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Electronic Structure and Size of TiO_2 Nanoparticles of Controlled Size Prepared by Aerosol Methods

Leonardo Soriano[1,*], **Petri P. Ahonen**[2], **Esko I. Kauppinen**[2],
Jorge Gómez-García[1], **Carmen Morant**[1], **Francisco J. Palomares**[3],
Marta Sánchez-Agudo[1], **Patrick R. Bressler**[4], and **José M. Sanz**[1]

[1] Departamento de Física Aplicada, Instituto de Materiales Nicolás Cabrera,
Universidad Autónoma de Madrid, E-28049 Madrid, Spain
[2] VTT Chemical Technology, SF-02044 Espoo, Finland
[3] Instituto de Ciencia de Materiales de Madrid, CSIC, E-28049 Madrid, Spain
[4] BESSY, D-12489 Berlin-Adlershof, Germany

Summary. A complete characterization of nanostructures has to deal both with electronic structure and dimensions. Here we present the characterization of TiO_2 nanoparticles of controlled size prepared by aerosol methods. The electronic structure of these nanoparticles was probed by X-ray absorption spectroscopy (XAS), the particle size by atomic force microscopy (AFM). XAS spectra show that the particles crystallize in the anatase phase upon heating at 500°C, whereas further annealing at 700°C give crystallites of 70% anatase and 30% rutile phases. Raising the temperature to 900°C results in a complete transformation of the particles to rutile. AFM images reveal that the mean size of the anatase particles formed upon heating at 500°C is 30 nm, whereas for the rutile particles formed upon annealing at 900°C 90 nm were found. The results obtained by these techniques agree with XRD data.

Keywords. Electronic structure; Nanostructures; Spectroscopy.

Introduction

Nanostructured materials are of enormous interest in many technological fields due to their unique properties caused by their reduced size. However, many questions, especially those concerning the correlation of their properties with their dimensions, remain still open. To answer these questions, a characterization of the electronic structure of the nanoparticles together with an accurate determination of their dimensions is required. Usually, the electronic structure of materials is probed by electron spectroscopies. However, this is not always an easy task since, as in the case of insulating nanostructured materials, various non-controllable effects such as charging, support-nanostructure interaction, size-effects, *etc.* can affect the spectra. In this work we report on the characterization of the electronic structure of

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[*] Corresponding author. E-mail: l.soriano@uam.es

TiO_2 nanoparticles by X-ray absorption spectroscopy (XAS). We will show below that XAS is an appropriate tool for the analysis of such nanoparticles. The fine-structure of the Ti $2p$ and O $1s$ XAS spectra allows to distinguish between the two stable TiO_2 phases, *i.e.* anatase and rutile. Moreover, XAS is able to detect and *semi*-quantitatively determine the phase composition. The particle size was determined by atomic force microscopy (AFM). The results obtained by these two surface techniques, *i.e.* TiO_2 phase structure and particle size, agree with those obtained by XRD.

In general, metal oxides are a fascinating family of materials with a large variety of electronic properties. Oxide surfaces and interfaces play an important role in many technological applications like catalysis, corrosion, sensors, *etc.* [1, 2]. In particular, titanium oxides have been widely studied due to their application as ceramics, catalysts, catalyst supports, optical coatings, gas sensors, pigments, *etc.* In all these cases, a large surface-to-volume ratio is of great importance, so that the study of TiO_2 nanoparticles seems well justified. Aerosol synthesis and, in particular, in-droplet hydrolysis of titanium alkoxide have proved to be a suitable method for the preparation of nanostructured TiO_2 particles [3, 4].

As mentioned above, the electronic structure of oxide surfaces and interfaces is usually experimentally studied by electron spectroscopies such as X-ray photoemission (XPS), *Auger* electrons (AES), electron energy loss (EELS), *etc.* [5]. The characterization of nanostructures requires techniques with adequate lateral/depth resolution. Although the lateral resolution of electron spectroscopies is progressively improving due to new technological developments, is still far from other techniques such as *e.g.* scanning tunnel microscopy (STM) that reaches atomic resolution. However, if the nanostructured material is homogeneously dispersed, electron spectroscopies can give averaged information on its electronic structure [6, 7]. XAS is an X-ray technique which probes unoccupied electronic states. In XAS, a photon is absorbed by a core electron, thus producing transitions to unoccupied states. These transitions are controlled by dipole selection rules so that only transitions to states with $\Delta l = \pm 1$ are allowed [8]. In the total electron yield detection mode, XAS is a surface sensitive technique with a mean probing depth of 40 Å [9] at the energy range used in this study (450–550 eV). This means that a near-surface region of about 20 nm depth can be probed.

Results and Discussion

Atomic force microscope images

The AFM images of the powders after annealing at 500 (a), 700 (b), and 900°C (c) are shown in Fig. 1. The images at the bottom are topographic, whereas those at the top are friction images. We have to note that previous characterization of the morphology of the powders by scanning electron microscopy (SEM) [3] had revealed spherical agglomerates (1–2 μm diameter) which showed structures in the nanometer scale. In general, the AFM images show that after pressing of the powders the initial spherical agglomerates are divided in individual nanoparticles (<200 nm) with some other bigger structures remaining. The particle size was statistically estimated for different images of the same powders. The particles

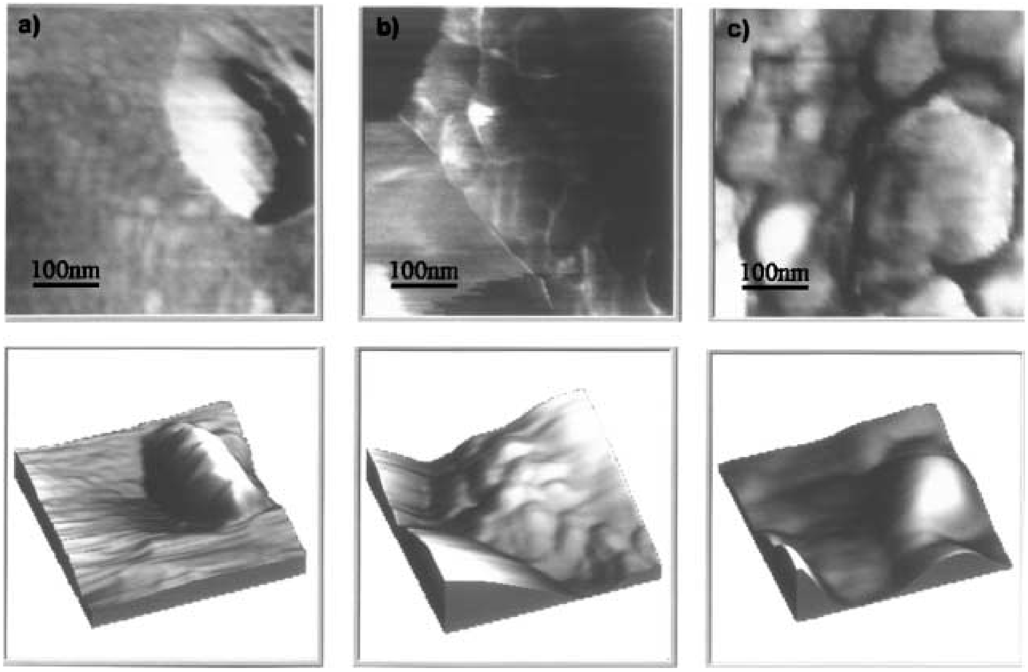

Fig. 1. AFM images of powders annealed at 500 (a), 700 (b), and 900°C (c); topographic images at the bottom, friction images at the top

Table 1. TiO_2 phase and particle size of powders annealed at different temperatures as obtained by X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray absorption (XAS)

Annealing temperature/°C	XRD [3]		AFM	XAS
	Particle size/nm	Phase	Particle size/nm	Phase
500	20	Anatase	30	Anatase
700	40–50	Anatase + Rutile	55–85	Anatase + Rutile
900	100	Rutile	90	Rutile

observed in Fig. 1a, corresponding to powders annealed at 500°C, have a mean size of 30 nm. Two average size populations were obtained for particles corresponding to powders annealed at 700°C (55 and 85 nm). For particles of powders annealed at 900°C, the mean size is 90 nm. These results are in good agreement with data obtained by XRD (Table 1). Summarizing the AFM results, we can conclude that annealing of the powders at 500°C produces very fine particles (30 nm). Posterior annealing of the powders produces an enlargement of the particle size. After annealing at 700°C, a broadening of the particle size distribution is observed, indicating that two different types of particles exist.

O 1s XAS spectra

The O 1*s* XAS spectra of the as-prepared powders and of those annealed at different temperatures are shown in Fig. 2. According to the properties of XAS

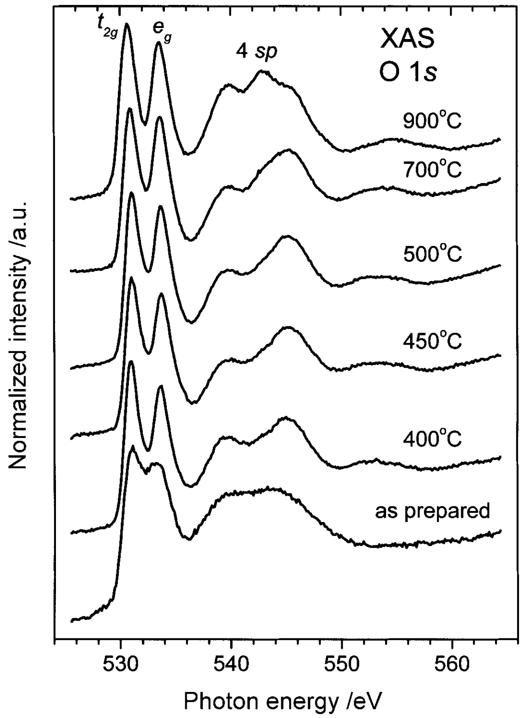

Fig. 2. O 1*s* XAS spectra of the powders as-prepared and after annealing at different temperatures

described above, these spectra correspond to unoccupied electronic states of O *p* character which are hybridized with unoccupied metal states. In fact, these spectra are mapping the metal states. In general, the spectra show two well defined sub-bands at the threshold (530–535 eV) and a broader band at higher energies (540–550 eV). The first double band originates from the hybridization of O 2*p* states with Ti 3*d* orbitals leading to the t_{2g} and e_g sub-bands. The energy splitting of these two bands, as measured in the O 1*s* XAS spectra, is very sensitive to the local structure and ligand coordination and a good estimation of the optical crystal field splitting (Δ_{CF}) [11]. The second band originates from the hybridization of O 2*p* states with Ti 4*sp* orbitals. This band appears at higher energies due to the larger overlap of the O 2*p* – Ti 4*sp* orbitals and is more sensitive to long-range order in the sample.

The spectrum of the as-prepared powders shows that the band at the threshold is broader with a lower splitting of the two sub-bands, *i.e.* a lower crystal field splitting. This is a clear indication of a weaker interaction between the Ti 3*d* and O 2*p* orbitals. According to the O 1*s* XAS spectra of Ti oxides previously reported [12] this can be interpreted in terms of a lower oxidation state of the Ti atoms corresponding to the titanium hydrous oxide as-prepared powders [3]. On the other hand, in the spectra of the annealed nanoparticles the two sub-bands at the threshold appear narrow and well defined with an energy separation of 2.6 eV, in agreement with other reported values for the crystal field splitting in TiO_2 [13]. These spectra are almost identical except for the 4*sp* band which shows three main

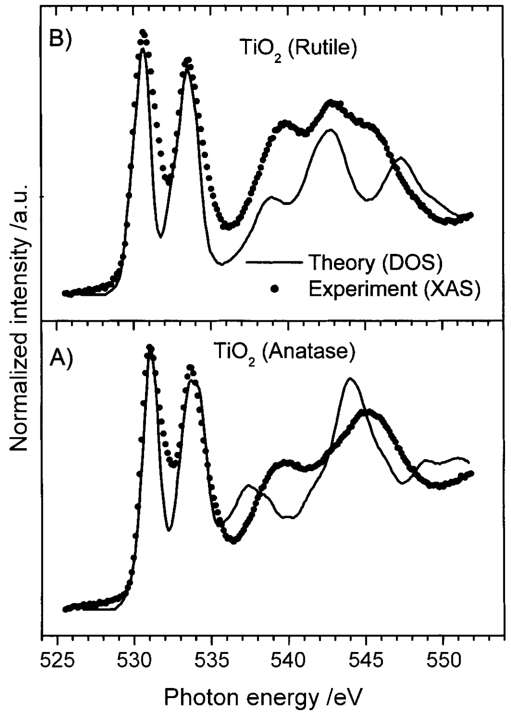

Fig. 3. A) Unoccupied density of states of O p character calculated in Ref. [14] for anatase (solid line) and O $1s$ XAS spectra of powders annealed at 500°C (dots); B) Unoccupied density of states of O p character calculated in Ref. [14] for rutile (solid line) and O $1s$ XAS spectra of powders annealed at 900°C (dots)

structures for the powders annealed at 900°C, but only two for the powders annealed at 500°C. The spectrum of the powders annealed at 700°C seems to correspond to a transition stage between those corresponding to annealings at 500 and 900°C.

To understand these differences in the $4sp$ band we have depicted the band structure calculations performed by *de Groot et al.* [14] for TiO_2 in both anatase (A) and rutile (B) phases in Fig. 3. The calculated density of states (DOS) of oxygen $2p$ character (solid line) is compared with the O $1s$ XAS spectra of the powders annealed at 500°C (A) and 900°C (B). It can be seen that the agreement of the experimental spectra with their corresponding DOS is good. The crystal field splittings of the t_{2g} and e_g bands predicted by the calculations are in complete agreement with the experimental spectra. The calculated $4sp$ bands show two main structures for the anatase phase, whereas for the rutile phase those bands show three different peaks. From the above comparison it is inferred that after annealing at 400°C anatase TiO_2 phase is formed, whereas after annealing at 900°C anatase is completely transformed to rutile. The spectrum of the powders after annealing at 700°C seems to indicate that at this temperature both phases are present. These XAS results are in complete agreement with the XRD results summarized in Table 1.

Ti 2p XAS spectra

According to the selection rules of XAS, the Ti $2p$ XAS spectra correspond to Ti $2p \rightarrow 3d$ and Ti $2p \rightarrow 4s$ transitions ($\Delta l = \pm 1$). However, the spectrum is dominated by transitions to Ti $3d$ states since the contribution of the Ti s states is negligible. Although in a first approximation the Ti $2p$ XAS spectra should map the unoccupied density of states of Ti $3d$ character, other final state effects affect the spectra. In particular, the hole created when a $2p$ electron is ejected to a narrow d band produces a potential which disturbs the original spectra; as a consequence, they cannot be explained by theoretical models based on band structure calculations. However other models based on atomic multiplets projected in the corresponding symmetry have been successfully used to explain most of the transition-metal $2p$ XAS spectra [15, 16]. The Ti $2p$ XAS spectra of TiO_2 have been interpreted as atomic multiplets of the $2p^63d^0 \rightarrow 2p^53d^1$ transitions projected in a crystal field according to the corresponding symmetry of the Ti atoms in each phase. In fact, as will be shown later, the different distortions of the octahedral symmetry of anatase and rutile give rise to an extra-splitting of the e_g bands in two sub-bands with different relative intensities.

The Ti $2p$ XAS spectra of the as-prepared and annealed powders are shown in Fig. 4. Once again, the spectra of the annealed powders differ from the spectrum of the as-prepared powders which is significantly broader and presents only four defined structures. The spectra of the annealed powders show five well defined structures (labelled from A to E) and two small peaks at the threshold. The spectra

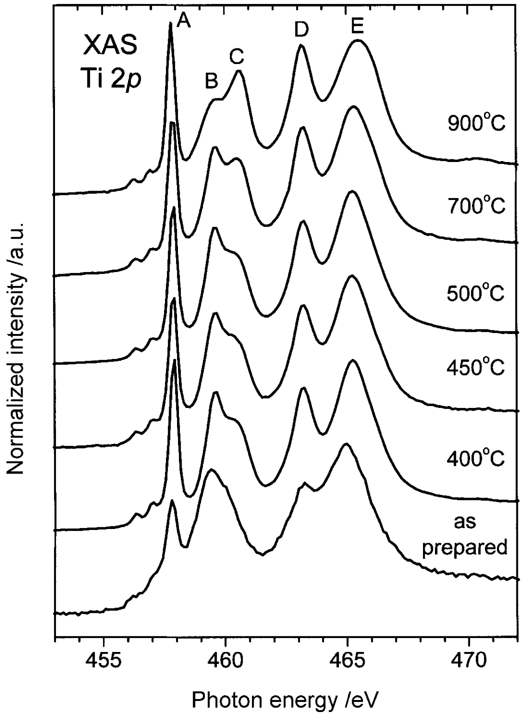

Fig. 4. Ti $2p$ XAS spectra of powders as-prepared and after annealing at different temperatures

of the powders annealed at temperatures of 400–500°C are identical and agree with other spectra published for anatase TiO_2 [10, 14], although the spectra shown in this work have a much better resolution which is a clear indication of both the good crystallinity of the nanostructured powders and a good performance of the monochromator. In these spectra, the band formed by peaks A, B and C originates from transitions from Ti $2p_{1/2}$ states, whereas the band of peaks D and E results from Ti $2p_{3/2}$ states. The different broadening of each band is related to the different lifetimes of the excited state. Peaks A and D correspond to transitions to t_{2g} states, whereas peaks B, C, and E relate to transitions to e_g states. On the other hand, the spectrum of the powders annealed at 900°C shows the same structures as the previous ones, but a different relative intensity of peaks B and C. In Fig. 5A, this spectrum is compared with atomic multiplet calculations for rutile in D_{4h} symmetry with a crystal field strength of 1.8 eV taken from Ref. [15], showing an excellent agreement. As mentioned above, the differences in the relative intensity of the B and C peaks in anatase and rutile are due to the different distorsions of the octahedrons formed in each phase [15].

According to the above XAS results we can conclude that upon annealing at 400–500°C the precursor powders crystallize to anatase TiO_2. By annealing at 900°C, anatase is completely transformed to rutile. It was demonstrated above that the Ti $2p$ spectra of anatase and rutile differ only in the relative intensity of the B

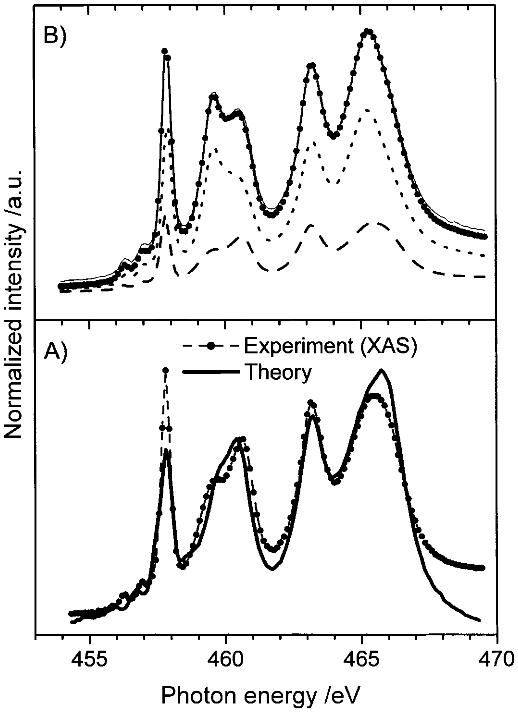

Fig. 5. A) Atomic multiplet calculations in D_{4h} symmetry for rutile with a crystal field strength of 1.8 eV taken from Ref. [15] (solid line) and Ti $2p$ XAS spectrum of powders annealed at 900°C; B) linear combination (solid line) of 30% rutile (dashed line) and 70% anatase (dotted line) compared with the Ti $2p$ XAS spectrum of powders annealed at 700°C (dots)

and C peaks. However, after annealing at 700°C the spectrum shows a relative intensity of these two bands different from those assigned to anatase and rutile. It is reasonable to think that at these temperatures anatase is only partly transformed to rutile, leading to a mixture of the two phases. In Fig. 5B the spectrum of the powders annealed at 700°C is compared with a linear combination of 30% rutile and 70% anatase. It is quite obvious that XAS is able even to quantify the relative amount of the two phases.

Conclusions

We have characterized the particle size and electronic structure of both as-prepared and annealed TiO_2 powders grown by aerosol methods. The combined AFM and XAS characterization indicates that after annealing at 500°C, particles of 30 nm size of anatase are formed. Annealing at 700°C causes 30% of the particles to be transformed to rutile with 85 nm particle size, whereas the 70% remaining anatase particles increase their size to 55 nm. Finally, annealing at 900°C produces a complete transformation to rutile particles of 90 nm size. Both XAS and AFM data are in complete agreement with XRD characterization.

Experimental

TiO_2 precursor powders were prepared by in-droplet hydrolysis of titanium alkoxide. More details on the aerosol preparation procedure can be found elsewhere [3]. The as-prepared powders were submitted to thermal annealing in air for 1 h at different temperatures up to 900°C. Crystal structure and particle size were determined by X-ray diffraction (XRD) using a Siemens D500 diffractometer. A summary of the XRD results is shown in Table 1.

XAS spectra were measured using a plane grating – varied line spacing monochromator (PGM-VLS) in the synchrotron radiation facility BESSY (Berlin, Germany). The estimated resolution of this monochromator at the Ti 2*p* edge (450 eV) was better than 100 meV. The powders were pressed on a suitable stainless steel sample holder to permit a vertical position for XAS measurements. The spectra were recorded in the total electron yield detection mode and corrected with the I_0 current measured from a gold net located at the entrance of the chamber. Then, the spectra were normalized for comparison. The absolute energy scale was calibrated according to the known position of the first peak of the Ti 2*p* EELS spectra of rutile TiO_2 [10].

A home-built atomic force microscope operating in air was used for AFM measurements. Pyramidal Si_3N_4 tips grown at the end of triangular levers (Park Scientific Instruments) were used with a normal constant force of 0.1 N/m. The powders were pressed on mica for AFM measurements. By this operation, as inferred from the AFM images, the original spherical agglomerates (1–2 μm diameter) originating from the droplet were crashed and dispersed on the surface of the mica substrate.

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