# Analyst

## ARTICLE

### Electron Energy-Loss Spectroscopic Tomography of $Fe_xCo_{(3-x)}O_4$ Impregnated $Co_3O_4$ Mesoporous Particles: Unraveling the Chemical Information in Three Dimensions

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Electron energy-loss spectroscopy – spectrum image (EELS-SI) tomography is a powerful tool to investigate the three dimensional chemical configuration in nanostructures. Here, we demonstrate, for the first time, the possibility to characterize the spatial distribution of Fe and Co cations in a complex  $Fe_xCo_{(3-x)}O_4/Co_3O_4$  ordered mesoporous system. This hybrid material is relevant because of the ferrimagnetic/antiferromagnetic coupling and high surface area. We unambiguously prove that the EELS-SI tomography shows a sufficiently high resolution to simultaneously unravel the pore structure and the chemical signal.

### SUPPORTING INFORMATION

In this work, 3D structural and chemical information was recovered from antiferromagnetic (AFM) mesoporous  $Co_3O_4$ nanocast replicas of SiO<sub>2</sub> KIT-6 templates impregnated with iron (III) nitrate precursor to form  $Fe_xCo_{(3-x)}O_4$ . In particular, SiO<sub>2</sub> KIT-6 templates<sup>1,2</sup> have a 3D cubic morphology presenting a double gyroidalmesostructure with channels running along the [100] and [111] directions, defining a 3D pore network, that are then replicated in the  $Co_3O_4$ .

Mesoporous KIT-6 silica was synthesized in acidic conditions using Pluronic P123 copolymer as surfactant and tetraethyl ortosilicate as the silicon source. The hydrothermal treatment was carried out at 90°C for 24 h in a sealed container and the solid obtained was filtered, copiously washed with water and finally calcined at 550°C for 5h to remove the organics. A detailed explanation of the material growth is given elsewhere<sup>3</sup>. For the synthesis of the  $Co_3O_4$  replica, a given amount of KIT-6 silica powder was put in contact with cobalt nitrate dissolved in ethanol. The mixture was stirred for 30 min in a crucible and left for ethanol evaporation overnight. The crucible was then placed in a tubular furnace and the impregnated silica was calcined at 375 °C. The silica host was removed with 30 mL of 2 MNaOH solution at 70 °C under stirring. The resulting mesoporous  $Co_3O_4$  powder was collected after centrifugation and decanted off the supernatant, copiously rinsed in ethanol, and finally dried.

The  $Co_3O_4$  replica was subsequently infiltrated with different amounts of iron (III) nitrate precursor, which underwent conversion into the corresponding oxide product at 375 °C. The Fe(III): $Co_3O_4$ molar ratio was varied in order to achieve different degrees of filling of the  $Co_3O_4$  host:

- 0.6 Fe(III):Co<sub>3</sub>O<sub>4</sub> molar ratio
- 1.2 Fe(III):Co<sub>3</sub>O<sub>4</sub> molar ratio
- 2.4 Fe(III):Co<sub>3</sub>O<sub>4</sub> molar ratio

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The formation of a ferrimagnetic (FiM)  $Fe_xCo_{(3-x)}O_4$  layer is expected on the surface of the channels, as the interest of the material lays in the AFM-FiM coupling between the two transition metal oxides. Previous tomographic results<sup>3</sup> using high angle annular dark field (HAADF) showed the growth of material inside the particles, however, the elemental distribution inside of the sample could not be determined.

The sample with lower iron concentration is chosen to demonstrate the capability of low-voltage EELS-SI tomography to retrieve the elemental distribution inside the sample. This sample is chosen to minimize the thickness of the sample, as it can affect the EELS signal.

The final dataset was obtained by acquiring 36 EELS-SI, with 63x63 spectra each, 2048 channels per spectrum, 200 ms per spectrum and an energy dispersion of 0.2 eV per channel. We employed a FEI Titan Low-Base microscope, working at 80 kV. This microscope is equipped with a Cs probe corrector and an ultrabright X-FEG electron source.

We used Hyperspy, a python based software toolbox for MVA of EELS data<sup>4</sup>, to perform weighted principal component analysis (wPCA). wPCA separates the components of a dataset according to their variance. Based on the supposition that the noise has lower variance than the signal, by keeping the highest variance signals we obtain a noise-reduced dataset. Hyperspy is capable of dealing with the whole dataset, applying the same treatment to all the images. First of all it is necessary to align the dataset in energy. This was done using the oxygen K edge. The GIF Tridiem EELS detector used in the experiment actually consists of two detectors, which, at the low integration times used, could not properly correct for gain. In order to mend this offset, which was measured to be always below 50 counts, the data was separated into two spectral ranges, removing 8 eV around the area where the intensity jump is found. Afterwards, the data were spliced together, re-scaling to avoid the intensity jump. Also, to avoid negative values caused by the noise in order to use Poisonian normalization in the wPCA decomposition, a constant intensity translation was used. For wPCA decomposition, a sparse algorithm was used, masking some of the data. The masked area lies where the intensity jump correction was applied, in the 660-668 eV range. From this analysis, 4 components were chosen to reconstruct a clean dataset.

From this clean dataset, the elemental maps can be extracted. Taking into account the number of images that required elemental extraction, the process was simplified by creating a script for Digital Micrograph which removed the background contribution and integrated the areas under the oxygen, iron and cobalt edges. As a result, individual maps of the three elements for every image could be extracted, plus an image using the background before the oxygen edge. These four signals were successfully reconstructed in 3D using FEI-Inspect 3D and 40 iterations of the SIRT algorithm.

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