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NiO and Ba²⁺ ions doped NiO Nanoparticles:Synthesis, Characterization and Microbial toxicity to Escherichia Coli

R.Shanaj Begum¹ and R.John Xavier²

Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli - 620 023, India.

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1. Introduction

Metal Oxides Nanoparticles exhibit unique physical and chemical properties due to their dimensions in nanoscale. Nanomaterials are more reactive because of their smaller size and greater surface area. Nickel Oxide is a transition metal oxide, a P-type semiconductor with a wide energy gap of 3.6 eV - 4 eV [1]. Due to its novel optical, electronic, magnetic, thermal, catalytic and mechanical properties [2], widely used in manufacturing magnetic materials, alkaline battery cathodes [3, 4] and etc. However, NiO NPs were previously reported as bactericidal and bacteriostatic agents [5]. Electrical and optical properties of a semiconductor can be modified by the doping process.

Several techniques such as Micro emulsions, Solgel, Spray Pyrolysis, Electrochemistry Deposition methods [6-9], have been developed to synthesize NiO NPs. Coprecipitation method [10] was used to synthesize undoped and doped NiO NPs.The effect of Barium doping into NiO and the influence of calcinations time on the structural, optical property of Ba:NiO nanoparticles were investigated and also the antimicrobial activity of undoped NiO and Ba:NiO (4hrs) nanoparticles is tested against E-Coli bacteria using disc diffusion method.

2. EXPERIMENTAL

2.1 Synthesis

Nickel (II) Chloride (Aldrich,98%) and Barium Chloride Dihydrate (Aldrich, 99%) in an appropriate amount of NiO $_{(0.2-x)}$ Ba $_x$ O (x=0 and 0.02 M) were dissolved in 100 ml of deionized water ,stirred for 2 hours.100 ml of Sodium Hydroxide (1.6 M) solution was added drop wise and stirred for 6 hours at 70°C. The resultant green precipitate was washed with double distilled water and ethanol, dried by heating at 90°C in the air. The pure NiO sample was calcined for 4 hrs at 700°C and the Barium doped samples were calcined for the different period of time (3hrs, 4hrs) at 700°C, the greenish sample turned into black color powder.

The decomposition of Ni (OH)₂ is represented as

Tele: 8870046786	
E-mail address: shanajbegum7@gmail.com	
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ABSTRACT

NiO NPs and Barium doped NiO NPs calcined for different periods of time (3hrs, 4hrs) at 700°C were synthesized through co-precipitation method. XRD analysis confirmed that all the samples exhibit FCC cubic structure. The doping of Barium and also increasing the calcinations time of Ba:NiO increases the crystallite size.Optical absorption spectra reveal that energy gap decreases from 3.75 eV to 3.35 eV due to the increase in crystallite size.PL spectral analysis shows that emission intensity decreases with decreasing grain size.The morphology of the NiO NPs and Ba:NiO NPs has been analyzed by FESEM and SEM respectively The results of antimicrobial activity of NiO NPs and Ba:NiO (4 hrs) against E-Coli indicated that NiO NPs have excellent inhibitory activity.

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NiCl₂ + 2NaOH $__{RT}$ Ni (OH)₂ + 2NaCl (1)

$$Ni(OH)_2$$
 calcinations $NiO + H_2O$ (2)

2.2 Characterization

Powder X-Ray Diffraction (XRD) of the samples was recorded using X'Pert PRO Diffractometer using Cu K_{α} radiation (0.15406 nm) at 2 θ angles, operated at 40 KV and 30 mA. Fourier Transform Infrared spectra, UV-Vis spectra (U-2900), Photoluminescence spectra (model-LS45) were recorded to analyze the functional groups and optical properties of the samples. FESEM and SEM characterizations are used to analyze the morphology of undoped and Barium doped NiO NPs. EDAX reveals the composition of NiO and Ba:NiO NPs. The antibacterial activity was performed by Disc diffusion method using the microbial strain, Gram-negative bacteria: Escherichia Coli (MTCC 119) Obtained from Microbial Type Culture Collection (MTCC) at the Institute of Microbial Technology (IMTECH), Chandigarh, India.

2.3 Antibacterial Studies

Nutrient agar (NA) medium prepared by dissolving 28 g of nutrient agar in 1L of distilled water and sterilized in an autoclave at 121°C for 15 minutes was poured into sterile Petri plates.Using sterile forceps, discs (6 mm diameter) impregnated with the stock solution of NiO NPs (50µl, 100 µl, 150 µl) were dispensed on the surface of the test organisms inoculated agar plates and incubated at 37°C for 24 hrs and at room temperature for 24-48 hrs. The antibiotic diffusion from these discs into Agar medium leads to inhibition of bacterial growth and the mean diameter of the zone of inhibition was recorded in mm. Chloramphenicol was used as the positive control. The same procedure was adopted to determine the antimicrobial potential of Barium doped NiO NPs(4hrs).

3. Results and Discussion

XRD patterns of pure NiO and Barium doped NiO NPs synthesized at the different calcination time 3 hrs,4hrs



designated as R1,R2 and R3 respectively are shown in Fig.1.Diffraction peaks of all the samples are indexed as (111), (200), (220), (311) and (222) crystal planes of NiO NPs (JCPDS: 78-0429, Fm-3m space group) .The samples R2 and R3 show a peak at 23.849° and 23.847° correspond to BaCO₃, formed due to the decomposition of BaCl₂ to BaO during calcinations at high temperature and then absorption of CO₂ from the atmosphere [10]. The crystallite size was estimated by Debye- Scherrer's formula

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$$\mathbf{D} = \mathbf{K}\lambda/\beta \operatorname{COS}(\theta) \tag{3}$$

Where k=0.9, D, β , θ and λ are the crystallite size, full width at half maximum intensity ,Bragg's angle and the wavelength of the Cu-K α radiation (1.5406 Å[°]).



Fig.1. XRD Pattern of NiO and Ba:NiO samples.

The average crystallite size of the samples R1, R2 and R3 are 22 nm , 28 nm and 31 nm respectively. The doping process increases the size of the crystallite ,decreases intensity of the peaks.Increase in the calcinations time of Ba:NiO NPs leads to increase in crystallite size since crystallite growth is thermally accelerated.

Fig.2. shows the FT-IR spectra of the samples R1, R2 and R3. The peaks in the range 3020 cm⁻¹–3650 cm⁻¹ correspond to the vibration mode of O–H bonds .The bands at 3378 cm⁻¹ and 1595 cm⁻¹ are due to O-H stretching vibration and O-H-O bending vibration mode. The bands of carbonate groups and C-O stretching bond are observed at 1434 cm⁻¹, 882 cm⁻¹ and 1036 cm⁻¹ respectively. The bands at 567 cm⁻¹, 415 cm⁻¹ are assigned to Ni-O stretching vibration mode.



Fig.2. FTIR spectra of NiO and Ba:NiO samples.

The samples R2 and R3 display the same functional groups with a slight change in the intensity and frequency. There is no peak signifying the presence of water. The weak bands at 1750 cm⁻¹,1716 cm⁻¹ which are the typical frequency of carbonyl group correspond to BaCO₃ and the peaks at 692 cm⁻¹ and 567 cm⁻¹ are assigned to Ni–O–H vibration mode and Ni-O stretching vibration mode respectively. The strong

bands exist at 493 cm⁻¹ for pure NiO NPs [11], 490 cm⁻¹ for Ba:NiO (4hrs) and 492 for Ba:NiO (3hrs) validate the formation of Ni-O [12].

The Tauc's plot and absorption spectra (inset) of the samples R1, R2 and R3 (Fig.3.) shows peak absorption intensity at 318 nm, 341 nm and 355 nm. The shift towards higher number indicates a decrease in band gap with increasing particle size [13]. The energy bandgap (E_g) calculated using Tauc's model

 $(Ah_V)^n = k (h_V - E_g)$ (4)



Fig.3. Tauc's Plot and Absorption spectra (inset) of the samples.

Where A , h_V is the absorbance and the photon energy and n = 2 for direct band gap. The energy band gap of R1, R2 and R3 determined from the graph of $(Ah_V)^2$ as a function of (h_V) by extrapolating the linear portion of the curve to energy axis are 3.75 eV, 3.52eV and 3.35 eV respectively . The decrease in band gap energy due to the increase in crystallite size is an evidence of the quantum confinement effect [14].

PL spectra of the samples R1, R2 and R3 excited by excitation energy 3.65 eV (Fig.4) illustrate UV emission peak of R1 at 357 nm due to electronic transitions of Ni²⁺ ions and the visible emissions of R2 and R3 at 426 nm and 439 nm respectively due to defects such as Ni interstitials and Oxygen vacancies present in the samples[15] and also confirm the substitution of Ba²⁺ ions into the NiO lattice. The decreasing particle size increases surface area:Volume ratio (Table.1) which in turn increases the number of intermediate energy states. The relaxation at these energy levels may be accountable for the fact that PL emission intensity decreases with decreasing particle size [16].





FESEM image and Energy dispersive X-ray spectra of NiO NPs shown in Fig.5 elucidate that NiO nanoparticles are nearly spherical and cubical in shape and are composed of Nickel (91.85%) and Oxygen (2.93%).SEM image and EDAX spectra of Ba:NiO (4hrs) NPs (Fig.6) indicate that the

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particles are irregularly-shaped and composed of Oxygen (28.71%,), Nickel (60.71%) and Barium (10.58%).



Fig.5. FESEM and EDAX of NiO sample.



Fig.6. SEM and EDAX of Ba:NiO (4hrs) sample.

The photographic images (Fig.7) and the size of zone of inhibition (Fig.8) of NiO NPs and Ba:NiO NPs (4hrs) against E-Coli expressed maximum inhibition at 150 μ l. The increased effect may be due to the toxicity of Ni²⁺ ions released continuously attached to the negatively charged bacterial cell wall due to the electrostatic force [17]. The positive control exhibited the zone of inhibition 12.82±0.86 mm and 12.80±0.89 mm for NiO and NiO:Ba (4hrs) respectively at 30 μ l.



Fig.7. Photograpic images of inhibition zone of NiO and Ba:NiO.



Fig. 8. Size of inhibition zone of NiO and Ba:NiO.

Since the size of NiO NPs is smaller than Ba:NiO (4hrs) the activity of NiO NPs against E. Coli is more than that recorded for Ba:NiO NPs since the decrease in size leads to increase in surface area to volume ratio (Table.1). The binding of small-sized NiO NPs on the surface of the bacteria [18] react much faster with cell wall and generate reactive Oxygen species (ROS) which ultimately cause damage to the membrane and kill bacteria [19].

Table 1. Comparison of Surface area / Volume of NiO andBa2+doped Nickel Oxide NPs.

Samples	D (nm)	Surface Area (nm) ²	Volume (nm) ³	SA / volume
NiO	22	1519.76	5572.45	0.2727
Ba:NiO (3hrs)	28	2461.76	11488.2	0.2143
Ba:NiO (4hrs)	31	3017.54	15590.6	0.1936

4. Conclusion

The incorporation of Ba^{2+} ions into NiO crystal lattice results in the increase of the crystallite size and changes the shape of the Ba:NiO (4hrs) NPs.PL spectra reveal that an increase in calcinations temperature causes the increase in PL intensity due to crystal growth. Furthermore, doping plays a vital role in controlling the particle size, which in turn modify structural and optical properties of doped NiO NPs. The antibacterial effect of NiO NPs against E.Coli reveals the high efficacy of NiO nanoparticles as a strong antibacterial agent. **References**

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