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Assembly and structure of Ni/NiO core–shell nanoparticles

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ABSTRACT

In this work it is reported a detailed investigation of the structure in Ni/NiO core–shell nanoparticles (NP). An experimental set-up was realized for the preparation and the study of pre-formed NP films. NiO shell was obtained with controlled dosing of O_2 gas in the experimental system. A comparison of HR-TEM experimental images with theoretical simulations shows that the Ni NP core has a regular multitwinned icosahedral structure, composed with single crystal tetrahedra with (1 1 1) faces. NiO phase is clearly observed forming islands on the NP surface. In order to better investigate the oxide shell, the exit wave reconstruction method was applied to the images. It was found evidence of oxide island formation with direct or opposite (twinned) stacking on Ni (1 1 1) surfaces.

1. Introduction

Fabrication of metal–metal oxide core–shell nanoparticles (NP) is an important research area, as it presents different and fascinating possibilities, like shell-driven magnetization stability [1–3] and improving contrast to enhance magnetic resonance imaging [4]. The magnetization stability can be achieved through exchange coupling at the interface between the Ferromagnetic (FM) metallic core and the antiferromagnetic (AF) oxide shell, giving rise to the exchange bias effect [2,3]. This effect is in principle tunable through control of structure, shape and size of the NP. Realization of size and shape selected NP combined with a thorough spectroscopy and microscopy analysis is therefore of fundamental importance. For these reasons, different methods for producing NP assemblies have been developed during the last years: chemical synthesis [4–6], lithography-based, self-assembling [7,8], atom deposition and thermally assisted precipitation in matrix [9,10]. One of the most established techniques is deposition of preformed metal NP's onto surfaces with gas aggregation sources, which allowed a systematic study of the properties of Fe and Co granular films [11–15]. More recently, this technique has been extended to the realization and study of Ni NP films [16,17], giving insights into the NP shape, films morphology and collective magnetic phenomena due to interparticle interactions.

Another relevant aspect is the fact that the fcc metal NP can be obtained in single or poly-crystalline form, depending on their rate of cooling into solid phase [18–24]. In particular, multi twinning during crystallization can give rise to a variety of shapes, like for instance decahedral, icosahedral, cuboctathedral and body centred tetragonal orthorhombic structures in Au NP [20–23], while in the case of FePt [23] and Ni [25,26], McKay [18] icosahedral NP were observed. Molecular dynamics simulation on Ni demonstrated that upon rapid cooling from liquid phase the icosahedral shape is favoured, while fcc and hcp single crystal phases can be obtained at slower cooling rates [24]. The formation of NP in form multi-twinned nanocrystals, can have important consequences on formation of oxides at their surfaces; in fact, the presence of increasing strain with distance of lattice planes from the centre of NP and vacancies at the facet edges can play an important role in nucleation and island formation of the oxide species. The phase and stability of the oxide shell is therefore strongly dependent on the structural properties of the NP core. Co-deposition of different metals in vapour phase and controlled oxidation allowed the possibility of obtaining Ni/NiO and Ni/MgO core–shell NP, that were investigated in details with in situ X-ray photoelectron spectroscopy (XPS) and high resolution and energy filtered-transmission microscopy (HR-TEM and EF-TEM), obtaining information on the NP shape, and on the stability and morphology of the shell oxide phases [25,26]. In this work, we concentrate on the structure of Ni core, and on the details of oxide formation by making use of HR-TEM, using in particular the exit wave reconstruction (EWR) method for image analysis [27,28], which allows a software correction of the lens aberrations and therefore a more direct determination of atoms locations as compared with conventional techniques.

2. Experimental

The Ni NP were generated and characterized in an experimental system with three interconnected vacuum chambers. The first

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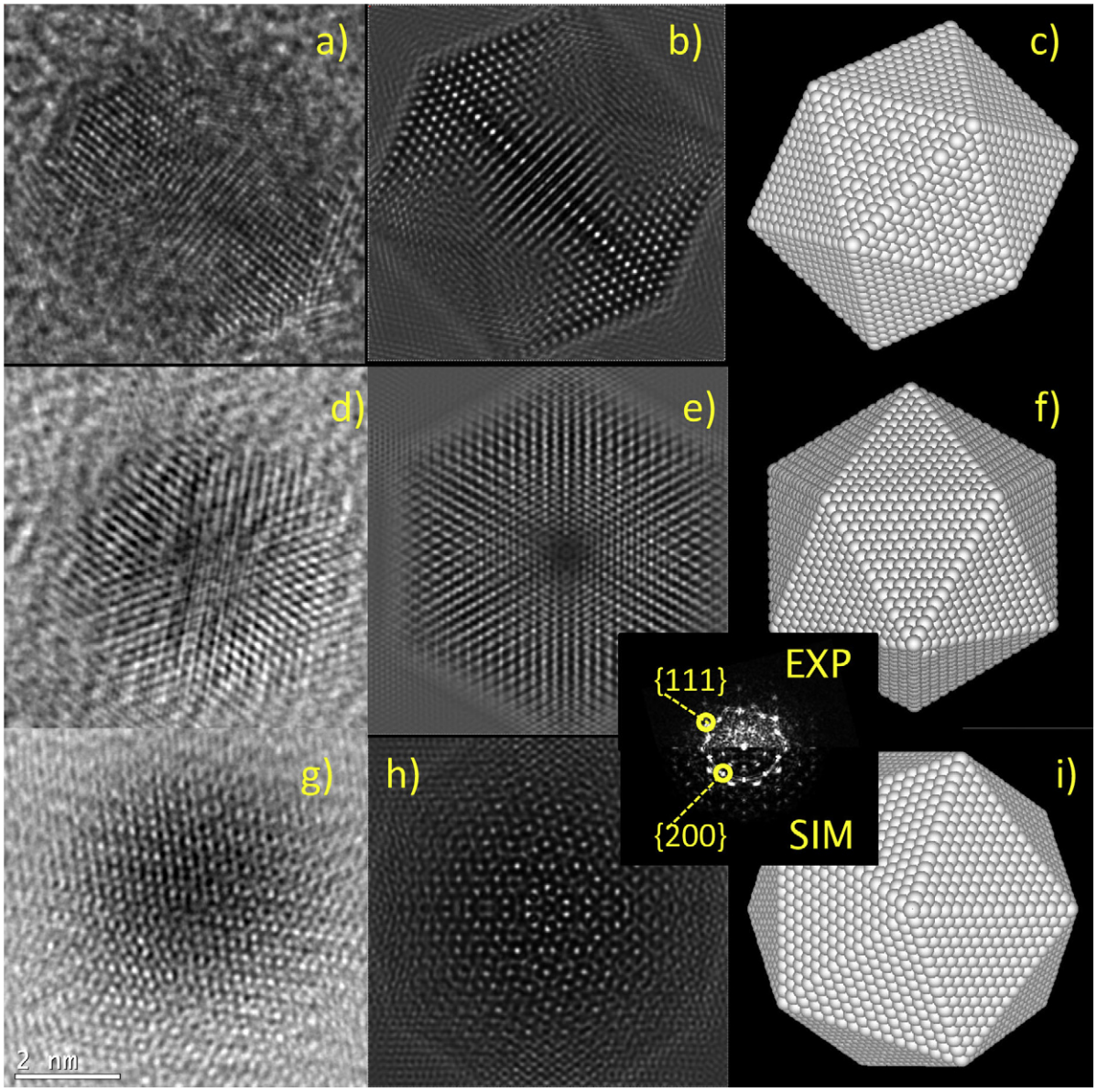

Fig. 1. (a), (d) and (g) Series of three experimental HR-TEM images taken from Ni NP with different orientations. (b), (e) and (h) Corresponding simulated HR-TEM images. (c), (f) and (i) Atomistic model of McKay icosahedron accordingly oriented. Inset: the peculiar pentagonal diffractogram corresponding to the orientation (g). Simulation and experiment show a very good agreement.

chamber is equipped with a NP source (NC200U, Oxford Applied Research) and a Quadrupole Mass Filter (QMF). In the source, Ni was evaporated by magnetron sputtering, and it was condensed into NP by an inert gas carrier (in our case, Ar). The charged NP in the produced beam were mass-selected by the QMF, and entered in the deposition chamber, where they could be deposited on a substrate. Deposition occurred in O_2 atmosphere (which was let in by a leak valve). The NP deposition rate was monitored with a quartz microbalance. We always checked the size distribution of the deposited particles with scanning electron microscopy (SEM) [17] and with TEM. After deposition, the samples could be transferred to the third chamber, for in situ XPS. During the experiments reported in this work, most of the samples were produced with a NP beam generated with a magnetron discharge power $P = 55$ W, and Ar flow $f \approx 80$ sccm. In these conditions we could obtain Ni NP with a linear size distribution between 3 and 8 nm, as measured from the QMF and directly verified looking at the TEM images. The typical size distributions have a width $\sigma = 1.2$ nm over an average diameter $\langle d \rangle = 5.5$ nm, as obtained by SEM images. Ni NP were either deposited in O_2 atmosphere or in base vacuum. Typical O_2 pressure values chosen for the Ni–O_2 deposition were $p_{O_2} = 1 \times 10^{-6}$ mbar. The substrates used during deposition were either highly oriented pyrolitic graphite (for some of the XPS analysis, chosen for its inertness) or carbon coated Cu grids for TEM. After the preparation and the XPS experiments, the samples were transferred in N_2 atmosphere. The TEM experiments were performed using a JEOL JEM-2200FS working at 200 keV and equipped with Schottky Field Emission Gun (SFEG) and Ω-filter for energy loss analysis. The instrument has an objective lens spherical aberration coefficient of 0.5 mm, permitting to obtain a point to point resolution of 0.19 nm. In order to remove delocalization effects focal series of 20 images have been acquired and processed with IWFR [27] software. The series were acquired for focal step between 10 and 15 nm starting form close to Scherrer conditions. The exact defoci have been determined for each image by detailed semi-automatic fitting of the amorphous rings within STEM CELL [29].