3D structure and chemical composition of Co-based nanoparticles casted inside carbon nanotubes

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The internal channel of carbon nanotubes represents a well defined confined space for performing experiments at the nanoscale by filling it with metallic or oxide nanoparticles [1]. In this work, magnetic Co-based nanoparticles (NPs) with homogeneous size have been selectively casted inside the channel of multi-walled carbon nanotubes (CNTs) using a solvothermal synthesis. For such a system, the channel acts as a “nanoreactor” allowing decomposing the metal precursor into metal-based solid nanoparticles [2]. This synthesis method allows one to fill carbon nanotubes with nanoparticles exhibiting quite regular sizes and shapes and generates nanostructures with a high load of Co or Co oxide, up to 60 % in weight, which can be potentially used for magnetic or catalysis purposes. The selective filling of the CNTs by oxide and/or metal nanoparticles is still a challenge and for optimizing the process a precise characterisation of the nanoparticle shape, crystallographic structure and chemical composition is required. To explore these characteristics in the three spatial dimensions, one of the most employed methodologies is a multi-selective approach which consists in combining high resolution TEM imaging, EELS spectroscopy and STEM-HAADF tomography.

The measurements have been performed using a JEOL 2100F TEM-STEM electron microscope equipped with a Cs probe corrector, GIF Tridiem filter and a tomographic set up. The traditional and high-resolution images were acquired in STEM HAADF and BF modes, as well as the acquisition of the tilt series for the tomographic reconstructions.

The first experiments were performed with CNTs having an inner diameter of ca. 50 nm filled with a chain of unique NPs and with CNTs having an inner diameter of ca. 100 nm (Fig. 1A) filled with a chain of pairs of NPs. A detailed analysis of a unique particle shows that it is made of several individual aggregated smaller crystals (Fig. 1B). The “fractured” internal structure of the NPs is confirmed by the analysis of STEM-HAADF images acquired on a typical specimen after a reduction process under an hydrogen flow, where the porous structure between the individual metallic Co crystals composing a NP is made more visible (Fig. 1C).

From a morphological point of view, the analysis of the Co-oxide NPs casted in the channels of the CNTs reveals two typical 2D shapes: hexagonal and rhombohedral volumes. Several EELS analysis performed in the line-scan mode across the NPs shows that the Co:O ratio is larger in the hexagonal NPs (5:1, see Fig. 2A) than it is in the rhombohedral ones (2:1, not shown here). In addition, the magnetization measurements indicate a systematic presence of a magnetic compound (Fig. 2B). As the presence of Co_3O_4 is excluded by XRD analysis and as CoO is antiferromagnetic, the magnetic compound can be assigned to metallic Co. In addition, the presence of oxygen in all the NPs suggests the existence of a core-shell structure.

Analyses were performed on the NPs having a rhombohedral shape on their 2D projections, which represents the majority of the NPs. The tomographic analysis showed that they present a 3D octahedral shape allowing a better understand of the 3D assembling of the nanocrystals within a NP (Figs. 3A, B). More precisely, the shape of individual grains and intergranular spaces indicate a preferential arrangement of the different nanocrystals. This observation was confirmed by the analysis of HR images (Fig. 3C), on which a crystallographic matching can be observed between the structures of two adjacent crystals and suggesting a supercrystal-type arrangement. Within an individual crystal, spatially resolved EELS analysis (not shown here) allowed to definitely conclude on the presence of a Co-CoO core-shell structure. This is in agreement with the XRD results, where a good Rietveld refining of the patterns was obtained by considering the presence of the two phases. For comparison, the XRD patterns and STEM-EELS spectra taken on NPs synthesized outside CNTs showed the presence of a unique single phase, namely CoO, demonstrating the role of CNTs nanoreactors which provide protection against oxidation, as it was already observed in other previous works performed on similar systems [3].

References

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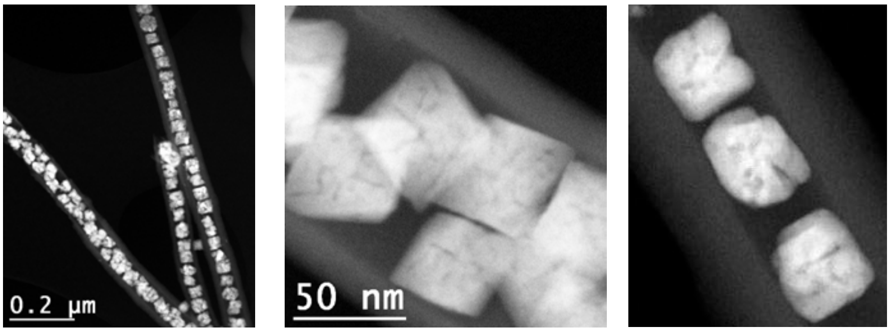
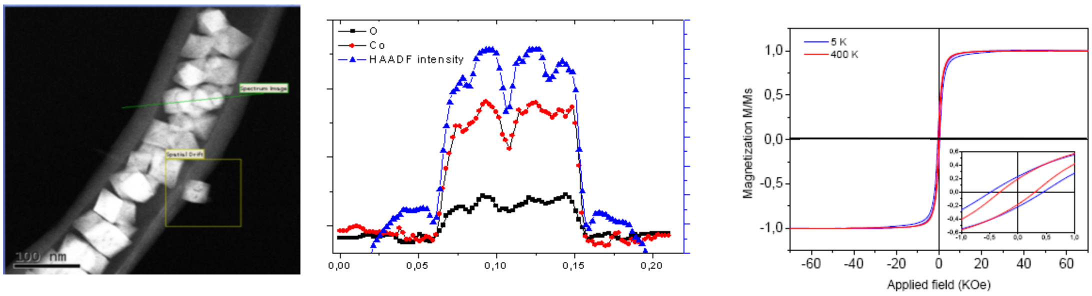


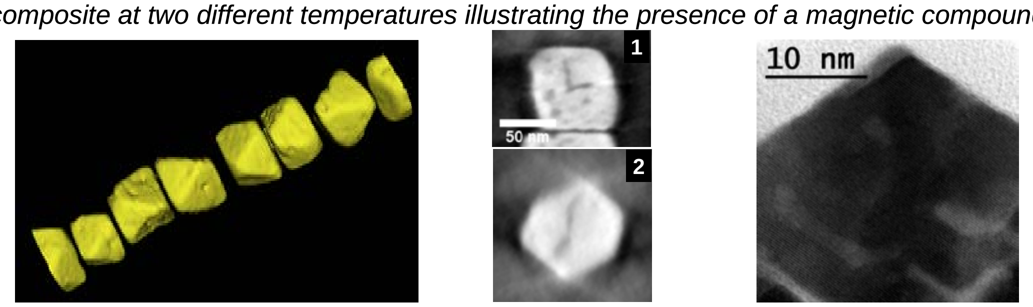
A) B) C)

Figure 1. *A) HAADF-STEM image acquired on three CNT with different diameters used as supports to insert Co-based nanopartcles through a solvothermal synthesis method. B) Zoom on a typical nanoparticle with a rhombohedral 2D shape. C) STEM-HAADF image taken on several Co-based nanoparticles submitted to a reduction process under hydrogen flow at low temperature.*



A) *B)*

Figure 2. *A) EELS analysis performed on three Co-based nanoparticles with a roughly 2D hexagonal shape (left) and O and Co concentration profiles (right) across the considered particles. B) Magnetization loop of the Co-CNT composite at two different temperatures illustrating the presence of a magnetic compound.*



A) *B)* *C)*

Figure 3*. A) 3D tomographic model of several Co-based nanoparticles with octahedral shape casted inside a carbon nanotube. B) Slices extracted from the reconstruction calculated from a tilt series of HAADF, corresponding to the sub-volume of an individual nanoparticle. C) HRTEM image on a typical nanoparticle.*