

ELNES: A promising method for structural and chemical nanoparticle analysis?

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Nanoparticles are of growing importance in material science and in industry, since they are present in some products or production processes, for example [1]. In order to understand and to control the fabrication process and the properties of nanoparticles, their structural and chemical characterization is essential. Up to now it is still a challenge to find the right method to obtain a complete set of data on a specific type of nanoparticles. A method which has been proven to be very successful in providing structural *and* chemical information on the nanometer scale is TEM in combination with Electron Energy Loss Spectroscopy (EELS). Especially the Energy Loss Near Edge Structure (ELNES) contains both, since it reflects the electronic structure of empty states in the conduction band, and is thus a very promising method for nanoparticle characterization. Up to recently ELNES was limited to 0.7eV in Field Emission Gun (FEG)-TEMs [2], while X-ray Absorption Near Edge Spectroscopy (XANES) performed using Synchrotron Radiation Sources was the best analytical method to probe the near edge fine structure with an energy resolution below 0.2 eV [3]. Unfortunately the spatial resolution in XAFS is at best around one micron, which is far too large to get information on individual nanoparticles. Thanks to the introduction of monochromators, high resolution energy filters and Cs probe correctors into the FEG-TEMs, the same energy resolution with far better spatial resolution (<1nm in STEM mode) can now be achieved with EELS [4]. Thus ELNES is the only possibility for fine structure analysis of nanometer size particles and a relevant alternative to XANES for bulk analysis. The drawback of high spatial resolution in Cs corrected STEM is the increased risk to introduce sample damage because of the large current density in the probe [5] focused on a small particle which is potentially less stable than the bulk. In this abstract we would like to demonstrate the advantages and the drawbacks of working with ELNES to obtain structural and chemical information on an industrially relevant nanoparticle system, i.e. TiO₂ rutile and anatase.

The Ti L₂₃ edge of rutile and anatase is a very relevant showcase for the success of ELNES in nanoparticle analysis (Fig. 1.) and has been studied before [6]. The fine structures of the Ti L_{2,3} white lines are specific for each TiO₂ modification. Hence the crystal structure of individual nanoparticles can be determined by the acquisition of a highly resolved EELS spectrum in STEM mode (Fig 2.). The spectra obtained from anatase nanoparticles are comparable to the bulk spectrum and do not change their aspect as a function of exposure times between 4s and 20s. On the contrary, after only 4s exposure, the ELNES spectrum of the rutile nanoparticles is not exactly identical to the rutile bulk spectrum. When the exposure time is increased from 4s to 8s, the rutile Ti-L_{2,3} edge fine structures changes dramatically. After 12s the fine structure shape stabilizes. Comparing to literature, we find that the stable rutile spectrum after 12s exposure shows similarities with the TiO₂-II phase X- ray

Absorption Spectrum (XAS) recorded by Ruus et al. [7] and with the brookite EELS spectrum recorded by Mitterbauer [8] suggesting the presence of one of those phases or maybe both of them. We believe that the crystal structure change is a consequence of the strong irradiation. This indicates that in nanoparticles the rutile phase is less stable than the anatase phase, although it is exactly the opposite in the bulk. The instability of rutile in comparison to anatase in nanoparticles has been already reported before [9].

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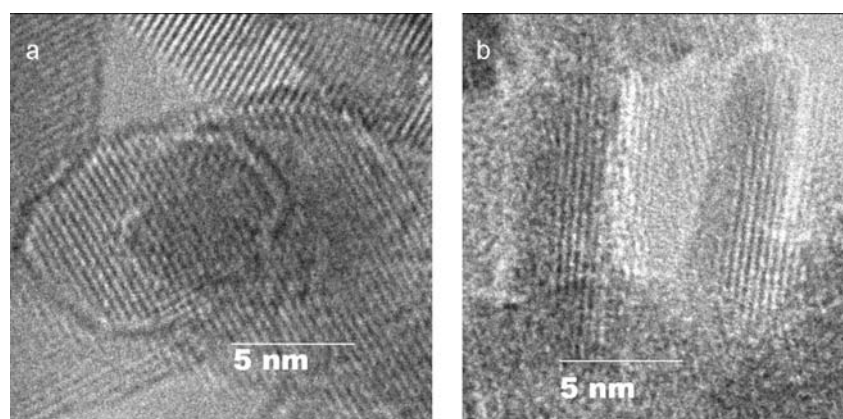


Figure 1. HRTEM images of the a) rutile and b) anatase nanoparticles. The crystal structure of the particles was checked by x-ray diffraction before bringing them onto a holey grid.

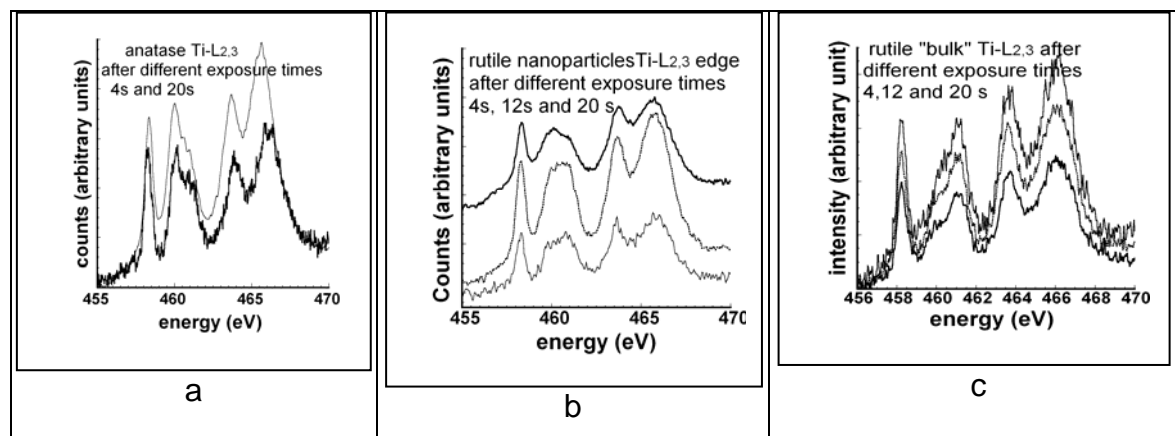


Figure 2. ELNES of Anatase (a) and rutile (b) nanoparticles and rutile bulk (c) at the $Ti-L_{2,3}$ edge obtained at exposure times of 4s, 12s and 20 s with a 0.2 nm probe in STEM mode.