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Structure and Phase Analyses of Nanoparticles using Combined Analysis of TEM scattering patterns

Boullay P.[1], Lutterotti L.[2], Chateigner D.[1]

[1]CRISMAT, CNRS UMR 6508, CAEN, France, [2]Department of Industrial Engineering, University of Trento, TRENTO, Italy

Email of the presenting author: philippe.boullay@ensicaen.fr

The development of materials science at the nanoscale questions the characterization techniques on their ability to describe small objects, either individually or as large assemblies. Transmission electron microscopy (TEM) appears as one of the techniques able to provide quantitative results using imaging, spectroscopic or diffraction methods. Aiming the structure, size and phase analysis of nanoparticles, a TEM approach would ideally combine these methods at the nanometer scale but analyses on individual particles are not ideal if one wants a representative statistical analysis.

Another approach would be based on the quantitative analysis of electron diffraction intensities similarly to what is done in X-ray Powder Diffraction (XPD). Selected Area Electron Diffraction patterns of an assembly of nanoparticles exhibit ring patterns analogous to those from XPD, hereafter called Electron Powder Diffraction patterns (EPD). Phase identification and structure refinement of such powder diffraction patterns can be reached by search-match routines followed by Rietveld analysis [1-2] or PDF (Pair Distribution Function) [3-4] methods. Besides the phase identification and structure refinement issue, we will show that the average size and shape of the crystallites (Fig. 1) as well as quantitative texture analysis (Fig. 2) can be obtained from EPD [5]. Using Rietveld analysis within the Combined Analysis methodology, almost routine analyses of nanoparticles in the form of powders and thin films can be achieved. Complementary measurements can be added, for instance Energy Dispersive X-ray Spectroscopy in order to constrain the refinements in cases for which elemental variations are of matter, and PDF, in order to quantify even amorphous structures [3,6].

This reciprocal space approach allows a fast access to statistically meaningful information about the average size and shape of an assembly of nanoparticles (agglomerated or not). It is thus very complementary to direct imaging of isolated nanoparticles. Fast and insensitive to sample drift, this approach shall be advantageously used for gaining quantitative information from in-situ environmental studies of dynamic processes involving nanoparticles.

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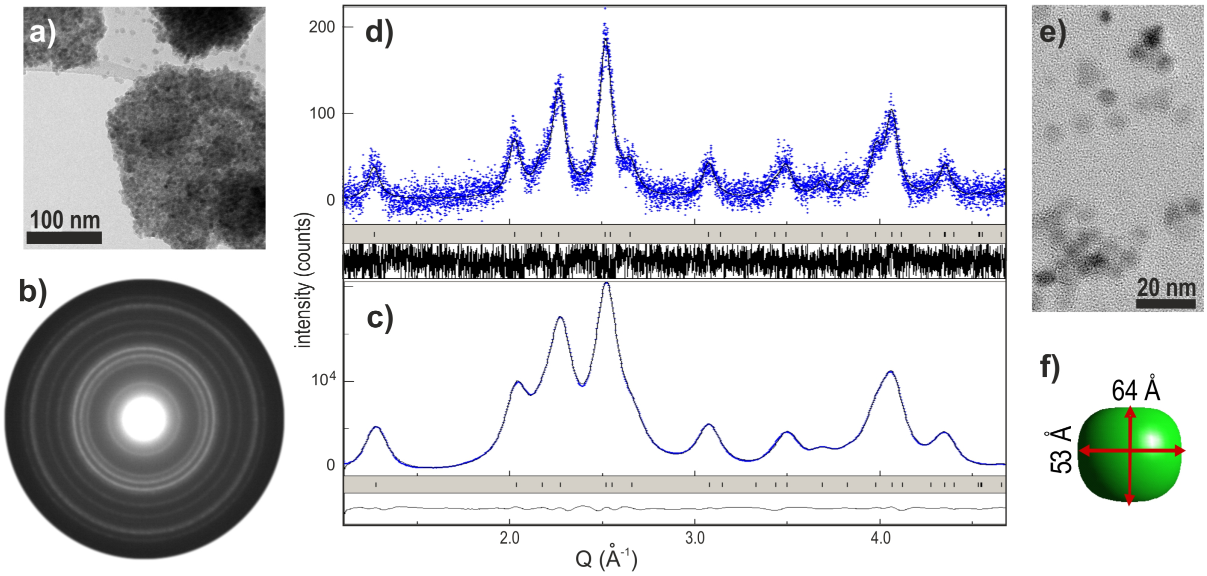

Fig. 1: a) Mn3O4 nanoparticle's aggregates. Associated EPD in b) and 1D plot in c) representing the full integration along the Debye rings. The profile is fitted (Rw=2.06% and RBragg=1.55%) considering the sample contribution and compared with XPD in d). e) TEM bright field image of isolated particles. f) Average size and shape of the Mn3O4 nanoparticles.

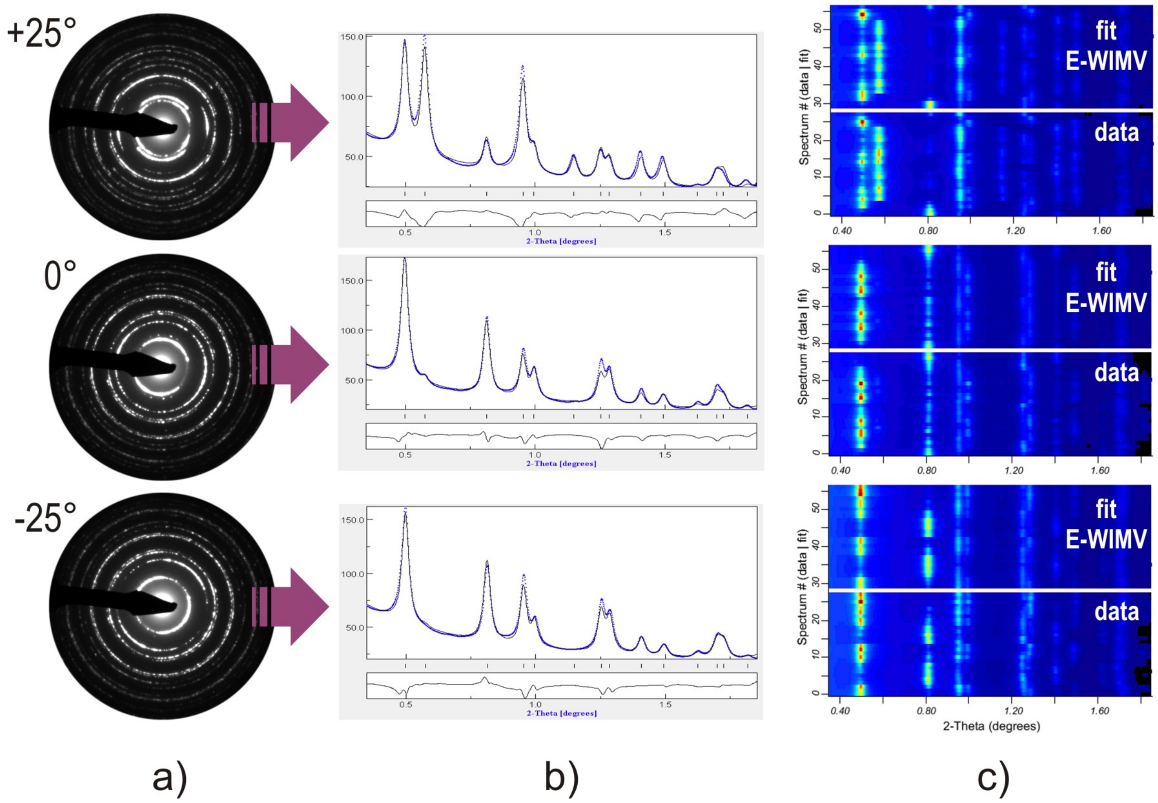

Fig. 2: a) EPD for 2 extreme and 0° sample tilts obtained on a Pt thin film deposited on a Si single crystal substrate. b) corresponding 1D patterns using Dh = 10° and for h = 180°. c) 2D plots for the 35 1D-patterns of each 2D pattern in a). Experimental data (bottom) and fits (up) are represented, Pawley pattern matching. Square root intensity scales.