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RESEARCH ARTICLE

Synthesis and Characterization of Ni Doped ZnO Nanoparticles and Study of their Antibacterial Activity

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Abstract

Objective: The current study focused on the synthesis of Nickel doped ZnO nanoparticles from the sol-gel technique. **Methods:** The pre-arranged nanopowder was described by XRD, FTIR, SEM, EDAX, and antibacterial investigations. The X-ray diffraction studies uncover that the incorporated nanoparticles have a wurtzite structure and the molecule size differs from 18 to 31 nm. A change in morphology, after being doped with Nickel, has been noticed. **Findings:** The Energy Dispersive X-Ray Analysis (EDAX) uncovers that the essential arrangement of arranged examples and the consolidation of the Ni particles into the ZnO cross-section. *Escherichia coli, Staphylococcus aureus, Aspergillus flavus*, and *A. niger* were used to test the antibacterial activity of Ni-doped ZnO nanoparticles using the plate dispersion method. **Novelty:** The antibacterial activity improvement with Ni doping effect is attributed to the enhancement of electronic defects including vacancy defect Ni and interstitial defect ZnO with Ni doping Concentration. These defects behave as electrons and holes source necessary for reactive oxygen species (ROS) responsible for bacteria's destruction.

Keywords: Antibacterial effect; Morphology behavior; NIckel doped ZnO Nanoparticles

1 Introduction

Zinc oxide has attracted an increasing interest due to its excellent semiconducting properties. ZnO is a direct wide band gap of 3.37 eV, it enjoys a large excitation binding energy (60 meV) at room temperature and thermal stabilities[1]. ZnO is becoming the most used semiconducting metallic oxide; it has attracted a large attention as a promising material in a wide range of technological applications namely: electronics, optics and optoelectronics devices transparent conducting oxide (TCO), gas sensing, waste water treatment, nanogenerator and antibacterial activity.

Nowadays microbial contamination is becoming a serious issue in healthcare and food industry. Annually 40% of the 50 million deaths in world were due to infectious diseases caused by bacteria's such as *Escherichia coli, Salmonella* etc.[2,3].

Therefore, developments of nanoparticles with antimicrobial properties are of considerable interest. In the last few years, multi-functional metals and metal oxides have attracted interest for their antimicrobial activities[4]. Metal oxide nanoparticles find many applications in physical, chemical and biological fields. Metal oxides nanoparticles, such as TiO_2, ZnO, CuO, SiO_2, SnO_2 and MgO have proven interesting antibacterial properties. ZnO has attracted a special interest due to its application in health care products, UV radiation blocking. The antibacterial activity of ZnO NPs was reported earlier[5]. It has been demonstrated that ZnO nanostructures can be successfully used against both Gram-positive and Gram-Negative bacteria[6,7].

Any antibacterial material action depends mainly on the production of reactive oxygen species (ROS) on the surface of the nanoparticles. The mechanisms of actions are based on the reactive oxygen species generation or the release of Zn^{2+} ions. These produced species interact harmfully with the bacteria's cell membranes to cause their death**.** Antibacterial nanoparticles have found several applications in antibacterial, photocatlytic activities, water treatment and food packaging[8].

It is well-established that ZnO impurity doping can control its properties and may improve its antibacterial activity. Several doping elements effect on ZnO antibacterial activity have been investigated in the literature. The antibacterial activity of Co doped ZnO, Fe doped ZnO, Ni doped ZnO, V doped ZnO, Sn doped ZnO, Ag doped ZnO, Mg doping, Mn doped ZnO, Sr doped ZnO, Sc doped ZnO, Se doped ZnO. Also, co-doping with F and Fe, La and Cu co-doped ZnO have been also investigated. To the best of our knowledge Ni doping effect on ZnO nanopowder antibacterial activity has not been investigated. The only complied work on Ni doped ZnO thin film were prepared by spray pyrolysis method.

Ni element has been used as an effective dopant of ZnO, it has been demonstrated that incorporation in ZnO network controls the material crystallinity and improves the material electrical conductivity to produce a transparent conducting oxide for solar cell and flat panel display[9,10].

In the present work we studied the antibacterial activity of Ni-doped ZnO nanocomposites fabricated via sol-gel technique. We investigate the antibacterial activity of the prepared nanocomposites against various pathogens such as *Escherichia coli, Staphylococcus aureus, Aspergillus flavus, Aspergillus niger* and the effect of Ni doping level on ZnO antibacterial activity efficiency.

2 Methodology

The zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) was dissolved in deionized water which was used as the starting solution (0.1 M). Nickel acetate tetra hydrate [Ni $(CH_3COO)_2$. $4H_2O$] was used as dopant precursor for Ni, correspondingly. The pH value of the beginning arrangement was kept up at 9 by adding the essential amount of NH_4OH arrangement, following Tri-ethanolamine ($C_6H_{15}NO_3$) is added as a surfactant to control the size and morphology of nanoparticles. The resulting mixture was heated to 60°C and magnetically stirred for 2 hrs. After finished the stirring process the precipitate was irradiated with a microwave oven (LG India, frequency employing 2.45 GHz) for 30 min, and washed several times with a combination of ethanol and water kept in the ratio of 1:3. Then the precipitate was separated carefully by filtration and the sample was heated at 80°C in a hot air oven for 6 hrs. Finally, using a muffle furnace, the powder was calcined at 700 °C for 2 hrs.

3 Characterization

X-ray analysis was carried out using X-ray diffractometry (XRD) using CuKα radiation (λ=1.5406Å) in the 2θ range from 20˚ to 80˚. The morphology was identified by Scanning Electron Microscope (SEM), and energy-dispersive X-ray absorption (EDAX) was carried out correspondingly. The pattern of the ZnO wurtzite phase and accessible molecular bonds were investigated by the FTIR spectrum. The anti-bacterial and anti-fungal activities were examined for Ni-doped ZnO nanoparticles against two pathogenic bacteria and two pathogenic fungi were investigated by the agar disk diffusion method[11]

3.1 Results and Discussion

3.1.1 Structural Study

The X-ray diffraction (XRD) patterns of undoped and Ni-doped ZnO nanoparticles with different dopant concentrations (0.1, 0.2, and 0.3M) of Nickel (Ni^{2+}) are shown in Figure 1. The structural property of nanoparticles as well as crystalline size was obtained from XRD spectra. The strong and clear peaks reveal the high clarity and crystallinity of the as-equipped powder. The sharp diffraction peaks matching to (100), (002), (101), (102), (110), (103), (112) and (201) planes indicate the crystalline ZnO with hexagonal wurtzite structure, which are in close conformity with the JCPDS card No. 36-1451,[12]. From the spectra, the broadening line indicates synthesized powders in nanoscale. In Figure 1, diffraction peaks occur at 31.80, 34.48°, 36.37°, 47.60°, 56.65°, 62.90°, 67.91°, and 69.01°, correspondingly. In meticulous, the intensity of diffraction peaks is improved drastically with rising of Ni^{2+} absorption. This action indicates that the increase in the doping concentration enhances the crystallinity, which may be ascribed to the disparity ionic radii of zinc and Nickel. With the increase of Ni concentration, it has been reported that the intensity of the diffraction peak decreased(13). The average crystallite size of nanopowders was obtained using Scherrer's formula

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

Where D is grain size (nm), λ is the wavelength of the X-ray, β is FWHM, and θ is the Bragg angle.

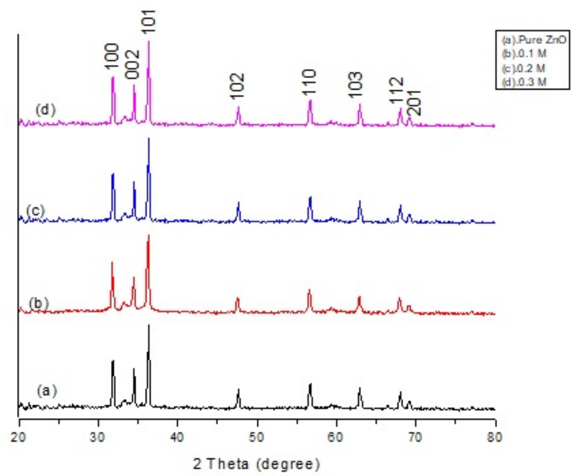

Fig 1. XRD Spectra Analysis of Undoped Ni doped ZnO Nanoparticles

The effect of high temperature very much influence the particle morphology of the as equipped ZnO nanopowder and Ni-doped ZnO nanoparticles in different molarities like 0.1, 0.2, and 0.3M. As the molarities concentration increases FWHM (Full Width Half Maximum) increases and at higher molarities concentration value FWHM (Full Width Half Maximum) decreases(14). The calculated grain size of undoped and Ni-doped ZnO nanoparticles is tabulated in Table 1.

Table 1. Structural parameters of Undoped and Ni doped ZnO Nanoparticles

Sample	Molarities Ratio	Grain size (D) nm
Pure ZnO	0.1 M	18
Ni doped ZnO	0.1 M	26
Ni doped ZnO	0.2 M	29
Ni doped ZnO	0.3 M	31

3.1.2 Functional Group Analysis

In the FT-IR spectra shown in Figure 2 the wide absorption band at ~3323.87 cm−1 corresponds to the O–H stretching vibrations of water present in ZnO and the other transmission band at ~3148.12 cm−1 is assigned to a residual organic component. The band at ~1587.23 cm−1 can be linked with the bending vibrations of H_2O molecules.

The transmission band at ~1392.04 cm−1 and ~1122.12 cm−1 in both the samples is due to the carbonyl groups of the carboxylate ions which force leftovers adsorbed on the surface of ZnO. The stretching of the band appear at 767.97 cm−1 confirms the formation of ZnO particles(15). The peaks that appear between 459.79 and 610.05 cm−1 are assigned to the metal-oxygen (M–O) stretching mode. Verges et al. already report that form of peaks in three different positions depends on the shapes of ZnO. The shape affects the location and intensity of the peaks.

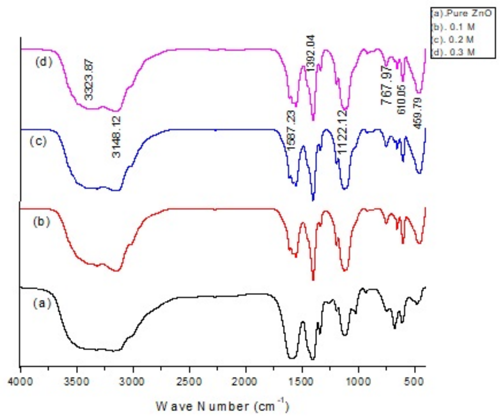

Fig 2. FTIR Analysis of Ni Doped ZnO nano particles

3.1.3 Morphological Analysis

The SEM images of undoped ZnO and Ni-doped ZnO nanopowders are shown in Figure 3. The grain sizes of all the samples are in the nanoscale and have a crystal-like closely packed arrangement. It is seen that the grain size increase with the increasing doping concentration [16]. The increase in the grain size is one of the reasons for the enhancement in the antibacterial activities of the synthesized doped ZnO nanopowders as discussed in Antibacterial studies.

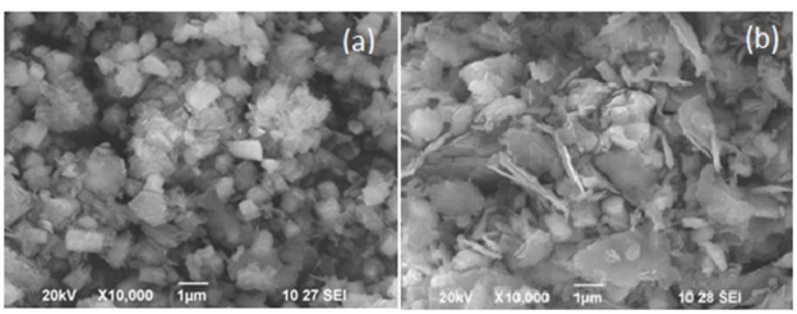

Fig 3. SEM Analysis of Pure and Ni doped ZnO nano particles

The EDAX analysis indicates the successful undoped and Ni-doped ZnO nanoparticles which are with the coincidence of XRD result. The EDAX spectra of undoped and doped samples are shown in Figure 4 Elemental analysis shows that the presents of elements such as Zn, Ni, O are confirmed the formation of Ni-doped ZnO nanoparticles. The Undoped ZnO contains only zinc and oxygen elements, whereas the doped samples contain zinc, oxygen, and nickel in the appropriate ratios [17].

3.1.4 Antibacterial Activity

The incorporated Ni-doped ZnO nanoparticles of discrete shape such as nano precious stone like structure by the sol-gel procedure. The nanoparticles were calcined for 2 hrs at 700°C. The antimicrobial movement of Ni-doped ZnO nanoparticles was examined against two pathogenic microorganisms strains, one Gram-positive (*Staphylococcus Aureus*) and one Gram-negative (*Escherichia Coli*) and two anti-fungal of parasitic strains (*Aspergillus flavus* and *Aspergillus niger*). Antibacterial and against

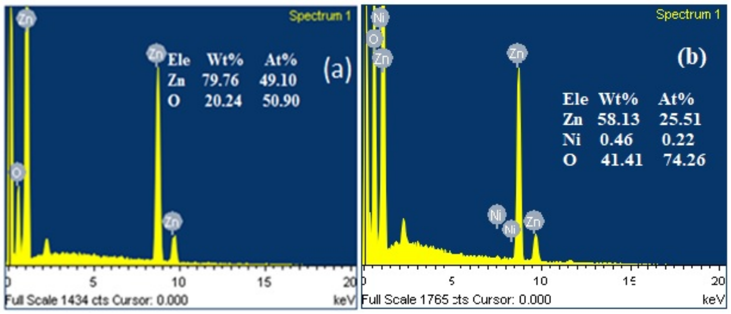

Fig 4. EDAX Analysis Pure ZnO and Ni doped ZnO nano particles

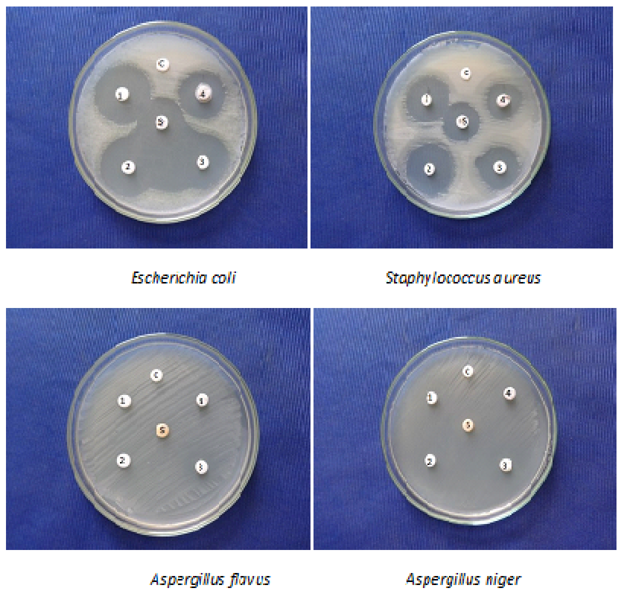

Fig 5. Antibacterial activity of Ni doped ZnO Nano particles

Table 2. Assay of Antibacterial Activity

Sl. No.	Bacteria	Zone of Inhibition (mm in diameter)					
		C	S*	1	2	3	4
1	*Escherichia coli*	-	22	21	23	25	27
2	*Staphylococcus aureus*	-	20	19	21	23	25
3	*Aspergillus flavus*	-	10	-	-	-	-
4	*Aspergillus niger*	-	11	-	-	-	-

**Amikacin for Bacteria; Amphotericin b for Fungi*

parasitic imminent Ni-doped ZnO nanoparticles were surveyed as far as zone of restraint of bacterial development[18]. The after effects of antibacterial and against contagious activities are introduced in Table 2.

According to the reported values in Table 3, Ni doping leads to better ZnO antibacterial activity, this might be due to larger ionic radius of Ni by comparison to the other studied metals, they are equal to 0.8 nm which are larger than Mn ionic radius (0.7nm), V ionic radius (0.7nm), Mg ionic radius (0.65nm), Co ionic radius (0.6 nm). Doping metal with larger radius ionic metal may introduces various electronic defects in ZnO band gap that play a crucial role in the antibacterial mechanism. This may suggest that the electronic defects in ZnO band gap play a crucial role in its antibacterial activity. Several mechanisms of ZnO action against bacteria have been suggested. These mechanisms are based on the decomposition of ZnO and formation of reactive oxygen species (ROS).

Table 3. Compilation of the inhibition zone diameter against various bacteria's recorded in ZnO material doped with different metallic elements

Components	Zone of inhibition	Tested micro-organism	References
Fe-ZnO	16.9	*E.coli*	[19]
V-ZnO	19.3 12	*P.aeruginosa, S. Aureus*	[20]
Mg-ZnO	10 10	*P.aeruginosa, S. Aureus*	[21]
Sn –ZnO	13 10	*E.Coli, S. Aureus*	[22]
Cu-ZnO	12 12	*E.Coli, S. Aureus*	[23]
Cu-Sn co-doped ZnO	16 15	*E.Coli, S. Aureus*	[24]
Mn- ZnO	8.8 11	*E.Coli, S. Aureus*	[16]
Mn doped ZnO	24 22 24	*E.Coli, Staphylococcus aureus, P.aeruginosa*	[25]
Ni doped ZnO	27 25	*Escherichia coli, Staphylococcus aureus*	Present study

4 Novelty statement

The synthesis and characterization of Ni doped ZnO nanoparticles and the study of their antibacterial activity present a unique approach to exploring the potential of these nanoparticles in combating bacterial infections.

5 Research finding

The research findings suggest that the Ni doped ZnO nanoparticles exhibit enhanced antibacterial activity compared to pure ZnO nanoparticles. The presence of nickel impurities in the ZnO lattice enhances the bactericidal properties, resulting in increased generation of reactive oxygen species (ROS). These ROS are known to have potent antibacterial effects, leading to effective inhibition of bacterial growth. The study also reveals that the antibacterial activity of the Ni doped ZnO nanoparticles is concentration-dependent, with higher concentrations showing stronger antibacterial effects. These findings highlight the potential of Ni doped ZnO nanoparticles as a promising candidate for the development of antibacterial agents in various applications, such as wound healing, water treatment, and medical devices.

6 Conclusions

The Undoped and nickel-doped ZnO nanoparticles were incorporated by the sol-gel technique. The result of primary, morphological, and essential examination of undoped and Ni-doped ZnO nanoparticles was researched. The XRD examination uncovers that the prepared particles were in hexagonal wurtzite structure with normal molecule size for undoped and doped ZnO nanoparticles under 31 nm. The surface morphology investigation was done utilizing SEM and EDAX. The substance gatherings of the examples were perceived by FTIR spectra and noticeable IR peak are investigated. In this way, the current doping strategy can be viewed as one of the productive procedures to adjust the ZnO nanoparticles. The outcomes were contrasted and standard anti-toxin drugs. In this work, Ni-doped ZnO nanoparticles were observed to be not dormant against Anti-bacterial, for example, Gram-positive and Gram-negative and inert for hostile to contagious movements.

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