticides, etc. [1]. Numerous Scientists claim that nanotechnologies offer more affordable, effective, efficient and durable ways of achieving specific nanoparticles for water treatment will allow manufacturers to prepare less toxic particles using the classical method. In an evolving world market, metal oxide (MO) - based semiconductor materials have taken on an exceptionally significant role due to their wide range of properties and applications. Their strong electron interactions, combined with their compositional simplicity and stoichiometric diversity, makes them

important model compounds for understanding the effects of strong correlation in physical and chemical phenomena and also have found use in many applications such as photocatalysis [2].

Photocatalysis is considered as a more advanced oxidation process to resolve environmental problems such as air pollution and textile industrial wastewater. The main idea behind photocatalysis includes the degradation of organic chemicals using UV rays with catalysts. Recently, the use of heterogeneous semiconductors as a photocatalyst for the degradation of organic pollutants in water has been given great importance. When semiconductors are illuminated with a light higher than their band-gap energy, an electron in the valance band gets shifted to the conduction band leaving behind positive holes in the valence band. These holes result in the generation of hydroxyl radicals which are highly oxidizing in nature. These holes on reacting with dye molecules, extract electrons and initiate the progress of degradation [3]. ZnO is an inexpensive, n-type semiconductor with a wide band-gap having optical transparency in the visible range. The n-type semiconductor behaviour is due to the ionization of excess zinc atoms in the interstitial positions and the oxygen vacancies, Surface defects play an important role in the photocatalytic activities of metal oxide as they increase the number of active sites [4]. As for as water detoxification is concerned, ZnO is more efficacious owing to the fact that it generates  $H_2O_2$  more persuasively. It has high reaction and mineralization rates. Hinging on its absorption efficiency ZnO exhibited an improved photocatalytic activity. The cause of this is an increase in the surface defects upon doping of transition metals with metal oxides. Besides, it affects the optical and electronic properties and can presumably shift the optical absorption towards the visible region. This can subsequently activate these modified metal oxide photocatalysts upon visible light irradiation [5].

Doping is an important way to enhance the separation of charge carriers in semiconductor photocatalysts. Many dopants such as Ni, Cu, Fe, Mn, etc. have been used to enhance photocatalysis efficiency [6]. Especially Ni was considered for the improvement of photocatalytic activity as one of the most effective doping elements for the improvement of the activity photocatalysts. In the present research work, Nickel doped zinc oxide nanoparticles were synthesized by the solvothermal method which was tested for the enhanced photocatalytic performance of Nickel doped nanoparticles as photocatalyst. as-synthesized The sample was characterized by X-ray diffraction (XRD), UV Visible spectroscopic technique, Fourier transform infrared spectroscopy (FTIR). The photocatalytic properties of the synthesized nanoparticles were evaluated through the degradation of Rhodamine solutions initiated by radiation.

## 2. MATERIAL AND METHOD

The acetate salts of zinc and nickel  $((CH_3COO)_2 Zn.2H_2O)$ ,  $(Ni(CH_3COO)_2)$ , were used as a source of metal ions, ethylene glycol, urea was also purchased. Rhodamine 6G indicator was the dye chosen. All the chemicals were from Merck, they were of analytical grade and utilized without further purification. double distilled water and acetone were used for the purification of the final product. Nickel-doped ZnO nanoparticles were prepared using the solvothermal method, zinc acetate dihydrate [Zn (CH<sub>3</sub>COO) <sub>2</sub>Zn.2H<sub>2</sub>O), nickel acetate (Ni(CH<sub>3</sub>COO)<sub>2</sub>), were used as the precursors. The solvent for dissolving the precursor material was ethylene glycol.

Ni-doped ZnO nanoparticles were synthesized for four different concentrations (x = 2%, 4%, 6% and 8%) by

changing the concentration of the precursors. Initially, the precursor materials like zinc acetate dihydrate, nickel acetate and urea were taken in the proposed ratios, mixed well in the ethylene glycol using a magnetic stirrer for about 1 hour. The solution was then microwave treated until the solvents were evaporated completely. The substance thus deposited on the ceramic bowl was cleaned about five times using double distilled water. Then, to remove the unwanted organic compound present, the sample was washed with acetone [7]. As a final step, the sample was calcinated at 300°C which gives the product required. The increase in concentration of Ni gives a strong change of colour in the final product (Fig. 1). With the advent of science and technology in the field of instrumentation, it is possible to scrutinize nanopowders at atomic level, in a very simple and efficient manner. In the present work, nickel doped zinc oxides were characterised by the following methods. The XRD patterns were recorded using XPERT-PRO Diffractometer system. The absorbed patterns were indexed with those available in the JCPDS database. The crystalline size was determined by Debye Scherrer's formula. The absorption spectra of the samples were analyzed using HITACHI UH 5300 UV-Visible Spectrophotometer. The FTIR spectra of the samples were determined in the range of 4000 to 400 cm<sup>-1</sup> on NICOLET IS5 KBR windows with AR diamond crystal plate. The surface morphology and composition of zinc, nickel and oxide were investigated by Field Emission Scanning Electron Microscope (EVO 18 SEM) and Energy Dispersive X-Ray Spectroscopy (QUANTA -FEG 250). The photocatalytic properties of Nickel doped Zinc Oxide nanoparticles were evaluated through the degradation of Rhodamine 6G initiated by 300W tungsten lamp visible.



Fig. 1: Variation of colour from light to dark green upon addition of Nickel

## 3. RESULTS AND DISCUSSION

# 3.1. Structural analysis of Ni doped ZnO nanoparticles

XRD patterns of Ni-doped ZnO nanoparticles are displayed in Fig. 2 (a). Most of the sharp intense peaks grabbed the properties of ZnO of JCPDS Files in Table 1 with the space group of  $P_{63}$ mc [8]. The synthesized Zn<sub>1</sub>. <sub>x</sub>Ni<sub>x</sub>O materials display hexagonal structure, Reflection from the predictable planes such as (100), (002), (101), (102), (110), (103), (201) and (202) match up with the peaks at  $2\theta = 31.76^{\circ}$ ,  $34.41^{\circ}$ ,  $36.23^{\circ}$ ,  $47.58^{\circ}$ ,  $56.69^{\circ}$ ,  $62.92^{\circ}$ ,  $69.18^{\circ}$  and  $77.05^{\circ}$ . Respective JCPDS File No, lattice parameter (a=b, c), Volume of the cell and

average crystalline size are tabulated (Table 1). For the hexagonal system, the volume of the cell is figured from the equation,  $V = 0.866 \times a^2 \times c \times sin (60^\circ)$ , where a and c are lattice parameters. With the increase in the Ni concentration (X= 2%- 8%), the lattice parameter values get decreased. This decrease in the lattice parameter might be due to the substitution of Ni ion with the ionic radius of 0.55 Å in the place of the Zn ion with ionic radius 0.60Å. The average crystalline size of the sample ranges from 26.79nm-34.69 nm using Debye Scherrer's equation. An increase in the intensity of the peak is absorbed with the increase in the concentration of the Nickel doping (Fig 2b).



Fig. 2: (a) XRD pattern of Ni doped ZnO nanoparticles, (b) Variation of intensity in XRD spectra

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Metal Oxide	JCPDS File. No	Lattice Parameters		Volume of the cell	Average Crystalline
		a = b(Å)	c(Å)	(Å <sup>3</sup> )	Size (nm)
0.08	01-079-2205	3.2495	5.2054	47.60	34.69
0.06	01-080-0074	3.2513	5.2059	47.66	33.35
0.04	01-076-0704	3.2517	5.2090	47.72	30.72
0.02	01-079-0206	3.2540	5.2118	47.77	26.79

Table 1: XRD Analysis of Ni doped ZnO nanoparticles

Field Emission Scanning Electron Microscope paves way for the conceptualization of morphology of the nanoparticle. FESEM images of as synthesized  $Zn_{0.92}Ni_{0.08}O$  was obtained as shown in Fig. 3. The average particle size of the sample was calculated as 16.04 nm. In order to confirm the formation of Nickel doped Zinc Oxide nanoparticles, EDX analysis was performed. During the EDX measurement of

 $Zn_{0.98}Ni_{0.02}O$  and  $Zn_{0.96}Ni_{0.04}O$ , different areas were focused and the corresponding peaks are shown in Fig. 4 (a) & (b). All three elements are seen in the microwave synthesized nanoparticles in the EDX spectrum. In Fig. 4 (a), the quantity of Zn, Ni and O were 36.27, 1.61 and 62.12 respectively, while in Fig. 4 (b), the values were 47.59, 3.50 and 35.06 for  $Zn_{0.98}Ni_{0.02}O$  and  $Zn_{0.96}Ni_{0.04}O$  NPs.



Fig. 3: SEM image of Zn<sub>0.92</sub>Ni<sub>0.08</sub>O nanoparticles

## 3.2. Optical analysis

Modification in the optical band-gap of ZnO due to Ni doping is given by extrapolating the linear portion of the  $(\alpha h u)^2 -h u$  plots to  $(\alpha h u)^2$  from absorbance spectra using UV-Visible absorbance spectrometer in the ranges of 300 to 800 nm. The tauc graph of Ni-doped ZnO is plotted in Fig 5 as obtained. The optical band-gap  $E_g$  of the ZnO doped Ni (X= 2, 4, 6 & 8%) are procured as 2.95eV, 3.08eV, 3.20eV and 3.33eV. It is inferred that there was an increase in the optical band-gap Eg of the material with the increase in the Nickel concentration. The introduction of Ni in the top of the valence band is considered as a reason for the increase in the optical bandgap [9].



Fig. 5: UV-VIS Tauc Plot of Ni doped ZnO Nanoparticles for X= (a) 8%, (b)6%, (c) 4% and (d) 2%

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Photoluminescence spectra investigations on Ni doped ZnO samples are arrayed in the Fig. 6. One or more defect-related emission peaks near the blue-green (480-550 nm), yellow (550-610 nm), and orange-red (610-750 nm) in the visible region one near band edge emission in the UV region is generally exhibited by ZnO. Oxygen vacancies (Vo), zinc vacancies (Vzn), oxygen interstitial (Oi), zinc interstitial (Zni), antisite oxygen (Ozn), and extrinsic impurities that form deep energy levels in the bandgap which makes an emission in the visible region [10]. But we obtained two peaks, one weak emission peak at 366 nm and a sharp emission peak at 655 nm as shown in the Fig. 6.



Fig. 6: Photoluminescence Spectra of Zn<sub>1-x</sub>Ni<sub>x</sub>O nanoparticles

It is quite common that the orange-red emission peak centered at 654.32 nm and at 653.74 nm is attributed to the presence of excess oxygen such as oxygen interstitials [11]. Taking the intrinsic point defect in the energy band of ZnO, the peaks about 654 nm may be due to (1) transition from the monovalent interstitial zinc (Zn+) or oxygen vacancy (Voo) to the monovalent vacancies (Vo+) and (2) transition from the conduction band to the monovalent vacancies (Vo+). It is seen that defects of oxygen interstitials (oxygen vacancies) represent the oxygen-rich (oxygen-deficient) state of ZnO. Our results are in good agreement with results already reported [12].

Fourier Transform Infrared spectroscopy is a technique to make a clear interaction with particles to analyse the chemical bonding, molecular structure, and functional group presence in the material. FTIR spectra of  $Zn_{1x}Ni_xO$  was recorded in the range of 4000cm<sup>-1</sup>-400cm<sup>-1</sup>. Fig. 7 gives the full transmittance spectra of Ni (2%, 4%, 6% and 8%) doped ZnO nanoparticles.

Avoiding the presence of  $CO_2$  in the atmosphere and absorption of water is not negligible. The peak at 3012cm<sup>-1</sup> represents the OH vibration and the presence of slight moisture in the sample. The peaks at 1738 cm<sup>-1</sup> , 1366cm<sup>-1</sup> and 1216cm<sup>-1</sup> correspond to C=O stretching, O-H bending and C-O stretching and broadband around 600cm<sup>-1</sup> to 400 cm<sup>-1</sup> represents the metal-oxygen bonding.



Fig. 7: FTIR Spectra of Ni doped ZnO Bottom to top 2% to 8%

#### 3.3. VSM studies

Magnetization Field (M-H loop) of Nickel (X=2%) doped ZnO was elucidated as shown in Fig. 8. The M-H curve impart the paramagnetic appearance. No such change was absorbed up on the addition of Ni on ZnO lattice. Coercivity, retentivity, magnetization and energy loss per unit volume were obtained as 270.84 G, 22.233E-6 emu, 1.4433E-3 emu at room temperature.



Fig. 8: M-H curve for Zn<sub>0.98</sub>Ni<sub>0.02</sub>O system

#### 3.4. Photocatalytic studies

Under visible light irradiation, the photocatalytic performance of the samples was estimated by the decomposition of the Rhodamine 6G dye. To prepare the samples for the photocatalytic analysis, first 0.1gm of Rh 6G was weighed. The 50ppm solution of Rhodamine 6G and 0.05gm of the catalyst Ni-doped ZnO were prepared for the photo reactor system. Initially, the solution was placed in the dark mode for 60 min and then under visible light irradiation. The degraded dye sample was collected in the interval of 15 min and tested for degradation of the dye. Afterward, the solution collected was tested for absorption spectra using a UHS300 spectrophotometer. The formula to calculate the degradation efficiency was, Degradation

Efficiency =  $\{(A_0 - A_{(t)})/A_0\} \times 100$ 

Where,  $A_0$  is the initial absorption of methyl orange solution and A(t) is the absorption of different UV irradiation times. Fundamentally, all the Ni-doped ZnO liberate photons with the irradiation of visible light when its energy is greater than or equal to the bandgap [13]. An equal number of electrons and holes in the conduction and valence band make possible for the existence of OH and O<sub>2</sub> free radicals. Of course, all the four ZnO with Ni doping evinced a satisfactory degradation of the dye molecule (Fig. 9 a, b). Out of them, Ni with a concentration of 8% prompted the best results with an efficiency of 83.85% in comparison with x= 2%, 4%, and 6% which gave the degradation efficiency of about 78.26%, 81.16%, and 83.11%.



Fig. 9: (a) plot between time vs. absorbance, (b) plot between time vs. degradation Efficiency

## 4. CONCLUSION

Nickel doped ZnO nanoparticles were synthesized by solvothermal method and their structural, optical, magnetic properties and photocatalytic activity were scrutinized. The hexagonally structured Ni doped ZnO shows the crystalline size around 16 nm, with the required elemental composition confirmed by EDS spectra an increase in crystalline size (26nm-34nm), decrease in band gap (3.33eV- 2.95eV) resulting in the increase of photocatalytic degradation efficiency (78% -83%) of Rhodamine 6G dye with increase in concentration of Nickel. The Ni doped ZnO nanoparticles prove to be efficient materials for degrading contaminated coloured waste water for reusing. It can be concluded that this work may provide the most efficient catalyst for the photodegradation of organic pollutants from waste water in industry and is expected to promote its practical applications in the other field of environmental science.

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## **Conflict** of interest

The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this paper.

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