Direct Observation of the Formation of Nanoparticles by in situ Time-Resolved X-ray Absorption Spectroscopy

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In situ time-resolved X-ray absorption spectroscopy was used to observe the first stage of NiO nanoparticle formation. The spectra of Ni K-edge (and their Fourier transforms) during heating show a systematic structural phase transformation (amorphous to crystalline) near 400 °C. Crystallization occurs during heating of solid solution (biopolymer) of nickel dispersed in gelatin. The experimental XANES spectra are compared to ab initio calculations using a multiple-scattering model (code FEFF).

Nanostructures display interesting properties from fundamental and technological points of view. The large surface to volume ratio enables development of new materials and devices. During the past decade, significant progress has been made in preparing nanostructures systems using numerous physical and chemical methods.[1] Recently, many studies have been dedicated to bio-inspired methods, where the biology is a source of inspiration for making nanostructures with specific properties.[2]

In situ extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) have been used to study catalytic activity in nanoparticles[3−7] and their electrochemical properties. Recently, XANES has been used for analysis in high-temperature catalytic studies,[3,4] in studies of structure and electronic behavior of inorganic compounds and metals in the form of nanoclusters,[3,4] in gas sensors,[5] and in surface investigations.[6] Using X-ray absorption spectroscopy (XAS) one can investigate the formation of the nanoparticle by studying the XANES absorption profile.

The main focus of the present study is to show and discuss results related to the first stage of crystallization of nickel oxide (NiO) nanoparticles using metal/gelatin systems in the form of films and their characterization by in situ EXAFS and XANES during heating. The XANES feature spectra are sensitive to changes in electronic and atomic structure of the absorbing atom[7] during nanoparticle growth. The process studied has already been used over recent years to obtain, for instance, nanoparticles of NiO, Cr_2O_3, and other oxides.[8−11]

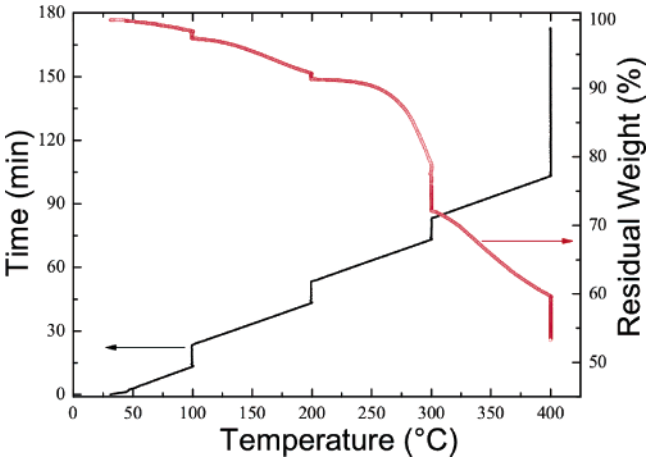

Figure 1. (right) TG of the Ni−gelatin system undergoing a (left) kinetic curve with plateau.

We also present ab initio XANES calculations for the NiO model compound, using the multiple-scattering code FEFF8,[12] that agree well with the experimental spectra and provide an interpretation of the features in the experimental spectra.

Gelatin solutions were prepared by dissolving gelatin grains (1.25 g, type B, SARGEL) in distilled water (20 mL) stirred continuously for 20 min at 40 °C. After complete dilution of the gelatin, nickel chloride hexahydrate (0.5 g

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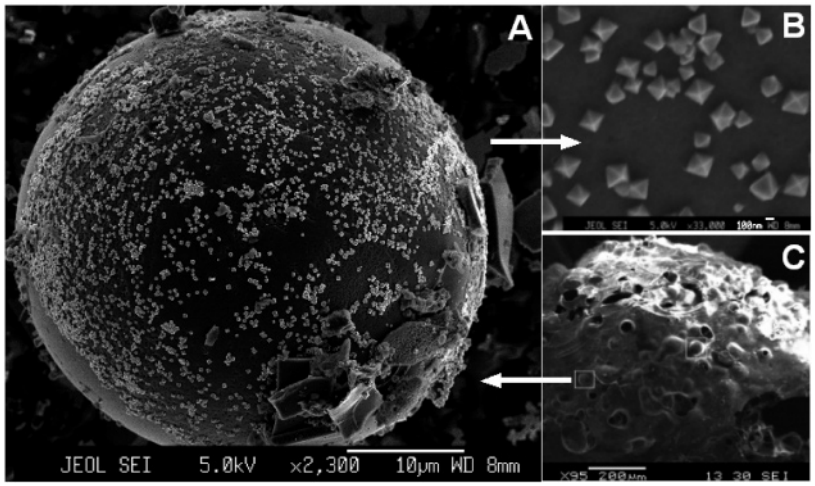

Figure 2. (A) Bubble (organic matrix) with NiO nanoparticles, (B) NiO nanoparticles of pyramidal shape (100 nm bar), (C) precursor material of the nanoparticles in puff state.

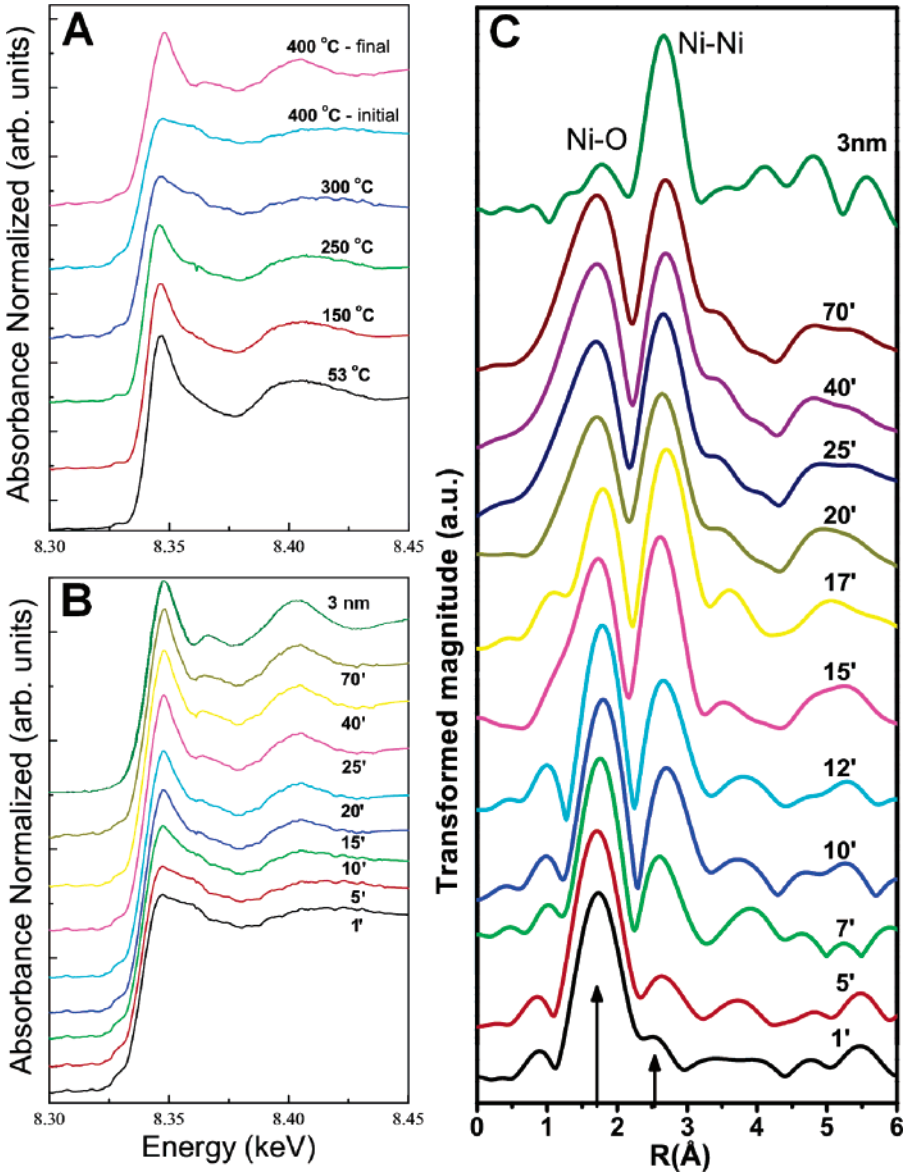

Figure 3. Ni K-edge XANES spectra measured at different temperatures (A) along the kinetic curve shown in Figure 1 and (B) at different times of the isothermal region at 400 °C, (C) Fourier transformed at different times of the isothermal at 400 °C.

$NiCl_2 \cdot 6H_2O$, Sigma-Aldrich) was added to solution and stirred at 60 °C for 10 min. Dried amorphous and brittle[13] samples were obtained after annealing at 80 °C for 36 h at atmospheric pressure.

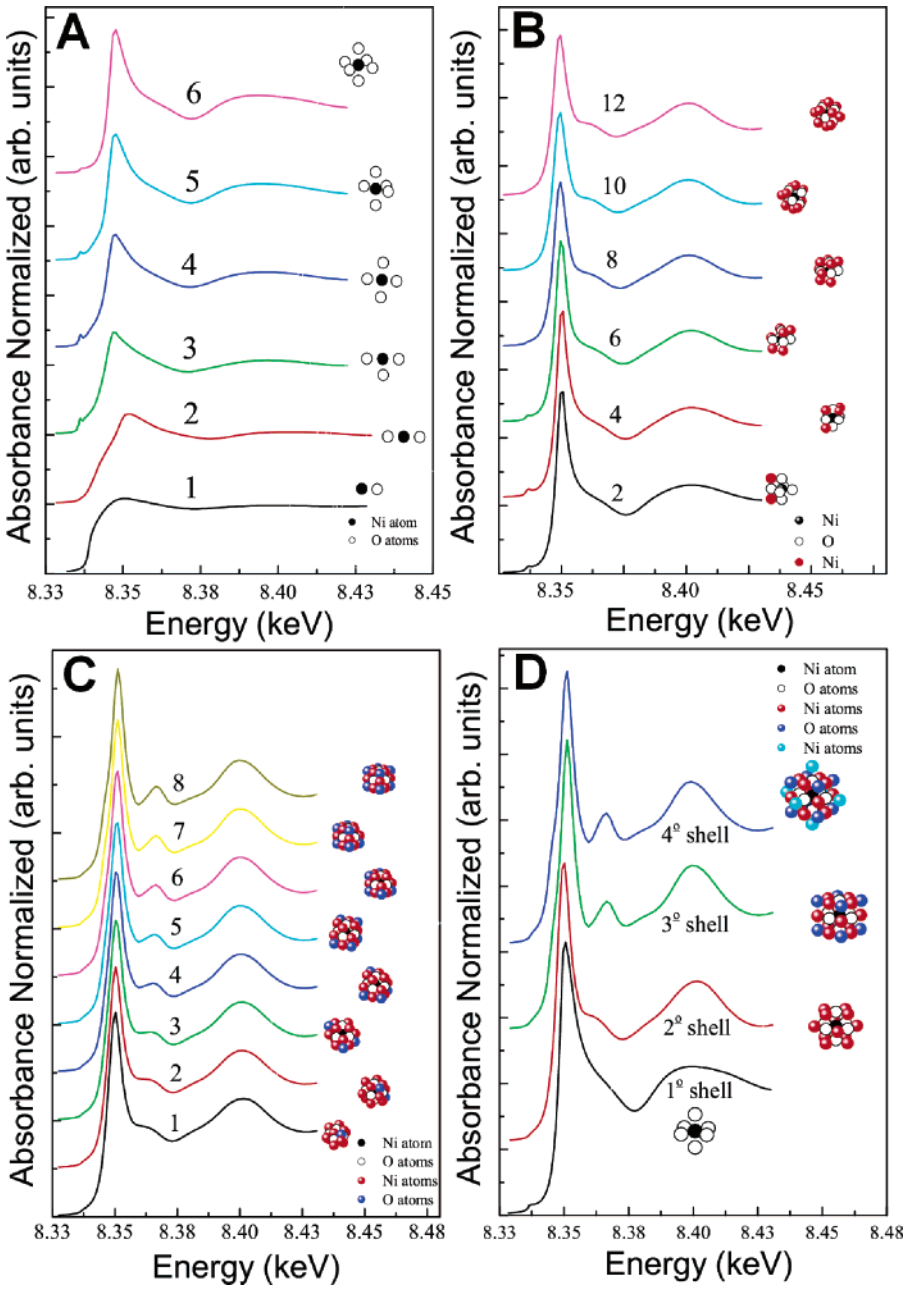

Figure 4. Ni K-edge XANES spectra calculated with the FEFF8 program around Ni for NiO model (A) filling the first shell, (B) filling the second shell, (C) filling the third shell, and (D) different clusters (7 atoms/first shell, 19 atoms/second shell, 27 atoms/third shell, 33 atoms/fourth shell).

We conducted thermal gravimetric (TG) analysis of the behavior of Ni-salt/gelatin solution under heating. TG experiments were performed (Shimadzu differential thermal analyzer) under synthetic air with a flow of 50 mL/min using a platinum crucible. The heating rate was 5°/min, over the temperature range from 25 to 400 °C, with plateaus at 100, 200, and 300 °C for 10 min and, finally, 400 °C for 70 min. The plateaus and ramps are shown in Figure 1(left). The TG curve in Figure 1 (right) shows weight-loss events due to water (structural and residual) elimination and later the breaking of gelatin chains. Note that the main event, around 270 °C, corresponds to the pyrolysis temperature expected for gelatin. Another TG result (not show) shows us that at nearly 600 °C, no more mass is lost.

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The mass loss between 250 and 300 °C, mainly near 300 °C, can be related to the breaking of metal−organic (nickel-salt/gelatin) compounds, mainly Ni linked to aminoacids, resulting in a great concentration of volatile gases, such as CO and CO_2. In this stage, the process of expansion of the organic precursor occurs, provoking a puff state that is similar to the bubble shape, containing gases, as shown in the Figure 2C. For temperatures above 300 °C, the bubbles are expelled separately, leaving a mixture of amorphous NiO dispersed in a carbon matrix. The nucleation process begins, and later, small NiO particles embedded in carbon, which act as a diffusion barrier during the growth of nanoparticles, are crystallized. SEM images of the sample synthesized at 350 °C for 6 h illustrate the morphology of theses particles. Figure 2A show several NiO nanoparticles in a pyramidal shape

(Figure 2B), with sizes between 80 and 250 nm, spread over the bubble surface.

In situ X-ray absorption (XANES and EXAFS) measurements were performed in transmission mode at the Laboratório Nacional de Luz Síncrotron facilities, LNLS (Campinas, Brazil),[14] by using an energy-dispersive spectrometer (beamline DXAS). The spectra in the Ni K-edge region (8333 eV) were collected in the CCD detector with 10 ms of time exposure and 100 accumulations for each frame.

Samples were heated under the same conditions as those of Figure 1 using a halogen lamp oven that is described in ref 15.[15] The oven was mounted on a translation (3D-*xyz*) table and the temperature readout was made by a K-type thermocouple installed inside the sample cell.

XANES data were analyzed on the basis of experimentally and theoretically determined reference files.[12] Fourier transform (FT) analysis was performed on several spectra measured at 400 °C, for different times of synthesis. FEFF8 code was used to simulate the XANES spectra by increasing the cluster by adding O and Ni shells around the central atom of Ni, always obeying the cubic (*Fm*3*m*) symmetry.

Figure 3A shows Ni K-edge XANES spectra of the biopolymer submitted to a continuous heating treatment from 53 to 400 °C. It ilustrates the evolution from biopolymer, formed essentially of Ni-salt/gelatin, to a NiO amorphous intermediate phase and aiding in a NiO crystalline phase. During biopolymer transformation to the NiO amorphous phase, a great quantity of mass is lost (approximately 50%), as seen in the TG curve of Figure 1. The crystalline phase formation starts at 400 °C; at this temperature, there is a large difference between the initial and final pos-edge peaks, which can be related to the beginning of the nickel oxide crystalline phase.

Figure 3B shows the absorption spectra collected after different times (total: 70 min) in the isothermal at 400 °C. After nearly 5 min, the Ni−O interactions increase, indicating that the number of neighbors surrounding the Ni atom is increasing; consequently, nanoparticle growth begins, as shown by the appearance of the modulation peak between 8.35 and 8.40 keV. This is made clear by the Fourier transform analysis (FT) of all XAS spectra shown in Figure 3C. The first and second peaks are related to first (Ni−O) and second (Ni−Ni) shells, respectively. The second peak grows continuously in intensity as a function of annealing time. This increase indicates that Ni atoms are recombining with oxygen atoms, in a process of formation and growth of NiO particles. Note that the particles are small, because the second shell is not formed completely, as shown by comparison with FT results for particles with an average size of 3 nm. This phenomenon agrees with the results obtained by Jimenez et al.,[6] who interpreted FT results for SnO_2 samples calcined at two different temperatures in an ex situ experiment.

Additional insight on NiO particle growth was obtained by simulation of the XANES spectra using the FEFF8 code, for different numbers of coordination shells considering multiple-scattering formalism.[12] Figure 4A shows the spectra calculated for 1−6 oxygen atoms around the central atom of Ni, always obeying the fcc NiO structure. The simulated XANES spectrum for 2 oxygen atoms is similar to the experimental spectrum in Figure 3B (at 400 °C for 1 min), suggesting that, at this time, the amorphous state exertd one strong contribution in the XANES spectrum. At later times (isotherm), both amorphous and crystalline phases contribute to experimental spectra. Panels B and C of Figure 4 are the spectra simulated by addition of further oxygen atoms to the structure and are similar to the intermediate experimental spectra in Figure 3B. After the third shell, we do not see any significant changes in the simulated spectra for clusters greater than 5 Å (see Figure 4D).

We conclude that in situ X-ray absorption using synchrotron radiation is a powerful technique for detecting the initial crystallization stage of the NiO nanoparticles and characterizing the amorphous to NiO nanocrystal phase transition. Furthermore, this technique is useful for determining the kinetic parameters of nanoparticle growth and may be a promising way of estimating the particle growth via the neighborhood number of the FT of the spectra.

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