

Synthesis and characterization of NiO and NiFe₂O₄ nanoparticles obtained by a sucrose-based route

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Abstract

Crystalline oxide powders were synthesized in nanoscale dimensions by a simple and novel chemical route, which is based on the use of sucrose as a chelating agent. The starting solutions were evaporated at 60 °C and the resulting gel was heated up to 300, 600 or 750 °C. The process was able to produce nickel oxide and nickel ferrite, characterized by structural and microscopic techniques. The average size of the particle was estimated by both Scherrer's equation and electron microscopy, and the results indicated that particles with a high crystallinity and a mean size in the range of 11–36 nm were obtained. This synthesis route was able to produce NiFe₂O₄ and NiO nanoparticles at temperatures as low as 300 and 350 °C, respectively.

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1. Introduction

Several methods (mechanical or chemical) have been used and developed for synthesizing crystalline oxide powders in nanoscale dimensions. In many of them, the main objective is to reduce the costs of chemical synthesis and to produce materials for technological applications [1–6]. Among the several methods, the ones that keep a high random distribution of the metal ions or complexes are based on the use of a matrix (solution, gel or “resin”). This characteristic increases the chemical homogeneity and avoids (or reduces) the segregation of a particular metal during the processing and crystallization of the multimetal oxides [7–9]. In these chemical methods, the metal ions (or complexes) are immobilized on an atomic scale (inside the matrix), which allows to obtain oxides at temperatures lower than the ones produced in solid state reaction. Due to the immobilization, the metal ions react with each other with a minimum diffusion; consequently, it is possible to

synthesize homogeneous and stoichiometrical oxides [7,8]. Sol–gel techniques are well known examples of routes with these characteristics [10,11]. In these techniques, the control of the particle size can be controlled by the formation and aggregation of the particles in the starting sol, which is dependent on the concentration of reagents, pH, temperature, solvent, electronegativity of the metals, etc. [12,13]. Such dependence can also be attributed to aqueous solution–gel-based methods, in which metal salts are dissolved in an aqueous solution. Both processes generate an amorphous three-dimensional gel network with metals dispersed in the matrix [4,10].

Besides the versatility and simplicity, and since water is the most polar solvent, the aqueous solution–gel method can offer a better chemical homogeneity compared to sol–gel techniques, which may present differences in solubility between the several chemical species in the sol [14]. Other advantages over the sol–gel techniques are the elimination of the aging, special atmospheres for preparing the solution and the low cost [4,15,16].

A few years ago, we were involved in the development of a patented process [17] to synthesize oxides in the form of

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powders and films [18–20] based on the use of coconut water. In this process, called proteic sol–gel [21], the function of the chelating agent in the solution was attributed to the protein, making it possible to obtain binary and ternary oxides. In this study, the oxides could be synthesized at low temperatures [18–20] without carbide presence, that is, without the formation of any double bond between the carbon and the metal. Nevertheless, an alternative that may have been considered is that sucrose (contained in coconut water) could also have acted as the main chelating agent, without discarding the protein effect. Therefore, a novel and cheap aqueous solution–gel synthesis method was tested to produce nanocrystalline powders. The chemical process is based on the use of sucrose as the chelating agent, and it stands out by its simplicity and low cost, using only sucrose and metal nitrates as reagents. The process can be considered similar to the amorphous complex method, often called amorphous citrate method [16,22]. In the amorphous complex routes, solutions of citrate are added to water and carbonaceous materials, generating a stable and homogeneous solution. The solvent is then evaporated at a moderate temperature and a sticky gel is obtained [16,22,23]. This gel is heated to remove the organic constituents, and a very thin homogeneous crystalline powder is formed [16,22]. In this synthesis method, citric acid is used as the chelating agent. In the process presented in this study, the chemical route is similar but sucrose is used as the chelating agent. The process can therefore be described as an “amorphous sucrose method”.

In this paper, nickel oxide (NiO) and nickel ferrite (NiFe₂O₄) nanoparticles were obtained in two different conditions. The former was synthesized without alterations in the heating rate, and the latter was synthesized with alterations in the heating rate.

2. Experimental

In the following procedures, as illustrated in Fig. 1, aqueous solutions were prepared to synthesize nanopowders of NiO and NiFe₂O₄. The reagents used for the synthesis of nanopowders were sucrose (SYNTH, 99.9% C₁₂H₂₂O₁₁), nickel nitrate (ECIBRA, 99.9% Ni(NO₃)₂·6H₂O) and ferric nitrate (ECIBRA, 99.8% Fe(NO₃)₃·9H₂O). The starting solution was prepared by dissolving sucrose (0.1675 mol L^{−1}) in a solution of metal salts, followed by mechanical stirring for some minutes. Because both metal salts [Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O] are hygroscopic, titration using EDTA was used to determine the concentrations of Ni²⁺ and Fe³⁺, and to minimize possible errors in the stoichiometric of the nickel ferrite [24,25]. The solution was prepared in the ratio of 1:2, Ni²⁺ and Fe³⁺, respectively.

The sucrose, nickel and iron salts aqueous solution (to synthesize nickel ferrite) presented small precipitated particles, probably due to the low pH of the solution, which disappeared when the solution was heated to 60 °C. The solution was kept in the oven until a solid sticky gel

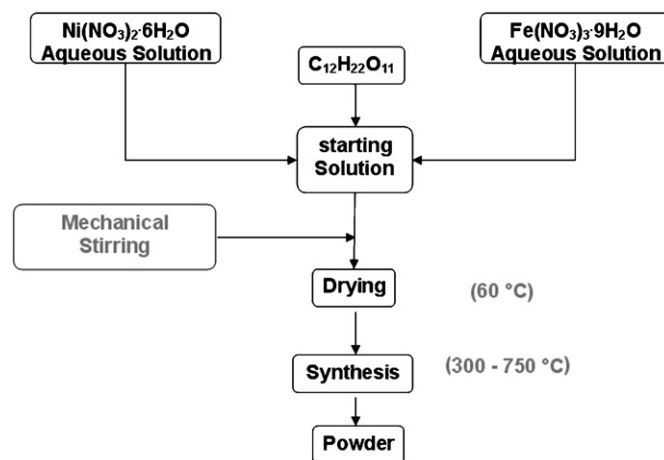


Fig. 1. Diagram of the chemical process based on the use of sucrose as the chelating agent.

was obtained due to evaporation of the solvent. This gel was annealed in a furnace at temperatures of 300, 600 and 750 °C.

An optical microscope Olympus BX 60M was used to observe the porous network of the sample soon after its synthesis. A field emission gun scanning electron microscopy JSM 6330F (FEG-SEM) was used to observe the morphology, distribution and particle sizes. The X-ray diffraction measurements were obtained using a Rigaku powder diffractometer with Bragg-Brentano geometry in continuous mode with scan speed of $\frac{1}{4}^\circ/\text{min}$. CuK α radiation tube with line focus was operated at 40 kV and 25 mA. The X-ray powder diffraction patterns were obtained in the range of 25–85°, and increments of 0.02°. The crystalline phases were identified using the International Centre for Diffraction Data (ICDD) catalogue. Rietveld refinement [26] procedures were done for all diffraction patterns using the DBWS9807, as described by Young and Wiles [27] and GSAS [28]. The full width at half maximum (FWHM) of the diffraction peaks obtained from the refinement was used to calculate the particle size. The pseudo-Voigt function was selected to fit the peak profiles for the identified crystalline phases. FWHM of the peaks, asymmetry coefficients, scale factors and lattice parameters for each phase and the background polynomial parameters were simultaneously refined.

The particle size, D , was calculated using the Scherrer's equation [29]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where k is the shape coefficient for reciprocal lattice point (here, assuming $k = 1$), β is the FWHM of the peak and θ is the Bragg angle.

The β parameter was corrected for the instrumental broadening using the following equation:

$$\beta = \sqrt{\beta_{\text{exp}}^2 - \beta_{\text{inst}}^2}, \quad (2)$$

where β_{exp} is the measured broadening and β_{inst} is the broadening due to the instrument. It was considered that the diffraction peaks profile presented Gaussian distribution. β_{inst} was obtained from LaB₆ (SRM660-National Institute of Standard Technology) powder standard using the Caglioti's equation [30]:

$$\beta_{\text{inst}} = \sqrt{U \tan^2 \theta + V \tan \theta + W}, \quad (3)$$

where U , V and W are the parameters obtained from the Rietveld refinement.

3. Results and discussion

It is known that the sucrose in aqueous solution is decomposed in two monosaccharides, glucose and fructose. Besides, monosaccharides can be oxidized by metal ions, generating carboxylic acid [31]. Therefore, the “amorphous sucrose method” can be related to the formation of chelates between the cations and the hydrocarboxylic acid formed in the solution [32]. Bose and Wu also investigated the use of sucrose as a chelating agent. In a recent study published by them [33], the solution was prepared using sucrose, nitrates and nitric acid. The nitric acid (not used in the present study) was employed to break down the sucrose to saccharic acid. Another paper, with similar research interests on the use of sucrose as a chelating agent [34], showed that the formation of saccharic acid was related to the use of oxidizing agents, which avoided the recrystallization of the sucrose. However, this procedure was not necessary to obtain the oxides produced in the present study.

At 60 °C condensation reactions took place, the water was evaporated and the constituents of the solution were polymerized until the solution became a black sticky gel. In the present study, this gel was heated to obtain the oxides. During the heating process, the organic constituents were evaporated and probably gases such as CO₂, N₂ and H₂O were expelled. The gases lead the sticky gel to expand more than 10 times, resulting in the formation of a highly porous three-dimensional network. Such network corresponded to nickel ferrite as shown in Fig. 2.

It was observed, by optical microscope, a regular porous macroscopic structure formed by rings. The bondings between the particles, which form the rings appeared to be weak, since they were easily broken with the manipulation.

The nickel oxide was synthesized in air at three different temperatures, 300, 600 and 750 °C, for 2 h using a heating rate of 10 °C/min. Fig. 3 shows the X-ray diffraction patterns of the nickel oxide nanoparticles. All nickel oxide samples showed a cubic structure (space group Fm3m) with $a = 4.1764 \text{ \AA}$ and density of 6.811 g/cm^3 , which is in agreement with JCPDS file 47-1049 [35]. The results were evaluated by simulations using the Rietveld method [26]. The factors $\chi^2(R_{\text{wp}})$ were: 1.09 (12.34%), 1.20 (13.76%) and 1.17 (12.12%) for the samples synthesized at 300, 600 and 750 °C, respectively.

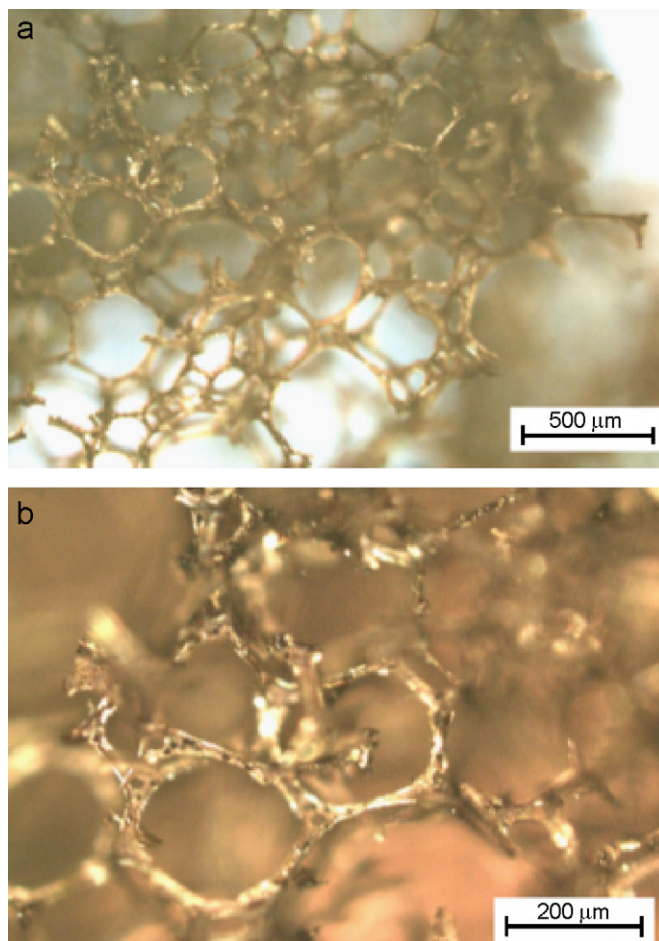


Fig. 2. Optical microscopy image of porous three-dimensional network of NiFe₂O₄. The bars in (a) and (b) represents 500 and 250 μm, respectively.

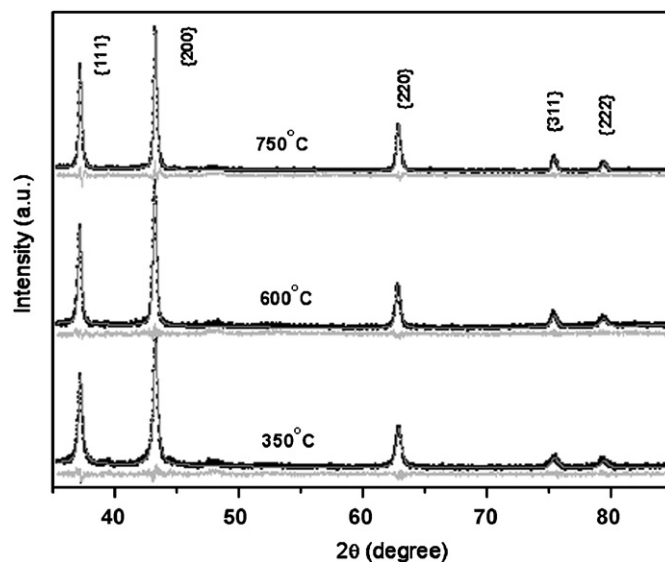


Fig. 3. X-ray diffraction pattern of the nickel oxide samples synthesized at 350, 600 and 750 °C.

The particle sizes of the nickel oxide samples in different crystallographic directions were calculated by Eq. (1). The mean particle sizes were 23, 27 and 34 nm for samples

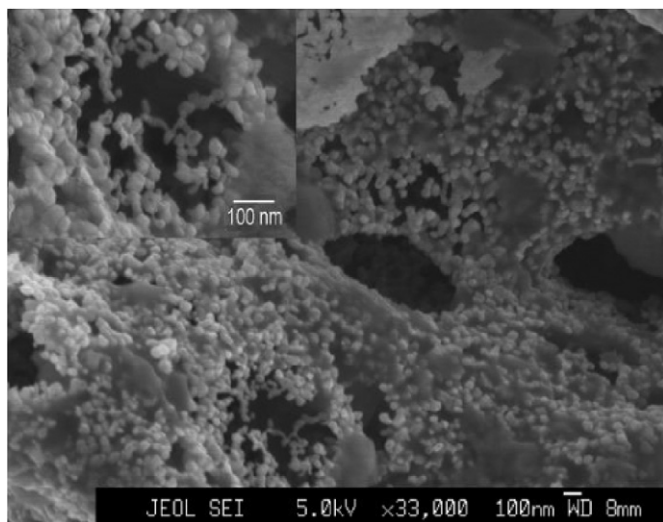


Fig. 4. SEM images of NiO synthesized at 750 °C. The inset shows the magnified image.

synthesized at 300, 600 and 750 °C, respectively (Table 1). Therefore, the higher the temperature, the higher the particle size. This behavior was expected because the heating facilitates the diffusion and agglomeration of the particles [36–38].

Fig. 4 shows the SEM images of the NiO particles synthesized at 750 °C. The particles seemed uniform and spherical. The nanoparticle sizes were in agreement with the values calculated by the Scherrer's equation.

The nickel ferrite was annealed in air at 300, 600 and 750 °C for 2 h using different heating rates of 5, 10 and 12.5 °C/min, respectively. The X-ray diffraction patterns of NiFe₂O₄, simulated by Rietveld refinement are shown in Fig. 5. It can be observed that the nickel ferrite was synthesized at temperatures as low as 300 °C.

Particle sizes of nickel ferrite (L_{hkl}) in different crystallographic direction $\{hkl\}$ were calculated by the Scherrer's equation [29] for all samples of NiFe₂O₄ (Table 2). The average size of the particle was 11 ± 1 nm for all samples. Through modifications in the heating rate, the particle size became independent of the temperature used. This behavior is explained by the increase in the heating rate, which favors densification instead of grain growth [39]. The expansion of the gases, which created the porous three-dimensional network, must also have impaired the agglomeration of the particle because the rings could have been able to decrease the contact area between the molecules, hampering the diffusion of particles and thus avoiding its agglomeration.

SEM images of the NiFe₂O₄ sample, synthesized at 750 °C, are presented in Fig. 6. It is not possible to observe the morphology of the particles with high precision due to the low resolution of the SEM. However, it is possible to verify that the particle size observed by SEM presents dimensions close to the ones calculated by the Scherrer's equation.

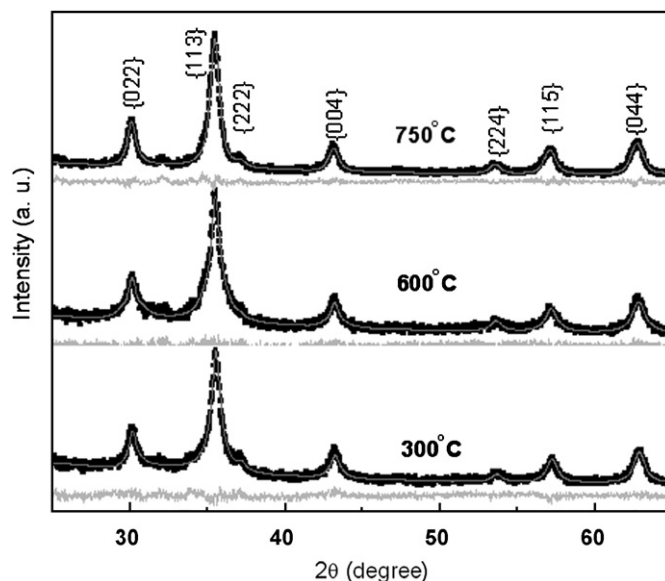


Fig. 5. X-ray diffraction pattern of the NiFe₂O₄ samples synthesized at 300, 600 and 750 °C.

Table 1
The particle sizes of the nickel oxide

Temperature (°C)	Particle size (nm)					
	Crystallographic planes					Average (nm)
	{111}	{002}	{022}	{113}	{222}	
300	27(1)	26(1)	22(1)	20(1)	19(1)	23(1)
600	28(1)	28(1)	27(1)	26(1)	25(1)	27(1)
750	36(1)	35(1)	33(1)	32(1)	32(1)	34(1)

The numbers in parenthesis represent the errors from the measurement.

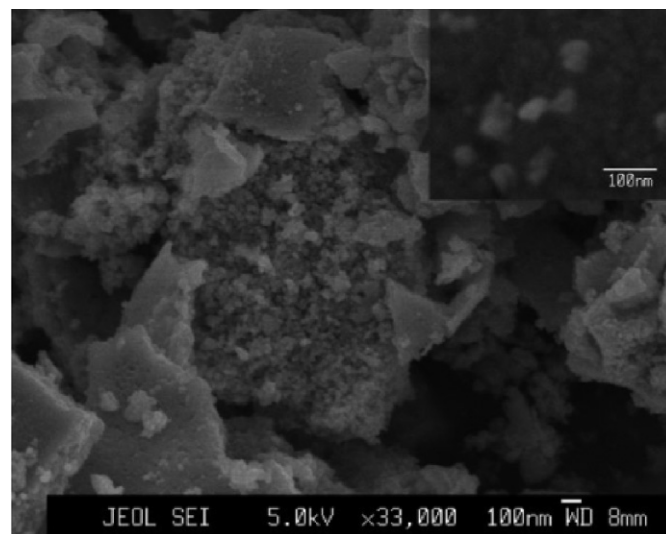


Fig. 6. SEM images of NiFe₂O₄ synthesized at 750 °C. The inset shows the magnified image.

Table 2
The particle sizes of the nickel ferrite

Temperature (°C)	Particle size (nm)					
	Crystallographic planes					
	{022}	{113}	{004}	{224}	{044}	Average (nm)
300	14(1)	12(1)	11(1)	10(1)	9(1)	11(1)
600	12(1)	12(1)	11(1)	10(1)	8(1)	11(1)
750	13(1)	12(1)	11(1)	9(1)	8(1)	11(1)

The numbers in parenthesis represent the errors from the measurement.

4. Conclusion

Nanoparticulate powders of the NiO and NiFe₂O₄ were synthesized by a simple and novel chemical route, which is based on the use of sucrose as a chelating agent. Both oxides were synthesized at 300, 600 and 750 °C, but in different conditions. The syntheses of all samples of nickel oxide were carried out with the same heating rate, whereas the heating rate of the samples of nickel ferrite were changed (Table 1). In the former, the higher the temperature, the higher the particle size. In the latter no changes were observed. The average particle sizes for these oxides, analyzed for both XRD and SEM, were between 11 and 36 nm.

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