

Synthesis and characterization of Pure and Cobalt-doped NiO Nanoparticles

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Abstract: Nanocrystalline pure and cobalt-doped NiO nanostructures were synthesized by co-precipitation method. The prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet- visible spectrometer (UV-Vis) and scanning electron microscopy (SEM) with EDX specifications. XRD pattern reveals that pure and Cobalt-doped NiO nanoparticles belongs to the face centered cubic crystal structure with the space group of Fm-3m. Electron microscopy studies clearly evidence the formation of cubical edged nanoparticles with an average particle size of 23 nm, emerges in the polycrystalline nature. UV-Visible absorption spectra of cobalt-doped NiO nanocrystals shows an absorption peak at 390nm. The bandgap value is calculated to be 3.2 eV.

Keywords : Nanoparticles, Co-precipitation method, Optical studies and morphological analysis.

1 Introduction

One of the most commonly used transition metal oxides for a wide range of applications is NiO. It is a NaCl-type anti-ferromagnetic oxide semiconductor. Furthermore it is considered to be a model semiconductor with p-type conductivity films due to its wide band gap [1]. Uniform sized with well dispersed NiO nanoparticles as a kind of functional material has attracted extensive interests due to its novel optical, electronic, magnetic, thermal and mechanical properties and potential applications in catalysis, battery electrodes, gas sensors, electro chromic films, photo electronic devices, magnetic materials and so on [2-7]. In these applications, it is still needed for synthesizing high quality and ultra- fine powders with required characteristics in terms of their size, morphology, optical properties, magnetic properties and so on.

The particle structural property (particle size, distribution and morphology) is closely related to the preparation techniques. Several methods have been used and developed for synthesizing crystalline oxide powders in nanoscale dimensions. In many of them, the main objective is to reduce the cost of chemical synthesis and to produce materials for technological applications. Many researchers have employed NiO nanoparticles by various methods such as evaporation [8-9], magnetron sputtering [10-12], sol-gel [13-14], surfactant-mediated synthesis [15], thermal decomposition [16], solvothermal [17], polymer-matrix assisted synthesis [18] and so on. Among various methods, the preparation of pure and Cobalt-doped NiO nanostructures through Co-precipitation method open a new view for chemists since there are many advantages such as simple process, control of process conditions, particle size, particle crystal structure and easiness to obtain high purity products. Hence it is quite promising and easy to use for industrial applications. NiO is a most exhaustively investigated transition metal oxide. It has a density of 6.67 gm/cm³ and green crystalline solid having a melting point of 1955^oC.

2 Experimental techniques

Pure and Cobalt-doped NiO nanoparticles were synthesized by co-precipitation method. All the chemical reagents used in our experiments were of analytical grade. NiO nanoparticles were successfully synthesized by Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Cobalt III Nitrate of various concentrations (1, 3 and 5 mol %) were dissolved in 40 ml of distilled water under constant stirring. The NaCl solution was added dropwise into the above solution over 15 minutes. Subsequently, green precipitate was filtered out. And stirring process was done in room temperature until pH approaches 7. Finally, the end product was separated by centrifugation and washed thoroughly with de-ionized water, ethanol and acetone consecutively. After drying at ambient temperature for 24 hours, the powder was calcinated at 400°C for 2 hours. For synthesis of pure NiO nanostructure, the same procedure was followed without Cobalt III Nitrate solution as mentioned above.

The purity and crystallinity of the as- synthesized pure and cobalt-doped NiO nanoparticles were examined by using powder X-ray diffraction (XRD). XRD pattern was taken from the BRUKER D5 phaser. The FTIR spectra of the samples were obtained from the Perkin FTIR spectrophotometer over the range of $450\text{-}4000\text{cm}^{-1}$ which showed several absorption peaks. The UV– Vis spectrophotometer (Varian, CARY 5000) was used to see the optical absorbance of the sample. The surface morphological studies and composition analysis of the samples were carried out using scanning electron microscope (HRSEM – FEI Quanta FEG 200).

3 Results and discussion

3.1 Phase analysis

Powder XRD pattern of chemically precipitated pure and cobalt-doped NiO calcinated at 400°C are shown in Fig.1. It clearly indicates the formation of face centered cubic NiO nanostructure with the space group of Fm-3m. The crystalline size of pure NiO and cobalt doped NiO nanoparticles are determined using Debye-Scherrer's relation [19].

$$D = k\lambda / \beta \cos\theta \quad (1)$$

Where β is the full width half- maximum value of the high intensity peak, k is the shape factor and λ is the wavelength of the X – ray source used in the XRD. The obtained d values are in the range of 7.7 nm to 8.3 nm. It is clear that the crystalline size of the samples increases with increasing dopant concentration of Ni. Also it is clear that the particle agglomerates due to van der wall's forces and they are responsible for ultrafine cobalt nanoparticles. The crystal structure of the samples are fcc. The Lattice parameter of the samples are $a = 4.17\text{\AA}$ and $\beta = 90^\circ$. These

values have very good agreement with the reported datas, which indicates the formation of pure NiO nanoparticle. From the XRD pattern, the most intense peak was observed at $2\theta = 43.33^\circ$. Also no impurity peaks were observed.

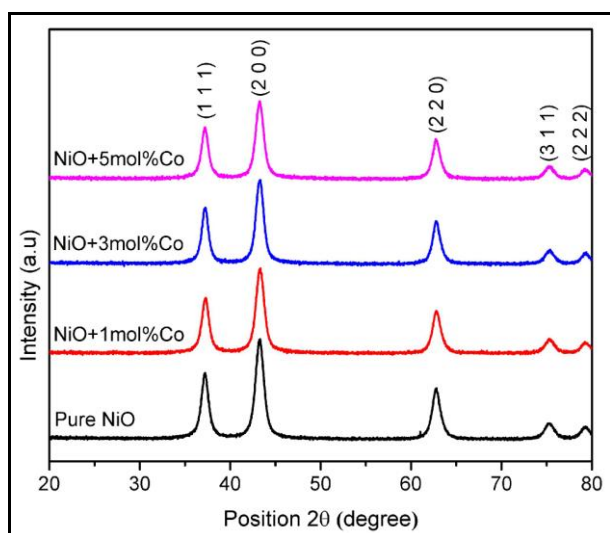


Fig. 1 XRD pattern of pure NiO and various concentrations of Co- doped NiO nanoparticles.

3.2 FTIR studies

Fig 2 shows the FTIR spectra of pure and cobalt-doped NiO nanoparticles. In order to determine the chemical structure of the sample, the FTIR spectra was observed over the frequency range of 450 – 4000 cm^{-1} . The absorption band in the region of 600 – 450 cm^{-1} is assigned to Ni – O stretching vibration mode [20]. The absorption of CO_2 from the atmosphere at the NiO surface was identified from the sharp peak positioned at about 1622 cm^{-1} in FTIR spectra. The broad absorption band centered at 3500 cm^{-1} is assigned to H – O – H bending vibrations mode were also presented due to adsorption of water in air. The broadness of the absorption band indicates that the NiO powders are nanocrystals and well crystallized. The size of samples used in this study was much less than the bulk form NiO, so that the NiO nanoparticles had its IR peak of Ni – O stretching vibration and shifted to the blue direction [21-22]. From the figure it can be seen that the intensity of Ni – O stretching band increases with increasing the concentration of Cobalt.

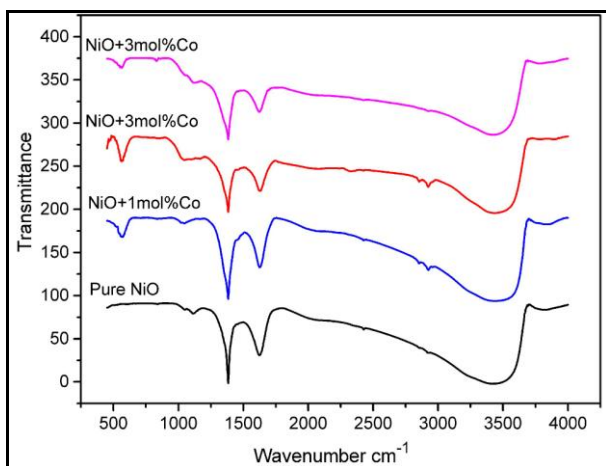


Fig. 2 FTIR spectra of pure and Co- doped NiO nanoparticles calcinated at 400^o C.

3.3 UV – Visible spectral studies

Optical absorption spectra of pure and cobalt-doped NiO nanoparticles heated at 400°C for various concentrations were illustrated in Fig 3. All samples exhibits the absorption maximum at around 350 – 450nm, confirms the strong UV absorption of the material. The absorption edges are seen to be shifted slightly towards lower wave number (blue shift). This shift indicates an increase in band gap, which can be attributed to a decrease in particle size. Blue shift was observed due to the quantum confinement effects. According to the data of the absorption spectra, the optical band gap (E_g) of pure and cobalt-doped NiO nanoparticles can be estimated by using the following equation.

$$(Ah\nu)^n = B(h\nu - E_g) \quad (2)$$

Where $h\nu$, A, B and n are photon energy, absorbance constant relative to the material and either 2 for direct transition or $\frac{1}{2}$ for an indirect transition respectively. Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the $(Ah\nu)^n - h\nu$ curve to zero. The band gap is determined by extrapolating the linear portion of the plot to the energy axis. The corresponding band gap energy was calculated to be 3.2 eV [23]. No linear relation was found for $n = \frac{1}{2}$, suggesting that the as-synthesized NiO nanostructures are semiconducting with direct transition at this energy [24].

The resulting emission characteristics shows the origination of one main strong emission peak centered at around 390 nm. The origin of the main strong peak attributed to the electronic transition of the Ni^{2+} ions. Optical absorption study reveals the existence of several transitions at energies below band gap in NiO [25-26]. The property of strong room temperature UV emission should be attributed to the high purity and perfect crystallinity of the as-synthesized cubic NiO nanostructures. The other peaks might be attributed to near band – to – band transition and oxygen related defects.

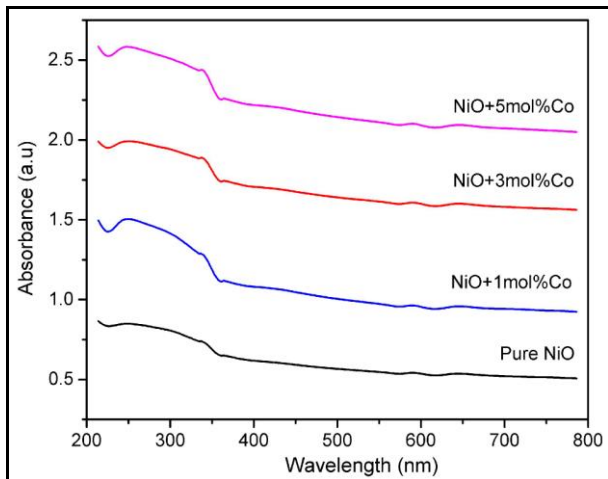


Fig. 3 UV-Vis absorption spectra of NiO nanostructure with various concentration of Cobalt

3.4 Electron microscopy analysis

The HRSEM images of the pure and 5mol% cobalt-doped NiO nanoparticles were taken at different magnifications are shown in Fig 4. The observed HRSEM images shows that the particles are cubical in shape and are polycrystalline. All the samples were showing nearly the same morphological features with an average particle size of 23nm. This infers that the addition of cobalt does not affect the crystal structure which confirms the incorporation of cobalt on to Ni lattice site. While increasing the doping concentration the particle size was considerably reduced and aggregated. The EDX spectrum for pure NiO and 5mol% cobalt-doped NiO nanoparticles were shown in Fig 5. They reveals that the presence of Ni, O and Co are the only elementary species in the sample. Moreover, no additional peaks corresponding to any other elements except Ni, O and Co were observed.

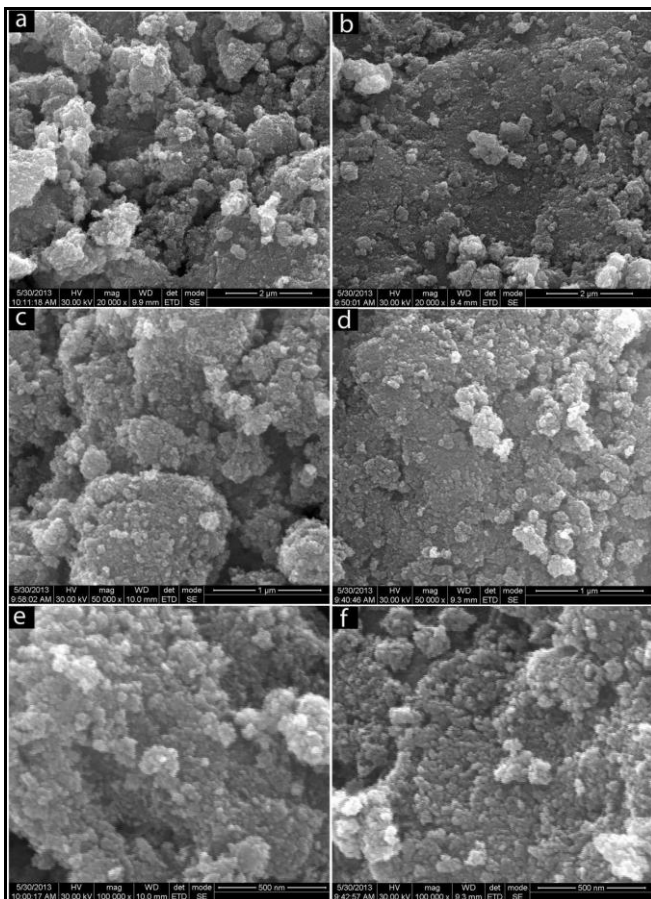


Fig. 4 HRSEM images of pure NiO (a,b,c) and 5mol% Co-doped NiO nanoparticles (d,e,f).

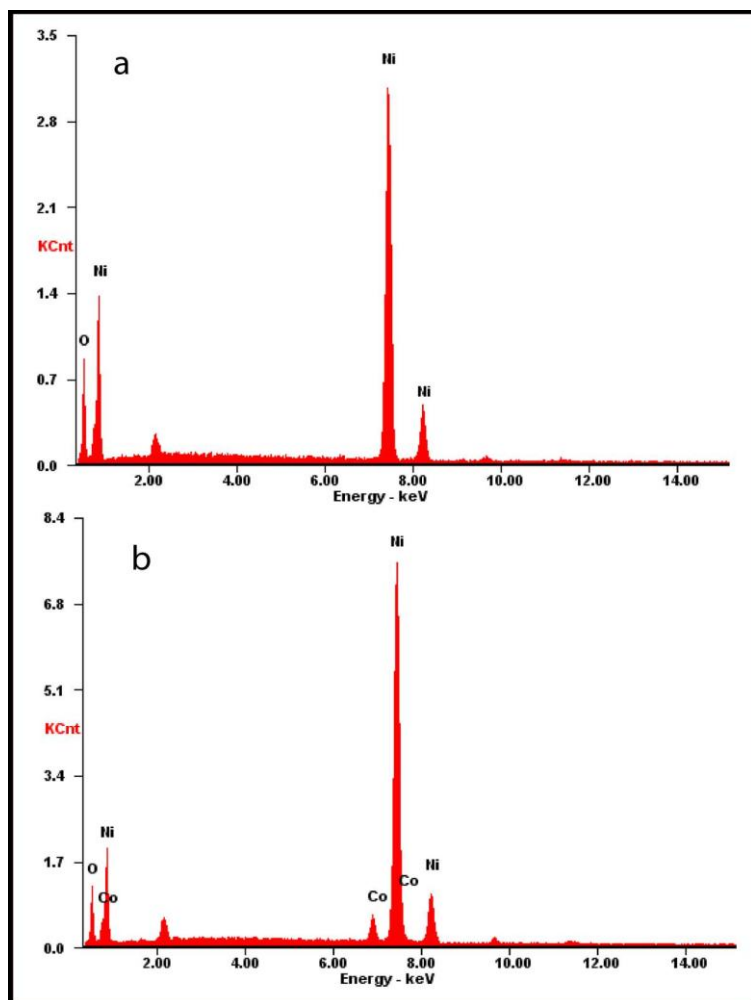


Fig. 5 EDX spectra of pure NiO (a) and 5 mol% Co-doped NiO (b) nanoparticles.

4 Conclusions

In this present investigation, we adopt the co-precipitation method to synthesis pure and cobalt doped NiO nanostructure. XRD pattern of the samples shows face centered cubic structure with polycrystalline nature. The UV-Vis shows an increasing absorption at the edge of UV – region and decreasing in the visible region for both pure and cobalt-doped NiO nanoparticles. The band gap of the material is estimated to be 3.2eV. FTIR shows the presence of NiO nanoparticles. SEM confirms that the particles are in nano size and the appearance of some particles are cubical in shape.

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