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Synthesis and characterization of nanocrystalline nickel oxide using NaOH and oxalic acid as oxide sources

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Abstract

Precursors of nickel oxide (NiO) nanoparticles were synthesized through a simple chemical precipitation method by changing the oxide source used for the synthesis. The synthesized precursors were subjected to thermo gravimetric analysis (TGA) to determine the temperature at which the precursors decompose into nickel oxide. The obtained results of TGA suggest that precursor NiO prepared using sodium hydroxide (NaOH) showed NiO formation at 600 °C, whereas, when oxalic acid was used as oxide source the formation of NiO took place at 400 °C. After calcinations of the precursors at respective temperatures, NiO nanocrystals have been harvested. The synthesized NiO powders were characterized by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL) spectroscopy, field emission scanning electron microscopy (FE-SEM), energy dispersive x-ray analysis (EDX), and vibrating sample magnetometer (VSM) analysis. An FE-TEM image of NiO prepared using oxalic acid showed spherical and elliptical particles with sizes in the range of 15 nm. The Williamson–Hall (W–H) plots were drawn for the annealed products to study their lattice strain and crystallite size. The sizes of NiO nanocrystals obtained from W–H analysis are well correlated with sizes estimated using Scherrer’s formula. The relatively low saturation magnetization of NiO confirms its super paramagnetic behavior.

Keywords: precursors, oxide source, calcinations, crystallite size, saturation magnetization
1. Introduction

In the past two decades, nanomaterials have gained more attention in fundamental and applied research owing to their peculiar physical and chemical properties. Among the nanocrystalline materials, nickel oxide (NiO), a p-type semiconductor material with a band gap of nearly 4.0 eV, finds its potential applications in gas sensors, lithium-ion batteries and super capacitors [1–6]. Usually, the properties of nanosized metal oxide materials depend on size, morphology, surface area and homogeneity which in turn depend on the method of preparation used. For the synthesis of metal oxide nanoparticles, different methods such as sol–gel [7], surfactant-mediated synthesis [8], thermal decomposition [9], solvothermal [10], polymer-matrix assisted synthesis [11] and chemical precipitation method are used [12]. Among the above-mentioned methods, chemical precipitation method has gained more advantages due to being low cost and less time consuming. NiO in nanosize is an important magnetic material and researchers have been taking efforts to reduce the size of NiO nanostructures, because of its particle size dependent magnetic properties. As per the available literatures, NiO nanostructures most probably exhibit a superparamagnetic behavior despite NiO bulk material exhibiting antiferromagnetic nature [10, 13]. Abul kalam et al have prepared spherical nanoparticles of NiO by thermal decomposition of nickel linoleate precursor in air at 400 °C [14]. Wide band gap nanocrystalline NiO powder was synthesized by Mohammadyani et al [15]. They have prepared nickel oxide with mean crystallite size of 20 nm via sonochemical route using sodium hydroxide and nickel nitrate. In nanoscale both crystallite size and lattice strain have their own contribution to x-ray diffraction (XRD) peak broadening and the peak broadening contributed by lattice strain is due to large volume of grain boundaries [16, 17]. Hence, the strain present in the nanomaterial affects the crystallite size measurement. In order to measure the crystallite size correctly and to study the modifications introduced by strain in the properties of nanomaterials, strain calculations are essential [18]. However, fitting the powder diffraction data completely and accurately is complicated and hence it attracts many indirect methods such as Williamson–Hall (W–H) method and Warren–Averbach analysis for estimating the lattice strain and crystallite size [19, 20].

In the present work, precursors of NiO were synthesized through simple chemical precipitation method using nickel nitrate and two different oxide sources, sodium hydroxide and oxalic acid. The synthesized precursors of NiO were analyzed by TGA to get the values of temperature at which the precursors decompose into nickel oxide. After proper calcinations, the obtained pure powders of NiO were characterized by techniques such as XRD, Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL), FE-SEM, field emission scanning electron microscopy (FE-TEM) and vibrating sample magnetometer (VSM). From the powder diffraction data, the crystallite size and lattice strain of the as-prepared precursors and NiO nanoparticles are accurately estimated from W–H plots.

2. Materials and methods

2.1. Chemicals

Nickel nitrate hex hydrate [Ni(NO$_3$)$_2$·6H$_2$O], sodium hydroxide [NaOH] and oxalic acid [C$_2$H$_2$O$_4$·2H$_2$O] were purchased from Merck and were used as-received since they were of
analytical reagent grade with 99% purity. Sample preparation and dilutions were made of ultrapure water.

2.2. Synthesis of NiO nanocrystals

In the preparation of NiO nanocrystals from nickel nitrate hexahydrate (Ni(NO$_3$)$_2$*6H$_2$O) and sodium hydroxide (NaOH), 0.5 M of Ni(NO$_3$)$_2$*6H$_2$O in 50 ml of deionized water and 2 M of NaOH in 50 ml water were mixed drop wise. The entire mixture was stirred magnetically until a green precipitate of nickel hydroxide hex hydrate was formed (equation (1)). The resultant precipitate was filtered and then washed alternately with deionized water and ethanol three times to remove the impurities. Further, for the harvest of NiO nanocrystals, the precipitate of nickel hydroxide hex hydrate (Ni(OH)$_2$*6H$_2$O) was dried in hot air oven at 100 °C for 2 h (equation (2)), and then calcined at 600 °C for 2 h. The obtained final product was named as sample A (equation (3)). The possible chemical reactions are briefly summarized as follows:

$$\text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 2\text{NaNO}_3 + \text{Ni(OH)}_2\cdot 6\text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{Ni(OH)}_2\cdot 6\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} \text{Ni(OH)}_2 + 6\text{H}_2\text{O}$$  \hspace{1cm} (2)

$$\text{Ni(OH)}_2 \xrightarrow{600^\circ\text{C}} \text{NiO} + \text{H}_2\text{O}$$  \hspace{1cm} (3)

In the same way, for the preparation of nickel oxalate dihydrate from nickel nitrate hexahydrate and oxalic acid dihydrate, 0.5 M of nickel nitrate Ni(NO$_3$)$_2$*6H$_2$O and 1 M of oxalic acid (C$_2$H$_2$O$_4$*2H$_2$O) were used. Finally, the prepared nickel oxalate dihydrate (NiC$_2$O$_4$*2H$_2$O) (equation (4)) was washed in the above-mentioned manner and then dried at 100 °C (equation (5)). Further, for the harvest of NiO nanocrystals the dried precipitate of NiC$_2$O$_4$ (nickel oxalate) was annealed at 400 °C. The final product was named as sample B (equation (6)). The possible chemical reactions are given below:

$$\text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O} + \text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O} \rightarrow \text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O} + 2\text{HNO}_3 + \text{6H}_2\text{O}$$  \hspace{1cm} (4)

$$\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} \text{NiC}_2\text{O}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (5)

$$\text{NiC}_2\text{O}_4 \xrightarrow{400^\circ\text{C}} \text{NiO} + \text{CO}_2 + \text{CO}$$  \hspace{1cm} (6)

2.3. Characterization

The prepared products were characterized by powder XRD on X’PERT PRO diffractometer with Cu-Ka radiation (k = 1.5406 Å). From the line broadening, the size of the particle was estimated by the Scherrer equation. Then, the estimated sizes were compared with the sizes calculated from W–H plots. FT-IR analysis was made to characterize the functional groups of the precursor and nanosized nickel oxide using SHIMADZU-8400 with a resolution of 4 cm$^{-1}$. The room temperature PL studies were carried out using VARIAN spectrophotometer. The morphological analysis was performed by JSM-6701F FE-SEM. To confirm the morphology and size of the nanocrystals of NiO prepared using oxalic acid FE-TEM (Model JSM 2100F JEOL, Japan) analysis was made. VSM is used to identify the nature of magnetic species in the material.
3. Results and discussion

3.1. Thermal analysis

To study the thermal behavior of as prepared Ni(OH)$_2$, TG and DTA analyses were performed simultaneously in the temperature range of 30–1000 °C. As shown in figure 1, the thermal decomposition of Ni(OH)$_2$ occurs in two major steps: 1, the removal of surface adsorbed water associated with the Ni(OH)$_2$ (30–220 °C) and 2, decomposition of nickel hydroxide into nickel oxide (220–570 °C). After 570 °C, the weight loss continued but gradually slowed and completely ceased at 600 °C; as a consequence the stable residue can be ascribed to NiO nanocrystals. The dehydration process involved in the first stage is given by the following chemical equation.

$$\text{Ni(OH)}_2 * X_{\text{ads}} * \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + X\text{H}_2\text{O}$$

(7)

In the first stage, the TG curve shows 7.53% of weight loss and using this weight loss, it is possible for us to estimate the amount of water existing in the as-prepared Ni(OH)$_2$. The amount of water existing in the sample can determine the crystal structure and electrochemical properties of the as-prepared Ni(OH)$_2$. As per the available literature [21], the water content for $\beta$-Ni(OH)$_2$ varies from 0 to 0.3 M fraction (moles of H$_2$O per mole of Ni(OH)$_2$) and for $\alpha$-Ni (OH)$_2$, it varies from 0.3 M to 0.7 M fraction.

In the present study, for the as-prepared Ni(OH)$_2$, the water absorption in molar fraction has been calculated from the TG curve as 0.29. Therefore, the possible dehydration reaction is modified as

$$\text{Ni(OH)}_2 * 0.29\text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + 0.29\text{H}_2\text{O}$$

(8)

From the calculated molar fraction value of water (0.29), it is concluded that the as-prepared Ni(OH)$_2$ is in $\beta$ phase. This result confirms the crystal structure detected from XRD patterns. In the second stage, the decomposition of Ni(OH)$_2$ takes place between 220 and 600 °C with a major weight loss of 19.2%. The entire decomposition reaction is given as

$$\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}$$

(9)
The DTA curve shows an endothermic peak with a maximum located at 300 °C. The temperature range of the endothermic peak in the DTA curve matches well with that of weight loss in the TG curve corresponding to the decomposition of Ni(OH)$_2$ into NiO.

The TG–DTA curves of nickel oxalate (NiC$_2$O$_4$·2H$_2$O) prepared using nickel nitrate and oxalic acid are shown in Figure 2. The TG curve shows two major weight losses. The initial weight loss between room temperature and 280 °C is attributed to the loss of two water molecules from anhydrous nickel oxalate. The second major weight loss in the range of 280–385 °C is due to conversion of anhydrous nickel oxalate to the nickel oxide. After these fragmentations at temperatures up to 385 °C, no thermal effects are observed in the TG curve indicating the formation of pure NiO nanocrystals. The DTA curve shows two endothermic peaks, one at 265 °C and the other at 350 °C. These peaks are supporting the weight loss in the TG curve corresponding to the removal of two water molecules and conversion of anhydrous nickel oxalate to the nickel oxide, respectively. These processes correspond to the following equations:

\[
\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O} \underset{300\text{--280} \degree\text{C}}{\longrightarrow} \text{NiC}_2\text{O}_4 + 2\text{H}_2\text{O} \tag{10}
\]

\[
\text{NiC}_2\text{O}_4 \underset{280\text{--385} \degree\text{C}}{\longrightarrow} \text{NiO + CO}_2 + \text{CO} \tag{11}
\]

Based on the TG—DTA results, the NaOH assisted synthesis showed NiO formation at 600 °C, whereas it is 400 °C for oxalic acid assisted synthesis.

3.2. XRD analysis

The XRD pattern of precursor prepared using NaOH is shown in Figure 3(a). All the diffraction peaks can be indexed to hexagonal structure of β-Ni(OH)$_2$ with lattice parameters $a = 3.1125$ Å, $c = 4.6357$ Å, which are consistent with JCPDS data (Card No: 74-2075). Scherrer’s formula [22] shows the crystallite size of β-Ni(OH)$_2$ as 4.67 nm. Figure 3(b) shows the diffraction pattern of precursor NiO prepared using oxalic acid. As shown in the figure, the diffraction peaks can be indexed to orthorhombic nickel oxalate (NiC$_2$O$_4$·2H$_2$O). The measured lattice constants ‘$a$’, ‘$b$’, and ‘$c$’ are 11.4469, 5.0433 and 15.6577 Å, respectively, and are consistent with the JCPDS values (Card No: 25-0582). The crystallite size estimated from Scherrer’s
formula is 18.19 nm. However, the diffraction patterns of samples A and B (figures 3(c) and (d)) indicate the formation of crystallographic planes such as (111), (200), (220) and (311) correspond undoubtedly to the cubic face-centered NiO phase with lattice parameter \(a = 4.1819 \text{ Å}\) and no discernible impurities. The absence of impurity peaks indicates that \(\beta\)-Ni(OH)\(_2\) and nickel oxalate are completely decomposed into nickel oxide at 600 and 400 °C, respectively. The obtained diffraction results agree with that of JCPDS card No: 89-7130. The average crystal size of NiO measured using Scherrer’s formula is found to be 18.19 nm for sample A, whereas the size is 13.40 nm for sample B. The smaller crystallite size of sample B suggests its large width of the XRD peaks.

3.3. Determination of lattice strain and crystal size using Williamson–Hall plots

In nanoscale, both crystallite size and lattice strain play an important role in XRD line broadening. W–H analysis is a simplified integral breadth method where both size induced and strain induced broadening are deconvoluted by considering the peak width as a function of 2\(\theta\). For the total peak broadening W–H suggested an equation which is given by

\[
\beta \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \tan \theta
\]  

(12)
Where, $\beta$ is the peak width at half-maximum intensity, $k$ is a constant equal 0.89, $\lambda$ is the wavelength of the radiation $D$ is the particle size in nanometer, $\theta$ is the peak position and $\varepsilon$ is the lattice strain. The average particle size and microstrain of the products were calculated using the W–H plotting, shown in figures 4(a), (b). When compared with sample B, sample A shows lesser scattering of points away from the linear fit, indicating that sample A has homogeneous size distribution and microstrain. Using the plots, the crystallite size was estimated from the $y$-intercept, and the strain from the slope of the fit. The calculated values of lattice strain and crystallite sizes are presented in table 1. From the table, it is noted that the average crystallite size estimated from Scherrer formula and W–H analysis shows a slight variation because of the difference in averaging the particle size distribution. Especially, the crystallite size of sample B estimated from the W–H plot is in agreement with the FE-TEM result as discussed in section 3.6. In addition, microstrain value of sample A is 20% greater than the strain value of sample B reflecting its greater contribution to strain induced broadening of the diffraction.

Table 1. Geometric parameters of as-synthesized and annealed NiO nanocrystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Lattice parameter (Å)</th>
<th>Strain estimated from W–H method ($10^{-3}$)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO (NaOH)</td>
<td>Cubic</td>
<td>$A = 4.1819$</td>
<td>1.5114</td>
<td>18.18</td>
</tr>
<tr>
<td>NiO (Oxalic acid)</td>
<td>Cubic</td>
<td>$A = 4.1819$</td>
<td>1.1711</td>
<td>13.41</td>
</tr>
</tbody>
</table>

Figure 4 (a, b) W–H plots of (a) sample A and (b) sample B.
peak. The lattice strain values of the present study are slightly less than the strain value of NiO recorded by Goncalves et al [23].

3.4. Optical properties

The room temperature PL spectra of samples A and B with 290 nm excitation are given in figure 5. Samples A and B show a UV emission band at 349 and 350 nm, respectively. And also, both samples show sharp visible emission at 598 and 600 nm, respectively. The UV emission is usually caused by the direct recombination of the excitons through an exciton-exciton scattering. The visible emission is recognized from the radiative recombination of photo generated hole with an electron occupying the nickel and oxygen vacancies [24]. Among the two samples, NiO synthesized from oxalic acid gives stronger UV and visible emissions than the product derived using NaOH. Strong emission indicates that NiO nanocrystals prepared from oxalic acid are good room temperature visible-light emitters.

The optical performance of a sample generally depends on the ratio of intensities between UV and visible emissions [25]. In the present study, sample A shows the optical intensity ratio of 1.32, whereas, for sample B the value is 1.74. The PL intensity ratio is evidence to evaluate the crystal quality. The higher the crystal quality, the greater should be the PL intensity ratio. Therefore, higher PL intensity value of sample B indicates its higher crystalline than its counter part, sample A.

3.5. Functional group analysis

FT-IR analyses have been recorded for the as-prepared and annealed samples in the range of 400–4000 cm⁻¹ and the results are shown in figures 6(a)–(d). In the IR spectrum of Ni (OH)₂ (figure 6(a)), a narrow and strong band at 3637 cm⁻¹ due to the γ (OH) stretching vibration, that
specifies OH groups in a free configuration, a strong band at 528 cm\(^{-1}\) corresponding to the hydroxyl group’s lattice vibration \(\delta\) (OH) and a band with weak intensity around 447 cm\(^{-1}\) resulting from the Ni-O lattice vibration \(\gamma\) (Ni-O) are predicted and are confirming the \(\beta\)-Ni (OH)\(_2\). It can be seen that a broad and intense band located at 3452 cm\(^{-1}\) can be ascribed to the O–H stretching vibration of the interlayer water molecules and their bending vibrations occur at 1643 cm\(^{-1}\). The presence of anions can be specified by the peak present at 840 cm\(^{-1}\). From the IR spectrum of nickel oxalate (figure 6(b)), a broad absorption band positioned at 3420 cm\(^{-1}\) is noted due to the O–H stretching vibration of water molecule. Vibrations at \(\sim\)1360 cm\(^{-1}\) are attributed to \(\sigma_s\) (C–O) + \(\delta\) (C–C), while the band at \(\sim\)1318 cm\(^{-1}\) corresponds to \(\sigma_s\) (C–O) + \(\delta\) (O–C=O). The bands at 830 cm\(^{-1}\) and 489 cm\(^{-1}\) are due to \(\delta\) (O–C=O) and \(\sigma\) (Ni–O) frequencies of the oxalate moiety, respectively.

The FT-IR spectrum of sample A shows the formation of Ni–O in nanosize (figure 6(c)). The presence of absorption at 3460 cm\(^{-1}\) describes stretching vibration of water molecules. The peak positioned at 2357 cm\(^{-1}\) is caused by –CH\(_2\). The absorption bands located at 1380 and 842 cm\(^{-1}\) are due to the NO\(_3^−\) anions. The decomposition of \(\beta\)-Ni(OH)\(_2\) into NiO nanocrystals is confirmed by intense absorption band at 424 cm\(^{-1}\). The formed particles are in nano form as bulk form of NiO can be expected between 390 and 403 cm\(^{-1}\) [26]. On the other hand, in the IR spectrum of sample B (figure 6(d)), the intensities of stretching and bending vibration bands of water molecules have been reduced considerably indicating the high purity of the product. At the same time, an intense peak of Ni–O has been predicted at 443 cm\(^{-1}\). Further, no absorption bands of anions were predicted in sample B indicating proper formation of crystalline NiO.
3.6. Microstructural analysis

The microstructural analysis of the samples A and B was carried out by FE-SEM analysis. The FE-SEM images of the samples are shown in figures 7(a) and (b). From the figures, it is observed that all the particles show almost spherical morphology. However, sample A has a higher degree of agglomeration than that of B. The diameter of the nanoparticles of sample A is in the range of 16–23 nm. But sample B has nanoparticles of diameters in the range of 23–27 nm. EDX analysis can be used to study the presence of nickel and oxygen, as is shown in figure 7(c). From the EDX spectrum, numerous well-defined peaks were predicted to Ni and O which clearly indicate that the synthesized particles are nickel oxide. Figure 8 shows an FE-TEM micrograph of NiO prepared using oxalic acid. As shown in the figure, the NiO nanoparticles are essentially little aggregated, but still appear to be spherical and ellipsoidal in
shape individually. The average grain size of the particles was about 15 nm, which testified to the estimated results from XRD pattern.

3.7. Magnetic study

Figure 9 shows the room temperature hysteresis loops of samples A and B. It can be observed that both formulations reveal typical paramagnetic behavior. The paramagnetic behavior of the prepared nanocrystals is clearly shown by coercivity ($H_c$), saturation magnetization ($M_s$) and remanent magnetization ($M_r$). The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field; beyond this field no further increase in magnetization occurs. High saturation magnetization magnetic materials are required for further
high-frequency inductors [27]. From the figure, it is noted that sample A has low saturation magnetization value of 6.45 emu gm\(^{-1}\) with remanent magnetization and coercivity values of 0.000 125 emu gm\(^{-1}\) and 479 Oe, respectively. However sample B has the saturation magnetization value of 6.92 emu gm\(^{-1}\) with remanent magnetization and coercivity values of 0.000 207 emu gm\(^{-1}\) and 32 Oe, respectively. Therefore, it was predicted that NiO nanocrystals synthesized using oxalic acid will lead to an increase in the saturation magnetization. Coercivity is the reverse magnetic field required to reduce the net magnetization to zero. For magnetic materials, it is necessary to reduce the coercivity as a way to control the energy losses. As seen earlier, sample B has relatively lower coercivity compared with that of sample A, which can be considered as a further improvement of the magnetic properties.

4. Conclusion

In summary, precursors of NiO were prepared using two different oxide sources viz sodium hydroxide and oxalic acid. The thermo gravimetric analysis results suggest the NiO formation at 600 and 400 °C for precursors prepared using NaOH and oxalic acid, respectively. After calcining at respective temperatures, the products obtained using NaOH and oxalic acid are termed as samples A and B. The XRD analysis indicates that both the samples A and B exhibit a cubic phase of NiO. From the W–H plots, it is concluded that sample B has less strain and particle size than sample A. The optical properties reveal that sample B exhibits higher optical intensity ratio than sample A. When compared with sample A, the FE-SEM micrographs of sample B show less agglomeration. FE-TEM analysis of sample B reveals spherical and elliptical particles with sizes in the range of 15 nm. The relative saturation magnetization behavior of samples A and B confirms their paramagnetic nature. However, sample B shows low coercivity value as compared with sample A. By considering the above results, among the two oxide sources oxalic acid could be used as a potential material for the preparation of NiO nanocrystals. The relative studies are in progress and will be reported in forthcoming publications.

References

Influence of Zn\(^{2+}\) ions incorporation on the magnetic and pseudo capacitance behaviors of NiO nanoparticles

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ABSTRACT

Reported here is the various levels of Zn\(^{2+}\) incorporated NiO nanocrystals derived from a simple chemical precipitation method. The synthesized products were analyzed for XRD, FTIR, FESEM, magnetic studies (VSM) and cyclic voltammetry (CV) measurements. Magnetic characterization shows a conversion of NiO from paramagnetic to ferromagnetic on the introduction of Zn\(^{2+}\) within NiO lattice. The cyclic voltammetry measurements showed higher rate of specific capacitance (876 F g\(^{-1}\)) for the NiO incorporated with 0.05 M of Zn\(^{2+}\) which made it promising electrode material for the super capacitor application.

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1. Introduction

The peculiar physical and chemical properties of nanoscaled materials have consumed ample space in materials science. Among various nanoscaled materials, nanocrystalline oxides of transition metals play an important role in advanced materials development. In the lineup of oxides of transient metals, NiO is an environment friendly semiconductor with ultra high specific capacity and high density which can be grown into a wide range of applications in lithium ion batteries and super capacitors [1–4], solar cells [5,6] anti-ferromagnetic layer [7], photo catalysts, electrochemical capacitors [8], electrochemical and optical coating [9]. In addition, nanosized NiO can exhibit super paramagnetic effect which can be used in drug delivery and MRI agent [10]. For the purpose of introducing new properties into these NiO nanocrystals attempts have been made to combine it with impurity atoms. A key concept is that the reactions leading to deposition of dopant ions must be balanced to succeed in incorporating dopants during crystal growth. Mishra and co-workers have studied the super paramagnetic behavior of Mn doped NiO nanocrystals [11]. Su and co-workers showed that nanocrystals of NiO can be used in electro chemical (EC) devices when properly doped with Cu [12]. Till date, there are no reports on Zn\(^{2+}\)-doped NiO nanocrystals. Herein, we present a chemical precipitation method for the successful preparation of Zn\(^{2+}\)-doped NiO nanocrystals with controlled Zn content of 0.025, 0.05, 0.075 and 0.1 M. In this preparation the surfaces of the Zn\(^{2+}\) doped NiO nanocrystals have a rich surface hydroxyl group, which means that they own excellent solubility and can be processed into nanostructures or devices more readily.

2. Materials and methods

2.1. Chemicals

Nickel nitrate hex hydrate [Ni(NO\(_3\)]\(_2\) \(\cdot\) 6H\(_2\)O], zinc acetate [Zn(\(\text{CH}_3\text{COO}\)]\(_2\) \(\cdot\) 2H\(_2\)O] and oxalic acid [C\(_2\)H\(_4\)O\(_4\)] \(\cdot\) 2H\(_2\)O] were purchased from Merck and were used as received since they were of analytical reagent grade with 99%
purity. Sample preparation and dilutions were made of ultrapure water.

2.2. Synthesis of NiO nanocrystals

In the preparation of NiO nanocrystals from nickel nitrate hex hydrate [Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O] and oxalic acid [C\textsubscript{2}H\textsubscript{2}O\textsubscript{4} \cdot 2H\textsubscript{2}O], 0.5 M of nickel nitrate hex hydrate and 1 M oxalic acid were mixed drop by drop. The entire mixture was stirred magnetically at 60 °C until the homogeneous solution was obtained. Finally, the prepared nickel oxalate dihydrate [NiC\textsubscript{2}O\textsubscript{4} \cdot 2H\textsubscript{2}O] was washed in the above said manner and then dried at 100 °C. Further, for the harvest of NiO nanocrystals the dried precipitate of NiC\textsubscript{2}O\textsubscript{4} (Nickel oxalate) was annealed at 400 °C. The final product was named as NiO nanoparticles. The possible chemical reactions are given below:

\[
\begin{align*}
\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + C_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O} & \rightarrow \\
\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + 2\text{HNO}_3 + 6\text{H}_2\text{O} & \rightarrow \\
\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} & \xrightarrow{\Delta 100\text{°C}} \text{NiC}_2\text{O}_4 + 2\text{H}_2\text{O} \\
\text{NiC}_2\text{O}_4 & \xrightarrow{\Delta 400\text{°C}} \text{NiO} + \text{CO}_2 + \text{CO}_2 \uparrow 
\end{align*}
\]

2.3. Synthesis of NiO: Zn\textsuperscript{2+} nanocrystals

For the synthesis of Zn\textsuperscript{2+}-doped NiO, 0.5 M of Nickel nitrate hex hydrate [Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O] in 50 ml of deionized water and an appropriate amount of zinc acetate [Zn (CH\textsubscript{3}COO)\textsubscript{2} \cdot 2H\textsubscript{2}O] (0.025, 0.05, 0.075 and 0.1 M) in 20 ml aqueous were mixed drop by drop. Then, 1 M of oxalic acid [C\textsubscript{2}H\textsubscript{2}O\textsubscript{4} \cdot 2H\textsubscript{2}O] in 50 ml of deionized water was added drop by drop to the above mixture. The entire mixture was stirred magnetically at 60 °C until the homogeneous solution was obtained. Finally, the product was dried in a hot air oven at 100 °C for 2 h, and then the dried precipitate was annealed at 400 °C.

2.4. Characterization

2.4.1. Materials characterization

The prepared products were characterized by powder X-ray diffraction (XRD) on an XPERT PRO diffractometer with Cu-Ka radiation (\(k = 1.5406 \text{\AA}\)). From the line broadening, the size of the particle was estimated by Scherrer equation. FT-IR analysis was made to characterize the functional groups of the product using SHIMADZU-8400 with a resolution of 4 cm\(^{-1}\). The morphological analysis was performed by a JSM-6701F field emission scanning electron microscope (FESEM). The dispersion of nickel, oxygen and zinc in the products was characterized by energy dispersive X-ray elemental analysis (EDX: Thermo Super Dry II). Vibrating sample magnetometer (VSM) is used to identify the nature of magnetic species in the material.

2.4.2. Electrochemical performance investigation

Electrochemical measurements were carried out in 0.2 M tetra butyl ammonium perchloride aqueous electrolyte using a three electrode system. The NiO was employed as the working electrode (WE), a platinum wire counter electrode (CE), and an Ag/AgCl reference electrode (RE). Cyclic voltammetry (CV) measurements were performed within a potential range of −0.6 to +1.8 V versus Ag/AgCl at a scan rate from 10 to 50 mV s\(^{-1}\) on the CHI 6060 electrochemical workstation. The specific capacitance (\(C_s, \text{ F g}^{-1}\)) was calculated from the cyclic voltammograms according to the following equation [13–15]:

\[
C_s = \frac{Q}{\Delta V. m} 
\]

where \(C_s\) is denoting the specific capacitance, \(Q\) the anodic and cathodic charges on each scanning, \(m\) is the mass of the electrode material (mg) and \(\Delta v\) is the scan rate (mV s\(^{-1}\)).

3. Results and discussion

3.1. XRD analysis

Fig. 1 displays the XRD patterns of undoped NiO and NiO doped with different levels of Zn\textsuperscript{2+} ions. The concentration of Zn\textsuperscript{2+} ions in the products was 0.025, 0.05, 0.075 and 0.1 M. In all the cases, only cubic structure of NiO was detected (JCPDS file no: 74-2075) and no signs of zinc oxides appear up to 0.05 M of doping, which indicates that phase pure doped nanocrystals were obtained by this synthetic scheme. The strong and sharp diffraction peaks demonstrate that the products are well crystalline. Furthermore, it can be seen that at higher doping concentrations (0.075 and 0.1 M) a secondary phase is noted and are specified by asterisks. The new phase corresponds to

![](image)
ZnO (JCPDS no: 36-1451). Therefore, the doping concentration of 0.05 M may roughly be considered as the solubility limit of Zn$^{2+}$ in NiO. At higher doping concentration i.e. beyond the solubility limit a few of Zn$^{2+}$ ions get segregated in the form of secondary phase. The formation of secondary phase induces some kind of modifications in the structural, magnetic and electrochemical properties. The variation observed in structural, magnetic and electrochemical properties are systematic when the doping concentration is below 0.075 M (single phase). Average size as estimated for undoped NiO nanocrystals using Scherrer formula [16] is found to be 13.4 nm. An increase in size is observed due to doping Zn$^{2+}$ in NiO nanocrystals (Table 1). As shown in Table 1, Zn$^{2+}$ doping is known to influence the lattice parameter of NiO. A suitable increase in the lattice parameter ‘a’ by 0.37% for Zn$^{2+}$-doped NiO (1 M) nanocrystals indicates expansion of the unit cell due to Zn$^{2+}$ inclusion in NiO nanocrystals. The ionic radius of Ni$^{2+}$ is (0.69 Å) [17] smaller than Zn$^{2+}$ (0.74 Å) [18]. The incorporation of Zn$^{2+}$ at Ni$^{2+}$ site generates strain and hence leads to an increase in the lattice constant. These findings essentially indicate the presence of Zn$^{2+}$ ions at cationic substitutional sites resulting in the cubic structure. We also notice from the data in Table 1 that there is about 1.1% increase in the specific volume as the particle size increases from about 13.4 to about 19.97 nm. This could be explained by the fact that as particle size increases, the effect of the surface forces on the bulk becomes progressively less.

### 3.2. Functional group analysis

FT-IR spectroscopy is an essential tool to study the presence of functional groups in the given sample. FT-IR spectra of undoped and Zn$^{2+}$ doped NiO nano crystals are shown in Fig. 2. The broad absorption bands at ~3430 and ~1630 cm$^{-1}$ encompass respectively to the O–H stretching and bending vibrations of absorbed water on the NiO surface [19]. All the samples show an absorption band at 2400 cm$^{-1}$ which can be ascribed to the existence of CO$_2$ molecules in the air. The presence of absorption band at around 1390 cm$^{-1}$ can be assigned to C–O stretching vibrations of acetate groups complexed with Ni–O. The strong absorption band between 443 and 432 cm$^{-1}$ can be attributed to the stretching modes of Ni–O [20]. The appearance of ZnO peaks in the diffraction patterns of higher concentration of Zn$^{2+}$ doping has not been seen in the FT-IR spectra and may be due to the trace content of ZnO molecules adsorbed on NiO: Zn$^{2+}$ architectures.

#### 3.3. Magnetic properties

Magnetic hysteresis curves of NiO and NiO doped with Zn$^{2+}$ recorded at room temperature are shown in Fig. 3 (a–e). The undoped NiO shows paramagnetic behavior with saturation magnetization 0.00920 emu/g. The saturation magnetization observed for 0.025 M of Zn$^{2+}$ doped NiO is 0.00242 emu/g, while for other doping concentrations (0.05, 0.075 and 0.1 M) it is 0.00256, 0.0174 and 0.043 emu/g respectively. It is clear that the magnetic moment in the case of doped samples is higher as compared to undoped samples. That is inclusion of Zn$^{2+}$ can increase the net magnetization. Note that with an increase in Zn$^{2+}$ concentration in NiO nanocrystals, paramagnetic behavior of undoped product has changed into super paramagnetic (0.025 and 0.05 M) and then finally reaching room temperature ferromagnetism (0.075 and 0.1 M). Especially, the NiO doped with 0.1 M of Zn$^{2+}$ does not saturate in high field due to lack of surface spins. This is explained by the fact that the magnetization consists of two components: an easily magnetized component in the low field region and a non-saturating component for the almost linear variation in the high field region. The easily magnetized component is associated with the uncompensated spins in the cores, and the non-saturating component is related to the surface spins. The primary reason to observe ferromagnetism is defects, most probably located at the surface and generated by the doping agents. It is observed that oxygen rich Zn$^{2+}$ doped NiO nanocrystals are super paramagnetic while oxygen poor products are ferromagnetic [21]. The obtained ferromagnetism is intrinsic and expected to arise from the exchange interaction between dopant ions mediated by defects like oxygen vacancy. Furthermore, the interactions of localized electrons.

### Table 1

Particle size and lattice parameters of NiO and NiO: Zn$^{2+}$ nanocrystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiO</td>
<td>13.40</td>
<td>4.1819</td>
<td>73.13</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$</td>
<td>16.67</td>
<td>4.1849</td>
<td>73.29</td>
</tr>
<tr>
<td>(0.025 M)</td>
<td>17.33</td>
<td>4.1911</td>
<td>73.62</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$</td>
<td>18.26</td>
<td>4.1932</td>
<td>73.69</td>
</tr>
<tr>
<td>(0.05 M)</td>
<td>18.26</td>
<td>4.1932</td>
<td>73.69</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$</td>
<td>19.97</td>
<td>4.1973</td>
<td>73.94</td>
</tr>
<tr>
<td>(0.075 M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0.1 M)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. FT-IR spectra of NiO and different levels (0.025, 0.05, 0.075 and 0.1 M) of Zn$^{2+}$ doped NiO nanocrystals.

Fig. 3. Magnetic hysteresis curve of NiO and NiO doped with Zn$^{2+}$ recorded at room temperature.
mediated by $V_0$ lead to pair the electrons either in the spin up or spin down state. In bound magnetic polaron (BMP) mechanism for transition metal oxides, the defect comes from the oxygen vacancy which could catch one itinerant electron to form a hydrogen-like orbit with a finite radius. When the defects increase in critical amount, the orbits overlap to form a narrow impurity band. The doped magnetic ions within the radius coverage correlate through the

Fig. 3. (a–e): Magnetic hysteresis loops of (a) NiO and (b–e) different levels (0.025, 0.05, 0.075 and 0.1 M) of Zn$^{2+}$ doped NiO nanocrystals.
impurity band electrons to become ferromagnetic. In the present case it is sure that ferromagnetic is induced by doping of Zn$^{2+}$. Further, in the XRD, all the intense peaks from Zn$^{2+}$-NiO could be indexed the same cubic structure as pure NiO NPs, the increase in lattice parameter as a function of Zn$^{2+}$ concentration is consistent with the substitution of Ni$^{2+}$ ions by Zn$^{2+}$ ions. The more Ni$^{2+}$ ions were substituted by Zn$^{2+}$, the greater lattice distortion of NiO would be generated, the more vacancies and lot interstitial should be getting. As a result, oxygen vacancy should be considered as the origin of ferromagnetism in our sample. In other words, when compared to pure NiO, Zn$^{2+}$ doping may increase the concentration of oxygen vacancies because of its larger ionic radius than Ni$^{2+}$ ions.

Coercivity is the reverse magnetic field required to reduce the net magnetization to zero. For magnetic materials, it is necessary to reduce the energy losses. As shown in Table 2, 0.05 M of Zn$^{2+}$ doped nickel oxide nanoparticles have a relatively lower coercivity compared that of undoped and other doped products, which can be considered as a further improvement of the magnetic properties. The decrease of the coercivity can probably be explained in terms of the effect of Zn–Ni bi-layers. Remanent magnetization is another quantity can be defined as the remaining magnetic momentum after realizing the magnetic field. Low remanent magnetic materials are classified as magnetically clean materials. In some distinct fields, low remanent magnetization is highly desirable for instance in data storage applications. As shown in Table 2, when compared to other products, 0.05 M of Zn$^{2+}$ doped product shows low remanent magnetization.

### 3.4. Electrochemical studies

The CV measurements on NiO and NiO doped with different levels of Zn$^{2+}$ were performed to evaluate the scan rate dependent super capacitive performance of the samples. The CV patterns of the samples are shown in Fig. 4(a–e). The CV patterns of all the samples show identical shapes, indicating that the capacitance characteristic was entirely deviated from that of the electric double layer capacitor that may generate CV curves of the ideal rectangular shape [22]. The presence of oxidation and reduction peaks indicates a pseudo capacitive behavior of the products resulted from reversible electrochemical reactions. The major advantage of pseudo-capacitance is its high energy transfer during the faradaic reaction and providing 10–100 times more capacitance than EDLCs [23]. The possible reversible chemical reaction may be due to the intercalation/de-intercalation of the tetra butyl ammonium cation (TBA$^{+}$) into/from NiO lattice.

\[
\text{NiO + TBA}^{+} + e^{-} \rightleftharpoons (\text{NiO})\text{TBA}
\]

As the scan rate increases, the potential of the anodic and cathodic peaks shift to more positive and negative directions, due to the limitation of the ion diffusion rate to satisfy electronic neutralization during the redox reaction. Applying the Eq. (4) the specific capacitance of the samples was calculated and summarized in Table 3. It is predicted from the table that the NiO has shown the specific capacitance of 318 F g$^{-1}$ at the scan rate of 10 mV s$^{-1}$. However, the specific capacitance of NiO drops as the scan rate increases, the specific capacitance is maintaining the value of 62 F g$^{-1}$ at the scan rate of 50 mV s$^{-1}$. The specific capacitance of NiO electrode calculated in the present study is greater than the values reported by other researchers. Patil et al., have presented the value of specific capacitance of NiO film electrode as 167 F g$^{-1}$ [24], whereas, Lokhande et al., have reported the value as 222 F g$^{-1}$ [22]. It is seen that in the present study at low scan rate, the specific capacitance is maximized. The potential reason for high specific capacitance at low scan rate could be resulted from the low faradaic reaction. At higher scan rates, the ionic diffusion takes place from the outer regions of the pores, whereas at low scan rate, both inner and outer surfaces are responsible in the calibration of specific capacitance and this leads to a higher value of capacitance at low scan rate.

As far as the doped NiO is concerned, on 0.025 M of doping, the calculated specific capacitance values for NiO at scan rates of 10, 20, 30, 40 and 50 mV s$^{-1}$ are 459, 184, 162, 133 and 71 F g$^{-1}$, respectively. Similarly, the specific capacitance values for NiO on 0.05 M of doping at the same scan rates are 876, 413, 317, 263 and 230 F g$^{-1}$ respectively. The increasing trend of specific capacitance of NiO on doping indicates that the incorporation of Zn$^{2+}$ ions into NiO system will help to increase the specific capacitance of spinel phase. As shown in the table, beyond 0.05 M of doping the specific capacitance decreases with the increasing the amount of Zn$^{2+}$. The decreasing trend of specific capacitance of Zn$^{2+}$ content exceeding 0.05 M can be attributed to the formation of secondary phase which are not electrochemical active. This is consistent with the XRD results in which secondary phase (ZnO)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation magnetization (emu/g)</th>
<th>Retentivity (emu/g)</th>
<th>Coercivity (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiO</td>
<td>0.00920</td>
<td>0.000567</td>
<td>135</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.025 M)</td>
<td>0.002420</td>
<td>0.000010</td>
<td>36</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.05 M)</td>
<td>0.002559</td>
<td>0.000009</td>
<td>35</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.075 M)</td>
<td>0.01745</td>
<td>0.000223</td>
<td>235</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.1 M)</td>
<td>0.043314</td>
<td>0.008617</td>
<td>183</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific capacitance (F g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiO</td>
<td>318 188 147 115 62</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.025 M)</td>
<td>459 184 162 133 71</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.05 M)</td>
<td>876 413 317 263 230</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.075 M)</td>
<td>239 119 93 83 47</td>
</tr>
<tr>
<td>NiO:Zn$^{2+}$ (0.1 M)</td>
<td>220 172 114 93 43</td>
</tr>
</tbody>
</table>
formation was seen at higher concentrations of Zn$^{2+}$ incorporation. The potential reason for the highest specific capacitance of NiO on 0.05 M of doping is due to its highly porous structure [25]. This highly porous structure rendered in better diffusion of ions and showed higher capacitance than other concentrations.

Fig. 4. (a–e): CV curves of (a) NiO and (b–e) different levels (0.025, 0.05, 0.075 and 0.1 M) of Zn$^{2+}$ doped NiO nanocrystals at different scan rates.
3.5. Micro structural analysis

The morphology of the NiO and NiO doped with 0.05 M of Zn$^{2+}$ was examined by the field emission scanning electron microscopy (FESEM) analysis. Fig. 5a displays the FESEM image of NiO. From the figure, it is observed that all the particles show spherical morphology with less degree of agglomeration. As seen in Fig. 5b, the surface area and porosity of the doped NiO samples are significantly higher than the undoped NiO. The formation of mesoporous structures of doped NiO in the present study may be due to various parameters such as hydrophobic interactions, hydrogen bonding, van der Waals forces, crystal face attraction, electrostatic and dipolar fields, intrinsic crystal contraction and Ostwald ripening contributing simultaneously during the product formation. The high porosity of doped NiO supposed to facilitate better transportation of electrolyte through their nanochannels for efficient redox reactions during the charge storage process. The EDS analysis was carried out on the pure and doped NiO and the results are shown in Fig. 5c and d. As shown in Fig. 5c, the energy dispersive spectroscopy (EDS) demonstrated that the synthesized NiO spheres consisted of carbon, nickel and oxygen, which is in agreement with those observed in the XRD pattern. In the EDS spectrum of doped NiO, well defined peaks of Ni, O and Zn were predicted which clearly indicate that the synthesized particles are incorporated with Zinc (Fig. 5d).

4. Conclusion

In conclusion, the structural, magnetic, and electrochemical properties of Zn$^{2+}$ ions doped NiO nanocrystals synthesized by the simple chemical precipitation method were studied. The substitution of parts of lattice Ni of NiO by Zn$^{2+}$ ions was confirmed by XRD. FT-IR spectra confirm the NiO vibrations. FESEM image showed the formation of mesoporous structure on doping. Magnetic curves of NiO showed paramagnetic behavior. However, on doping, paramagnetic behavior of undoped products was changed into superparamagnetic and they finally reach room temperature ferromagnetism. The observed ferromagnetic behavior is an intrinsic characteristic of the sample and has been explained on the basis of bound magnetic polaron mechanism, where the ferromagnetic ordering arises due to indirect interaction between localized electrons of Zn ions mediated by defect like oxygen vacancy. The electrochemical measurement showed that the capacitance of NiO electrode was significantly increased from 318 F g$^{-1}$ to 876 F g$^{-1}$ at low scan rate by incorporation of
0.05 M of Zn$^{2+}$ ions, making NiO: Zn$^{2+}$ a promising material for electrochemical capacitors.

**Acknowledgments**

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**References**

Opto, magnetic and electrochemical characterization of Ni$_{1-x}$Co$_x$O nanocrystals

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Abstract This manuscript describes the synthesis and characterization of Ni$_{1-x}$Co$_x$O with $x = 0.025, 0.05, 0.075$ and $0.1$ M. The structure and chemical compositions of the products were characterized by X-ray diffraction, energy dispersive spectrum and Fourier transform infrared spectroscopy. The obtained products were identified to be of face-centered-cubic structure. The optical properties of the products were studied by room temperature photoluminescence (PL) measurements. The PL spectra reveal a continuous suppression of both UV and green emissions by increasing the concentration of dopant ion. The suppressed green emission indicates the quenching of surface defects present in the nanostructures. The morphology of the doped product was analyzed by the scanning electron microscope and confirmed by field emission transmission electron microscope. Magnetic measurements show an enhancement in ferromagnetism at higher concentration of cobalt doping. The electrochemical characterization showed that the NiO doped with 0.05 M of cobalt exhibited much improved specific capacitance than that of pure NiO.

1 Introduction

The materials in nanoscale are of great importance in the fields of both fundamental and advanced research due to their outstanding physical and chemical properties. Especially, semiconductors of transition metal oxides have attracted the scientific community owing to their potential applications in spintronics and optoelectronics [1–3]. Among the metal oxides, NiO in nanoscale has gained more attention because of its anomalous magnetic properties such as magnetic enhancement, large coercive, spin glass freezing, and unusual hysteresis behavior [4–8]. NiO is basically an insulating material with a band gap of nearly 4.0 eV, but it shows p-type semiconducting behavior due to the presence of Ni$^{2+}$ vacancies or when it is doped with other cations [9]. The peculiar electronic properties of NiO introduce it an excellent material in applications such as anodes for lithium ion batteries [10, 11], solar cells [12, 13] and in chemical (gas) sensing [14–16]. Doping or alloying nanocrystals produces another fundamental approach to modify the properties of nanoparticles by means of tailoring the crystal compositions. When the dopant concentration is on the order of 1 per 10,000 atoms, the doping is referred to as heavy or high. The dopant concentration of the doped nanocrystals can be as high as a few percent and is some cases, even over ten percent which in fact form alloyed nanocrystals. Knowledge on the formation of the doped nanocrystals is still limited. The effect of Co on the supercapacitor behavior of NiO has been studied by other researchers [17, 18], however they failed to study the magnetic behavior of Co doped NiO nanocrystals. Zhang et al. [19], have shown that NiO doped with 1 % of Co exhibits excellent electrochemical performances than undoped NiO film. With the aim of improving the magnetic and electrochemical properties of NiO, we suggest a simple chemical precipitation method to prepare various levels of cobalt doped NiO nanocrystals. The synthesized products were characterized through different techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL), electron microscopy (SEM) fitted with EDX, field emission transmission electron microscopy (FE-TEM) and hysteresis measurements. The effect of Co on the super capacitance behavior of NiO has been performed using CV.
2 Materials and methods

2.1 Chemicals

Nickel nitrate hex hydrate [Ni(NO$_3$)$_2$·6H$_2$O], cobalt nitrate [Co(NO$_3$)$_2$·6H$_2$O] and oxalic acid [C$_2$H$_2$O$_4$·2H$_2$O] were purchased from Merck and were used as received since they were of analytical reagent grade with 99% purity. Sample preparation and dilutions were made of milli-Q water.

2.2 Synthesis of NiO and NiO: Co$^{2+}$ nanocrystals

For Co$^{2+}$-doped NiO, 1 M of oxalic acid [C$_2$H$_2$O$_4$·2H$_2$O] solution as precipitant agent was slowly dropped into constantly magnetic stirred mixture containing 0.5 M of nickel nitrate hex hydrate [Ni(NO$_3$)$_2$·6H$_2$O] with an appropriate amount of cobalt nitrate [Co(NO$_3$)$_2$·6H$_2$O]. The solution of the resultant mixture was stirred magnetically at 60°C until a precipitate was formed. The obtained precipitate was purified by dialysis against milli-Q water and ethanol several times to remove the impurities. The final product was then dried at 100°C and further calcined at 400°C for 2 h. A similar method of preparation without the addition of cobalt was used to synthesize undoped NiO nanocrystals.

2.3 Characterization

2.3.1 Materials characterization

X-ray diffraction (XRD) patterns of the synthesized nanocrystals were recorded by an X-ray diffractometer (X’PERT PRO) with Cu-Kα radiation (λ = 1.5406 Å). The photoluminescence (PL) emission spectra of the samples were recorded with a spectrofluorometer (Jobin–Yvon, FLUOROLOG–FL3-11). FT-IR analysis was made to characterize the functional groups of the nanocrystals using FT-IR spectrometer (SHIMADZU-8400) with a resolution of 4 cm$^{-1}$. The surface morphology and composition of the synthesized nanocrystals were investigated using a scanning electron microscope (SEM; JEOL-JSM-56100) equipped with an X-ray elemental analysis system (EDX: Thermo Super Dry II). Field emission transmission electron microscopy (FE-TEM: JSM2100F JEOL) measurements of Co$^{2+}$ doped NiO nanocrystals were performed to confirm the morphology. Magnetic parameters of undoped and doped nanocrystals were studied using vibrating sample magnetometer (VSM).

2.3.2 Electrochemical performance investigation

Electrochemical properties of the nanocrystals were investigated by cyclic voltammetry (CV) performed on an electrochemical work station (CHI 6060) between −0.6 and +1.8 V at room temperature with a scan rate of 10 mV s$^{-1}$. Electrochemical measurements were carried out in 0.2 M tetra butyl ammonium perchlorate with a standard three electrode configuration consisting of a sample (working electrode), an Ag/AgCl (reference electrode) and a high platinum wire (counter electrode). The specific capacitance ($C_s$, F g$^{-1}$) can be calculated from the CV curves using the equation [20–22] below:

$$C_s = \frac{Q}{\Delta v \cdot m}$$

where, $C_s$ is the specific capacitance, $Q$ the anodic and cathodic charges on each scanning, $m$ is the mass of the electrode material (mg) and $\Delta v$ is the scan rate (mV s$^{-1}$).

3 Results and discussion

3.1 X-ray diffraction

Figure 1 depicts the XRD patterns of Ni$_{1-x}$Co$_x$O nanocrystals. For the NiO, the peaks appearing at 37.22, 43.25, 62.86 and 75.43°C correspond to the reflections from (111), (200), (220), and (311) crystal planes, respectively. All the above mentioned peaks can be indexed with a face centered...
cubic crystalline structure [JCPDS card. No: 89-7130]. After the addition of cobalt in NiO, the spectra remain the same up to \( x = 0.05 \) M. This means that the cubic structure is not modified by the addition of Co into the NiO matrix. However, for \( x = 0.075 \) M, the diffraction from (311) plane of NiO was absent, but a small reflection of \( \alpha\)-Co(OH)\(_2\) was appearing at 2\( \theta = 23.6^\circ \) [JCPDS card No: 02-0925]. Further, for \( x = 0.1 \) M, the diffraction pattern exhibits only three features from (111), (200), and (220) reflections of NiO. The incorporation of dopant into the NiO matrix is further confirmed by the shrinkage and expansion of the lattice parameters of NiO in response to Co\(^{2+}\) incorporation (Table 1). The expansion of the lattice has been attributed to a number of possible phenomena, including confinement effects, grain surface relaxation, formation of point defects, and uncompensated coulombic interactions; lattice contractions have only been reported in a handful of metal oxide nanoparticles in structural phases significantly distorted from the bulk material. As shown in Table 1, the average crystallite size estimated from Scherrer’s formula decreases from 13.40 to 4 nm as the doping increases from 0.025 to 0.1 M. This is consistent with the fact that the addition of impurity in the semiconductor nanoparticles is known to affect the growth behavior and hence responsible for reduction in size after doping.

### Table 1: Particle size and lattice parameters of NiO and NiO: Co\(^{2+}\) nanocrystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiO</td>
<td>13</td>
<td>4.1819</td>
<td>2.5178</td>
</tr>
<tr>
<td>NiO: Co(^{2+}) (0.025 M)</td>
<td>5</td>
<td>4.2503</td>
<td>7.4550</td>
</tr>
<tr>
<td>NiO: Co(^{2+}) (0.05 M)</td>
<td>7</td>
<td>4.1886</td>
<td>4.8671</td>
</tr>
<tr>
<td>NiO: Co(^{2+}) (0.075 M)</td>
<td>5</td>
<td>4.1571</td>
<td>6.5568</td>
</tr>
<tr>
<td>NiO: Co(^{2+}) (0.1 M)</td>
<td>4</td>
<td>4.2069</td>
<td>8.9193</td>
</tr>
</tbody>
</table>

#### 3.2 Photoluminescence

The PL spectra of undoped and Co\(^{2+}\) doped NiO nanocrystals were measured at room temperature with an excitation wavelength of 290 nm, as shown in Fig. 2. The undoped product exhibits a sharp and intense UV emission at 400 nm and a broad green emission at 527 nm. The UV emission is attributed to the near band edge emission of NiO, originating from the excitonic transitions between the electrons in the conduction bands and holes in the valence bands [23]. The green emission at 527 nm is probably ascribed to oxygen vacancies. The intensity of the green emission actually determines the oxygen vacancy concentration of NiO [24]. Compared with pure NiO, the doped products show no clear difference in the peak positions; the
Fig. 4 Magnetic hysteresis loops of a NiO and b–e different levels (0.025, 0.05, 0.075 and 0.1 M) of Co$^{2+}$ doped NiO nanocrystals.
only difference was in the luminescence intensity. As illustrated in Fig. 2, the PL spectra reveal a non-monotonic suppression of UV and visible emission intensities by increasing the concentration of dopant ions. The results of the present study contradict the results of Sharma et al. [25], who have observed enhanced visible emission on ZnO as the concentration of Co increases. Actually, transition metal doping can introduce shallow donor or acceptor levels, which may be responsible for quenching of band edge luminescence in the case of doped NiO nanocrystals. Generally, at a high Co concentration of Co incorporation, the cobalt atoms have a tendency to form clusters around oxygen. The formation of these clusters will cause passivation of the surface of NiO and may provide competitive pathways for recombination resulting quenching of broad green emission, which means that the oxygen vacancy concentration in Co-doped samples decreases with higher Co content. Among the different concentrations, 0.075 M of doping yields maximum intensity quenching for both UV and visible bands owing to the secondary phase formation as confirmed by XRD analysis.

3.3 Functional group analysis

FT-IR analysis is a suitable technique to evaluate the functional groups present in the samples subjected to analysis. Figure 3 shows the FT-IR spectra of pure and different levels of Co-doped samples. All the samples show absorption bands at about 3,430 and 1,630 cm\(^{-1}\) can be attributed to hydrogen bonded OH stretching [26] and bending vibrations [27], respectively, indicating the presence of water molecule in the structure. The presence of intense absorption at about \(\sim 2,358\) cm\(^{-1}\) can be assigned to atmospheric CO\(_2\) [28]. The appearance of the band at 1,380 cm\(^{-1}\) is the characteristic peak of interlayer nitrate. A small band at \(\sim 1,022\) cm\(^{-1}\) can be ascribed to the deformation vibration of C=O. Generally, metal oxides give absorption bands below 1,000 cm\(^{-1}\), due to inter atomic vibrations. In the present case, pure NiO shows an absorption band at 443 cm\(^{-1}\), which is assigned to the Ni–O stretching vibration mode [29]. However, for Co\(^{2+}\)-doped products stretching vibrations of NiO are shifted to lower frequencies (except 0.1 M). The gradual shifts in the frequency with different levels of cobalt doping are caused by differences in the bond lengths that occur when Co ions substitute the position of Ni ions in the NiO lattice. It is interesting to note that there are additional peaks at 660 and 820 cm\(^{-1}\) for NiO doped with 0.05 M of cobalt. The band at 660 cm\(^{-1}\) is due to the \(\delta_{\text{Ni-O-H}}\) vibrations [30–33] and the absorption band at 820 cm\(^{-1}\) is attributed to the \(\delta\text{(O=C=O)}\) bridging oxolate group. Especially, on 0.075 M of doping, the samples have the mixed behavior of NiO and Co(OH)\(_2\). The formation of \(\alpha\)-Co(OH)\(_2\) is confirmed by the presence of non-hydrogen bonded hydroxyl groups at 3,597 cm\(^{-1}\). The prediction of \(\alpha\)-Co(OH)\(_2\) by FT-IR is consistent with the result of XRD. Further, when the level of doping was increased to 0.1 M, the samples show well defined vibrations between 660 and 1,460 cm\(^{-1}\) indicating the characteristic peaks of intercalated anions present in the cobalt nitrate.

3.4 Magnetic studies

The magnetic curves of the NiO and Ni\(_{1-x}\)Co\(_x\)O are shown in Fig. 4. The values of the magnetic parameters estimated from the curves are presented in Table 2. From the Fig. 4a, it is noted that the pure NiO is antiferromagnetic. The same antiferromagnetic behavior of NiO was predicted by Farhadi et al. [34]. On low levels of Co\(^{2+}\) doping (\(x = 0.025\) and 0.05 M) the magnetic curves of NiO exhibit the non-saturation of the magnetization which is the characteristic of superparamagnetic (weak ferromagnetic) ordering of the spins in the nanoparticles. Nickel oxide nanoparticles are made of small magnetic domains and each magnetic domain is characterized by its own magnetic moment oriented randomly. The total magnetic moment of the nanoparticles is the sum of these domains coupled by dipolar interactions. The coercivity values of NiO at low levels (\(x = 0.025\) and 0.05 M) of doping are higher than the value reported by other researchers [35]. Manikandan et al., have also reported the superparamagnetic behavior of NiO with coercivity value of 9.14 Oe. However, on higher amounts of Co\(^{2+}\) incorporation (\(x = 0.075\) and 0.1 M) magnetic curves of NiO showed the strong ferromagnetic behavior. The strong ferromagnetic behavior of the present samples may be originated from the three possible reasons,

| Table 2 Magnetic behaviors of NiO and NiO: Co\(^{2+}\) nanocrystals |
|-------------------------|-------------------|-------------------|-------------------|
| Sample                  | Saturation magnetization (emu gm\(^{-1}\)) | Retentivity (emu gm\(^{-1}\)) | Coercivity (gauss) |
| Pure NiO                | 0.00920           | 0.000567          | 135               |
| NiO: Co\(^{2+}\) (0.025 M) | 0.25266          | 0.001728          | 49                |
| NiO: Co\(^{2+}\) (0.05 M)   | 0.24361          | 0.001762          | 51                |
| NiO: Co\(^{2+}\) (0.075 M)  | 0.47116          | 0.043192          | 192               |
| NiO: Co\(^{2+}\) (0.1 M)   | 0.28101           | 0.037058          | 268               |
Fig. 5 CV curves of a NiO and b–e different levels (0.025, 0.05, 0.075 and 0.1 M) of Co\(^{2+}\) doped NiO nanocrystals at different scan rates
the first is the formation of Co(OH)$_2$, the second is the smaller grain size and the third is defects like oxygen vacancy. The surface-to-volume ratio of particles increases with a decrease in the nanoparticle size. Therefore, the ratio of surface spins increases with a decrease in the particle size. The RTFM in the smaller particles suggests that the magnetization of the nanoparticle is mainly from the surface spins. In the present case, the third reason is discarded since the PL measurements exhibited depletion of oxygen vacancies. Therefore the strong ferromagnetism in the present case may be ascribed from the synergistic effect of smaller size and impurity phase formation.

3.5 Electrochemical property

The CV curves of NiO and Ni$_{1-x}$Co$_x$O electrodes were recorded at different scan rates ranged from 10–50 mV s$^{-1}$. Figure 5a–e presents the CV curves of NiO and NiO: Co$^{2+}$ electrodes. The shapes of the CV curves indicate the capacitance characteristics are quite different from electric double layer capacitance, where the CV curve is normally close to an ideal rectangular shape. The difference in shape indicates that the capacity is mainly associated with the pseudocapacitive properties of the material and can be ascribed to redox mechanism. The peaks present in the voltammogram substantiates that a redox mechanism is involved during capacitance measurement due to the reversible electrochemical reactions. The possible reversible chemical reaction may be due to the intercalation/de-intercalation of the tetra butyl ammonium cation (TBA$^+$) into/from NiO lattice.

NiO + TBA$^+$ + e$^-\rightarrow$(NiO) TBA

It should be noted that the oxidation and reduction peaks of the Co$^{2+}$ doped samples are sharper than that of pure NiO, suggesting the higher activity of Co$^{2+}$ doped NiO. Applying the Eq. (1) the specific capacitance of the samples were calculated and summarized in Table 3. It is predicted from the table that the NiO has shown the specific capacitance of 318 F g$^{-1}$ at the scan rate of 10 mV s$^{-1}$. However, the specific capacitance of NiO drops as the scan rate increases, the specific capacitance is maintaining the value of 62 F g$^{-1}$ at the scan rate of 50 mV s$^{-1}$. The specific capacitance of NiO electrode calculated in the present study is greater than the values reported by other researchers. Patil et al. [36], have presented the value of specific capacitance of NiO film electrode as 167 F g$^{-1}$, whereas, Lokhande et al., have reported the value as 222 F g$^{-1}$ [37]. It is seen that in the present study, at low scan rate, the specific capacitance is maximized. The potential reason for high specific capacitance at low scan rate could be resulted from the low faradaic reaction. At higher scan rates, the ionic diffusion takes place from the outer regions of the pores, whereas at low scan rate, both inner and outer surfaces are responsible in the calibration of specific capacitance and this leads to a higher value of capacitance at low scan rate. Compared to undoped NiO, on 0.025 M of doping, the calculated specific capacitance values for NiO at scan rate of 10, 20, 30, 40 and 50 mV s$^{-1}$ are 496, 390, 305, 252 and 226 F g$^{-1}$ respectively. Similarly, the specific capacitance values for NiO on 0.05 M doping at the same scan rates are 530, 377, 275, 225 and 194 F g$^{-1}$ respectively. The increasing trend of specific capacitance of NiO on doping arises due to the intercalation of the Co$^{2+}$ ions with the TBA$^+$ ions of electrolyte which intercalates/deintercalates at the surface of the NiO nanocrystals and also into it through the channels and the pores of the nanocrystals. However, the obtained value is lesser than the value reported by Purushothaman et al. For amorphous nanoporous NiO$_{0.095}$Co$_{0.05}$O films, they have reported the value of 1,982 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ [38]. As shown in Table 3, on 0.075 M of doping, NiO shows a meager increase in the specific capacitance value. The meager increase can be attributed to the formation of impurity phase, which are not electrochemical active. The formation of impurity phase is also confirmed from the CV curves. For the CV curves of the 0.075 M of Co$^{2+}$ doped NiO sample, two oxidation peaks are observed in the high scan rates, which are believed to be associated with the formation of α-Co(OH)$_2$. This is also consistent with the results of XRD and FT-IR. However, further increase in Co$^{2+}$ doping (0.1 M) provides an appreciable improvement in capacitance for all scan rates indicating the removal of impurity phase.

3.6 Surface morphological analysis

The morphology and microstructure of the doped product were characterized in detail by SEM (Fig. 6a). The SEM image reveals the existence of spherical particles with lot of pores. The higher pore content may facilitate better transportation of electrolyte through their nanochannels for efficient redox reaction during the charge storage process. This is evidenced by the higher value of capacitance.

Table 3 Specific capacitance of NiO and NiO: Co$^{2+}$ nanocrystals at different scan rates

<table>
<thead>
<tr>
<th>Samples</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiO</td>
<td>496</td>
<td>136</td>
<td>113</td>
<td>78</td>
<td>66</td>
</tr>
<tr>
<td>NiO: Co$^{2+}$ (0.025 M)</td>
<td>496</td>
<td>390</td>
<td>305</td>
<td>252</td>
<td>226</td>
</tr>
<tr>
<td>NiO: Co$^{2+}$ (0.05 M)</td>
<td>530</td>
<td>377</td>
<td>275</td>
<td>225</td>
<td>194</td>
</tr>
<tr>
<td>NiO: Co$^{2+}$ (0.075 M)</td>
<td>388</td>
<td>322</td>
<td>245</td>
<td>203</td>
<td>179</td>
</tr>
<tr>
<td>NiO: Co$^{2+}$ (0.1 M)</td>
<td>500</td>
<td>355</td>
<td>265</td>
<td>216</td>
<td>184</td>
</tr>
</tbody>
</table>
recorded from the CV curves. Figure 6b gives a typical EDS spectrum of Co$^{2+}$ doped NiO samples, suggesting that the synthesized products are composed of Ni, O and Co elements. For morphological confirmations, FE-TEM images were recorded for undoped and doped NiO. The FE-TEM micrographs of undoped and doped NiO are given in Fig. 7a, b, respectively. As shown in figure, pure NiO shows nearly spherical particles with an average size of 15 nm, whereas, the doped products reveal the well separated individual spherical particles with sizes of about 7 nm. The sizes of the undoped and Co$^{2+}$ doped NiO are in good agreement with the XRD data.

4 Conclusions

Nanocrystals of Ni$_{1-x}$Co$_x$O ($x = 0, 0.025, 0.05, 0.075$ and $0.1$ M) have been successfully synthesized by the simple chemical precipitation method. The X-ray diffraction result suggests that cobalt ions substitute Ni in the NiO matrix and shows the formation of secondary phase at a higher level of doping. The formation of secondary phase was confirmed by FT-IR and CV measurements. The room temperature PL spectra reveal the intensity quenching for both UV and visible emissions by increasing the concentration of dopant ion. The results of magnetization curves reveal that weak ferromagnetic behavior of NiO is retained up to 0.05 M of cobalt doping, whereas, at higher cobalt content (0.075 and 0.1 M) NiO exhibits a strong ferromagnetic behavior. The influence of Co incorporation on the supercapacitance performance of NiO was investigated. It is obvious that incorporation of cobalt ions plays an important role in enhancing the capacitance behavior of NiO. Especially, the sample doped with 0.05 M of cobalt presented best electrochemical performance among the materials studied.

References


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Synthesis and characterization of Cu$^{2+}$ doped NiO electrode for supercapacitor application

K. Sathishkumar · N. Shanmugam · N. Kannadasan · S. Cholan · G. Viruthagiri

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Abstract Nanocrystals of Ni$_{1-x}$Cu$_x$O have been synthesized by a simple chemical precipitation method. X-ray diffraction studies showed that the samples have pure cubic phase and the average size of the nanocrystals is found to be in the range of 6.52–13.4 nm. The morphology of NiO nanocrystals analyzed by SEM showed a considerable change from nanoparticles to nanorods on doping and confirmed by FE-TEM analysis. The energy dispersive X-ray analysis results showed that the compositions of the elements are relevant as expected from the synthesis. The optical properties of the nanostructures were also investigated by Photoluminescence spectra. The magnetic properties were investigated at room temperature using the vibrating sample magnetometer and the hysteresis loops confirmed the ferromagnetic behavior of NiO on doping due to smaller size effect. The specific capacitance behavior studied by cyclic voltammetry measurements showed higher specific capacitance on lower concentration of doping which made it as promising electrode material for supercapacitor application.

Graphical Abstract

Keywords Nanorods · Nanostructures · Electrode · Supercapacitor · Photoluminescence
1 Introduction

The chemical and physical properties of materials in nanoscale are greatly improved than their bulk counter parts. Nanosized transition metal mono oxide NiO, the object of growing interest because of interesting physical properties and potential applications such as solar cells [1, 2], photocatalysts, electrochemical capacitors [3], antiferromagnetic layer [4] and optical coating [5]. NiO is basically an antiferromagnetic insulating material. The replacement of the cation by other 3d elements in NiO can generate the ferromagnetic phase. The magnetic properties of NiO are affected with reduction in size, shape and synthesis route [6–10]. Different geometrical shapes such as nanoparticles, nanorods, and core–shell structure of NiO are prepared by sol gel [11], reverse micelle [12], spray pyrolysis [13] and hydrothermal method [14–16]. However, many of the above mentioned methods that have been reported require more complex devices, multiple steps and a careful execution. Therefore, it is quite challenging to adopt a simple and convenient method for the preparation of NiO nanoparticles. Chemical precipitation method is one among the effective approaches to synthesize the NiO nanostructures since this method is simple and cost effective. As per the available literature almost a very few have attempted to study the magnetic and electrochemical properties of Cu doped NiO. Guohui et al. [17] studied the effect of copper doping on the capacitance behavior of NiO, and have shown that the capacitance of NiO has been improved on doping. In this paper, we explore a simple chemical precipitation route to prepare Ni$_{1-x}$Cu$_x$O nanocrystals. Moreover, the magnetic and electrochemical properties of Cu$^{2+}$ doped NiO nanocrystals are investigated in detail.

2 Materials and methods

2.1 Chemicals

Nickel nitrate hex hydrate [Ni(NO$_3$)$_2$·6H$_2$O], copper acetate [C$_2$H$_3$CuO$_4$·2H$_2$O] and oxalic acid [C$_3$H$_2$O$_4$·2H$_2$O] were purchased from Merck and were used as received since they were of analytical reagent grade with 99% purity. Sample preparation and dilutions were made of milli-Q water.

2.2 Synthesis of NiO and NiO: Cu$^{2+}$ nanocrystals

For the preparation of doped NiO, 1 M of oxalic acid [C$_2$H$_2$O$_4$·2H$_2$O] solution as precipitant agent was slowly dropped into constantly magnetic stirred mixture containing 0.5 M of nickel nitrate hex hydrate [Ni(NO$_3$)$_2$·6H$_2$O] with an appropriate amount of copper acetate [C$_4$H$_6$CuO$_4$·2H$_2$O]. The solution of the resultant mixture was stirred magnetically at 60 °C until a precipitate was formed. The obtained cyan colored precipitate was purified by dialysis against milli-Q water and ethanol several times to remove the impurities. The final product was then dried at 100 °C and further calcined at 400 °C for 2 h. A similar method of preparation without the addition of copper was used to synthesize undoped NiO nanocrystals.

2.3 Characterization

2.3.1 Materials characterization

X-ray diffraction (XRD) patterns of the synthesized nanocrystals were recorded by an X-ray diffractometer (X’PERT PRO) with Cu-K$_x$ radiation ($\lambda = 1.5406$ Å). The photoluminescence (PL) emission spectra of the samples were recorded with a spectrophurometer (Jobin–Yvon, FLUOROLOG–FL3-11). FT-IR analysis was made to characterize the functional groups of the nanocrystals using FT-IR spectrometer (SHIMADZU-8400) with a resolution of 4 cm$^{-1}$. The surface morphology and composition of the synthesized nanocrystals were investigated using a scanning electron microscope (SEM; JEOL-JSM-56100) equipped with an X-ray elemental analysis system (EDX: Thermo Super Dry II). Field emission transmission electron microscopy (FE-TEM: JSM2100F JEOL) measurements were performed to confirm the morphology of the doped product. Magnetic parameters of undoped and doped nanocrystals were studied using vibrating sample magnetometer (VSM).

2.3.2 Electrochemical performance investigation

Electrochemical properties of the nanocrystals were investigated by cyclic voltammetry performed on an electrochemical work station (CHI 6060) with a scan rate of 10 mVs$^{-1}$ between −0.6 and +1.8 V at room temperature. Electrochemical measurements were carried out in 0.2 M tetra butyl ammonium per chloride with a standard three electrode configuration consisting of a sample (working electrode), an Ag/AgCl (reference electrode) and a high platinum wire (counter electrode). The specific capacitance (Cs, Fg$^{-1}$) can be calculated from the CV curves using the equation [18–20] below:

$$Cs = \frac{Q}{\Delta v \cdot m}$$

where, Cs is the specific capacitance, Q the anodic and cathodic charges on each scanning, m is the mass of the electrode material (mg) and $\Delta v$ is the scan rate (mV s$^{-1}$).
3 Results and discussion

3.1 Structural analysis

Figure 1 depicts the XRD pattern of precursor NiO prepared using oxalic acid as oxygen source. As shown in the figure, the diffraction peaks can be indexed to orthorhombic nickel oxalate (NiC$_2$O$_4$·2H$_2$O). The measured lattice constants ‘a’, ‘b’ and ‘c’ are 11.4469, 5.0433 and 15.6577 Å, respectively, and are consistent with the JCPDS values (No: 25-0582). Figure 2 shows the XRD patterns of NiO and NiO doped

![Fig. 1 X-ray diffraction pattern of precursor NiO](image1)

![Fig. 2 X-ray diffraction patterns of NiO and different levels of Cu$^{2+}$ doped NiO nanocrystals annealed at 400 °C](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>13.40</td>
<td>4.1819</td>
</tr>
<tr>
<td>NiO: Cu$^{2+}$ (0.025 M)</td>
<td>6.52</td>
<td>4.1923</td>
</tr>
<tr>
<td>NiO: Cu$^{2+}$ (0.05 M)</td>
<td>7.31</td>
<td>4.1945</td>
</tr>
<tr>
<td>NiO: Cu$^{2+}$ (0.075 M)</td>
<td>7.78</td>
<td>4.1913</td>
</tr>
<tr>
<td>NiO: Cu$^{2+}$ (0.1 M)</td>
<td>9.96</td>
<td>4.1692</td>
</tr>
</tbody>
</table>

![Fig. 3 PL emission spectra of undoped and different levels of Cu$^{2+}$ doped NiO nanocrystals annealed at 400 °C](image3)

![Fig. 4 FT-IR spectra of NiO and different levels of Cu$^{2+}$ doped NiO nanocrystals annealed at 400 °C](image4)
with different levels of Cu$^{2+}$ ions. As shown in figure, all the diffraction peaks in the pattern can be indexed to cubic NiO as reported in the JCPDS file [No: 89-7130], and no other crystalline phases were detected at low level of (0.025 M) Cu$^{2+}$ incorporation. As the concentration of Cu$^{2+}$ increases (>0.025 M), the appearance of impurity phase was detected at 20 of about 44.42° and 51.32° corresponding to copper hydroxyl nitrite [Cu$_2$(OH)$_3$(NO$_2$)] and is in good agreement with the JCPDS data [No: 82-0059]. The intensity of impurity phase increases with dopant concentrations. It introduces constrain to the level of Cu$^{2+}$ doping in the NiO matrix so as to obtain a single phase and should be ≤0.025 M. Furthermore, on increasing the concentration of doping, the shifting of diffraction peaks to the lower angle side is predicted as a result of increased lattice constants. The lattice parameters of the doped products calculated from the XRD data are to some extent greater than those of undoped NiO (Table 1). The increase in lattice constants is due to expansion of the crystal structure as the slightly larger ionic radius of Cu$^{2+}$ (0.73Å) [21] substituted that of Ni$^{2+}$ (0.69Å) [22] in octahedral co-ordination of NiO cubic structure. The crystallite sizes of various NiO samples are estimated from full width at half maximum (FWHM) of the XRD peaks using Scherrer’s formula and the values are given in Table 1. As shown in the table, the size of the particles decreases with the increase of Cu$^{2+}$ concentration.

Fig. 5 SEM images of (a) NiO annealed at 400 °C (b) Cu$^{2+}$-doped (0.025 M) NiO annealed at 400 °C and (c) corresponding EDX pattern.
3.2 PL emission

The PL spectra of undoped and Cu\textsuperscript{2+} doped NiO nanocrystals were measured at room temperature with an excitation wavelength of 290 nm, as shown in Fig. 3. The undoped product exhibits a sharp and intense UV emission at 400 nm and a broad green emission at 527 nm. The UV emission is attributed to the near band edge emission of NiO, originating from the excitonic transitions between the electrons in the conduction bands and holes in the valence bands [23]. The green emission at 527 nm is probably ascribed to oxygen vacancies. The intensity of the green emission actually determines the oxygen vacancy concentration of NiO [24]. Compared with pure NiO, the doped products show no clear difference in the peak positions; the only difference was in the luminescence intensity. As illustrated in Fig. 3, the PL spectra reveal a non-monotonic suppression of UV and visible emission intensities by increasing the concentration of dopant ions. Actually, transition metal doping can introduce shallow donor or acceptor levels, which may be responsible for quenching of band edge luminescence in the case of doped NiO nanocrystals. Generally, at a high Cu\textsuperscript{2+} incorporation, the copper atoms have a tendency to form clusters around oxygen. The formation of these clusters will cause passivation of the surface of NiO and may provide competitive pathways for recombination resulting quenching of broad green emission, which means that the oxygen vacancy concentration on doped products decreases with increasing Cu\textsuperscript{2+} content. Among the different concentrations, 0.1 M of doping yields maximum intensity quenching for both UV and visible bands owing to the enhanced impurity phase formation as confirmed by XRD analysis. The quenching of emission intensity with increase in impurity phase suggests the low quality of the crystal. As the exciton moves through the materials, it encounters defects, and the exciton tends to decay in the vicinity of these centers.

3.3 Functional group analysis

FT-IR spectra of undoped and doped NiO nanoparticles were recorded in the range of 4,000–400 cm\textsuperscript{-1} and presented in Fig. 4. As shown in figure, bare NiO showed IR absorption bands at 3,431, 2,358, 1,627, 661 and 443 cm\textsuperscript{-1}. The bands at 3,431 and 1,627 cm\textsuperscript{-1} are respectively correspond to stretching and bending vibrations of O–H mode [25]. The intense absorption at around 2,358 cm\textsuperscript{-1} can be ascribed to CO\textsubscript{2} molecules. The band at 661 cm\textsuperscript{-1} is due to Ni–O–H bending and the band at 443 cm\textsuperscript{-1} is due to Ni–O stretching [26, 27]. The gradual shift in the NiO stretching vibration frequency which varies with Cu\textsuperscript{2+} concentration is caused by the difference in the bond length that occurs when Cu\textsuperscript{2+} ions substitute the position of Ni ions in the NiO matrix. In the IR spectrum of samples with Cu\textsuperscript{2+} concentration greater than 0.05 M few additional peaks are observed at 3,577, 1,406, 1,645, 950 and 837 cm\textsuperscript{-1} [28]. The presence of sharp band at 3,577 cm\textsuperscript{-1} can be attributed to α-Cu(OH\textsubscript{2}) whereas, the peak at 950 cm\textsuperscript{-1} indicates the O–H bending vibrations combined with metal atoms. The peak at 840 cm\textsuperscript{-1} indicates the formation of nitrite groups. The appearance of above mentioned functional groups, confirming the formation of copper hydroxyl nitrite as impurity phase. The absorption bands at 1,406 and 1,645 cm\textsuperscript{-1} correspond to

![Fig. 6 (a, b) FE-TEM images of Cu\textsuperscript{2+}-doped (0.025 M) NiO annealed at 400 °C](image-url)
Fig. 7 Magnetic hysteresis loops of (a) NiO and (b–e) different levels (0.025, 0.05, 0.075 and 0.1 M) of Cu$^{2+}$ doped NiO nanocrystals annealed at 400 °C.
C = O stretching of carboxylate ions [29]. These carboxylate ions act as monodentate ligands with metal ions to form relatively stable Ni\(^{2+}\) complexes, which can control the NiO crystal growth towards the rod-like structure.

### 3.4 Morphological study

Figure 5a, b shows the scanning electron microscope images of the pure and Cu\(^{2+}\) doped NiO nanocrystals. The surface morphology of the pure NiO shows the presence of spherical particles, whereas, the Cu\(^{2+}\) doped NiO shows the formation of nanorods of nickel oxide. The rods formed are non-uniform with a wide distribution in length and diameter. The possible growth mechanism is explained as follows: as copper acetate is added into the precursor solution, the complexing agent oxalic acid in the deposition solution will react with Ni\(^{2+}\) and Cu\(^{2+}\) cations to form nickel chelate ligand Ni\(^{2+}\)[C\(_2\)O\(_4\)\(^{2-}\)] and copper chelate ligand Cu\(^{2+}\)[C\(_2\)O\(_4\)\(^{2-}\)] metastable complex phases. In the absence of copper, Ni\(^{2+}\) combine with OH\(^{-}\) in the solution to form Ni(OH)\(_2\), which are absorbed onto NiO seed surface and nucleation process starts. As Cu\(^{2+}\) ions are added into the solution, Cu\(^{2+}\) react with OH\(^{-}\) group to form Cu(OH)\(_2\). Now the chelate ligand Cu\(^{2+}\)[C\(_2\)O\(_4\)\(^{2-}\)] competes with Ni\(^{2+}\)[C\(_2\)O\(_4\)\(^{2-}\)] in the solution for the absorption sites in the seed layer surface. The competition inhibits the NiO heterogeneous nucleation sites. Also copper complexes cannot act as a new nucleation centers for NiO crystals to grow due to surface energy state. Thus, NiO can grow in the form of nanorod. Figure 5c shows the EDX spectrum of Cu\(^{2+}\) doped NiO, which indicates the presence of Cu, Ni and O in the sample. The measurement of FE-TEM was carried out to further confirm the morphology of NiO on doping. The FE-TEM images show that the obtained nanocrystals are rod-like structure (Fig. 6a, b). The diameters of these nanorods are about 10–20 nm, and the lengths are about 40–60 nm.

### 3.5 Magnetic behavior

Magnetic behavior of the synthesized nanocrystals was studied at room temperature. Figure 7a–e depicts M-H curves of the pure and doped NiO nanocrystals. It is interesting to note that magnetic curve of NiO exhibits antiferromagnetic behavior and the curve does not saturate even in higher field. This indicates that the magnetization consists of two components; an easily magnetized component in low field region and a non-saturating component responsible for almost linear variation in high field region. The easily magnetized component is associated with the uncompensated spins in the cores and the non-saturating component is related with the surface spins. However, on Cu\(^{2+}\) doping, all the samples exhibit the antiferromagnetic to ferromagnetic transition. The values of saturation magnetization were 0.009201, 0.014528, 0.035115, 0.049062 and 0.052835 emu/g for the samples with x = 0, 0.025, 0.05, 0.075 and 0.1 M respectively. It is clear that the values of saturation magnetization increase with increasing copper concentration. There are three possible origins of the ferromagnetism in Ni\(_1-x\)Cu\(_x\)O that we should consider. The first case is size induced ferromagnetism. The second one is impurity phase related ferromagnetism. The third possible origin is the defects like oxygen vacancies related ferromagnetism. We should discard the third possibility in the present case because the magnitude of oxygen vacancies decreases with increase of Cu\(^{2+}\) doping as shown in PL emission. The magnetic parameters of undoped and doped NiO nanocrystals exhibit an increasing trend as particle size decreases (Table 2). If smaller the particle size greater should be surface-to-volume ratio. Therefore, the ratio of surface spins increases with a decrease in the particle sizes. The larger values of saturation magnetization, remnant magnetization and coercivity in the smaller sized nanoparticles suggest that the magnetization of the nanoparticles is mainly from the surface spins. In addition, for samples with x > 0.025 M, the formation of impurity phase is confirmed from the diffraction data. Therefore, occurrence of ferromagnetism in NiO on Cu\(^{2+}\) doping can be due to synergistic effect of smaller sized particles and impurity phase formation.

### 3.6 Electrochemical characterization

The electrochemical behavior of NiO and Cu\(^{2+}\) doped NiO electrode has been investigated. Figure 8a–e shows the cyclic voltammetry (CV) curves of undoped and doped products recorded at different scan rates (10–50 mVs\(^{-1}\)). The CV patterns of NiO show the oxidation peaks for all

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation magnetization (emu/gm)</th>
<th>Retentivity (emu/gm)</th>
<th>Coercivity (Gauss)</th>
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<tbody>
<tr>
<td>NiO</td>
<td>0.009201</td>
<td>0.000567</td>
<td>135</td>
</tr>
<tr>
<td>NiO: Cu(^{2+}) (0.025 M)</td>
<td>0.014528</td>
<td>0.003177</td>
<td>153</td>
</tr>
<tr>
<td>NiO: Cu(^{2+}) (0.05 M)</td>
<td>0.035115</td>
<td>0.007092</td>
<td>155</td>
</tr>
<tr>
<td>NiO: Cu(^{2+}) (0.075 M)</td>
<td>0.049062</td>
<td>0.010512</td>
<td>140</td>
</tr>
<tr>
<td>NiO: Cu(^{2+}) (0.1 M)</td>
<td>0.052835</td>
<td>0.010516</td>
<td>159</td>
</tr>
</tbody>
</table>
Fig. 8 CV curves of (a) NiO and (b–e) different levels (0.025, 0.05, 0.075 and 0.1 M) of Cu$^{2+}$ doped NiO nanocrystals annealed at 400 °C for different scan rates.
scan rates. However, a pair of well-defined redox reaction peak is visible in the CV curves of Cu$^{2+}$ doped NiO nanocrystals, indicating that the electrochemical capacitance of NiO and NiO: Cu$^{2+}$ mainly results from the pseudocapacitance [30]. The major advantage of pseudocapacitance is its high energy transfer during the faradaic reaction and providing 10–100 times more capacitance than EDLCs [31]. Applying the Eq. (1) the specific capacitance values were calculated and summarized in Table 3. It is predicted from the table that the NiO has shown the specific capacitance of 318 F g$^{-1}$ at the scan rate of 10 mV s$^{-1}$. However, the specific capacitance of NiO drops as the scan rate increases, the specific capacitance is maintaining the value of 62 F g$^{-1}$ at the scan rate of 50 mV s$^{-1}$. The specific capacitance of NiO electrode calculated in the present study is greater than the values reported by other researchers. Patil et al. [32], have presented the value of specific capacitance of NiO film electrode as 167 F g$^{-1}$, whereas, Lokhande et al., have reported the value as 222 F g$^{-1}$ [30]. It is seen that in the present study at low scan rate, the specific capacitance is maximized. The potential reason for high specific capacitance at low scan rate could be resulted from the low faradaic reaction. At higher scan rates, the ionic diffusion takes place from the outer regions of the pores, whereas at low scan rate, both inner and outer surfaces are responsible in the calibration of specific capacitance and this leads to a higher value of capacitance at low scan rate. As far as the doped NiO is concerned, on 0.025 M of doping, the calculated specific capacitance values for NiO at scan rates of 10, 20, 30, 40 and 50 mV s$^{-1}$ are 372, 208, 146, 114 and 93 F g$^{-1}$, respectively. It is obvious that doping Cu$^{2+}$ can increase the specific capacitance of NiO effectively for all scan rates. The potential reason is that Cu$^{2+}$ takes the sites in NiO lattice, which induces plenty of positive defect. Thus the probability of protons transporting is increased, and electron can escape from Ni much more easily. Therefore, the chemical activities of electrode material are improved. As shown in the table, beyond 0.025 M of doping the specific capacitance decreases with the increasing amount of Cu$^{2+}$. The decreasing trend of specific capacitance of Cu$^{2+}$ content exceeding 0.025 M can be attributed to the formation of impurity phase which are not electrochemical active. This is consistent with the XRD results in which impurity phase formation was seen at higher concentrations of Cu$^{2+}$ incorporation.

4 Conclusion

We have successfully synthesized nanocrystals of NiO and NiO doped with different levels of Cu$^{2+}$ ions by a simple chemical precipitation method. The XRD results suggest that the doping limit of Cu$^{2+}$ into NiO matrix as 0.025 M. The rod like morphology of the doped product was analyzed by SEM and confirmed by FE-TEM analysis. The paramagnetic behavior of NiO has been changed into ferromagnetic on all concentrations of doping which is resulted from the synergistic effect of smaller particle size and impurity phase formation. At low scan rate, the super capacitance performance of the NiO has been increased from 318 to 376 F g$^{-1}$ on 0.025 M of doping. However, further increase in Cu$^{2+}$ doping decreases the specific capacitance of NiO due to the formation of impurity phase. The improved supercapacitance performance of NiO with Cu$^{2+}$ doping through simple preparation process renders NiO a promising electrode for practical application in supercapacitors.

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References