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# The effect of anion on the magnetic properties of nanocrystalline NiO synthesized by homogeneous precipitation

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#### ARTICLE INFO

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Keywords: Nanocrystalline oxide Nickel oxide Homogeneous precipitation Magnetic measurement The effect of using different anions (nitrate, chloride, sulfate, and acetate) during the precursor synthesis, by homogeneous precipitation, on the magnetic properties of the final product (nanocrystal-line NiO), has been studied. The precursors and the oxide were characterized by various analytical techniques including powder X-ray diffraction, FT-IR spectroscopy, thermal gravimetry (TGA), and magnetic measurements. The synthesized NiO samples possess crystallite size in the range,  $\sim 2-6$  nm, depending on the anion of the nickel salt. The nickel oxide nanoparticles exhibit superparamagnetic behavior. Acetate and sulfate anions lead to NiO with higher saturation magnetization ( $\sim 1.2-1.8$  emu/g), while chloride and nitrate anions lead to NiO nanoparticles with lower saturation magnetization ( $\sim 0.1-0.4$  emu/g) values. The observed magnetic behavior has been attributed to the size effect.

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## 1. Introduction

The magnetic properties in the nanoscale regime differ considerably from those observed in bulk macro-crystalline materials [1] and the magnetic behavior of nanoparticles has been attributed to their size, shape, and surface effects [2–4]. The interesting properties of magnetic nanoparticles include increased magnetic moments [5], spin wave behavior [6], quantum tunneling [7], etc. The magnetic nanoparticles are of interest from the point of view of fundamental research [8], and applications such as magnetic recording [9], biomedicine [10], magnetic resonance imaging and drug delivery [11], separation [12], sensors [13,14], magnetic bar codes [15], etc. Among the magnetic nanoparticles, antiferromagnetic nanoparticles (AFN) are promising candidates for spin valves [16], magnetic random access memory [17], etc. Among the AFN, NiO nanoparticles have been extensively studied to understand the finite size and surface effects [18], spin glass behavior [19], surface anisotropy [20], and magnetic anomalies [21]. In the present study, the effect of using different anions, during the precursor synthesis, on the magnetic properties of nanocrystalline NiO (the final product) was studied. To the best of author's knowledge, this effect has not been studied before. Nanocrystalline NiO (NC-NiO) was synthesized by thermally decomposing  $\alpha$ -Ni(OH)<sub>2</sub>, a layered precursor, synthesized by homogeneous precipitation starting from different nickel salts.

## 2. Experimental methods

The synthesis of the precursor to NC-NiO was carried out by homogeneous precipitation as follows [22,23]. In a 250 ml beaker, about 5.2 mmol of a nickel salt (nickel nitrate, nickel chloride, nickel sulfate, and nickel acetate) was dissolved in about 80 ml of distilled water. To this, 0.083 mmol (5g) of urea was added and the contents were heated to 80 °C and kept for 4 h at this temperature. During the reactions, green precipitates were formed. The precipitates were filtered, washed with distilled water many times followed with ethyl alcohol and then dried at room temperature in air. The yield of the precursors was about 0.5 g. The precursors prepared using nickel nitrate, nickel chloride, nickel sulfate, and nickel acetate will henceforth be referred as precursor-1, precursor-2, precursor-3, and precursor-4, respectively. The thermal gravimetric analysis (TGA) showed that the green precursor powders, decompose at about 330-350 °C; the observed overall weight loss percentage ranged from 28 to 36. So the precursor powders were subjected to calcination at about 350 °C for 1 h inside a muffle furnace. Black powders were obtained in all the cases which were analyzed by various analytical techniques. The nickel oxide samples will be referred to as NiO-1 to NiO-4.

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu–K $\alpha$  radiation ( $\lambda = 1.5418$  Å) with a scan speed 2°/min. FT-IR spectroscopy measurements were done using a Thermo Nicolet Nexus FT-IR spectrometer using KBr technique. TGA measurements were carried out on a Perkin Elmer Thermal Analyzer (Pyris Diamond) under nitrogen with a heating rate of 10°/min in the

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Fig. 1. Powder XRD patterns for the precursors synthesized by homogeneous precipitation. (a), (b), (c), and (d) are the samples prepared from nickel nitrate, nickel chloride, nickel sulfate, and nickel acetate, respectively. The crystallite size of the precursor is also indicated.

 Table 1

 Elemental analysis data of precursors obtained by CHNS and AAS analyses.

S. no	Sample <sup>a</sup>	Percentage of elements					Total weight loss % from TGA	Stoichiometry
		С	Н	Ν	S	Ni		
1 2 3 4	Ni(OH) <sub>2</sub> -1 Ni(OH) <sub>2</sub> -2 Ni(OH) <sub>2</sub> -3 Ni(OH) <sub>2</sub> -4	5.9 (5.4) 5.6 (5.8) 4.4 (4.5) 4.5 (4.9)	1.9 (2.0) 2.4 (1.8) 2.0 (1.9) 1.9 (1.8)	5.9 (5.8) 6.4 (6.2) 4.4 (4.5) 5.2 (5.2)	- - 0.5 (0.0) -	53.5 (52.4) 51.5 (51.5) 55.8 (55.6) 53.5 (54.5)	36 (34) 32 (34) 28 (29) 30 (30.5)	$ \begin{array}{l} [{\rm Ni}({\rm OH})_{1.46}]({\rm OCN})_{0.46}\ ({\rm CO}_3)_{0.04}({\rm H}_2{\rm O})_{0.4}\\ [{\rm Ni}({\rm OH})_{1.4}]({\rm OCN})_{0.5}\ ({\rm CO}_3)_{0.05}({\rm H}_2{\rm O})_{0.2}\\ [{\rm Ni}({\rm OH})_{1.6}]({\rm OCN})_{0.34}\ ({\rm CO}_3)_{0.03}({\rm H}_2{\rm O})_{0.2}\\ [{\rm Ni}({\rm OH})_{1.52}]({\rm OCN})_{0.4}\ ({\rm CO}_3)_{0.04}({\rm H}_2{\rm O})_{0.22} \end{array} $

<sup>a</sup> Ni(OH)<sub>2</sub>-1 to Ni(OH)<sub>2</sub>-4 refer to precursors obtained from different nickel salts. The values in the parentheses indicate those calculated using the molecular formula of the precursors given in the last column.

temperature range, 25–600 °C. Atomic absorption spectrometric measurements were done using a Perkin Elmer atomic absorption spectrometer (AAnalyst 800). The carbon, hydrogen, nitrogen, and sulfur (CHNS) analysis was performed using a Vario EL III CHNSO elemental analyzer. TEM measurements were performed using a FEI Technai 2G electron microscope operating at 200 kV. The sample powders were dispersed in ethanol, under sonication, and TEM grids were prepared using a few drops of the dispersion followed by drying in air.

#### 3. Results and discussion

First, the precursors were characterized using an array of experimental techniques. The NiO samples, obtained by the thermal decomposition of the precursors, were then characterized. The powder XRD patterns recorded for all the precursors prepared using different nickel salts are shown in Fig. 1. From the analysis of XRD data, the product formed in all cases is  $\alpha$ -Ni(OH)<sub>2</sub> (JCPDS file: 38-0715) with a interplanar distance of ~7.3 Å, calculated using (003) reflections.  $\alpha$ -Ni(OH)<sub>2</sub> is a layered hydroxy deficient compound with anions in the interlamellar space for charge compensation [24–27]. The asymmetric nature of the (101) reflections in the XRD pattern indicate the turbostratic nature of the phases. The percentage of nickel, as determined by

atomic absorption spectrometry (AAS), and the percentage of other elements, as determined by the CHNS analyzer along with their stoichiometries are given in Table 1. The FT-IR studies on the precursor powders indicate the presence of characteristic vibrations due to CO<sub>3</sub><sup>2–</sup>, OCN<sup>–</sup>, Ni–OH, and H<sub>2</sub>O. On changing the anions during the precursor synthesis, the stoichiometries show minor variations with respect to the amount of anions in the interlayer space and intercalated water molecules (Table 1). The stoichiometry of the precursor samples are close to those reported in the literature [24-27]. The TEM images recorded for all the precursor samples are shown in Fig. 2. The TEM images show features characteristic of turbostratic phases such as aggregation of thin nanosheet-like structures. This is in accordance with what has been usually observed for  $\alpha$ -Ni(OH)<sub>2</sub> [24–27]. The mean length and mean thickness of the precursors from TEM measurements (Fig. 2) are given in Table 2. The mean length of the precursor particles increases from about 87 nm in precursor-A to about 307 nm in precursor-D. The mean thickness of the precursor particles also increases from about 6.5 nm in precursor-A to about 18 nm in precursor-D. The average crystallite size calculated using Debye-Scherrer formula using full-width at halfmaximum of the most intense reflections (003) are also given in Table 2. The average crystallite size of the precursor particles from XRD can be compared to the thickness of the precursor since (003) is the stacking direction for  $\alpha$ -Ni(OH)<sub>2</sub>, the precursor. The



Fig. 2. TEM images for the precursors prepared from different nickel salts by homogeneous precipitation method: (a) nickel nitrate, (b) nickel chloride, (c) nickel sulfate, and (d) nickel acetate.

#### Table 2

Summary of particle/crystallite size of precursors and NiO samples.

	Mean length from TEM (nm)	Mean thickness from TEM (nm)	Average crystallite size (nm) <sup>a</sup>
Precursor			
A	87.2±9.9	$6.5 \pm 1.7$	6.7
В	$92.7 \pm 18.3$	8.3±2.1	8
С	181.7±113.6	$11.7 \pm 10.6$	5
D	$306.9 \pm 170.8$	$17.9 \pm 13.9$	9.3
NiO-samples			
NiO-1	$228.3 \pm 148.9$	$5.6 \pm 2.1$	4
NiO-2	$169.8 \pm 70.1$	$8.4 \pm 1.3$	6.3
NiO-3	$274.5 \pm 186.3$	$9.6 \pm 10.5$	1.9
NiO-4	117.3±36.7	3.6±1.6	2.3

<sup>a</sup> From XRD measurements.

observed mean thickness values from TEM images are slightly larger compared to that obtained from the XRD data and this is attributed to agglomeration.

After calcination of the precursors at 350 °C for 1 h, the XRD patterns were recorded and they are shown in Fig. 3. By comparing the XRD patterns with the JCPDS Data, it was found that the product is nickel oxide (JCPDS file no: 73–1519). All the diffraction peaks are broad indicating the nanocrystalline nature of the material. The crystallite size of NiO was calculated using Debye–Scherrer formula using (200) reflections, and it is in the range, ~2–6 nm. The NiO samples obtained from precursor-1 and

precursor-2 possess relatively higher crystallite sizes (3.8 and 6.3 nm, respectively) compared to NiO obtained from precursor-3 and precursor-4 (1.9 and 2.3 nm, respectively). The size of nanocrystalline NiO prepared in the present study is comparable to that obtained by chemical methods such as sol-gel process (3–22 nm) and reverse micro-emulsion method ( $\sim$ 8 nm) but smaller than that obtained by techniques such as spray pyrolysis (14–30 nm), and microwave method (5–35 nm). The observed TEM images for the nanocrystalline NiO samples are shown in Figs. 4 and 5. The TEM images indicate the sheet-like nature of the nanocrystalline NiO. The nanosheet morphology of the precursors



Fig. 3. Powder XRD patterns of nanocrystalline NiO samples obtained by thermal decomposition of the precursors. (a), (b), (c), and (d) are the NiO samples prepared from precursor-1, to precursor-4, respectively.



Fig. 4. TEM images of nanocrystalline NiO obtained by calcination of the precursors, (a), and (b). a1, and b1 refer to the corresponding SAED patterns.



Fig. 5. TEM images of nanocrystalline NiO obtained by calcination of the precursors, (c), and (d). c1, and d1 refer to the corresponding SAED patterns.

(see Fig. 2) is retained even after calcination. The selected area electron diffraction (SAED) patterns (Figs. 4 and 5) indicate the crystalline nature of the samples. The discrete diffraction spots in the pattern indicate highly oriented nature of nanocrystalline NiO. This is observed for the NC-NiO obtained from precursor-2, and precursor-4. In the remaining cases (i.e. NC-NiO's from precursor-1 and precursor-3), the observed diffraction rings indicate polycrystalline nature of the samples. After calcination of the precursors, the mean length of the NiO particles from TEM measurements (Table 2) has increased from about 117 nm to about 275 nm except in the case of precursor-D where a decrease is observed. The mean thickness of the NiO particles varies from about 3.6 nm (NiO-4) to about 9.6 nm (NiO-3) and is relatively lower when compared to the thickness of the precursor particles which varies from 6.5 to 18 nm.

The magnetization versus applied magnetic field (M-H) curves for nanocrystalline NiO samples obtained from different precursors are shown in Fig. 6. All the NiO samples show superparamagnetic behavior. Bulk NiO is an antiferromagnet with a Neel temperature of 523 K and a two sub-lattice model has been used to explain its magnetic properties [28]. In the nanoscale size region, the two sub-lattice model fails. The nanoparticles are proposed to have multiple sub-lattice magnetic structure, e.g. consisting of 4-, 6- or 8-sub-lattices [29]. Nanocrystalline NiO is an example, where surface effects can dominate the net magnetic behavior. The nanoparticles possess uncompensated spins due to a higher fraction of surface atoms present on the surface of nanoparticles [30] leading to the net magnetization; smaller the crystallite size, greater will be the surface spins with low coordination and broken exchange bonds, and greater will be the net magnetization. The NiO samples, prepared in the present study, possess smaller crystallite size ( $\sim$ 2–6 nm). This would lead to increased surface uncompensated spins leading to *M* vs. *H* curves expected for superparamagnetic nanoparticles (Fig. 6).

In general, the NiO samples with smaller crystallite size, NiO-3, and NiO-4 with crystallite sizes 1.9 and 2.3 nm, respectively, show higher saturation magnetization at 10 kOe ( $\sim$ 1–1.8 emu/g). However, the NiO samples with larger crystallite size, NiO-1 (3.8 nm), and NiO-2 (6.3 nm) possess lower values of saturation magnetization at the same applied field ( $\sim 0.1-0.4 \text{ emu/g}$ ). When the nanoparticles are small, it is not easy to distinguish the surface and core effects; the surface/interface effects become more prominent as particle size decreases. Nanoparticles of NiO with smaller crystallite size (NiO-3 and NiO-4) possess a higher fraction of surface uncompensated spins as compared to nanoparticles with bigger crystallite size (NiO-1 and NiO-2) and thus possess higher saturation magnetization values. The observed magnetic behavior is in agreement with that reported for NiO nanoparticles. For example, Richardson et al. [31] have reported that NiO with less than 100 nm exhibits superparamagnetism. Khadar et al. have [32] reported that NiO with particle size 2–3 nm exhibits superparamagnetic behavior while NC-NiO with particle size 13-18 nm exhibits superantiferromagnetism. Rao et al. have reported that NiO with average particle size 3-24 nm exhibits superparamagnetism [33].



Fig. 6. Magnetization versus applied magnetic field plots for nanocrystalline NiO samples prepared from four different precursors. NiO-1 to NiO-4 refers to nickel oxides obtained from precursor-1 to precursor-4, respectively.

The present study is an attempt to study the influence of anions, during the precursor synthesis by homogeneous precipitation, on the magnetic properties of nanocrystalline NiO. Using acetate and sulfate leads to smaller NiO nanoparticles ( $\sim 2 \text{ nm}$ ) with increased saturation magnetization values compared to nitrate and chloride anions which produce relatively larger NiO crystallites (~4-6 nm) with smaller saturation magnetization values. Using different anions during the synthesis lead to precursors with different dimensions (Table 2). For example, on going from nitrate to chloride to sulfate, the mean thickness of the precursor particles (from TEM measurements) increases from 6.5 to 8.3 to 18.0 nm, respectively. Similar trend is observed even after conversion of the precursors to nanocrystalline NiO, except in the case of CH<sub>3</sub>COO<sup>-</sup>. The anion affects the agglomeration/growth kinetics during the homogeneous precipitation process leading to precursor particles of different dimensions. The anions present in the solution interact with the initially formed smaller colloidal particles thus providing a barrier for further growth resulting in smaller particles.

It has been reported in the literature that variation in heat treatment temperature of the precursor materials can also lead to variation in crystallite size of NiO nanoparticles. For example, calcination of precursors such as nickel oxalate dihydrate [34], nickel citrate [35], and nickel carbonate hydroxide [36] at different temperatures can lead to variation in the crystallite size of the NiO. Calcination of nickel oxalate dihydrate yields NiO crystallites of size 4.1-22 nm (calcination temperature:  $300-600 \,^\circ\text{C}$ ), nickel citrate yields NiO crystallites of size 8.1-52.4 nm (calcination temperature:  $400-550 \,^\circ\text{C}$ ) while nickel carbonate hydroxide hydrate yields NiO crystallites of size 5-38 nm (calcination temperature:  $350-650 \,^\circ\text{C}$ ). However, NiO nanocrystallites of very small size ( $\sim 2-6 \text{ nm}$ ) are difficult to obtain by the method of variation in heat treatment conditions. This is an advantage of the present method.

## 4. Summary

The use of different anions during synthesis of the NiO precursors and their effect on the magnetic properties of

nanocrystalline NiO was studied. The precursors and the oxide samples were characterized by powder XRD, FT-IR, TGA, elemental analysis, TEM, and magnetic measurements. The crystallite size of NiO is in the range  $\sim$ 2–6 nm; NC-NiO samples with smaller crystallite size ( $\sim$ 2 nm) were obtained using nickel sulfate, and nickel acetate, while use of nickel nitrate or nickel chloride lead to relatively bigger crystallite size ( $\sim$ 4–6 nm). Magnetic measurements on nanocrystalline NiO indicate superparamagnetic behavior for all the samples. NiO samples with smaller crystallite size possess higher saturation magnetization ( $\sim$ 1.2–1.8 emu/g), compared to those with bigger crystallite size that show lower saturation magnetization values ( $\sim$ 0.1–0.4 emu/g). The present method is one of the ways to produce very small nanocrystallites of nickel oxide.

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