Poster Presentation

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Exotic structures and morphology control in nanomaterials: PDF insights

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The elaboration of simple metallic nanoparticles from organometallic precursors in solution chemistry is routine since years. Soon the next step was control of chemical order in bimetallic systems (typically for the optimization of magnetic or catalytic properties). Another challenge was the growth of extended objects of controlled size and shape (e.g. rods, stars, urchins...) and their eventual self organization in superstructures.
A limited set of tools was available, and could be operated on a narrow practical range: precursors, solvent, reducing and stabilizing agents. The stabilizing ligands are essential for size control but must allow the delicate structural adjustments leading to the final form.
Remarkable achievements could be obtained but the processes at work have not been so much explored, and regarding the structural side, difficulties pile up: since the objects of interest are nanosized and often affected by strong structural disorder, classic XRD is practically blind. EXAFS is essential to solve the chemical ordering issue, but its limited range makes the technique of limited interest to evidence the atomic structure. Moreover, the fine tuning of growth control required for morphology control makes in many cases the material metastable and difficult or impossible to characterize using TEM.
PDF analysis is in practice the technique of interest to evidence the structure in relatively safe conditions.
These different techniques have been applied to different sophisticated nanomaterials of high catalytic and magnetic interest and PDF revealed unexpected structural organizations at early stages of synthesis, however obviously related to their very final shapes and properties. A well defined structure close to the one observed in the beta phase of manganese was found ubiquitous in very small metallic particles but highly difficult to observe by TEM [1]. Another structural signature could be observed for different magnetic nanoparticles with sizes ranging from 4.6 nm to 15 nm in size [2,3], so relatively large. However coherence length from PDF was found much shorter, and the structure remained undefined until very recent new measurements pointing to metallic glasses. The repeated observation of such exotic structures at very early stages of syntheses leading to extended highly organized objects is actually very puzzling. The correlation between synthesis conditions and the onset of these specific organizations, and the transition to objects of higher symmetry and larger dimensions (e.g. supercrystals, nanowires...) are still to explore. Current results and recent advances will be presented.
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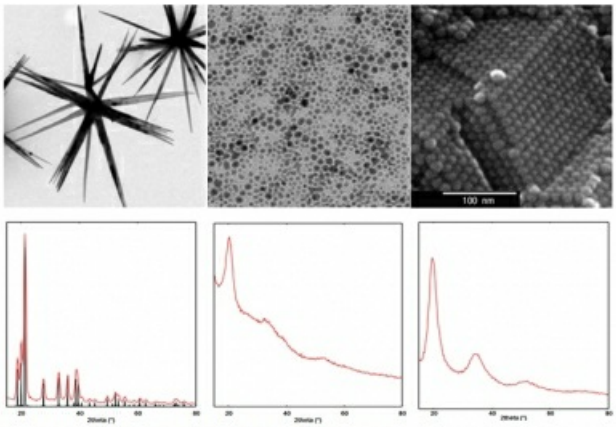

Shape of cobalt nanoparticles depending on the addition rate of cobalt precursor to stabilizing ligands (but similar reducing conditions) - left: fast addition, right: slow addition.

Supercrystal of self-organized FeCo nanoparticles.

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