Effect of the capping agents on cobalt nanoparticles

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Abstract The achievement of high information density and fast recording rate in memory devices crucially depends on the structure of magnetic domains. In this paper cobalt nanoparticles are synthesised using two capping agents (TOA, ODA) and two different preparation routes: thermal decomposition (TD) and Solvated Metal Atom Dispersion (SMAD). The interaction of capping agents with free metal clusters and their influence on Co nanoparticles size, atomic structure and oxidation state is investigated by means of X-ray diffraction and X-ray absorption spectroscopy.

1. Introduction

Cobalt exhibits a peculiar magnetic behaviour related to complex structural properties. Bulk Co is ferromagnetic while nanoparticles (np) below a critical size are superparamagnetic. Bulk metal cobalt, as powder and foil, exhibits a complex structure constituted of a mixture of hexagonal close packing (hcp) and cubic close packing (ccp) phases. Nanostructured cobalt often presents a cubic close packing (ccp) of atoms, but it is also possible that both ccp and hcp arrangements are present in the same sample and that the compact sequences of atomic layers are distorted by stacking faults [1]. The application of cobalt nanoparticles in high density and fast recording memory devices depends on the availability of a synthesis route enabling a strict control on various structural features such as average size, size distribution, close packing sequences and morphology. A crucial role is played by the capping agent, necessary to prevent merging and oxidation of the Co np [2]. In this paper we present the results obtained in the synthesis of Co np using trioctylammine, TOA, and octadecylammine, ODA, as capping agents and two different routes: thermal decomposition (TD) [3] [4] and solvated metal atom dispersion (SMAD) [5] [6]. In the case of SMAD, the metal clusters are directly obtained in the vapour phase and are subsequently coated by the capping molecules, while in TD a direct interaction between Co and capping molecules takes place during the growth process. The structural characterization carried out by X-ray diffraction and X-ray absorption demonstrates the relevance of the capping agent in determining the structural-morphological properties of Co np.

2. Experimental

The syntheses of Co nanoparticles were carried out using commercially available reagents. Metal cobalt (99.9%) and dicobalt octacarbonyl were used as precursors; trioctylammine (TOA) and octadecylammine (ODA) were used as capping agents. The SMAD procedure involved: (a) deposition of an organic solvent (toluene) on the walls of the reactor cooled at 77 K; (b) vaporization of the cobalt (about 200 mg) under Ar atmosphere (about 10⁻³ mbar); (c) injection of the capping agent solution in the reactor; (d) warming to room temperature. The TD route was carried out through the
following steps: (a) 1 g of Co$_2$(CO)$_8$ was put into 50 mL of solvent (toluene or mesitylene) at boiling temperature under argon flow; (b) after 20 minutes TOA or ODA was added; (c) the resulting solution was kept for 2 hours under stirring. The products of SMAD or TD were then dried by a rotary evaporator under vacuum at 350 K, so obtaining powder samples.

### Table 1. Investigated samples. Synthesis route, solvent, capping agent and number of Co atoms per capping molecule are specified.

| sample | synthesis | solvent   | capping agent | Co atoms per capping molecule |
|-------|-----------|-----------|---------------|------------------------------|
| 1     | TD        | toluene   | TOA           | 1000                         |
| 2     | TD        | mesitylene| ODA           | 180                          |
| 3     | TD        | mesitylene| ODA           | 1000                         |
| 4     | SMAD      | toluene   | TOA           | 1400                         |

High resolution X-ray diffraction (XRD) patterns were recorded at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble) in transmission geometry with incident wavelength 0.4 Å. The samples were loaded in 0.6 mm glass capillaries. The diffracted radiation was measured in the 2°-38° 2θ range. A reference Co powder pattern was also collected in the same conditions. The data analysis was carried out with GSAS [7]. The XAS data at the Co K-edge (7.7 keV) were collected at the BM26 beamline of the ESRF and at the XAFS beamline of Elettra (Trieste). In both experiments the spectra were measured at 25 K in transmission geometry, using N$_2$/Ar gas ionization chambers. The analysis of the EXAFS data was carried out using GNXAS [8].

### 3. Result and Discussion

The XRD patterns, reported in Figure 1, show evidence of ccp and hcp sequences and, with the exception of sample 2, also of cobalt oxide phase, which is easily identified by the peak at about 9.4°. According to a qualitative XRD data analysis, the samples containing TOA are more oxidized than those prepared with ODA and the SMAD sample 4 exhibits a prevalent hcp arrangement. GSAS allows the quantitative analysis of the crystalline phases present in a powder sample; in this case, it was used to determine the relative amount of hcp, ccp and cobalt(II) oxide. An average particle size was also obtained, although an explicit distribution function was not calculated. The results are summarized in Table 2. By inspection of Figure 1, it is possible to notice that the GSAS fittings are not satisfactory, mainly because the stacking faults disorder, affecting the peak intensity ratios, widths and angular positions [9], is not suitably modelled. It is also possible that non-crystallographic structures, such as icosahedral and decahedral clusters, are present to a significant extent. Actually, procedures allowing to thoroughly model the XRD patterns of Co nanoparticles are under way.

![Figure 1. XRD experimental, calculated and reference patterns, shifted for clarity.](image-url)
Table 2. Particle size and percentage of hexagonal, cubic and oxide phases obtained by fitting XRD data with GSAS.

|        | hcp % | d_{hcp} [nm] | ccp % | d_{ccp} [nm] | CoO % |
|--------|-------|--------------|-------|--------------|-------|
| Co powder | 65    | 265          | 35    | 265          | -     |
| 1      | 44    | 10           | 15    | 26           | 40    |
| 2      | 52    | 17           | 48    | 25           | -     |
| 3      | 50    | 5            | 40    | 11           | 10    |
| 4      | 58    | 10           | 9     | 18           | 32    |

In agreement with the XRD analysis, a satisfactory fitting of the EXAFS data could only be obtained taking into account the presence of both hcp and ccp clusters. In the R-space, the shells in the range 3.5-5 Å allow to distinguish the two metal arrangements (Figures 2-3). To fit cobalt foil and powder, the coordination numbers were fixed to the bulk values; to calculate the EXAFS spectra of the samples, we refined for each phase: a) the first neighbour distance, to which the farther distances are geometrically related; b) the Debye-Waller factor of the first shell; c) the relative amount and the average size, so that the coordination numbers were determined as a function of the average size, using the Borowski’s equation [10]. The limited number of the refined parameters, compared to the modeled data range, enabled a robust fitting and reliable results, since all the interatomic distances and disorder factors were expressed as a function of the first shell. Figures 2-3 show the results of the fitting in R-space, and Table 3 summarizes the refined parameters. Sample 1 was not analysed using this approach, since its spectrum (Figure 2) shows definite and large contributions from next neighbours CoO shells. Therefore, the results relative to the hcp-ccp analysis would not be reliable. On the contrary, sample 4 was analysed because the next oxide shells are absent.

By inspection of Table 3, it can be noticed that the SMAD sample 4, in agreement with the literature [1,11], is characterized by larger hcp clusters and smaller ccp ones. Actually, in the SMAD route already grown free clusters are coated by the capping agent, while in the TD route the Co-capping molecule interaction takes place during the cluster growth. This observation suggests that the capping agent can influence the growth process and in particular the close packing sequences.

Figure 2. Fourier transform magnitude, shifted for clarity, of calculated and experimental signal of samples.

Figure 3. Two data and hcp and ccp components, shifted for clarity, of a sample fit. The FT is uncorrected for phase shift.
Table 3. Parameters refined in EXAFS best fits.

| R$_1$ [Å] | $\sigma^2$ [Å$^2$] | % hcp | d$_{hcp}$ [nm] | % ccp | d$_{ccp}$ [nm] |
|------------|-----------------|-------|---------------|-------|---------------|
| Co foil    | 2.49            | 0.004 | 55            | -     | 45            |
| Co powder  | 2.49            | 0.003 | 54            | -     | 46            |
| 2          | 2.50            | 0.004 | 59            | 4     | 41            | 5               |
| 3          | 2.49            | 0.004 | 60            | 3     | 40            | 5               |
| 4          | 2.50            | 0.005 | 54            | 8     | 46            | 5               |

The results from XRD and EXAFS do not agree as concerns the relative amount of hcp and ccp phases. This difference should be ascribed to various reasons: in particular, it was already noticed that the GSAS Rietveld refinement is not well suited to analyze the XRD patterns of cobalt nanoclusters, due to the lack of an effective procedure to model stacking faults; moreover, XRD is sensitive to long-range interactions, while EXAFS is a nearsighted technique, sensitive to the short range neighbourhood of the absorber. Therefore, even with a satisfactory modelling of the XRD patterns, a discrepancy between the EXAFS and XRD analysis of hcp and ccp sequences can be envisaged.

According to the XRD results, it is possible to conclude that ODA protects the Co nanoparticles from oxidation better than TOA; further studies involving X-ray photoelectron spectroscopy are underway to elucidate this difference. EXAFS substantially confirms that samples 1 and 4 show a remarkable amount of cobalt oxide.

To the best of our knowledge, this paper represents the first attempt to study by EXAFS the close packing of atomic layers in metals. The Co third and fourth coordination shells are to this concern well suited due to their different shape in correspondence to hcp and ccp sequences. The analysis relative to sample 4, showing that the hcp clusters are larger than the ccp ones, is in agreement with several literature data reporting that very small Co clusters prefer the ccp packing. The opposite behaviour of samples 2 and 3 can be explained by the direct interaction of cobalt with the capping agent during the cluster growth.

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