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# Proteic sol-gel synthesis, structure and magnetic properties of Ni/NiO core-shell powders

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ABSTRACT

Core-shell structured magnetic Ni/NiO powders were prepared by a proteic sol-gel route. Commercial gelatin and nickel nitrate were used as precursor materials. The synthesized material was calcined in air at 500 °C and further investigated by XRD, VSM and TEM. In order to investigate the effects of the structure on the magnetic properties, NiO powders were synthesized by three other methods for sake of comparison: citrate method, nitrate calcination and combustion method. XRD results revealed that the core-shell structured material is composed of 84.8 wt% NiO and 15.2 wt% Ni, while the samples from other methods are single phase. Hysteresis loop at room temperature showed a strong ferromagnetic behavior for samples prepared by proteic sol-gel and citrate methods. Powders from nitrate calcination and combustion showed weak ferromagnetic behavior most likely attributed to unpaired moments in their nanoparticles. The overall results showed that the proteic sol-gel method is a versatile chemical way to prepare Ni/NiO core-shell powders with high ferromagnetic signals.

## 1. Introduction

Nickel oxide (NiO) is a versatile material that has found technological application in catalysis, gas sensor, solid oxide fuel cell anodes, supercapacitors and electrochromic windows [1–5]. Despite the fact that Bulk NiO is an antiferromagnetic (AF) material below a Néel temperature of 523 K [6], AF + ferromagnetic(FM)/asperomagnetic or superparamagnetic properties are exhibited when nanosized [7–9]. It has been postulated that this behavior is probably caused by uncompensated magnetic moments due to absence of cell periodicity at the nanoparticle surfaces and defects at nanoparticle cores [10,11]. On the other hand, bulk Ni exhibits FM properties below a Curie transition at 627 K. Therefore, Ni/NiO composites have been used in several technological applications combining intrinsic properties of each phase [12,13].

The effects of different synthesis routes on the particle size and magnetic properties of NiO and Ni/NiO composites have been widely reported in literature [9,12–15] showing that phase composition and particle morphology are key parameters to control magnetic performance. Accordingly, a structural study of NiO nanoparticles synthesized with commercial flavorless gelatin as an environmentally friendly precursor was reported elsewhere [16]. The gelatin is a natural polymer composed by a mixture of high molecular weight polypeptides and proteins usually obtained by hydrolysis of collagen.

The present paper is the first report on the magnetic characterization of core-shell structured Ni/NiO powders synthesized by proteic sol-gel method using gelatin as chelating and polymerizing agent. Structure and magnetic properties of NiO samples prepared by citrate, nitrate calcination and combustion methods were also investigated.

## 2. Experimental

Nickel oxide (NiO) powder samples were synthesized by four different methods, namely: citrate, nitrate calcination, combustion and proteic sol-gel. The citrate synthesis started by dissolving nickel nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich, 99%] in distilled water and further complexation with citric acid [$C_6H_8O_7{\cdot}H_2O$], using a acid – to – Ni molar ratio of 3.5. The resulting solution was stirred at 80–90 °C for 2 h to allow the formation of Ni-chelates. Afterwards, a thermal treatment was applied consisting of heating at 350 °C in air, for 1 h with

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a heating rate of 1 °C min$^{-1}$. In order to obtain NiO by nitrate calcination, a nickel nitrate aqueous solution was thermally treated at 350 °C under the same conditions used in the citrate method. It was used equimolar amounts of nickel nitrate and urea as precursor materials on third synthesis method (combustion, with self-ignition occurring in 3 min). The fourth synthesis method (proteic sol-gel), which has been already used before [17–19], was prepared using an aqueous solution of flavorless gelatin (Farmafórmula, Brazil) at 50 °C. Then, nickel nitrate was added to this solution, which was stirred at 90 °C for 1 h. Afterwards, the gel was thermally treated at 350 °C for 2 h with a heating rate of 1 °C min$^{-1}$. Hence, the as-prepared precursor powders derived from citrate, nitrate calcination and proteic sol-gel routes were grounded and further treated at 500 °C for 2 h in air, while material synthesized by combustion method was heat-treated at 500 °C for 3 min.

In order to examine crystal structure of synthesized materials, powder X-ray diffraction (PXRD) data were collected by a Bruker D2 Phaser diffractometer equipped with Linxeye PSD using zero-background silicon sample-holder. Data were collected between 30 and 70° 2θ theta range with 0.02° step sizes, 3 s each step, using Cu K$\alpha_{1,2}$ radiation (λ = 1.5418 Å). Quantitative phase analysis, lattice parameter and crystallite size were obtained from Rietveld refinement of PXRD using TOPAS software with fundamental parameters approach. FT-IR spectra were obtained by using a Shimadzu IRAffinity-1 spectrometer. Room-temperature magnetic measurements were performed on a commercial vibrating sample magnetometer (VSM), Lakeshore 7400. Before starting measurements, VSM sample holder was carefully cleaned using a diluted HCl solution and washed several times with distilled water in an ultrasonic bath. Then, particle size and a selected area electron diffraction (SAED) pattern of the proteic sol-gel synthesized material were obtained from Transmission Electron Microscopy (TEM) images, Hitachi H9000.

## 3. Results and discussion

Refined PXRD patterns of powders synthesized by citrate, nitrate calcination and combustion methods (Fig. 1) revealed a single phase with diffraction peaks belonging to the cubic phase of NiO (*Fm*-3*m*, JCPDS card file n° 47-1049) with sodium chloride type crystal structure. However, the material obtained by the proteic sol-gel method exhibits an additional phase of Ni metal (*Fm*-3*m*, JCPDS card file n° 04-0850), suggesting that proteic sol-gel method using gelatin might probably be a suitable chemical route to prepare NiO/Ni composites. Despite heat treatment in air at 500 °C, formation of zerovalent Ni particles is probably due to $Ni^{+2}$ reduction, which could be caused by a local hydrogen from amine groups in gelatin and to CO/$CO_2$-rich atmosphere produced from the precursor material decomposition [20,21].

From Table 1, it can be noticed that $\chi^2 = R_{WP}/R_{EXP}$ values indicate good agreement between experimental and calculated data. Despite no substantial difference in lattice parameters of cubic NiO phase may be seen regardless of the synthesis method, which is in agreement with previous reported ones [22], crystallite sizes ($D_{XRD}$) of NiO phase ranged from 16 to 78 nm, with the smallest one related to that sample prepared by combustion method (16 nm). Once powder obtained by the proteic method exhibited a Ni content of 15.2 wt%, it is important to mention that concentrations of obtained phases are greater than XRD detection limit, which typically is of the order of a few percent of crystallinity by mass [23]. Therefore, crystalline phases with masses smaller than a few percent will not appear in the diffractogram.

FT-IR spectra reveal absence of C-N, C-H and N-H bonds, confirming removal of organic species (Fig. 2). The band at 1380 cm$^{-1}$, attributed to the symmetrical O-C=O stretch from $CO_2$, may result from the decomposition of organic matter [24], nevertheless the bands at 3460 and 1635 cm$^{-1}$ are due to the (O–H) stretching vibrations of the adsorbed water and (O–H) deformation vibrations, respectively. Lastly, the peak around 528 cm$^{-1}$confirms the presence of Ni–O bond [25].

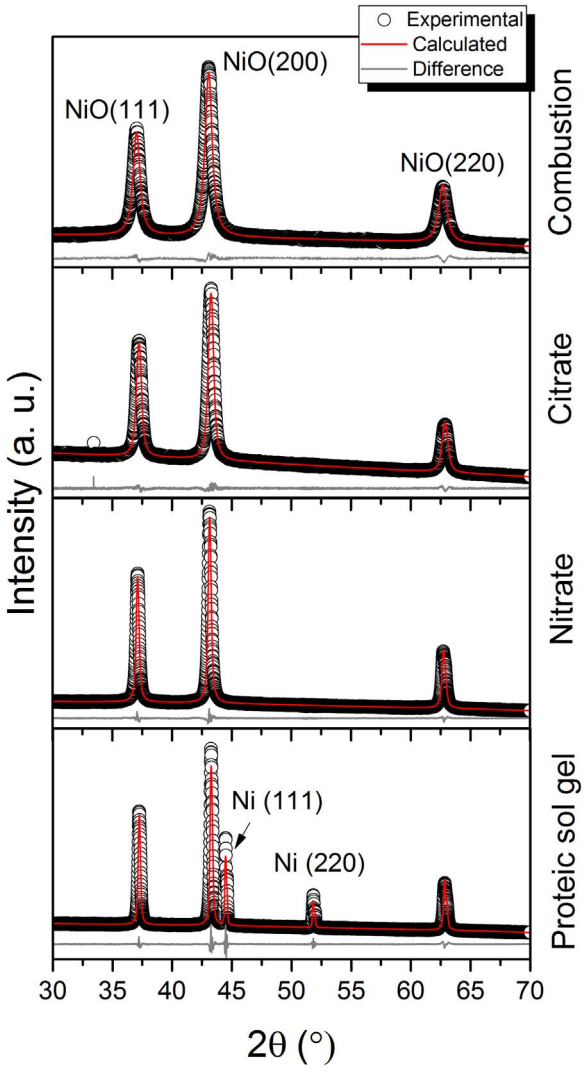


**Fig. 1.** Refined XRD patterns of samples synthesized by citrate, nitrate, calcination, combustion, and proteic sol-gel methods.

**Table 1**
Crystallite size ($D_{XRD}$), lattice parameters (a), quantitative phase analysis, and Rietveld agreement indexes for samples obtained by different synthesis methods. Data inside brackets correspond to the mass fraction of each phase.

| *Synthesis method* | *NiO phase* | | *Ni phase* | | *Agreement factors* | | |
|---|---|---|---|---|---|---|---|
| | $D_{XRD}$ (nm) | a (Å) | $D_{XRD}$ (nm) | a (Å) | $R_{wp}$ (%) | $R_{exp}$ (%) | $\chi^2$ |
| Citrate | 30 [100%] | 4.18 | – | – | 1.62 | 1.20 | 1.35 |
| Nitrate calcination | 47 [100%] | 4.18 | – | – | 1.51 | 0.90 | 1.68 |
| Combustion | 16 [100%] | 4.17 | – | – | 1.44 | 0.91 | 1.58 |
| Proteic sol-gel | 78 [84.8%] | 4.18 | 266.8 [15.2%] | 3.53 | 2.95 | 1.04 | 2.84 |

It can be seen that hysteresis curves of citrate, nitrate calcination and combustion samples do not saturate at the maximum applied field of 15 kOe (see Fig. 3a). On the other hand, the sample prepared by the proteic sol-gel method exhibits a ferromagnetic saturated regime. Despite at first glance it seems that combustion-based and nitrate calcined samples have their magnetization curves increasing linearly with applied field, without displaying hysteresis loop, suggesting an AF behavior, as expected for bulk NiO [15], careful examination of hysteresis