Electronic Structure of TiO_2 Nanoparticles as Observed by X-ray Absorption Spectroscopy (XAS)

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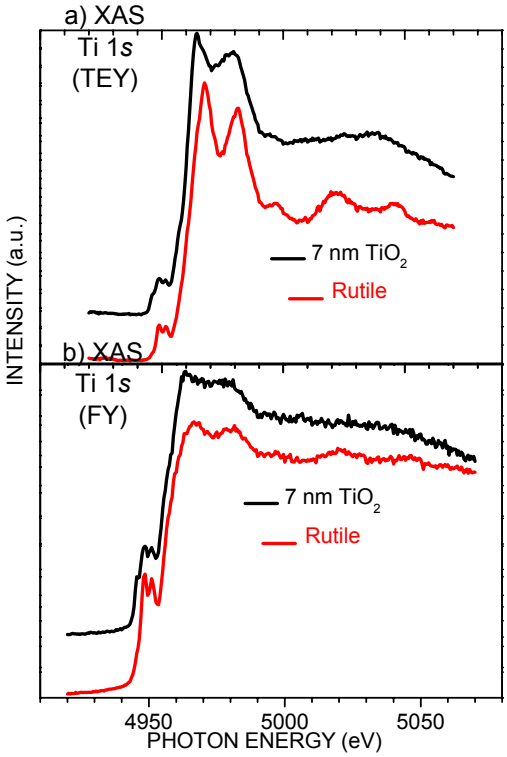
It is well known that when materials are arranged in nanometric dimensions, their physical and chemical properties could change with respect to those of the same bulk materials. These changes are produced by changes in their electronic structure induced by size effects. So that, the study of the electronic structure of nanoparticles materials is a hot topic in nanotechnology nowadays. Questions like why do the materials change their properties or what is the critical size at which their properties change, are of enormous interest.

In this work we study the electronic structure of TiO_2 nanoparticles by means of X-ray Absorption Spectroscopy (XAS). The large variety of properties of Titanium oxides gives this family of oxides relevant importance in many technological applications such as catalysis and photocatalysis, sensors, optical coatings, paintings, etc. On the other hand, the sensitivity of XAS to the local order range makes this technique suitable for such analysis.

TiO_2 nanoparticles have been grown by the inverse micro-emulsion of water and oil method[1]. The powder obtained was analyzed by X-Ray Diffraction giving the pattern of the anatase structure and a particle size of 10 nm was derived from the width of the diffraction lines. For XAS measurements, the powders were pressed into a suitable sample holder of dimensions according to the manipulator in the spectrometer. The Ti K edge was measured at the KMC1 beam-line in both, total electron yield and fluorescence yield. The Ti $L_{2,3}$ and O K edges were measured at the PM3 beam-line in near-total electron yield, that means by tuning the electron analyzer at the kinetic energy of the main secondary electron bump (10 eV). In the case of the Ti 2*p* edge, it was also measured in the partial yield detection mode. This means that the electron analyzer was tuned at the kinetic energy of the Ti LMM Auger peaks. It is known that partial yield spectra are more surface sensitive than those obtained in the total yield mode. The experimental spectra were corrected with the I_0 current taken from a gold grid. Other spectra of rutile and anatase measured in a different beam-line at BESSY (VLS-PGM) are shown for comparison.

The Ti K edges of the TiO_2 nanoparticle sample in both, total electron yield (a) and fluorescence yield (b), are shown in Fig. 1. Also the same spectra of a rutile single crystal are shown for comparison. In general, the spectra of the TiO_2 nanoparticles are very similar to those of rutile, except for the small peaks at the edge. The spectra of the TiO_2 nanoparticles show clearly three peaks whereas those of rutile show only two. This



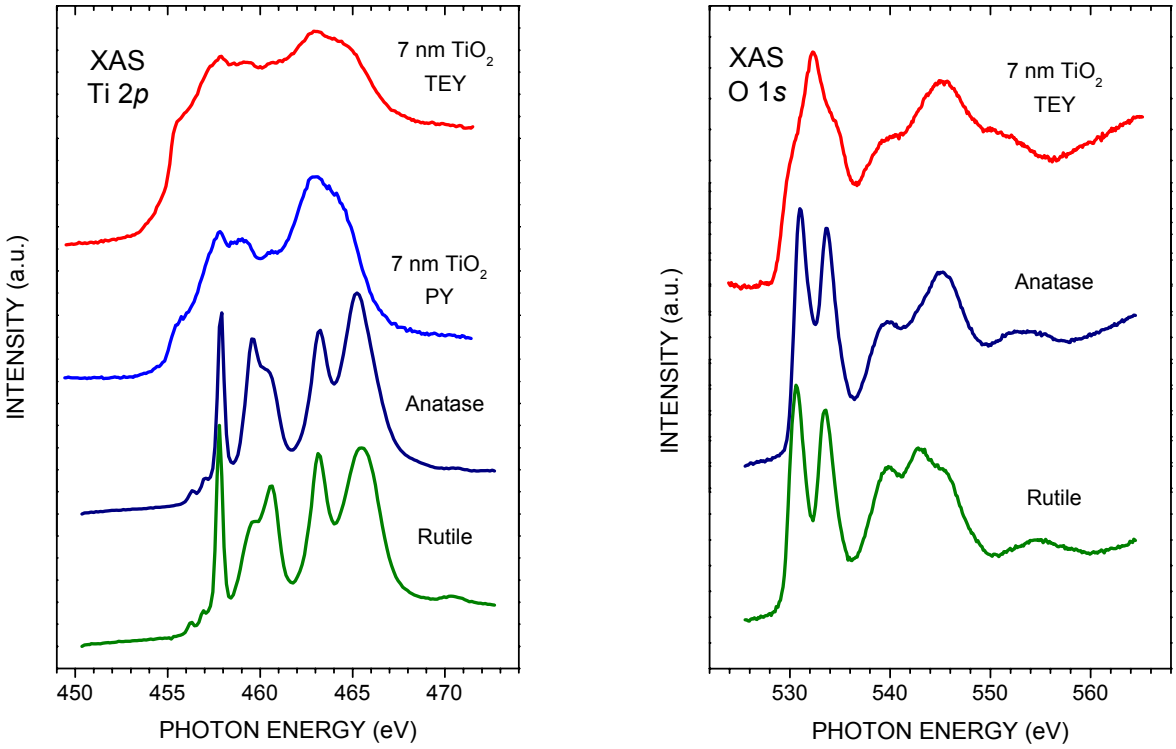
is more clearly observed in the spectra of fluorescence yield which presents the absorption edge more resolved than in the total yield spectra. On the other hand, it is clearly seen that both, total yield and fluorescence spectra, coincide for each sample. The spectrum of the nanoparticles agrees with other published spectra for the Ti K edge in anatase[2].

So that, these results confirm that the nanoparticles show the anatase structure in agreement with XRD data of the nanoparticles. It is worthy to note here that FY spectra are volume sensitive whereas TEY spectra are more surface sensitive, although the probing depth of XAS in TEY mode at these energies (5 KeV) is probably larger than the size of the nanoparticles.

The Ti 2p XAS spectra of the TiO_2 nanoparticles are shown in Fig. 2. We show the spectra taken in total yield and in partial yield by tuning the electron analyzer at the kinetic energy of the Ti LMM Auger peak. The reason is that, even though the total Ti 2p XAS spectra taken in total yield are more surface sensitive than those of the Ti 1s edge because the lower incident photon energy, the partial yield spectra are even more surface sensitive since the Auger electrons are only collected from the outer most region of the sample. By comparing both, total and partial yield spectra they show exactly the same structures although the partial yield spectra has a lower background as the secondary electrons are not collected. This indicates that at the depth of these techniques, the Ti atoms have the same local structure.

The main point now is to assign these spectra to a Ti oxide. We also show in Fig. 2 the corresponding spectra of rutile and anatase samples. As it is seen, the spectrum of the nanoparticles does not agree with the reference rutile and anatase spectra. However, if one compare this spectrum with that measured by Lusvardi *et al.*[3] in FY for TiO (Ti^{2+}), the agreement is excellent.

The O 1s XAS spectrum of the nanoparticles is shown in Fig.3. The spectra of the reference rutile and anatase samples are also depicted. It is seen that, as in the case of the Ti 2p spectra, the nanoparticles do not seem to be associated to rutile nor to anatase. In this case the higher photon energy region of the spectrum agrees in some way with that of anatase but the lower photon energy region of the spectra differs from that of anatase. The splitting of the two sub-bands (2.6 eV for anatase and rutile)[4], associated with the t_{2g} and e_g states via hybridization does not appear in the spectrum of the nanoparticles. An extra peak centered between the t_{2g} and e_g bands arises to dominate the spectrum. This extra peak can be associated to the O 1s spectrum of TiO shown in the literature[3].



In summary, the above results seem to indicate that whereas the bulk of the nanoparticles remains as TiO_2 in the anatase form, the surface of the nanoparticles seems to be strongly reduced to TiO (Ti^{2+}). Of course, the existence of some amount of Ti^{3+} species at the surface cannot be neglected. However, and what it is more important, this result is contradictory with respect to Ti oxides surfaces. It is well known that the surfaces of the lower oxidation state oxides in contact with atmosphere tend to oxidize up to the larger oxidation state, i.e. Ti^{4+} but here the process is just the contrary: the surface of a higher oxidation state Ti oxide (Ti^{4+}) is strongly reduced.

This preliminary result require more investigation by using surface sensitive characterization techniques.

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