	Experiment title: Oxidation state information of Ag@Co and Pd@Co nanoparticles synthesized in polymeric matrix	**Experiment number**: 25-01-753
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Shifts: 9	**Local contact(s):** Jon Ander GALLASTEGUI MANARICUA <jon_ander.gallastegui_manaricua@esrf.fr> ▶	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*[1]Amanda Alonso (Main Proposer)

[2]Jorge Macanás

[1]Julio Alonso Bastos

[1]Centre GTS, Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain
[2] Chemical Engineering Department, Escola d'Ingeniería de Terrassa, ES Enginyeria, C/Colom, 1, 08222 Terrassa, (Barcelona), Spain

Report:

The development of nanometer sized particles has been intensively pursued because of their technological and scientific importance. Within these materials, Metal Nanoparticles (MNPs) have drawn great interest due to their unusual electrical, optical, magnetic, and chemical properties that are different from those of their bulk counterparts and which arise from the quantum size effects and large surface areas [1] and their multiple applications. The synthesis of metal nanoparticles may be done by various synthetic routes. In some of them, stabilizers play a crucial role in controlling both the size and the shape of nanoparticles [2]. That is why, the incorporation of MNPs into polymeric matrices has drawn a great deal of attention within the last decade.

The MNPs of the platinum group metals (PGM) are widely applied in several applications such as catalysis, water treatment and so on. Furthermore, the design of bimetallic nanocomposite materials with core-shell structure (consisting of a cheap metal core coated with a PGM shell) is of particular interest. For instance, the heterogeneous catalysis is known to occur on the catalyst surface and, consequently, the central part of the catalytic MNPs does not participate in the catalytic process. This means that the central part of the nanocatalytic MNPs could be composed by another inexpensive metal coated with a PGM shell of desired thickness providing the needed catalytic activity [dalton]. Besides, if the core of the core-shell MNPs is made of a ferromagnetic metal, the nanocomposite might be easily recovered from the reaction mixture and reused in the successive reaction cycles. In addition, taking into account the concerns associated with a possible uncontrollable leak of MNPs into the medium under treatment and/or to the environment, the synthesis of ferromagnetic MNPs with desired functionality is even of more interesting [3,4], taking into account the stability added by the polymer matrix.

It important to notice that several parameters affect the MNPs nature: reduction step, polymer functional groups, metal precursor, pH, Tª, environment. Based on those conditions, it is known that size, structure, distribution, oxidation state, etc. can vary. So, the main objective of the performed experiment is to obtain information about the nature of the metals contained in nanoparticles stabilized in polymer matrix versus some parameters. In the case of core-shell nanoparticle, one of the most interesting aspect is to prove and to know exactly the structure of them and the metals proportions which sometimes is difficult to determine by electron microscopy analyses.

For this porpouse, EXAFS/XANES techniques were used. XANES spectra allows us to know atomic organisation and chemical bonding around by spectras comparison (linear combination) with the standards,. EXAFS technique permit to get information about the local environment of an atomic impurity in a matrix of different atomic species by comparison of spectras using Fourier Transform. This knowledge can permit us a better understanding on the material applications and to follow in our research to improve the synthesis and properties on metal nanoparticles [4].

Its important to notice that a range of all possibilities of combinations has been analysed in this experiment as it is is shown in the following matrix of samples (Table 1).

	Ag	Ag@Co	Pd	Pd@Co	Co
Sulfonic membrane					
Sulfonic fiber					
Carboxylic fiber					
Sulfonic resin					
Carboxylic resin					

Table 1. Combination of MNPs and all kind of matrices studied in this experiment

The samples under study, synthesized by our group in their PhD thesis work, were analysed by means of XANES technique at BM25A. Samples consist on Ag-, Co-, Pd-, Ag@Co or Pd@Co-PSNMPs, with different matrix form. In this report, we show the results of some representative samples (Table 2), taking into account that the same procedure was done for the rest of the samples (Table 1). Moreover, it is shown just XANES samples. EXAFS spectras were obtained for some samples but their discussion requier more data analysis, which will published in the following months. All samples were analysed mostly on transmittance mode. Some samples with low absorption signal intensity were performed using a fluorescence detector.

Spectra	Scan (sum)	Metal	MNPs composition Carboxylic fiber
merge3	148-152	Ag	Ag@Co
merge4	32-39	Co	Ag@Co
merge	41-43	Co	Co

Table 2. Representative samples shown in this report.

Some standards are measured in order to calibrate the energies of the edge positions for Ag, Co and Pd in different environments. The molecules used as standards represent the possible oxidation state of the metals of MNPs in salt form, oxides or even nanoparticles. In Table 3 is shown some of the standards analysed which are used in the results shown in this report.

Scan	Metal	Method	Code	Type	Composition	salto (eV)	K-edge (eV)
118	Ag	Transm	Ag foil	std	Ag^0 foil		25514
125	Ag	Transm	P12	std	$Ag(NO_3)$	0,6	25514
7	Co	Transm	Foil Co	std	Co^0 foil	1,2	7709
11	Co	Transm	P6	std	$CoSO_4 \cdot 7H_2O$	0,5	7709
17	Co	Transm	P20	std	Co_3O_4	1,8	7709
84	Pd	Transm	Foil Pd	std	Pd^0 foil	0,5	24350
92	Pd	Transm	P2	std	$Pd(NH_3)_4(NO_3)_2$	0,3	24350

Table 3. Representative metal standards to spectra comparison for the analysis of samples shown in Table 2.

In Figures 1, 2 and 3 are represented the edge energy for different metal standards (the most representative ones) of all metals of our interest (Ag, Co and Pd, respectively) showing the main peak of the each element. The line spectra named as "merge" correspond with the sum of all replicates for the sample (see Table 2). By comparison, we can determine the state of the corresponding metal in each sample.
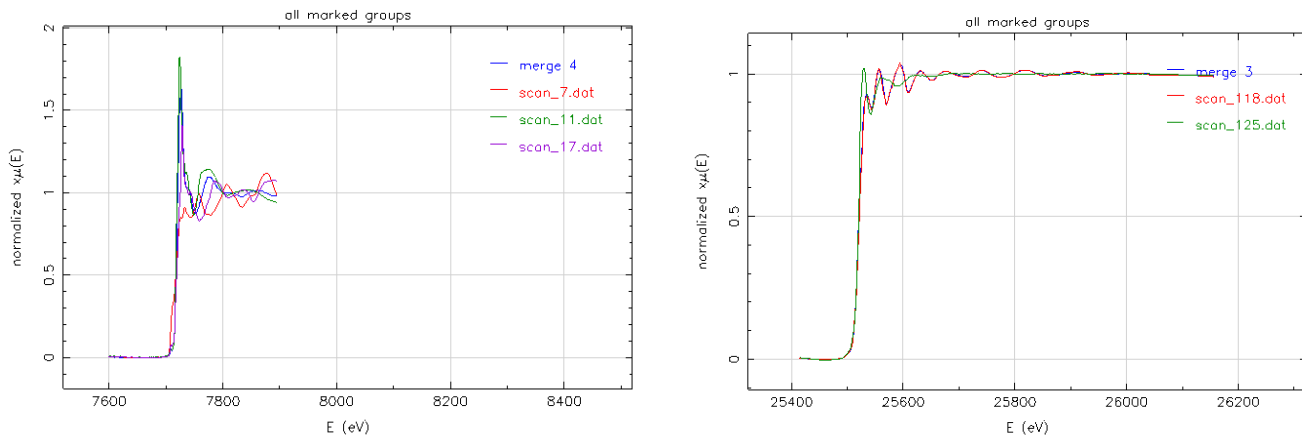
Figure 1. Co (a) and (b) spectra comparion (merge 4 and merge 3, respectively) with Co and Ag standards for Ag@Co carboxylic sample.
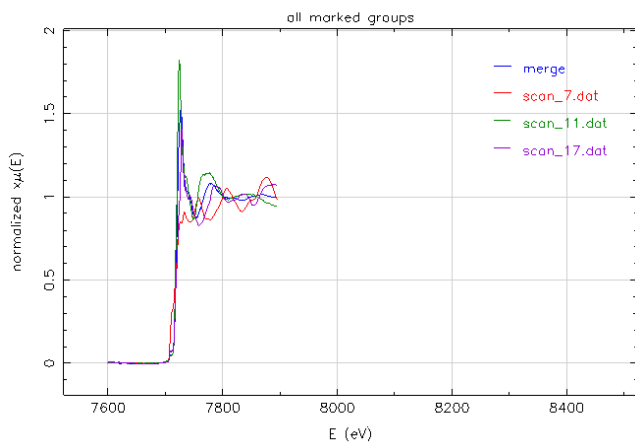

Figure 2. Co spectra comparion (merge) with Co standards for Co-carboxylic sample.

Figure 1a shows that the merge spectra for Co is between Co_3O_4 and $CoSO_4$ elements. It could be because of the Co partial oxidation to +2 state and +3. The similar spectra to Co_3O_4 could be done by the presence of O from the COO$^-$ functional groups of the matrix. It is shown in other samples, analysed in this experiment, based on sulfonic membranes, a similar spectra to $CoSO_4$. In this case, this result is done because of the presence of SO_3^- groups from the matrix.

Figure 1b, based on the sample than we discussed above, clearly shows the presence of Ag^0. With these both results, we can affirm the presence of Ag metal, which is optimal for the applications of these samples, but an oxidation process that takes place during the nanocomposite synthesis method. With the data analysis of this sample we will be able to know the exact composition of Co.

The merge's spectra shown in Figure 2 is pretty similar to the one shown in Figure 1. This result leads to know that the oxidation of the Co could be done during the Co-loading or the following reduction step, and it is not (exclusively) because of the silver loading process (or because of the silver reduction potential).

Further data analysis is it required to do with the goal of knowing the exact Co oxides composition and the environment of all samples (by EXAFS results). Moreover, we will conclude the matrix effect over the final nanocomposite material. The following experiments and characterization are focused on the synthesis of magnetite core MNPs covered by Ag or Pd shell as well as Co-core synthesis surface modified with some ligand molecule to avoid Co oxidation. Besides, different kind of polymeric matrices are under studying for the Pd@Co MNPs synthesis.

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[2] A. Alonso. Environmentally-safe polymer-metal nanocomposites with most favorable distribution of catalytically active and biocide nanoparticles, *Nanocomposites*, ISBN 978-953-308-55-0 (chapter under revision).

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