Analysis of individual nanostructures : clusters, small particles and nanotubes

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The coupling of a narrow probe of high-energy electrons (100 keV) in a STEM (Scanning Transmission Electron Microscope) instrument with an efficient PEELS (Parallel Electron Energy Loss Spectroscopy) system is quite well suited to the exploration of the structural, chemical and electronic properties of individual nanostructures and interfaces [1], see also M. Tencé et al., these Proceedings. Major technical improvements have opened the field of spectrum-imaging and chrono-spectroscopy [2]. As a consequence, spatially resolved analysis at the subnanometer level has become currently accessible. Furthermore the high rate of EELS spectrum acquisition (up to 100 Hz) is a prerequisite for performing dynamic studies.

These possibilities have been used for mapping the composition of nano-objects, to the limit of single-atom identification [3]. When considering characteristic core edges, specific processing routines [4] have been developed and tested on different types of nanoparticles of mixed composition. In figure 1 the well-established background subtraction technique for each pixel has been used, while in figure 2 each B-K edge recorded in a spectrum-image sequence has been fitted via a NNLS fit to several reference B-K edges [5]. In this latter case, one maps bonding rather than elements, because the detailed profile of the EELS fine structures can be associated to the unoccupied electron density of states, and therefore to the local environment and bonding properties at specific atomic sites. In the low energy-loss range from a few eV to a few tens of eV, the behavior of the electron gas (for example, its response to an external perturbation, either as collective or individual excitations) is also modified by the presence of surfaces, the role of which becomes dominant for nanostructures. The interaction of the incident electron beam with the involved bulk and surface plasmon modes can be monitored in a typical near-field approach, providing direct access to the local dielectric properties of a nano-object. Figure 3 shows an example extracted out of a study of the band gap variation in individual BN nanotubes with different diameters and numbers of walls [6].

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These new possibilities can be used for investigating local electronic and structural properties in individual nano-objects of simple geometries (nanotubes, nanowires, onions, nanobubbles, nanoparticles, quantum dots...), as well as in interfaces, multilayers and tunnel junctions. The field of present and potential applications therefore spans a wide range of scientific domains, encompassing not only electronics, photonics, magnetic systems, catalysts, but also more original situations in mineralogy, environment, biomineralization issues.

[1] C. Colliex and O. Stéphan, in *Handbook of Microscopy for Nanotechnology*, Yao Nan and Wang Zhong L., (Eds.) Kluwer Academic Publishers (2005) pp. 653-681
[2] C. Jeanguillaume and C. Colliex, Ultramicroscopy 28 (1989) 252
[3] K. Suenaga et al. Science 290 (2000) 2280
[4] M. Tencé et al., Ultramicroscopy 58 (1995) 42
[5] O. Stéphan, EMAG Oxford 2002, IoP. Conf. Ser. 179 (2003) 437
[6] R. Arenal de la Concha et al., submitted (2005)

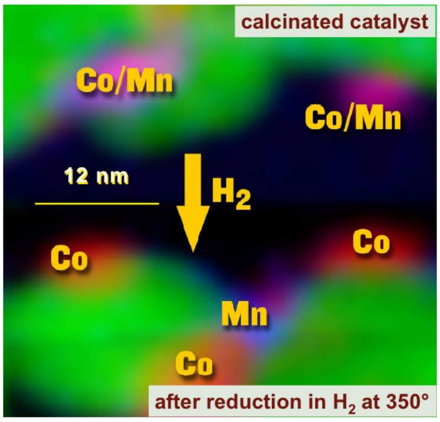

Figure 1 : Montage of two STEM-EELS chemical maps of Ti (green), Co (red) and Mn (blue) showing the mixing of Co and Mn phases before and their segregation after a H_2 reduction treatment of Co based catalyst nanoparticles dispersed on TiO_2 surfaces (courtesy F. Morales et al., PCCP 7 (2005) 568).

Figure 3 (below) : Low energy loss spectra recorded on (or at the surface of) individual BN nanotubes with 1, 2 or 3 walls (see corresponding BF images), compared with dielectric coefficients of hex BN, in order to extract band gap values.

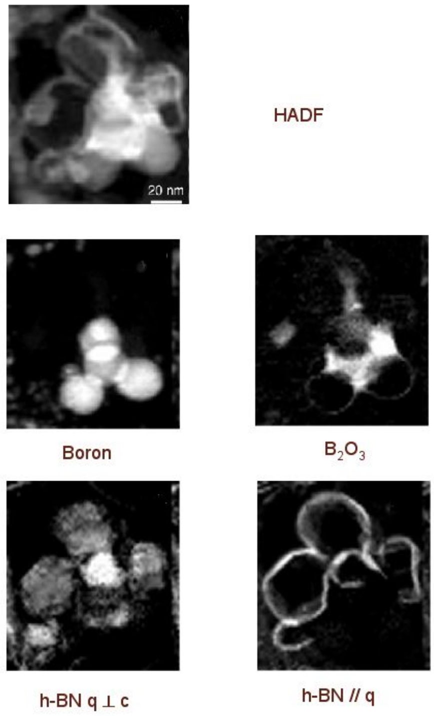

Figure 2 : Chemical maps (compared with the HADF image) of an ensemble of nanoparticles collected during the preparation of BN nanotubes. The method uses NNLS fits with reference B K edges for different compounds (B, B_2O_3, hex BN of different orientations).