ORIGINAL ARTICLE

Structural, morphological, optical and electrochemical aspects of novel synthesized Nickel Oxide and Cobalt doped Nickel Oxide nanoparticles–An alternate electrode material for energy storage devices

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Abstract
Nickel oxide (NiO) and cobalt doped Nickel oxide (Co-NiO) nanoparticles were successfully synthesized by cost effective, environmentally friendly, and scalable eco-precipitation method. The prepared nanoparticles were investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDAX), Fourier Transform Infrared Spectroscopy (FTIR), Optical spectroscopy (UV) and Cyclic voltammetric (CV). The structural characterization was carried out by X-ray diffraction which confirmed the polycrystalline nature of the particles with cubic structure. SEM analysis of the particles enabled the conclusion that the prepared particles were polycrystalline, irregularly spherical in shape, and agglomerated. The chemical bond and functional group were identified from FTIR spectroscopy and the elemental composition of prepared particles was identified by EDAX analysis. From UV-Vis absorbance spectra and Tauc relation, the type of transition and band gaps of the particles were estimated. The electrochemical performance was investigated using Cyclic Voltammetry (CV), Galvanostatic charge discharge (GCD), and Electrical Impedance Spectroscopy (EIS) in presence of 1M KOH as an electrolyte. The NiO and cobalt doped NiO coated electrodes provide promising applications as electrode materials for energy storage devices.

Keywords: *Cobalt-Doped NiO; Cyclic Voltammetry; Energy Storage Device; Nickel Oxide Nanoparticles; Supercapacitors.*

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INTRODUCTION

In this rapidly changing world, all the application that people use in daily bases are made electronically applicable such as communication system, wearable devices, Transport system, energy storage devices such as supercapacitors, batteries and fuel cells. Supercapacitors now-a-days lavishly used in many applications because of its low cost, environment sociable, portable have good power densities, current densities, capacitive properties, therefore best electrode material chosen is important for better performance and cyclic stability.

Supercapacitor is classified into three types based on their charge storage mechanism namely Pseudo-capacitors, Electric Double layer capacitors (EDLC), Hybrid capacitors, which are electrochemically, electrostatically and both respectively. Electrode material is important element for supercapacitors application, mostly of metal oxide and their composites are used with carbon material for better results. Transition Metal Oxides (TMOs) like Manganese oxide (MnO_2), Vanadium pentoxide (V_2O_5), Cerium oxide (CeO_2), Cobalt oxide (CoO_2), Iron Oxide (Fe_2O_3) Nickel oxide (NiO) were used for designing the electrode material. In various TMOs, NiO metal

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oxide is available in low cost and prepared at low temperature. Two or more metal combines to form composite (binary, ternary, quaternary etc) which shows good results when compared single metal-oxides to increase further more electrochemical performance carbon-based materials are used, which includes carbon nanotubes (CNTs), graphite, activated carbon materials were used for better stability and enhance the surface area of the electrode [1].

NiO electrode is of particular interest due to its cost effectiveness and excellent redox activity. However, NiO electrode suffered from high internal resistance, which reduces its electrochemical performance [2]. Strategies such as doping with a cation or compositing with carbon materials or other metal oxides help to mitigate this problem. Doping with a guest element increases the electrochemical active sites due to the introduction of lattice defects. It also helps to prevent NiO particles from agglomeration leading to a more porous structure. Many attempts have been undertaken to improve the electrochemical performance of NiO electrode through doping with other elements [3]. Among various d-block and rare earth metals, Cobalt (Co) doping was found to have a significant impact on the morphology of NiO materials. Here we are interested in improving the electrochemical properties of NiO electrode by doping with cobalt ion and preparing a highly porous nanostructure. In this paper we reported, the synthesis NiO and cobalt doped NiO nanoparticles and from electrochemical studies cobalt doped NiO coated electrode provide promising application as electrode materials for energy storage devices [4].

Nazir Ahmad Mala *et al.* prepared Zn and Mn, co-doped NiO nanostructures by co-precipitation method and their electrochemical study showed the pseudocapacitive nature with specific capacitance of 846.71 F/g[5]. Hao Xu *et al.* synthesised Co–doped NiO@WCNTF was prepared via facial chemical process and obtained specific capacitance of 1244 F/g [6]. Shyamli Ashok *et al.,* synthesised Cobalt doped NiO nanostructures by one step solution combustion method, obtained specific capacitance of 1244 F/g [7]. Juan Wang et al. synthesised 3DCo-doped Ni by hydrothermal method, exhibits a specific capacitance of 1300F/g[8]. Shang Jiang *et al.* prepared Co-Ni bimetallic nanoparticles by sulfurization/phosphorylation transformation method. The

electrode developed a 1739.3 F g^{-1} specific capacitance [9].

In the present wok, a simple efficient co-precipitation technique was used for synthesis of NiO and Cobalt doped NiO nanoparticles. Co-precipitation method has allows the mixing of particles at the molecular level and the processing of precursors at room or low temperature. The structural, morphological, and optical properties of the synthesized NiO and Cobalt doped NiO nanoparticles have been investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDAX), UV/Vis spectrophotometry and Fourier-transform infrared (FTIR) spectroscopy, spectroscopy techniques. The effect of doping on the electrochemical properties has also been studied by cyclic voltammetry (CV) Galvanostatic charge discharge (GCD) and Electrical Impedance Spectroscopy (EIS).We have analysed the electrochemical measurement of NiO and Cobalt doped NiO nanoparticles in which it revels the specific capacitance of Cobalt doped NiO electrode which shows efficient electrode material for energy storage application when compared to earlier researchers [5-9].

EXPERIMENTAL SECTION
Materials
Nickel Nitrate hexahydrate (Ni (No$_3$)$_2$.6H$_2$O), Sodium hydroxide (NaOH), Cobalt Nitrate Hexahydrate (Co (NO$_3$)$_2$.6H$_2$O), acetylene black, polyvinylidene difluoride (PVDF), n-methyl-2-pyrrolidinone were purchased from nice brand.

Synthesis of NiO and Cobalt doped NiO nanoparticles
Nickel Oxide (NiO) nanoparticles were synthesized by co-precipitation method. 0.3M (8.7243 g) of Nickel Nitrate Hexahydrate was dissolved in 100ml of double distilled water the solution was stirred for 30 minutes at room temperature. After 30mins of stirring, 1.199g of Sodium Hydroxide (NaOH) is dissolved in 100 ml of doubled distilled water added drop wise until the solution reaches pH of 9. Formation of precipitate (green colour) took place and continued stirring for few more minutes. Then the precipitate was kept undisturbed for 2 hours for the settlement of the particle. The precipitate was washed several times with distilled water followed by ethanol and then centrifuged. Then the particles were collected and dried at 100 ºC in hot air oven for 5 hours. The

dried particles were grained in mortar - pestle to get uniform fine powders and the particles were calcinated in muffle furnace for 2 hours at 550ºC. Finally black colour powder (NiO) was obtained and prepared NiO nanoparticles were used for analysis. For the synthesis of cobalt doped NiO nanoparticles, 0.3 M of Nickel Nitrate Hexahydrate and 10 wt% (0.87g) of Cobalt nitrate hexahydrate was dissolved in 100 ml of double distilled water. Now the solution was stirred in magnetic stirrer for 60 minutes. Next steps followed as similar as in the preparation of NiO nanoparticles, Fig. 1 represents the schematic procedure in the synthesis of Cobalt doped nanoparticles.

Preparation of working electrode

Electrochemical analysis such as cyclic voltammetry, electrochemical impedance, and galvanostatic charge–discharge measurements were carried out using an electrochemical workstation (Gamry, Interface 1000; Warminster, PA, USA). NiO nanoparticles were coated in Ni foam, Ag/AgCl, and platinum were used as working, reference, and counter electrode in a three-electrode cell system. All electrochemical studies were carried out in presence of 1 M KOH as electrolyte at room atmosphere. The working electrode was prepared by uniform mixing of NiO nanoparticles (75 wt%), acetylene black (15 wt%), and polyvinylidene difluoride (PVDF) (10 wt%) in 1-methyl-2-pyrrolidinone (solvent) under sonication to obtain slurry. An adequate amount (15 μl) of slurry was used to deposit on Ni foam with coating area of 1×1 cm^2 and dried at 50° C. Before this process, Ni foam was washed with

acid, detergent, ethanol, and deionized water to remove all surface impurities.

Characterization

A Shimadzu X-ray diffractometer (D8 ADVANCE) with a vertical goniometer fitted with vanadium filter and copper radiation (CuKα λ=1.54 Å) with a step size of 1.01°was used for the structural analysis of the synthesised nanoparticles. FTIR spectrophotometer, (JASCO FTIR spectrometer model FT/IR- 4600 series) ranging 500 cm^{-1} to 4000 cm^{-1} was used to determine chemical bonding and functional group present in the synthesised nanoparticles. The morphological characterization of the synthesized NiO was studied using (Jeol 6390LV) Scanning Electron Microscopy (SEM). A JASCO V-770UV double beam spectrophotometer was used for optical studies in the wavelength range 400-2500 nm.

Electrochemical measurements

The electrochemical analysis, cyclic voltammetry was carried out with (Metrohm Autolab M204) potential window-0.1 to +0.5 at room temperature. The electrochemical analysis has been done with three electrode system, Nickel foam (substrate) was used as a working electrode, Ag/AgCl as reference electrode, Platinum electrode (Pt) electrode as counter electrode.

RESULTS AND DISCUSSION
XRD Analysis

X-Ray diffraction patterns of NiO and cobalt doped NiO nanoparticles synthesized by co-precipitation method are presented in the Fig. 2
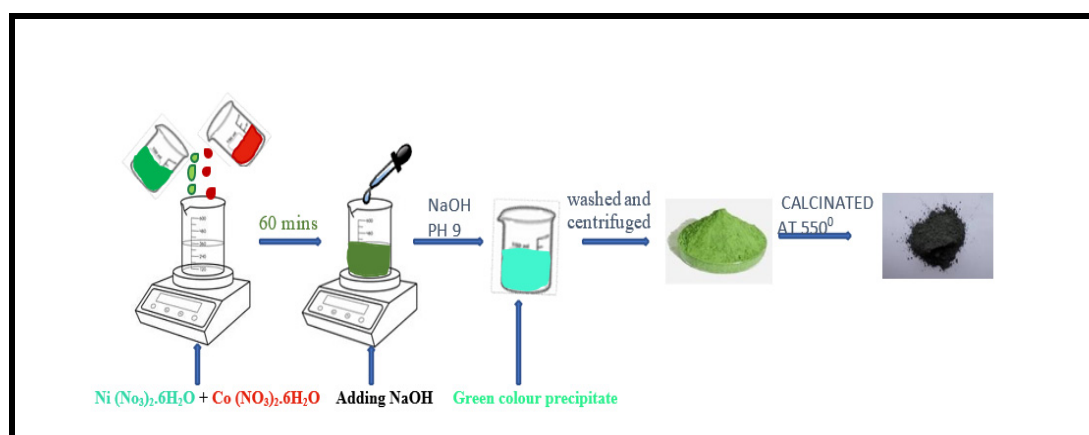

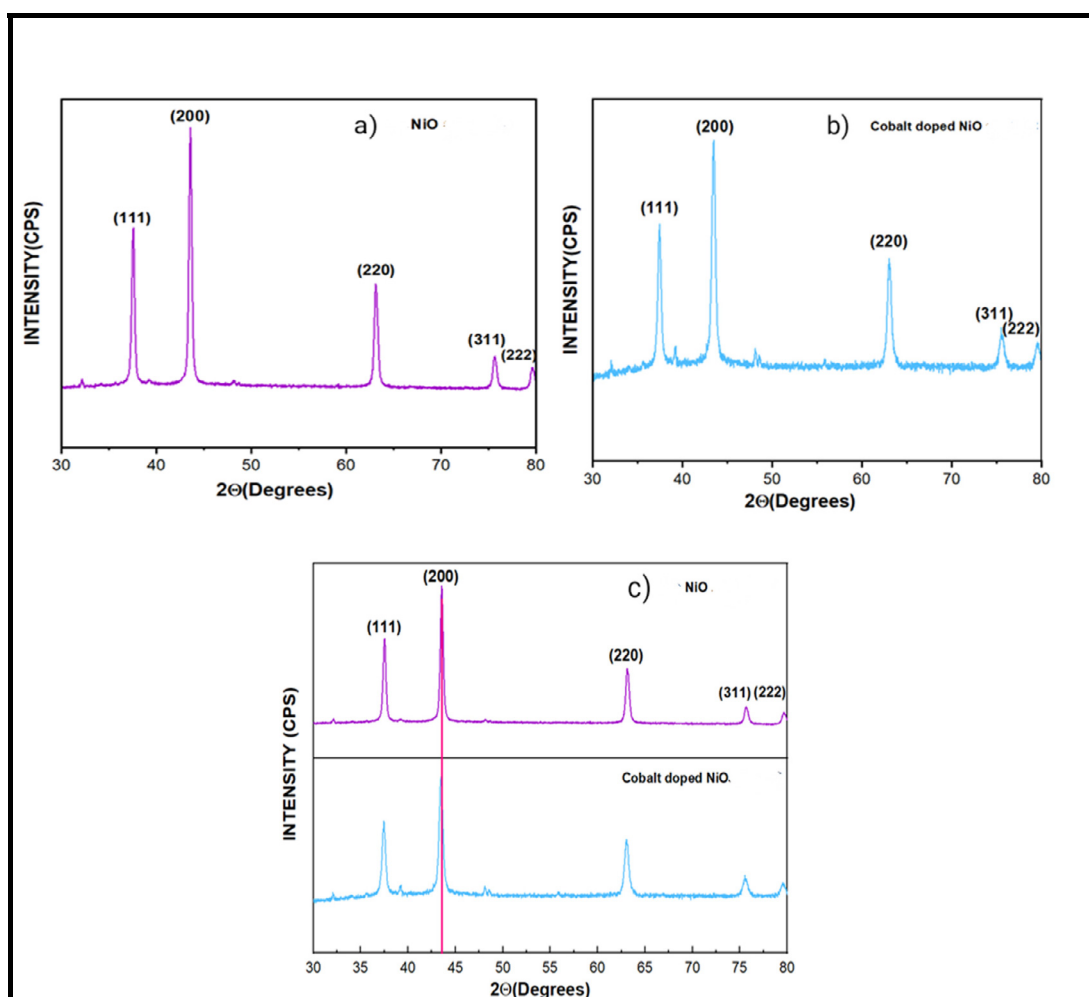Fig. 1. Schematic representation of synthesis of cobalt doped NiO nanoparticles.

Fig. 2. XRD diffractograms of (a) NiO nanoparticles (b) Cobalt doped NiO nanoparticles (c) Shift in peaks of NiO andCobalt-doped NiO nanoparticles.

(a,b).The predicted peaks (111), (200), (220), (311), and (222) were reported as the identifying peaks for NiO and cobalt doped NiO nanoparticles by earlier researchers [10-17] and (JCPDS card no 00-07-1049). The presence of these prominent peaks confirmed that the synthesized nanoparticles were polycrystalline in nature with cubic structure (FCC). The diffraction pattern exhibited no extra peaks which confirmed that there were no impurities in the synthesized nanoparticles.

From the diffraction profiles Fig. 2 (a, b), it has been observed that cobalt doped NiO nanoparticles have peaks with less intensity and widened as compared to NiO nanoparticles. This may be due to presence of defects such as dislocation density

and micro-strain caused due to interstitial doping [18-21].Both the defects increased when Cobalt was doped in NiO nanoparticles and presented in Table 1.

Fig. 2 (c), shows the shifted peak of both NiO and Cobalt-doped NiO nanoparticles. It has been observed that cobalt doped NiO nanoparticles slightly shifted towards smaller 2q value compared to NiO nanoparticles [Table 1] and this shift confirms that the crystallites are slightly strained [21-24]. The shift in the peak position is presented in Table 1.

From the observed 'd' spacing and (hkl) planes the lattice constant was evaluated using the relation

Table 1. Structural parameters of NiO and Cobalt doped NiO nanoparticles.

Sample name	d spacing Å	2θ	hkl plane	Lattice constant (a) Å	Crystalline size (D) 10^{-9} m	Volume(a^3) Å³	Micro strain (ε) 10^{-3}	Dislocation density(δ) 10^{15}lines/m²
NiO	2.4120	37.486	(111)	4.177	27.480	72.8774	1.3876	1.3243
	2.0890	43.520	(200)	4.178	28.189	72.8774	1.3789	1.2584
	1.4768	63.090	(220)	4.177	26.980	72.8774	1.5702	1.3737
	1.2594	75.609	(311)	4.176	27.639	72.8774	1.6528	1.3090
	1.2058	79.599	(222)	4.177	25.419	72.8774	1.8486	1.5476
					Average=27.57		**Average= 1.5676**	**Average=5.639**
Cobalt doped NiO	2.4120	37.411	(111)	4.177	21.69	72.8774	1.7573	2.1255
	2.0890	43.437	(200)	4.178	21.33	72.8774	1.8226	2.1979
	1.4768	63.001	(220)	4.177	21.25	72.8774	1.9922	2.2145
	1.2594	75.492	(311)	4.176	17.23	72.8774	2.6489	3.3684
					Average=20.37		**Average=2.0552**	**Average=7.38**

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{1}$$

were, d – interplanar spacing a – lattice constant, (hkl) plane from the observed 'd'spacing various structural parameters such as crystalline size, dislocation density and strain have been estimated using the expressions, The crystalline size of nanoparticles were determined using Debye Scherrer' relation [15],

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{2}$$

Where, β - the full width half- maximum value of the high intensity peak, θ- Braggs angle in radians K - the shape factor(K= 0.94) λ- the wavelength (1.54Å) of the X-ray source used in the XRD.

The micro strain (ε) was calculated using the equation

$$\varepsilon = \frac{\beta\cos\theta}{4} \tag{3}$$

The dislocation density(δ) was calculated using the equation,

$$\delta = \frac{1}{D^2} \tag{4}$$

From the observed 'd' spacing, (hkl) planes, the lattice constants, crystalline size (D), micro strain (ε) and dislocation density (δ) were calculated using the respective equations (1–4) and presented in the Table 1.

Morphological Analysis

Scanning Electron Microscopy (SEM) was employed to analyse the morphology and growth features of NiO and cobalt doped NiO nanoparticles synthesised by coprecipitation method. Fig.3(a, b, c)shows the morphology of NiO nanoparticles and Fig. 3 (d, e, f) shows the morphology of cobalt doped NiO nanoparticles with different magnifications. From Fig. 3 (a, b, c) it can be observed that the prepared particles are polycrystalline in nature and spherical (irregular) in shape with different sized particles due to agglomeration. As particles are agglomerated, hence it is difficult to do size distribution analysis. The agglomeration is mainly due to the owing to the strong chemical bonds adopted, strong surface energy and small dimensions. Fig. 3 (d, e, f)shows the same morphological features as in NiO nanoparticles which infers that the addition of cobalt does not affect the crystal structure which confirms the incorporation of cobalt on to Ni lattice site as observed by earlier researchers [25, 26].

EDAX Analysis

Energy Dispersive X-ray analysis (EDAX) of NiO and Cobalt doped NiO was carried out to obtain the elemental composition of the synthesised nanomaterials. Composition of synthesised materials shown in the form of peaks (Fig. 4(a)) represents the EDAX spectra of NiO nanoparticles and (Fig. 4(b)) of cobalt doped NiO nanoparticles synthesized by Co-precipitation method. The spectrum effectively shows the presence of Ni, Co, O confirms NiO and cobalt doped NiO nanoparticles. But sodium (Na) presence is due to the addition of sodium hydroxide (NaOH) for the adjustment of pH during synthesis. Presence of impurity N and Al in small amount may be due to the environmental circumstance during synthesis [12-14].
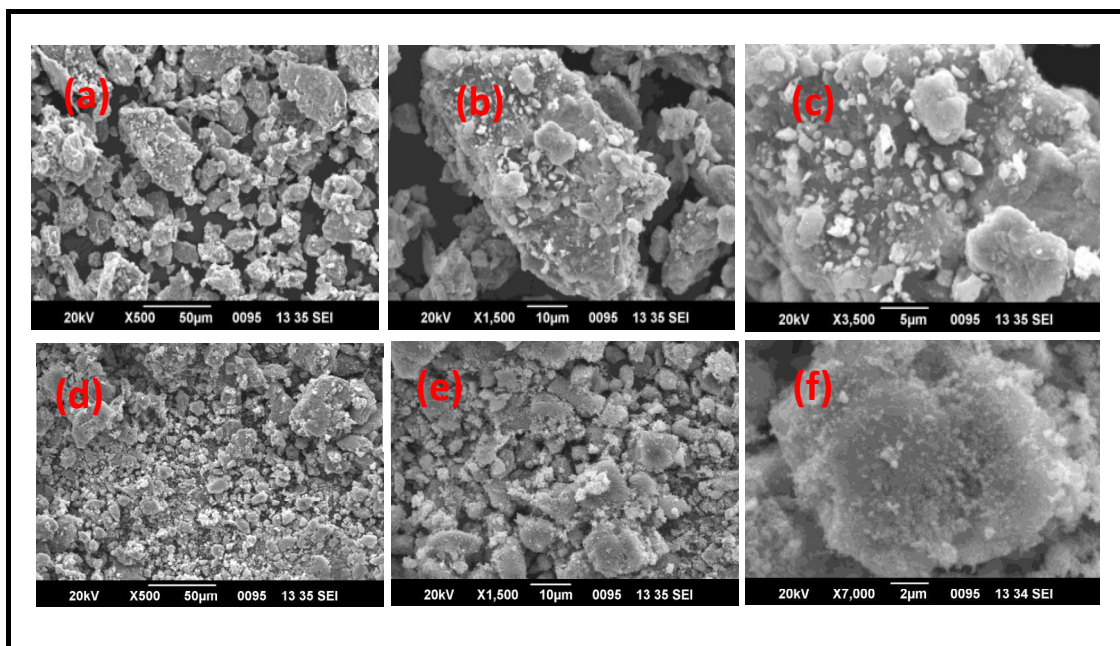
Fig. 3. SEM micrographs of (a, b ,c) NiO nanoparticles, (d,e ,f) Cobalt doped NiO nanoparticles of different magnifications.
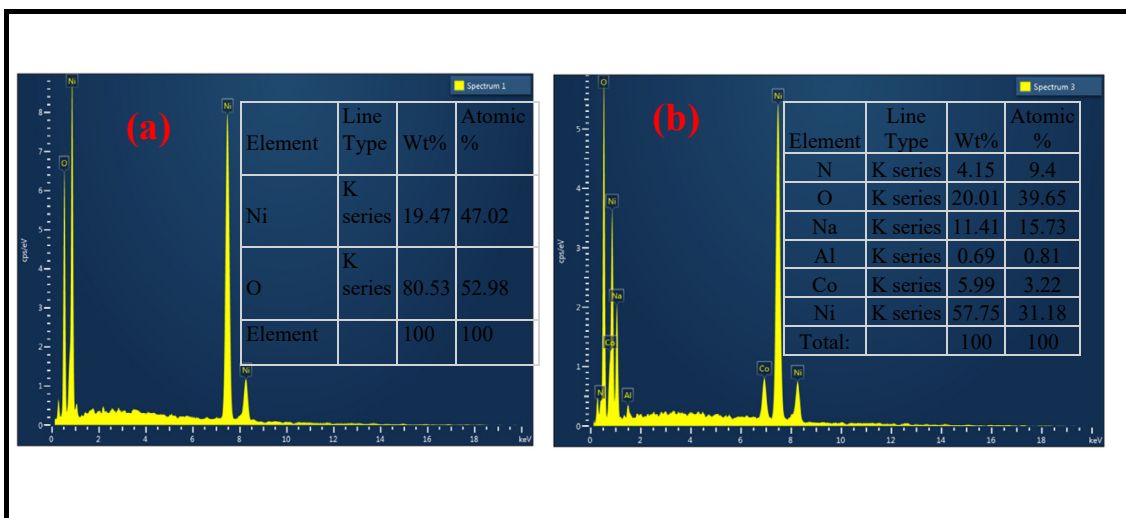

Fig. 4. EDAX spectra of (a) NiO nanoparticles, (b) Cobalt doped NiO nanoparticles.

FT-IR Analysis

The FTIR spectroscopy is technique used to identify the functional group and other chemical bonds present in the final product. Fig.5 (a) shows the FTIR spectra of synthesized NiO nanoparticles. The vibrational frequencies of the various chemical bonds in the particles can be assigned from FTIR spectra in terms of the peak positions. By the assignments of stretching and bonding modes of vibrations to the observed frequencies conformational preference of the molecule can be identified. NiO stretching vibrations was found in the range between 600-400 cm^{-1} and NO^{3-} interlayer vibrations around 1300cm^{-1}. The peak around 1600 cm^{-1} and 3500 cm^{-1} has been assigned to H-O-H bending vibrations and the peak around 1700 cm^{-1} assigned to IR band related to NaNO$_3$ as a by-product as reported earlier [11-13]. The
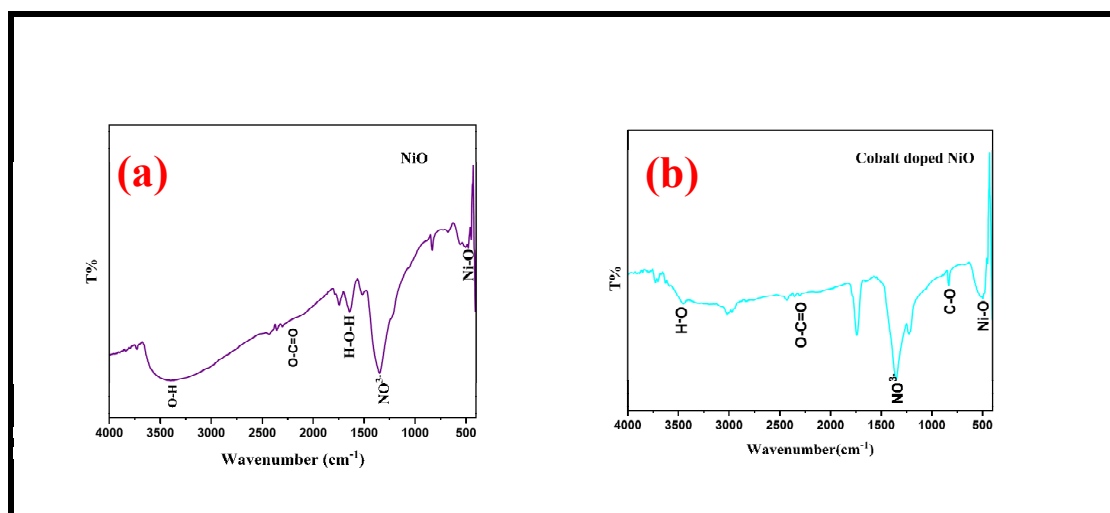
Fig.5. FTIR spectra of (a) NiO nanoparticles, (b) Cobalt doped NiO nanoparticles.

Table 2. Functional group of NiO and Cobalt doped NiO nanoparticles.

Sample name	Wave number (cm^{-1})	Functional group
NiO nanoparticles	555	NiO stretching vibration
	1347	NO_3^- interlayer
	1642	H-O-H bending vibrations
	2355	O-C=O symmetric and asymmetric stretching vibrations
	3395	O-H bending vibrations
Cobalt-doped NiO nanoparticles	500	NiO stretching vibration
	831	C-O vibrations
	1350	NO3- interlayer
	2429	H-O-H bending vibrations
		O-C=O symmetric and asymmetric stretching vibrations
	3020	O-H bending vibrations

peak around 2000 cm^{-1} was assigned to O-C=O symmetric and asymmetric stretching vibrations and presence of water was confirmed due to O-H stretching vibrations at 3400 cm^{-1}.

Fig. 5 (a) shows the FTIR spectra of synthesized cobalt doped NiO nanoparticles. From the spectra it was observed that an additional peak around 650 cm^{-1} has been assigned to Cobalt oxide [18] along with the peaks of NiO nanoparticles as stated below and presented in Table 2**.**

Optical Analysis

The optical property and bandgap of synthesized NiO and Cobalt doped NiO nanoparticles were done by UV-Vis Absorption Spectroscopy. Energy band of materials was related to absorption coefficient α by the Tauc relation equation 5.

$$\alpha h\nu = A\,(h\nu - Eg)^n \qquad (5)$$

where A is absorbance, α is absorption coefficient, $h\nu$ is the photon energy (eV), E_g is optical band gap (eV) and n is the number characterizing the nature of the transition process; n=2 for direct transition and n=1/2 for indirect transition [25].

A plot of $(\alpha h\nu)^2$ versus ($h\nu$) of NiO and Cobalt doped NiO nanoparticles is shown in Fig. 6 (a, b). The straight line extrapolated to cut the energy axis, the band gap has been estimated. The estimated band gaps are 3.10 eV and 2.89 eV for NiO and Cobalt doped NiO nanoparticles. Table.3 shows the variation of crystalline size and optical band gap of NiO and Cobalt-doped NiO nanoparticles, confirmed that band gap decreases crystalline size also decreases the band gap from 3.10 to 2.89 eV. However, when the band gap decreases on addition of donor impurities contributes electron energy levels high in the semiconductor band gap, so the electron can be
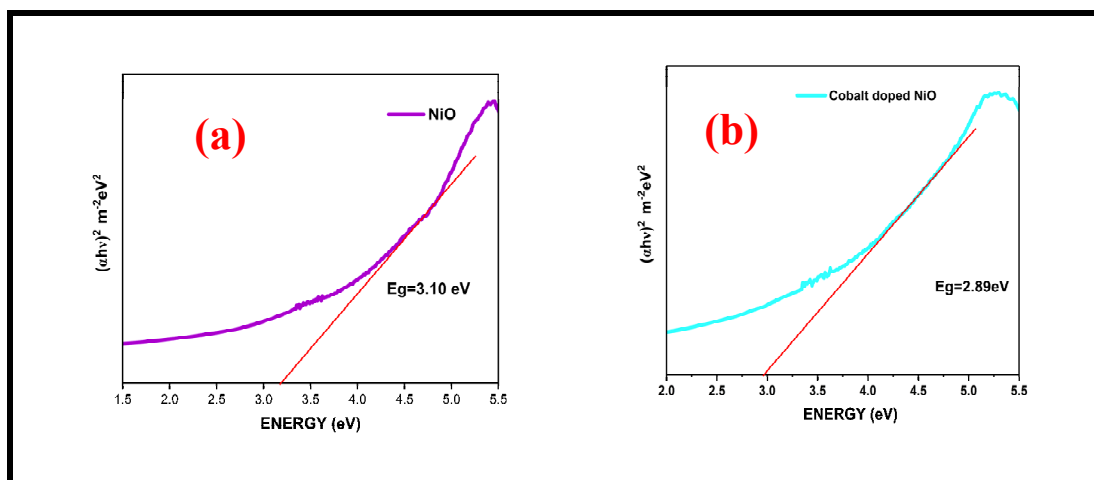
Fig. 6. Plot of $(\alpha h\nu)^2$ vs ($h\nu$) of (a) NiO nanoparticles, (b) Cobalt doped NiO nanoparticles.

Table 3. Variation of crystalline size and optical band gap of the NiO and cobalt-doped NiO nanoparticles.

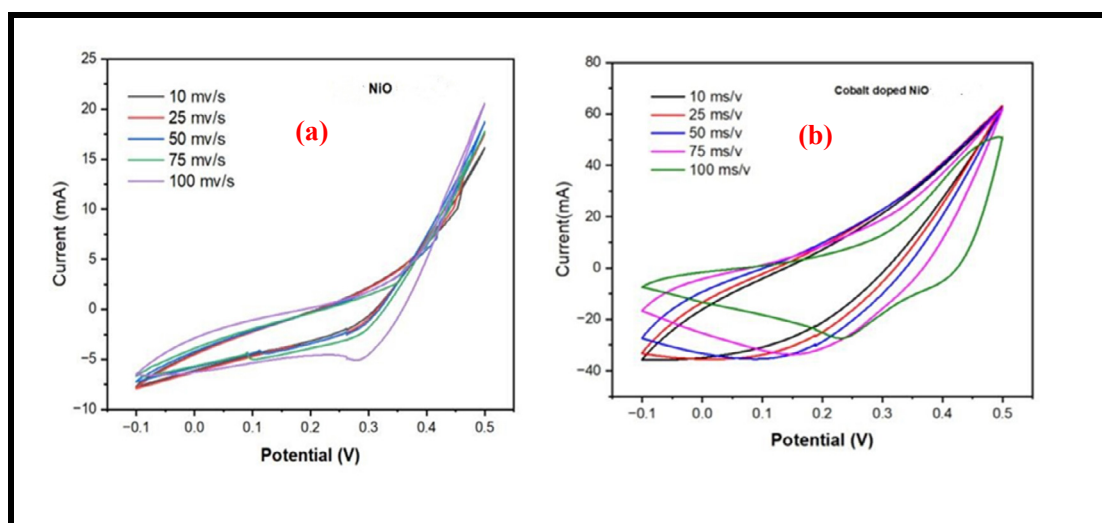| Sample	Crystalline size 10^{-9}m	Band gap(eV)
NiO	27.57	3.10
Cobalt-doped NiO	20.37	2.89

Fig. 7. Cyclic Voltammograms at different scan rate of (a) NiO nanoparticles, (b) Cobalt doped NiO electrodes.

easily excited into conduction band as reported by earlier researchers [23-28].

Electrochemical measurements of NiO and Cobalt-doped NiO

The synthesised NiO and cobalt doped nanoparticles was examined via electrochemical measurements. CV curves of NiO and Cobalt doped NiO nanoparticles of voltage ranging from -0.1 to +0.5 at different scan rates (10, 25, 50, 75 and 100 mV/s) was displayed in (Fig. 7 (a, b)). The electrode set up was three electrode systems in which nickel foam act as a working electrode, Ag/AgCl as reference electrode and Platinum electrode as counter electrode and 1M KOH act as electrolyte.

The electrode revealed the anodic and cathodic sides of NiO and cobalt-doped NiO (Figs.7 (a, b))

Table 4. Estimation of specific capacitance of NiO and cobalt doped nanoparticles.

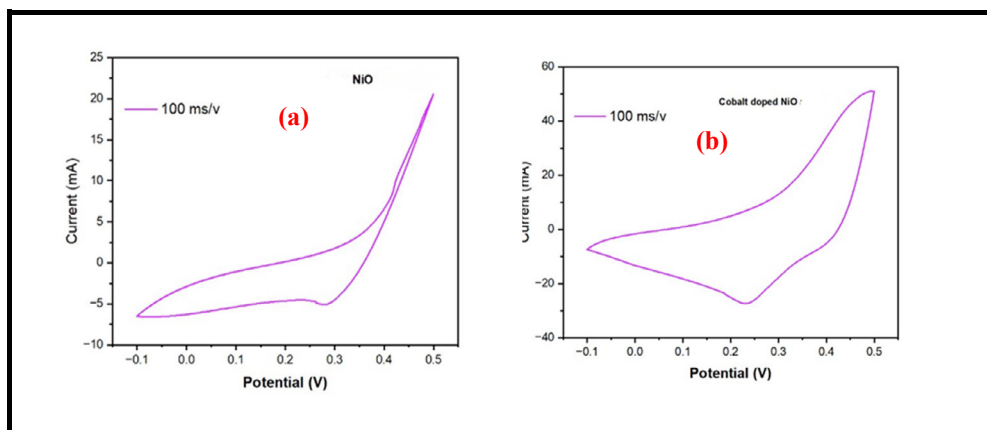| Samples	Area (AV)	Scan rate (mV/s)	Specific Capacitance(f/g)
NiO nanoparticles	2.114782365	100	444.1042966
Cobalt doped NiO nanoparticles	14.17814437	100	2977.410318

Fig. 8. Cyclic Voltammograms at 100ms/V scan rate of (a) NiO nanoparticles, (b) Cobalt doped NiO electrodes.
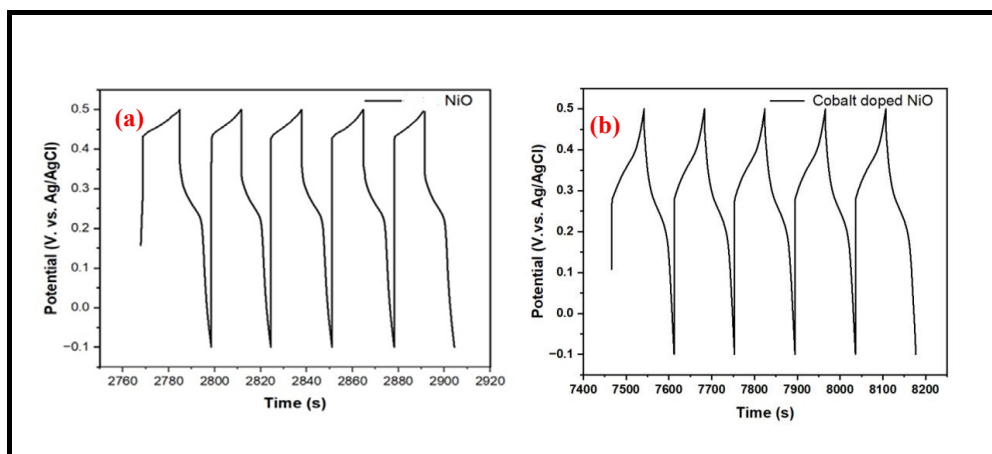

Fig. 9. Galvanostatic charge–discharge curves of (a) NiO electrode, (b) cobalt doped NiO electrodes.

suggesting typical Electric double layer capacitors (EDLC) behaviour with respect to the non-faradaic redox reaction of NiO electrode. It shows that the capacity increase with the increase of cycling times. From the curve it was observed that, even the voltage sweeps out at the rate of 100 mVs^{-1}, the CV curve still retain the rectangular shape, results the unrestricted motion of electrolyte in the pores at the slow double-layer formation situation as reported by earlier researchers. The improvement in cyclic performance was observed on cobalt-doped NiO electrodes as rectangular and in NiO electrodes as triangular galvanostatic charge–discharge (GCD) curves [27-34].

Specific capacitance was calculated from the below equation.6. and Table 4 for 100th scan rate for both and Cobalt doped NiO Fig. 8 (a, b)shows better specific capacitance, for NiO shows 444 f/g after doping with Cobalt the specific capacitance increases to 2977 f/g which shows better capacitance after doping.

Formula to calculate C$_P$ (Specific Capacitance) [35]
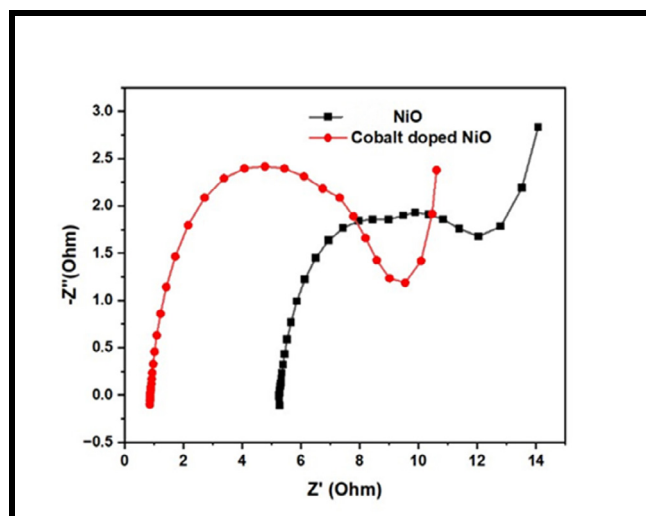
$$C_P = \frac{A}{2*k*m*\Delta V}\, f/g. \tag{6}$$

Fig. 10. Nyquist (EIS) plot of NiO and Cobalt doped NiO electrodes.

A = area under CV curve, k= scan rate (mV/s), m=mass of the active material (g)

ΔV= difference in Potential window (V_2-V_1) (v)

Figs. 9 (a, b) shows the Galvanometric charge discharge (GCD) graph of NiO and cobalt doped NiO electrodes. GCD profiles of NiO and cobalt doped NiO electrode displayed an approximately triangular shape at10 A/g current density in 0.1M KOH solution. Additionally, GCD profile could still be maintained as a triangle under a high current density, demonstrating desirable capacitive behaviour as observed by earlier researchers [28, 29]. Schematics of Electrochemical Impedance Spectroscopy (EIS) was presented in Fig.10 and from the results Nyquist plot is drawn between imaginary part Z and imaginary (-Z'') as a function of the real part Z and real (Z') of the complex impedance of an electric double layer capacitor (EDLC). It consists of a semi-circle at high frequencies between points a non-vertical line at intermediate frequencies and a nearly vertical line at low frequencies beyond point [36-42].

CONCLUSION

NiO and Cobalt doped NiO nanoparticles have been synthesized by novel method called Co-precipitation method. The synthesized nanoparticles were calcinated at 550°C. XRD reveals the polycrystalline in nature with the cubic structure (FCC). The structural parameters such as lattice constant, crystalline size, volume, dislocation density and strain were calculated and well agreement with JCPDS 00-07-1049 and by

the earlier researchers. Morphology of NiO and Cobalt doped NiO nanoparticles were observed from SEM analysis and it has been observed that is spherical in shape with different sized particles due to agglomeration. EDAX analysis confirms the presence of atomic percentage of Ni, Co and O in NiO and Cobalt doped NiO nanoparticles. Functional groups of NiO and Cobalt doped NiO nanoparticles were confirmed from FTIR analysis. UV-VIS analysis confirms the nature of transition as direct bandgap for NiO and cobalt doped NiO nanoparticles and Obtained band gap is about 3.10 and 2.87eV. Cyclic voltammetry was done to calculate specific capacitance, for NiO was about 444 f/g and for Cobalt-doped NiO 2977f/g. After doping Cobalt ions, the electrochemical performance of the Cobalt doped NiO electrode material shows outstanding electrochemical performance with capacitance up to 2977 f/g at 10 A/g current density, shows the behavior of Electric double layer capacitor (EDLC).Finally, it has been concluded that after introduction of Cobalt ions in NiO nanoparticles shows the improvement in electrochemical performance. Cobalt doped NiO electrode provide promising application as electrode material for energy storage devices.

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CONFLICTS OF INTEREST

The authors do not have any conflicts of interest.

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