Fe oxidation state 3D mapping of core-shell nanoparticles.

Torruella P.[1], Arenal R.[2,5], Saghi Z.[3], Yedra L.[1,4], Eljarrat A.[1], de la Peña F.[3], Midgley P. A.[3], Estradé S.[1,4], Peiró F.[1]

[1]LENS–MIND-IN2UB, Dept.d'Electrònica, Universitat de Barcelona. Barcelona - Spain . Email: pautorruellabesa@gmail.com
[2]LMA, Instituto de Nanociencia de Aragon, Universidad de Zaragoza. Zaragoza - Spain.
[3]Department of Materials Science and Metallurgy, University of Cambridge. Cambridge - United Kingdom.
[4]CCiT, Universitat de Barcelona. Barcelona - Spain.
[5]Fundacion ARAID. Zaragoza - Spain.

The aim of this work was to characterize a sample consisting on FeO-Fe3O4 core-shell cubic-shaped nanoparticles. Because of the similarities in the composition and effective atomic number of the core and the shell, high angle annular dark field (HAADF) imaging could not be used to resolve the structure.
As an alternative, EELS fine structure can be used to obtain information on the oxygen and iron oxidation state, thus making it possible to distinguish between FeO and Fe3O4. However, there is the limitation that EELS projects the information of the 3D nanoparticle into a 2D map.
To overcome this limitation there is the possibility to consider EELS spectrum image data-sets as suitable for 3D tomographic reconstruction, not only containing information on the chemical composition of the sample (as in [1]) but also on the oxidation state of Fe at each voxel.
A tilt series of spectrum images (SI) was acquired every 4 degrees in the range from -67 to +69 degrees on a probe corrected FEI Titan, equipped with a XFEG source and operated at 80 kV acceleration voltage. Then the images were treated with Hyperspy to obtain independent spectral components from the iron edge, with could be correlated with the different iron oxides. However, because of sample contamination, only a few of these images were useful. In order to improve the quality of the reconstruction, a new reconstruction algorithm based on the mathematical theory of compressed sensing (CS) was used. CS tomography has recently shown its ability to robustly reconstruct tilt series with as few as 9 projections at adequate angles [2], minimizing the typical artifacts. To our knowledge this is the first time that the CS algorithm has been used to reconstruct an EELS core-loss spectrum image data-set.
The CS reconstructions of two EELS datasets are consistent and show a shell thickness of 9nm around the core. The 3D reconstruction proves a total shell coverage of the core and that there has been no appreciable phase mixing.

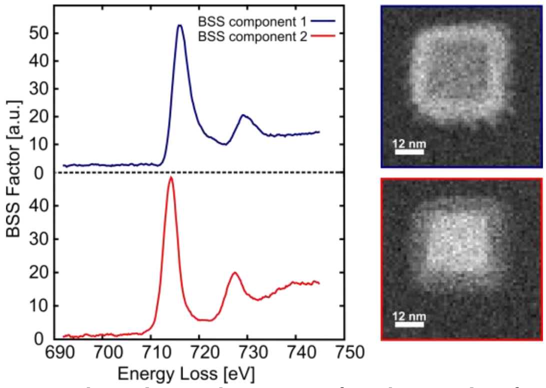

Fig. 1: Obtained spectral components from the iron edge after performing PCA and ICA with Hyperspy.

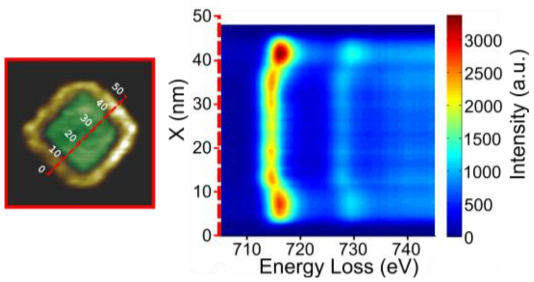

Fig. 2 : Demonstration of the spectrum volume. A spectrum line is extracted from one reconstructed slice.

References

[1] Ll. Yedra et al., *Ulramicroscopy*, **122** (2012), pages 12-18.

[2] Z. Saghi et al., *Nano Letters*, **11** (2011), pages 4666-4673.