Structural Optical Magnetic And Photocatalytic Properties of Ferromagnetic *P-Type* NiO: *N-Type* ZnO Nanocomposites

G. Kavitha

University of Madras

K. Thanigai Arul

AMET Deemed to be University

Manikandan Elayaperumal (✉ maniphysics@gmail.com)

Thiruvalluvar University <https://orcid.org/0000-0002-3307-5776>

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Abstract

The semiconductor-transition conducting metal oxides (p-type NiO: n-type ZnO) nanocomposites (NCs) called (NZO) are successfully prepared by a simple wet-chemical route followed by the systematic sintering at different temperatures such as 400°C, 500°C, 600°C, and 700 °C. The structure and morphology of the samples were characterized by X-ray diffraction (XRD), high-resolution scanning/transmission electron microscopy (HR-SEM/TEM), and energy-dispersive X-ray spectrometry (EDX) techniques. XRD analysis reveals that the average crystallite size of the NZO NCs was found to be in the range 16-18 nm. The synthesized sample discloses a ferromagnetic behavior. The photocatalytic degradation of rhodamine B in an aqueous solution was superior at the NZO NC at 600 °C in comparison with other samples. Here, the NZO NCs display to be good candidates for magnetic and photocatalytic application.

1. Introduction

In the recent years, coupled metal oxide semiconductor nanomaterials have been received a lot of interest owing to its potential applications in optoelectronic devices, sensors, solar cells, photocatalysis and biological imaging, etc. [1–5]. It is well known that zinc oxide (ZnO) is an efficient photocatalyst, with a band gap of around 3.2 eV and it is one of the low-priced *n-type* semiconductors and a large exciton binding energy (60 MeV) [6, 7]. Nickel oxide (NiO) is one of the most usually used photocatalysts with a wide range of applications as a p-type semiconductor with a wide band gap (3.6-4.0 eV) [8]. However, both the ZnO and NiO nanomaterials possess disadvantages of having a wide band gap ≤ 3.2 eV, therefore, the photo-excitation process requires UV region of the electromagnetic spectrum [9]. Nowadays, the coupled metal oxide semiconductors, i.e., two different metal oxides together act as a hetero-junction demonstrate improved photocatalytic activity. It is mainly due to the simultaneously excitation of the present metal oxide semiconductors, and improve their electron–hole pair separation, which enhances the photocatalytic efficiency [10]. Moreover, the efficiency of the photocatalytic activity depends upon the life time of the photo-generated electron/hole pairs [11]. A wide variety of synthesis routes have been used to prepare metal oxide nanoparticles, such as precipitation, microwave irradiation, mechanical milling, solution combustion, pulse laser deposition and vapour transparent deposition [12–14]. Different synthesis procedure yields different morphology of the sample such as nanorods, nanowire, nanoflower, nanocube and nanosheet, which altering its optical, electrical and magnetic properties have been reported [15–17].

Sun et al. [18] developed a novel dumb-bell shaped ZnO photocatalyst by hydrothermal method. The results indicated that the prepared dumbbell-shaped ZnO microcrystal exhibits superior photocatalytic activity and it could be considered as a promising photocatalyst for dye effluent degradation. Tong et al. [19] synthesized quasi-sphere-like ZnO by ice-water bath. This hierarchically nanostructured ZnO shows significantly improved photocatalytic activity than ZnO nanopowder. ZnO nanostructures in the shape of particles, rods, flower-like and micro-sphere synthesized using a facile hydrothermal method and the effect of morphology on the decolorization of acid red dye solutions under sunlight was studied by

Mohajerania et al. [20]. Sobana et al. [21] reported that Ag NPs doped TiO₂ for the degradation of direct red 23 and direct blue 53. Improved photocatalytic activity of Ag-TiO₂ was found to be due to electron trapping by Ag particle. Neppolian et al. [22] reported ZrO₂-TiO₂ binary oxide semiconductor nanoparticles for the application of photocatalyst.

In this present work, the ZnO-NiO NCs are prepared by wet chemical route and further the samples are sintered at different temperatures viz 400°C, 500°C, 600°C and 700°C. The prepared samples were characterized by X-ray diffraction (XRD), high resolution scanning electron microscopy (HR-SEM), high resolution transmission electron microscopy (HR-TEM), diffuse reflectance spectroscopy (DRS) and vibrating sample magnetometer (VSM) and photocatalysis. Under light irradiation, sintered sample (600°C) degrades rapidly due to higher transfer of electrons to conduction band from valence band and forming hole at valence band that providing superoxide for the degradation of the dye.

2. Materials And Methods

2.1 Preparation

Analytical reagent grade of nickel chloride, zinc acetate dihydrate and sodium hydroxide (NaOH) were obtained from Merck and used without any purification. Nickel chloride (1 M) and zinc acetate dihydrate (1 M) and NaOH (2.5 M) were prepared using appropriate amount of distilled water separately in a beaker. Then, the solution of nickel chloride was kept on a magnetic stirrer and the zinc acetate solution (1 M) was added drop wise to the nickel chloride solution. To the above mixture, the NaOH solution was added drop wise till the turbidity occurred for 3 h. Thus, the green gel was formed that was washed thrice using distilled water. Eventually, the sample was permitted to dry in an oven for 3 h at 80°C. In this step, the mixture of zinc hydroxide and nickel hydroxide was formed during the following reaction (1):

The ultimate precipitate was heated for 3 h in a muffle furnace at various temperatures namely, 400°C, 500°C, 600°C and 700°C and denoted as NZO-400, NZO-500, NZO-600 and NZO-700 respectively. The following reaction (2) took place in the dehydration phase:

2.2. Characterization

The structural characterization of ZnO-NiO samples was performed using a Philips X'pert X-ray diffractometer with CuK_α radiation at λ = 1.540 Å. Particle size and energy dispersive X-ray analysis of ZnO-NiO have been performed with a Jeol JSM6360 high resolution scanning electron microscopy. The transmission electron micrographs and photoluminescence of the samples were carried out by Philips-TEM (CM20) and Varian Cary Eclipse Fluorescence Spectrophotometer respectively. The surface area

was derived from the nitrogen adsorption–desorption isotherms using liquid nitrogen at 77 K using an automatic adsorption instrument (Quanta chrome Corp. Nova-1000 gas sorption analyzer). The magnetic properties of the samples were investigated using vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from -10000 to +10000 Oe using a PMC MicroMag 3900 model vibrating sample magnetometer (VSM) equipped with 1 Tesla magnet.

2.3. Photocatalytic activity

A photoreactor fitted with four 8 W medium pressure mercury vapor lamps emitting at 365 nm (Sankyo Denki, Japan) was used to determine the photocatalytic activities of the doped and undoped samples. The set of lamps was covered outside by a highly polished anodized aluminium reflector to preserve the light intensity. A borosilicate glass tube of 15 mm inner diameter placed at the centre of the photoreactor was used as the reaction vessel. The reactor was cooled by fans that mounted inside it. The light intensity was determined by ferrioxalate actinometry. Fresh solution of rhodamine B was used for the photodegradation. After the addition of the nanoparticles to the dye solution, air was bubbled through the solution and, further the nanoparticles are stirred at constant motion. The dissolved oxygen was measured by an Elico dissolved oxygen analyzer PE 135. After the illumination, the nanoparticles were recovered by centrifugation and the dye was analyzed by spectrophotometrically at 552 nm. The calibration curve was constructed by measuring the absorbance of rhodamine B at different ppm.

3. Results And Discussion

3.1. X-ray diffraction

The crystal structure and phase purity of ZnO-NiO nanoparticles are analyzed by X-ray diffraction. The XRD patterns of the as-synthesized ZnO-NiO nanoparticles are shown in Fig. 1. The diffraction peaks are corresponding to both ZnO (JCPDS No. 36-1451) [23] and NiO (JCPDS No. 47-1049) [24] are noticed. The peaks around 37°, 43°, 62.4° and 74.7° are corresponding to the NiO planes (111), (200), (220) and (311). Similarly, the peaks around 31.6 °, 34.2 °, 36.19 °, 47.4 °, 56.6 °, 67 °, 68.9 ° and 78.8 ° are related to the planes of ZnO (100), (002), (101), (102), (110), (112), (201) and (202) respectively. As the temperature increases, the intensity of diffraction peaks is enhanced that revealing high crystallinity. The peak around 36.19° is split and its intensity varied with the sintering temperature due to the modulation of crystal growth orientation. Here, the planes of NiO are predominant compared with the planes of ZnO. Similar trend was explained in the composite of ZrO_x/ZnO metal oxides by hydrothermal method [24].

The average crystallite size was calculated using Scherrer’s formula given in Eq. (1)

$$L = \frac{0.89 \lambda}{\beta \cos \theta}$$

..... (1)

where L is the crystallite size, λ, the X-ray wavelength, θ, the Bragg diffraction angle and β, the full width at half maximum (FWHM). From the Table-1 it was clear that as the temperature increases the average

crystallite size gradually increases from ~ 16 to 26 nm. XRD pattern of pure and nanocomposites of NZO diffraction were given in the supplementary materials.

Table -1: Particles Size Determination of HTCMOs NCs

Calcination Temperature (°C)	Particle Size (nm) [Characteristic Peaks]	
	ZnO	NiO
300	10.087	10.873
400	16.135	16.135
500	17.611	18.261
600	20.175	20.174
700	25.525	26.913

3.2. Morphological analysis

The morphology of the prepared ZnO-NiO was examined by SEM. Growth of the nanoparticles cannot be controlled in this method leading to the variation of particle sizes. Fig. 2a shows the SEM micrographs of ZnO-NiO nanoparticles, which are of irregular spherical shape with varying sizes between 15 and 20 nm. The composition of ZnO-NiO nanoparticles was analyzed by energy dispersive X-ray analysis (EDX). The EDX results showed the presence of Zn, Ni and O without any other characteristic peaks (Fig. 2b). The HRTEM image showed the presence of abundant nearly flakes-like particles that were self-assembled (Fig. 2c) and the lattice fringes of ZnO-NiO nanoparticle are shown in Fig. 2d. The flakes-like particles have an average size in the range 16-18 nm.

3.3 VSM

Magnetization measurements on the synthesized nanoparticles were carried out and shown in Fig. 3. A weak ferromagnetic behaviour of the synthesized sample (NZO-400) was confirmed by the shape of hysteresis loop. From the VSM measurements, the coercive field (H_c) and the remanent magnetization (M_r) of the sample were estimated to be 27.47 O_e and 0.004 emu/g respectively. The low H_c and M_r confirmed the soft and weak ferromagnetic nature of the sample. The saturation magnetization (M_s) of

sample was found to be 0.200 emu/g which confirmed its ferromagnetic behaviour. Because of sintering, the particle size was reduced thereby formation of different magnetic domain which orient in the direction of magnetic field. The ferromagnetic behavior of the nanocomposite can be explained by dimensional factor as well as generation of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ solid solution. The present results coincide with the results obtained by Schwartz et al [25, 29].

3.4. Photocatalytic activity

In order to determine the photocatalytic activity of coupled metal oxides ZnO-NiO NCs, a series of experiments were carried out with rhodamine B in aqueous suspension under the light of wavelength 552 nm. The photocatalytic degradation follows a pseudo-first order reaction and its kinetics can be expressed using $\ln(C_0/C_t)=kt$, where k is the apparent reaction rate constant, C_0 is the initial concentration of rhodamine B, the reaction time (t) and C_t is the concentration of rhodamine B at time t . Fig. 4 shows the kinetic fit for the degradation of rhodamine B over the coupled ZnO-NiO NCs with the catalyst dosage of 30 mg, rhodamine B concentration of 75 mg/L and at pH 5. At 600°C, the sample rapidly degrades the dye owing to higher transfer of electrons to conduction band from valence band and forming hole at valence band under light irradiation that providing superoxide to the dye compared with other samples [26]. Here, the $h\nu B^+$ (hole at valence band) and eCB^- (electron at conduction band) are dominant oxidizing and reducing agents, respectively. The $h\nu B^+$ interacts with the dye (organic compounds) leading to form CO_2 and H_2O as end products. The $h\nu B^+$ also oxidizes the organic compounds by interacting with water for the generation of hydroxyl radical ($\cdot\text{OH}$). This radical is an electrophilic nature that can oxidize all electron rich organic molecules to convert them to CO_2 and water. The photocatalytic degradation of organic pollutants is a crucial one that can be achieved effectively by the process of reduction of oxygen and the oxidation of the dye that are continued simultaneously in order to avoid the build up of electron in the conduction band. This leads for the reduction of the rate of recombination of eCB^- and $h\nu B^+$ [27–28] and the reaction rate given in the supplementary materials.

4. Conclusions

In the present work, the ZnO-NiO NCs are successfully prepared by a simple wet chemical route with cost effective manner in the RT. It was found that the generation of NZO NCs commences at 400°C and as the temperature rises, the size of the composites gradually reduced. The flakes like morphology were observed from the electron microscope from the synthesized NZO NCs were confirmed by HR-SEM and HR-TEM analyses. The magnetization versus field strength behaviors of curve of ZnO-NiO NCs showed a hysteresis characteristic of ferromagnetic materials due to the dimensional effect of NiO nanoparticles. Besides, the ZnO-NiO NCs showed high photocatalytic efficiency for the degradation of *rhodamine B* dye under the light irradiation. Thus, the prepared ZnO-NiO sample is a potential candidate for photocatalytic applications.

Declarations

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Informed Consent

Informed consent was obtained from all individual author for this study.

Authors' Contributions

GK aimed and conceived of the study, formulated its design, coordinated the conduct of the study including materials synthesis, data collection, analysis and interpreted the data, and drafted the manuscript; KT participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; EM and JK participated in the design of the studies like magnetic and electron microscopic measurement etc assisted in interpreting the data, and helped to draft the manuscript. All authors read and approved the final manuscript.

Compliance with Ethical Standards

Conflicts of Interest

The authors report no conflicts of interest. When the editor or individual reader's need the original scientific data/images needed from this study. We will provide based on the genuine and ethical standard.

Research Data Policy and Data Availability Statements

The data that support the findings of this study are available from, but restrictions apply to the availability of these data, which were used under license for the current study, and so are not publicly available. Data are however available from the authors upon reasonable request and with permission.

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Figures

Figure 1

XRD patterns of ZnO-NiO nanocomposites of (e) NZO-400, (f) NZO-500, (g) NZO-600 and (h) NZO-700

Figure 2

ZnO-NiO nanocomposite (a) SEM image (b) EDX, (c) HR-TEM image and (d) lattice fringes.

Figure 3

Magnetic hysteresis loop of ZnO-NiO nanocomposites at 400 °C.

Figure 4

PCD efficiency (%) of ZnO-NiO nanocomposites.

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