

Results Report. Experiment 25-01-774:

"XANES study on nanostructured semiconductor templates loaded with Iron and Cobalt magnetic nanoparticles"

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Introduction

The development of hybrid materials is a current topic with many applications in several fields (i.e. optoelectronics, catalysis, biomedicine). Concretely, the hybridization of semiconductors with ferromagnetic material such as Cobalt, Iron and Nickel gives the possibility to obtain materials that combine semiconducting and magnetic properties [1]. Porous semiconductors, such as porous silicon (PS), present additional advantages like high surface area and porous structure [2].

In this experiment we aimed to the study of oxidation state and crystalline structure of Cobalt and Iron in Cobalt/Iron-Porous Silicon (Co-PS/Fe-PS) hybrid materials. Both elements have been infiltrated inside the PS matrix by electrochemical methods [3].

Results

1. Previous Studies of the hybrid materials

Preliminary structural studies of Co-PS and Fe-PS hybrid systems were carried out by TEM. As Fig.1&2 shows, Co and Fe infiltrates inside the PS matrix and forms spherical nanoparticles (NP) into the pores. In case of Co, NP of circa 5 nm are formed, in case of Fe, NP of circa 20 nm are observed. STEM images plus EDX analysis of these Systems (Fig.3) allows the identification of both elements in the NP.

Magnetic properties of both hybrid Systems were evaluated by Alternating Gradient Field Magnetometry (AGFM). In case of Co-PS, results point to the possibility of controlling the magnetization of Co-PS by controlling the amount of Co inside the PS matrix (Fig.4). This was achieved by controlling the number of electrodeposition pulses during the synthesis process. Coercivity of the material depends on the amount of Co in the hybrid material: less concentrated systems has lower coercivity values than bulk Co [4,5]; systems with higher Co concentration present higher values. In case of Fe-PS systems (Fig.5), magnetization has a weak dependence with Fe concentration. Coercivity does not vary with the amount of Fe in the system.

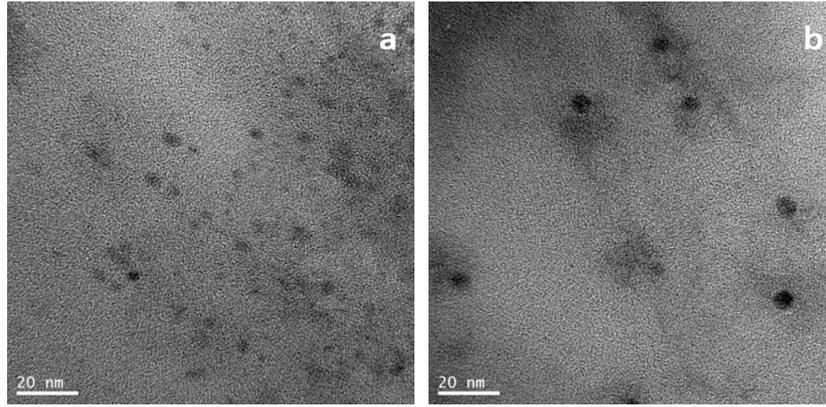


Fig.1. TEM images of the Co NP hosted inside the PS matrix for the Co-PS systems. a&b represent different magnification of the same systems.

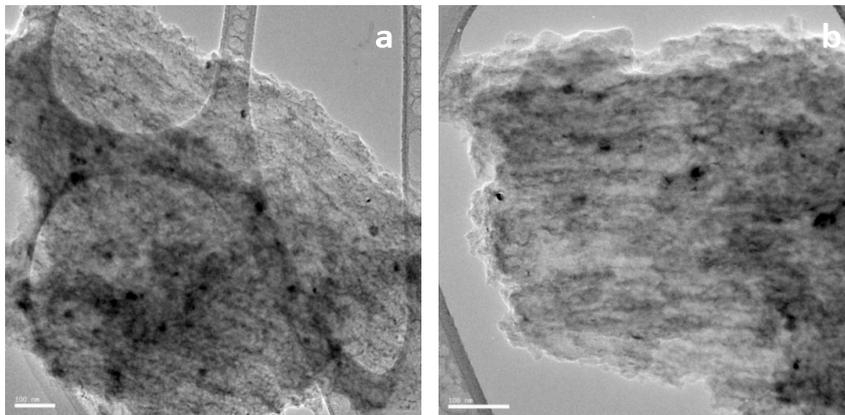


Fig.2. TEM images of the Fe NP hosted inside the PS matrix for the Fe-PS systems. a&b represent different magnification of the same systems.

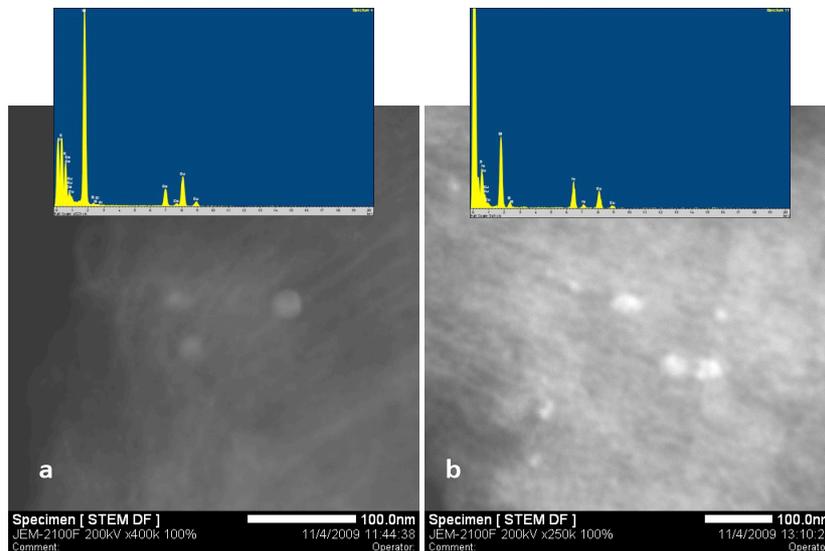


Fig.3. STEM images of: a) Co-PS system and b) Fe-PS system, showing respectively Co and Fe NP inside the PS matrix. Insets present EDX elemental analysis of the NP.

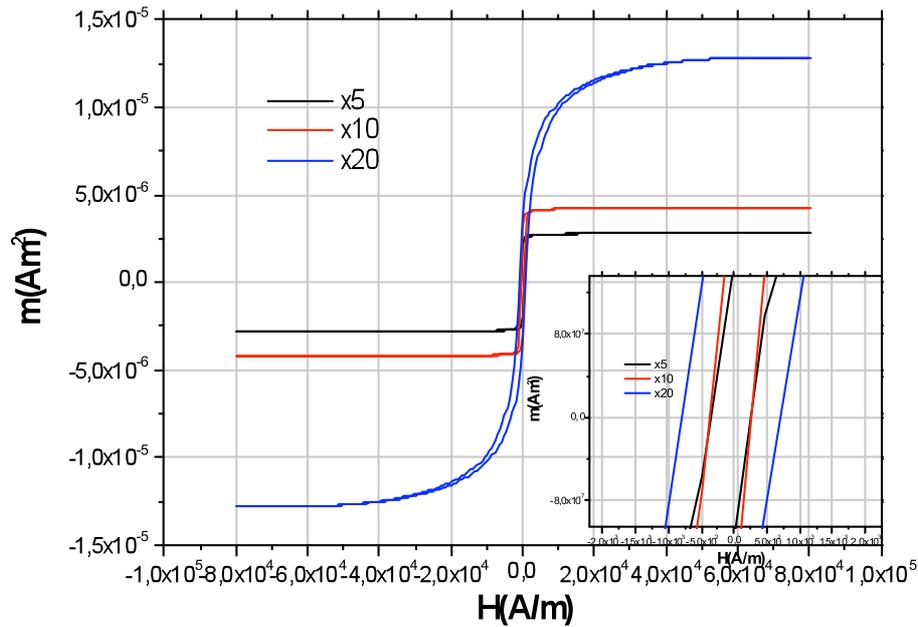


Fig.4. Hysteresis cycle for Co-PS systems with increasing Co concentration inside the matrix, obtained from increasing number of electrodeposition pulses: 10, 20 and 40.(inset) Axis detail showing coercivity dependence.

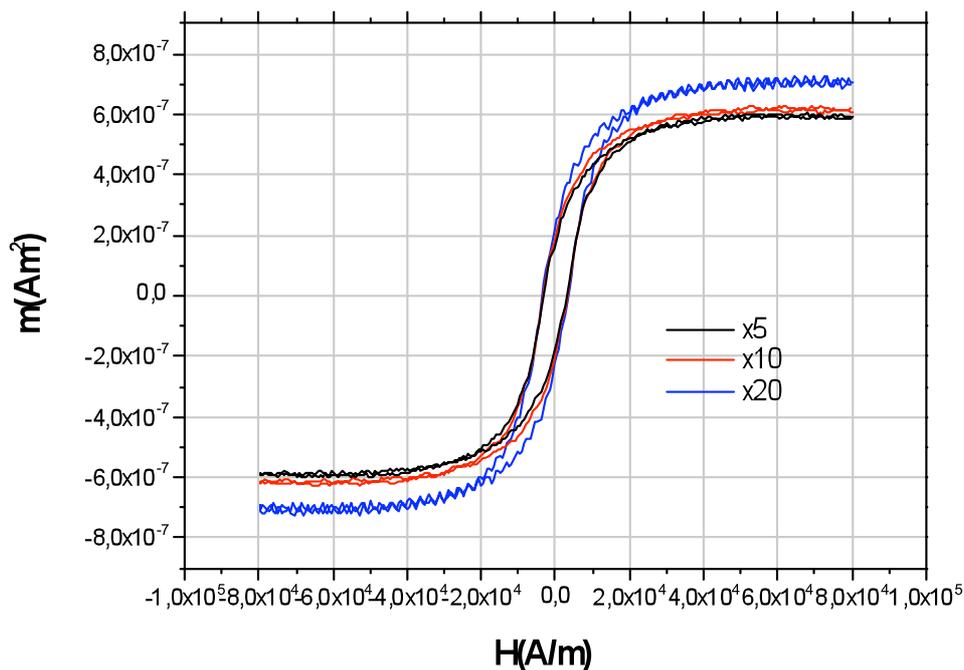


Fig.5. Hysteresis cycle for Fe-PS systems with increasing Fe concentration inside the matrix, obtained from increasing number of electrodeposition pulses: 10, 20 and 40.

2. Results derived from experiments in the ESRF

2.a. Cobalt-PS systems

Once studied the magnetic potential of Co-PS systems, the protective effect of the PS matrix against the oxidation of Co is determined. Magnetic properties of Co strongly depend on the oxidation state and therefore determine the possible applications of this

hybrid systems [6]. For this purpose a multilayer PS is fabricated and infiltrated with Co. Two multilayer configurations were made, as fig.6 shows, one with a negative porosity gradient (Co-PS-n) and other with a positive one (Co-PS-p). These systems are studied by XANES (Fig.7). XANES spectra of both systems show clear differences in oxidation state. Co and Co oxides references are obtained for comparing and fitting the experimental spectra to those of reference materials. From the fitting of the experimental data to references it can be observed that in Co-PS-n, present Co is mainly metallic (close to 90% at.) and the other 10%at. is Co_3O_4 . Besides, studying Co-PS-p it shows to be composed by a mix of Co (40%at.), CoO (50%at.) and Co_3O_4 (10%at). EXAFS data are not enough to extract conclusions about structure of Co deposits.

The elemental concentration profile of these systems was studied by Rutherford Back Scattering (RBS). RBS spectra and elemental profiles of both systems are showed in Fig.8. It can be deduced that in Co-PS-n, Co is uniformly distributed along the multilayer, and the oxygen concentrates mainly near the surface. This means that metallic Co is hosted in deeper zones of the multilayer and Co_3O_4 is concentrated in outer zones of the matrix. For Co-PS-p systems, on one hand Co penetrates to less deep zones, on the other hand the O concentration keeps fairly constant along the multilayer. This should be due both to the presence of O bubbles inside the matrix and the coexistence of a mix of Co oxides.

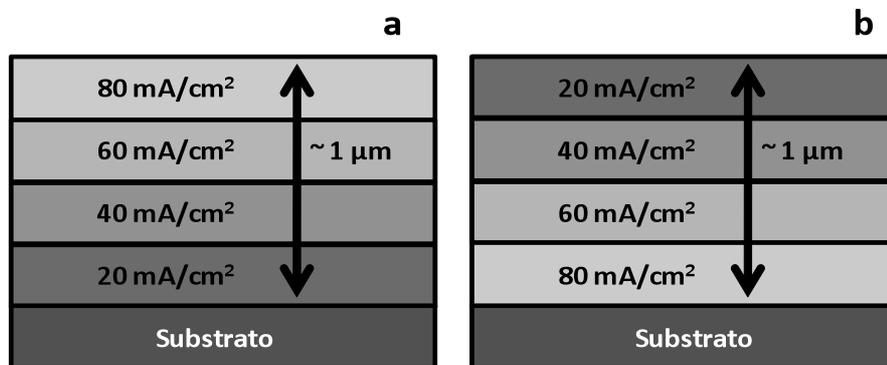


Fig.6. Scheme of the configuration of the PS multilayer's used for the XAS experiment: a) negative gradient configuration, Co-PS-n; b) positive gradient configuration, Co-PS-p..

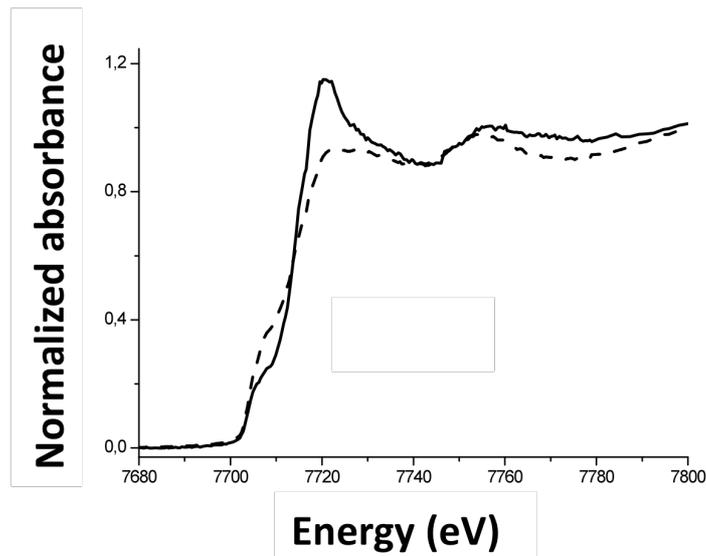


Fig.6. XANES spectra of the Co infiltrated inside Co-PS systems for the two selected multilayer configurations: Co-PS-n (dashed line) and Co-PS-p (continuous line).

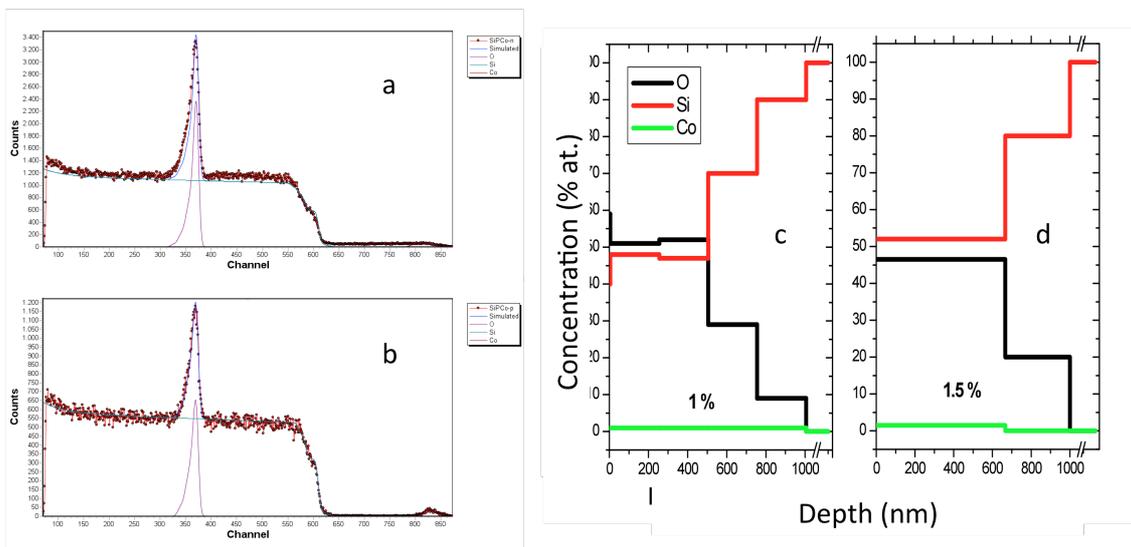


Fig.8. a&b) RBS spectra of Co-PS-n and Co-PS-p, respectively showing experimental data (dots), and simulation (lines). c&d) Elemental concentration profiles of Co-PS-n and Co-PS-p, respectively obtained from simulations in a&b.

2.b. Iron-PS Systems

Resulting from AGFM measures is clear that oxidation and crystalline state of Fe in Fe-PS systems need a deeper characterization. By XAS-synchrotron spectroscopy both features are explored. Fig. 9.a shows the normalized absorbance derivative of a set of Fe oxide references and Fe-PS. In upper side of the figure thermally treated Fe-PS systems are represented. Non-treated Fe-PS has not a well-defined oxidation state as is deduced from this representation [7]. For increasing temperature of the treatments, oxidation state shows evolution to a well-defined one, equivalent to hematite/maghemite. From the oscillations in the EXAFS spectra it has been possible

to obtain the radial distribution function (RDF) from the Fourier transform. For the same set of systems RDF is obtained and show that the non-treated Fe-PS is mainly composed by amorphous Fe and partially crystallized. Moreover, presence of a small portion of amorphous Fe-Si composites is detected [8]. Consecutive thermal treatments in the systems promote the disappearance of Fe-Si composites and the crystallization of the Fe lattice [8, 9]. For highest temperature treatments, structure of the Fe set close to corresponding to hematite/ maghemite.

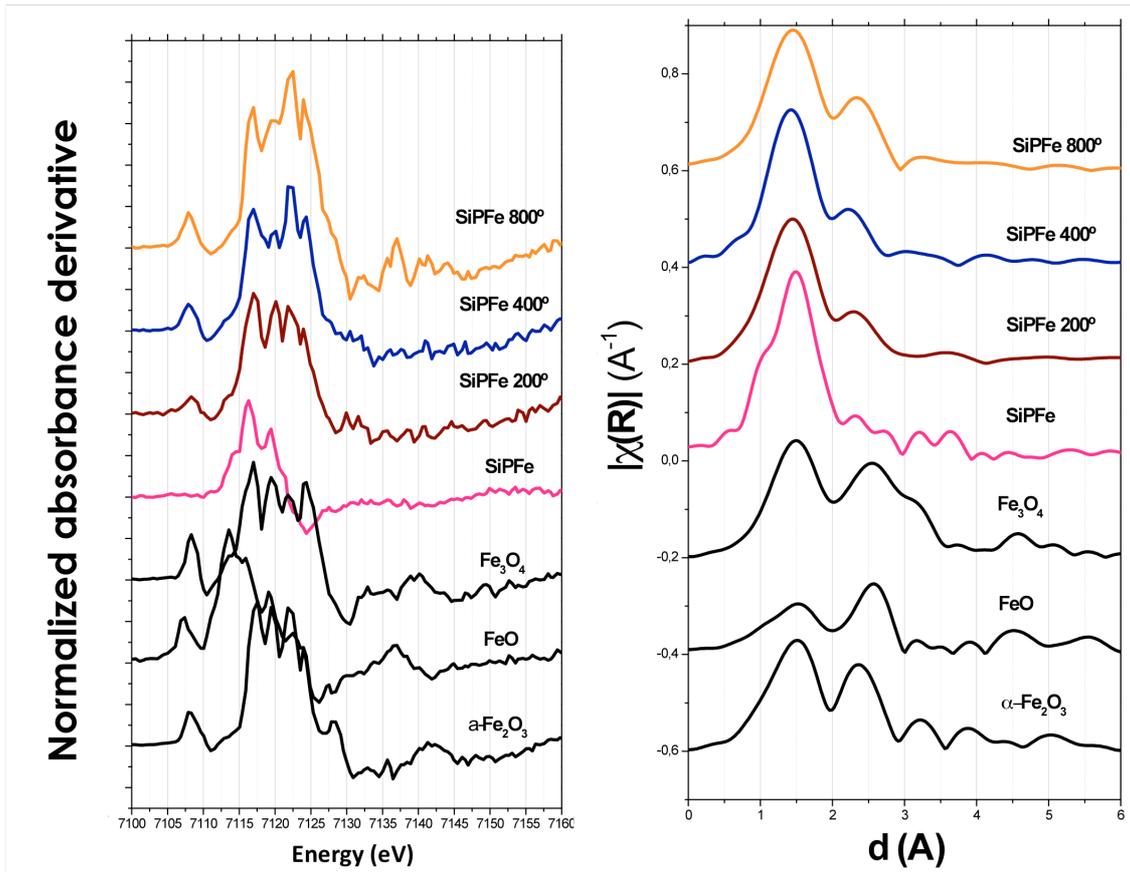


Fig.9. Results from XAS measures of Fe-PS. a) Derivative of the normalized absorbance of the XANES spectra for a set of Fe oxides, non post-treated Fe-PS and thermally treated Fe-PS to increasing temperatures.

Perspectives

The predominant metallic state of Cobalt inside the Co-PS systems has been proved by XANES spectroscopy. Moreover, the possibility of minimize the oxidation of Co in such systems have been pointed out by this technique and RBS.

Once studied the oxidation state and structure of Fe deposit by XAS spectroscopy, the absence of magnetic order in this systems is clearer. Formation of amorphous oxides, even presence of antiferromagnetic oxides explain this observed feature.

As general conclusion, to characterize Metal-PS hybrid systems XAS spectroscopy has probed to be determinant in the study of such diluted systems.

Publications derived from ESRF experiments

Results of these experiments have been published in one PhD thesis: "Hybrid structures of porous silicon-metal/metal oxide: Synthesis, characterization and Biomedical applications" in the Universidad Autónoma de Madrid (Madrid, Spain) by Álvaro Muñoz Noval presented in June 2011.

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