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Experimental report

In operando nanothermometry of magnetic nanoparticles by combining XRD and XAS using an X-ray compatible cell for magnetic hyperthermia

The local temperature at the nanoscale of individual magnetic nanoparticles (MNPs) based on iron oxide under magneto-thermia conditions was determiend through the measurement of temperature-dependent structural and vibrational atomic parameters by means of using two synchrotron techniques: X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

Results:

The experimental setup consisted in an *ad hoc* designed X-ray compatible configuration where the sample was placed to apply both structural techniques under an alternating magnetic field excitation.

i) XRD measurements were performed using a beam wavelength of 0.8 Å (15 keV) after optimizing the diffraction conditions (angle range, resolution and intensity). First, we performed a calibration of a drop of γ-Fe_2O_3 nanoparticles (iron oxide nanoparticles, IONPs) contained in a capillary tube. The diffraction spectra of the sample at room temperature corresponded to an inverse spinel structure (space group Fd-3m) (Figure 1A). This part of the experiment was carried out with the aim to correlate the position of diffraction peaks with temperature (from 20 to 140 ºC). The thermal environment was provided by a cryostat operative in that range. The thermal readout was implemented with an infrared thermographic camera.

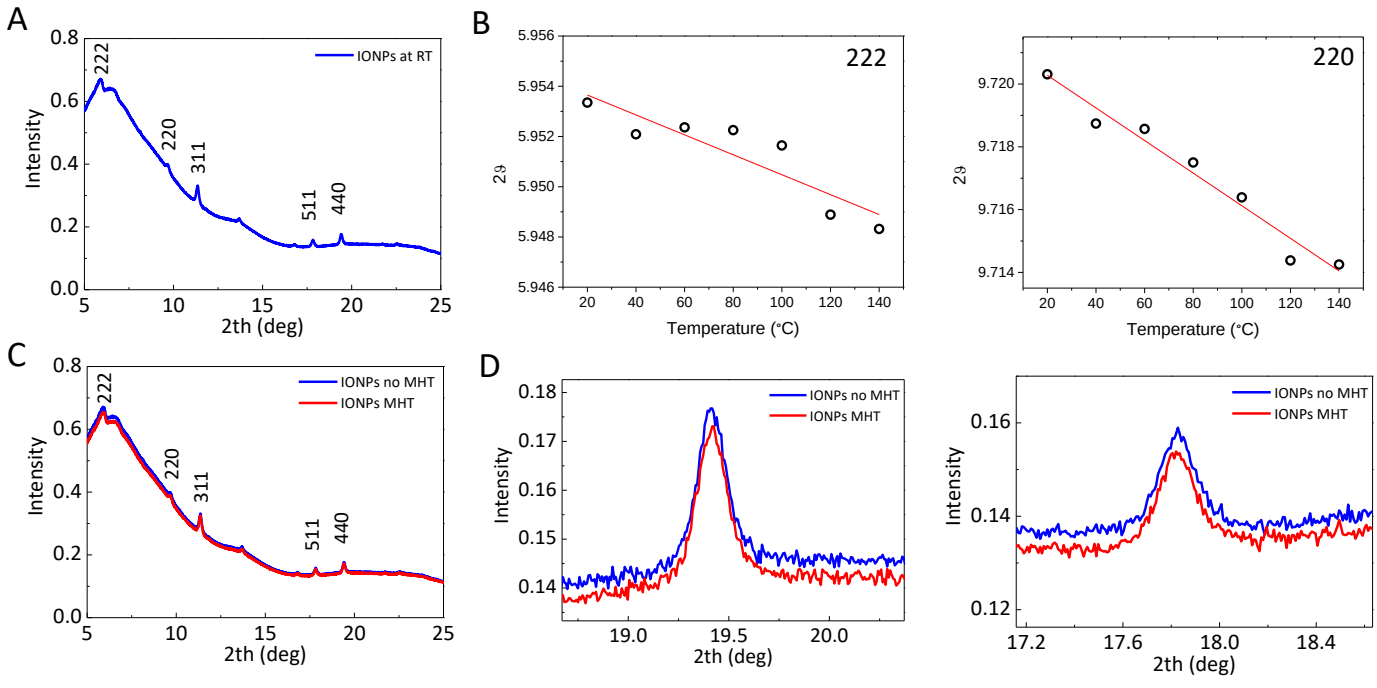

Figure 1. (A) Diffractogram of γ-Fe_2O_3 nanoparticles (IONPs) at room temperature. (B) Calibration curve of the IONPs (222) and (220) diffraction peak positions with temperature (from 20 to 140 ºC). (C) Diffractogram of γ-Fe_2O_3 nanoparticles (IONPs) at room temperature and subjected to magnetothermal induction. (D) Evolution of the diffraction peak positions with and without magnetothermal excitation.

The change on the X-rays diffraction pattern with temperature (in the range from 20 to 140 ºC) is depicted in Figure 1B regarding (222) and (220) diffraction peak positions. Calibrations of these positions are then

presented in the same figures. Figure 1C shows the diffractograms of IONPs at room temperature and under magnetic field application (measured at the steady state). Evolution of the diffraction peak positions with and without magnetothermal excitation. The local temperature that is generated at the surface of the IONPs after the alternating field excitation is then being subjected to analysis.

ii) XAS spectra were measured at the Fe K-edge (7112 eV) in transmission and fluorescence mode. First, a temperature-dependent XAS measurement on IONPs was performed with the help of a cryostat and a thermographic infrared camera to provide a calibration curve. Measurements were collected at different temperatures (from 20 to 50 ºC) in order to avoid the liquid evaporation and bubbles.

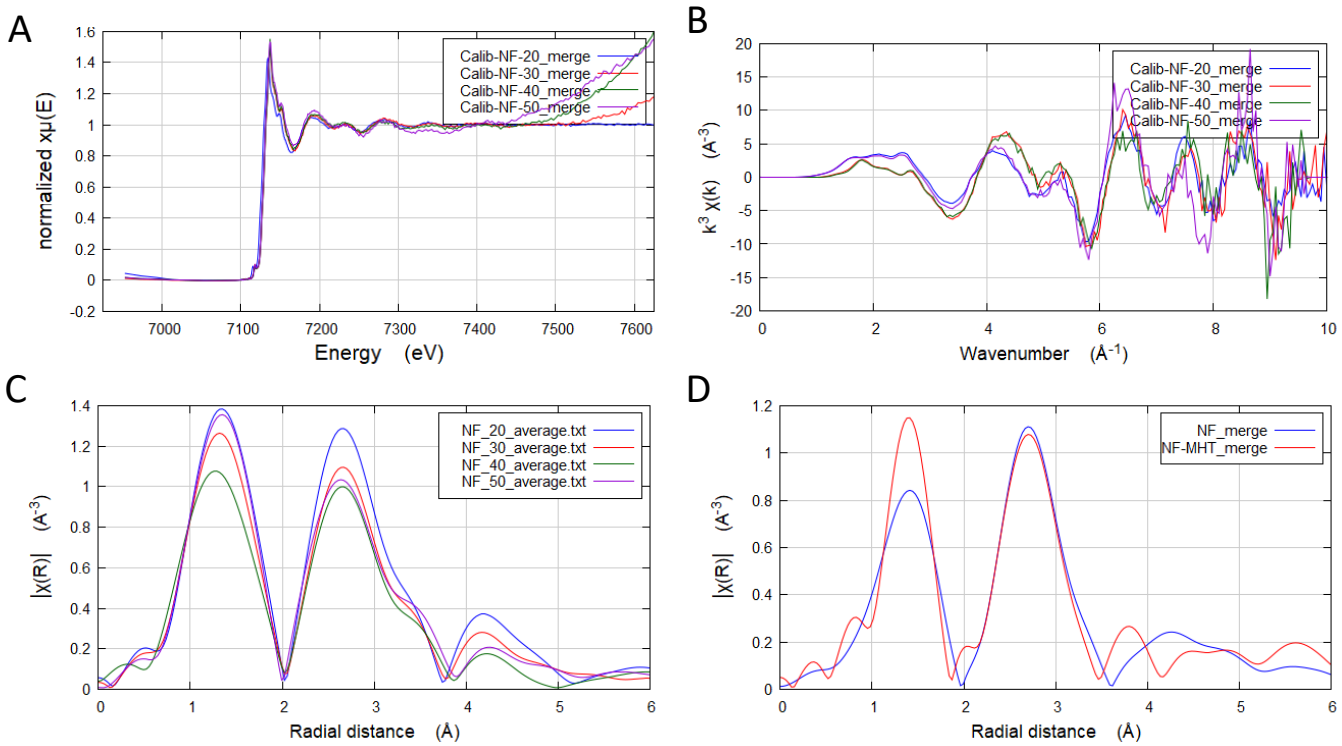

Figure 2. (A). XAS spectra at the Fe K-edge (7112 eV) of IONPs from 20 to 50 ºC obtained during the calibration curve measurements. (B) EXAFS spectra and (C) Fourier transform of the EXAFS signal of IONPs from 20 to 50 ºC. (C) Fourier transform of the EXAFS signal of IONPs subjected to magnetothermal induction.

We are performing the analysis of the local temperature obtained by the two techniques. We have then checked the validity of our hyperthermia setup that requires some improvements. We have also explored the measurements conditions, optimized experimental parameters and duration in time. We have concluded that the use of both techniques requires time to refine the conditions and therefore it limits the number of samples. These results shed light in the pursue of find new methodologies to monitor the local temperature of materials in hyperthermal conditions.[1-2]

References

1. Espinosa, A.; Castro, G. R.; Reguera, J.; Castellano, C.; Castillo, J.; Camarero, J.; Wilhelm, C.; García, M. A.; Muñoz-Noval, A. l., Photoactivated Nanoscale Temperature Gradient Detection Using X-ray Absorption Spectroscopy as a Direct Nanothermometry Method. *Nano Letters* **2021,** *21*, 769.

2. Faure, S.; Mille, N.; Kale, S. S.; Asensio, J. M.; Marbaix, J.; Farger, P.; Stoian, D.; van Beek, W.; Fazzini, P.-F.; Soulantica, K., Internal Temperature Measurements by X-ray Diffraction on Magnetic Nanoparticles Heated by a High-Frequency Magnetic Field. *The Journal of Physical Chemistry C* **2020,** *124* (40), 22259-22265.