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Citation: [AIP Conference Proceedings](#) **1365**, 437 (2011); doi: 10.1063/1.3625396

View online: <http://dx.doi.org/10.1063/1.3625396>

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TXM-NEXAFS of TiO₂-Based Nanostructures

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Abstract. In this work, electronic properties of individual TiO_x-pristine nanoribbons (NR) prepared by hydrothermal treatment of anatase TiO₂ micro-particles were studied using the HZB transmission x-ray microscope (TXM) at the BESSY II undulator beamline U41-FSGM. NEXAFS is ideally suited to study TiO₂-based materials because both the O K-edge and Ti L-edge features are very sensitive to the local bonding environment, providing diagnostic information about the crystal structures and oxidation states of various forms of titanium oxides and sub-oxides. TXM-NEXAFS combines full-field x-ray microscopy with spectroscopy, allowing the study of the electronic structure of individual nanostructures with spatial resolution better than 25 nm and a spectral resolution of up to $E/\Delta E = 10000$. The typical image field in TXM-NEXAFS measurements is about $10 \mu\text{m} \times 10 \mu\text{m}$, which is large compared to the individual nanoparticle. Therefore, one image stack already contains statistically significant data. In addition, the directional electric field vector (\vec{E}) of the x-rays can be used as a “search tool” for the direction of chemical bonds of the atom selected by its absorption edge.

Keywords: X-ray microscopy, NEXAFS, fabrication and characterization of nanoscale materials

PACS: 68.37.Yz, 61.05.cj, 81.07.-b

INTRODUCTION

Low-dimensional TiO_x-based nanostructures, such as nanowires, nanotubes, and nanorods, bring to reality the possibility to fine-tune chemical reactivity as the system structure, and the occupation of the outermost energy levels can be tuned by changing preparation parameters. Several structures have been proposed for these structures, including scrolling of anatase sheets, trititanate H₂Ti₃O₇ exfoliated sheets, (Na,H)₂Ti₂O₄(OH)₂-based layers, and lepidocrocite titanate-like sheets. Based on x-ray diffraction and transmission electron microscopy (TEM) experiments, it is currently believed that the structure is closely related to the family of layered titanate H₂Ti_nO_{2n+1} materials, where $n = 3, 4, 5$ or even ∞ for the end-member composed of flat layers of octahedral. The exact structure is still a matter of debate.

Conventional spectroscopy methods, such as photoemission spectroscopy and x-ray absorption spectroscopy, have shown to be particularly well-adapted probes to study electronic properties of nanostructures. However, these conventional techniques typically sample an area of some μm^2 , thus preventing the analysis of a single nanostructure. Moreover, signals originating from impurities that are usually present in the nanostructure powder (amorphous material, particles, and catalysts) cannot be avoided. Spectroscopy combined with high spatial resolution overcomes these problems.

In this work, electronic properties of individual TiO_x-pristine nanoribbons (NR) prepared by hydrothermal treatment of anatase TiO₂ micro-particles were studied using the NEXAFS capabilities of the HZB TXM at the undulator beamline U41 [1]. NEXAFS is ideally suited to study TiO₂-based materials because both the O K-edge and Ti L-edge features are very sensitive to the local bonding environment, providing diagnostic information about the crystal structures and oxidation states of various forms of titanium oxides and sub-oxides. TXM-NEXAFS

combines microscopy with spectroscopy, allowing investigation of the electronic structure of individual nanostructures with spatial resolution better than 25 nm [1-3]. The typical image field in TXM-NEXAFS measurements is about $10\ \mu\text{m} \times 10\ \mu\text{m}$, which is large compared to an individual nanostructure. Therefore, one image stack already gives statistically relevant information (Fig. 1). The exposure time per image is in the range of a few seconds. In addition, the directional electric field vector (\vec{E}) of the x-rays can be used as a “search tool” for the direction of chemical bonds of the atom selected by its absorption edge [4]. The electronic structure of these nanoribbons is discussed in terms of the crystal field splitting. Reference anatase and rutile samples are used as templates for the interpretation of the spectroscopic signatures of the nanoribbon.

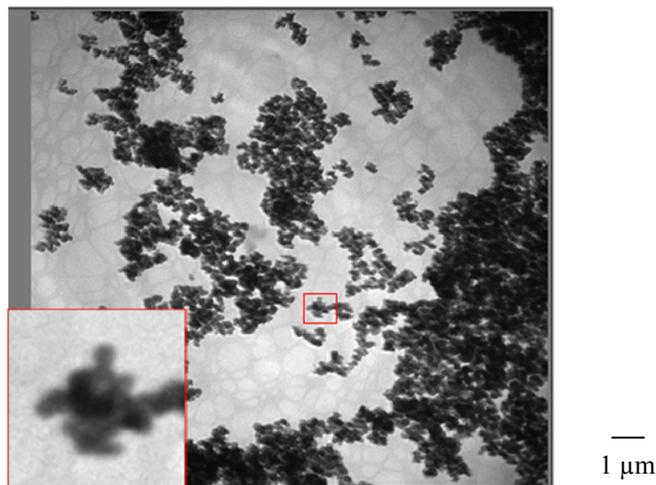


FIGURE 1. TXM image (stack) of anatase at $h\nu = 460\ \text{eV}$. An adequate number of nanoparticles in one stack give statistically relevant information.

RESULTS

NEXAFS spectra are clear fingerprints of titanium oxides. They show significant differences depending on the crystallographic phase as well as on the Ti reduction. TiO_2 single-crystal spectra show well-resolved peaks in the range between 455 and 470 eV corresponding to the various Ti $2p \rightarrow 3d$ transitions [5]. The Ti L-edge shows two groups of peaks arising from the spin-orbit splitting of Ti $2p$ core level into $2p_{3/2}$ and $2p_{1/2}$ levels with $\sim 6\ \text{eV}$ energy separation. These levels are further split due to crystal-field effects. The Ti $L_{2,3}$ edges recorded on rutile TiO_2 micro-particles (Fig. 2(a)), anatase TiO_2 micro-particles (Fig. 3(a)), and the ribbon have similar form (Fig. 4(a)): the L_3 and L_2 edges are separated by the $2p$ core hole spin orbit coupling around 5 eV. The L_3 and L_2 edges are both split by the strong crystal field splitting arising from the surrounding oxygen atoms.

The experimental splitting of the L_2 line for anatase and the nanoribbon are of comparable magnitude ($\sim 2\ \text{eV}$), and the splitting for rutile is somewhat larger ($\sim 2.6\ \text{eV}$). The separation between the t_{2g} and e_g orbitals is about 1.8 eV for anatase and 2 eV for rutile, in accordance with previously reported results [6].

The O K-edges for the rutile (Fig. 2(b)), anatase (Fig. 3(b)), and ribbon (Fig. 4(b)) are characterized by two main features. For anatase these are split by 2.5 eV whereas for rutile it is 2.75 eV. For the ribbon the splitting is around 2.5 eV, which is closer to anatase. This suggests that the crystal field splitting of the titanate ribbons is close to that of the anatase phase.

Figure 4 illustrates the oxygen $1s$ (K-edge) and titanium $2p$ ($L_{2,3}$ -edge) absorption edges recorded on the nanoribbon in two experimental geometries: \vec{E} parallel and perpendicular to the principal axis of the nanostructure. The Ti $2p$ spectra are similar to those reported for the TiO_2 anatase phase [7], with the main discrepancy in the single structure at 460 eV, which appears split in the TiO_2 . This structure results from transitions to the final state $(2p_{3/2})^{-1}d(3e_g)^1p^6$; the e_g states are formed by $d(z^2)$ and $d(x^2-y^2)$ orbitals, which are directed towards ligand anions, and are sensitive to deviations from $\text{Ti } O_h$ symmetry and the stacking of the octahedra units. Consequently, the absence of splitting of e_g states into $d(z^2)$ and $d(x^2-y^2)$ suggests that for TiO_x -nanoribbon, Ti atoms may occupy sites with different degrees of distortion and/or different stacking of the octahedra units from the one observed in the distorted O_h symmetry in TiO_2 -anatase.

The normal incidence NEXAFS spectra were measured with \vec{E} parallel and perpendicular to the principal axis of the nanostructure. No strong evidence for anisotropic distribution of Ti sites can be observed. Conversely, the O 1s spectra suggest anisotropic distribution of O sites. The O 1s transitions identified as t_{2g} and e_g in the spectra result from transitions to final states, $3d(2t_{2g})^1(1s)^{-1}p^6$ and $3d(3e_g)^1(1s)^{-1}p^6$. The energy separation between t_{2g} and e_g (crystal field splitting) is 2.5 eV, in close agreement with the value measured in the Ti 2p spectrum.

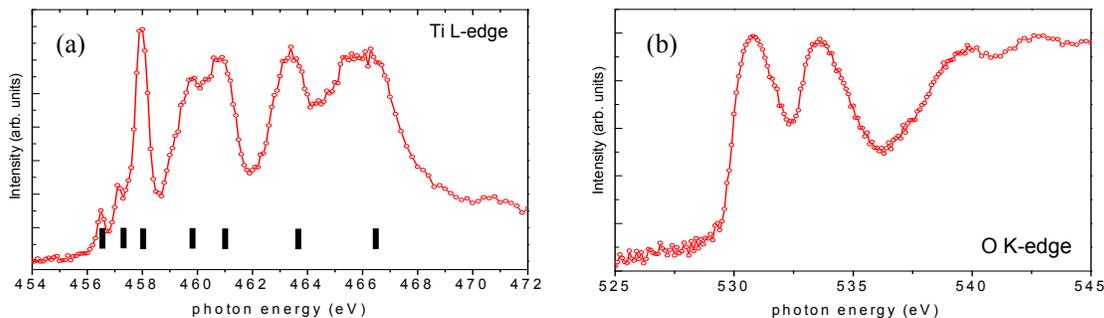


FIGURE 2. TXM-NEXAFS spectra recorded on TiO₂ rutile particles powder: (a) Ti L-edge, (b) O K-edge.

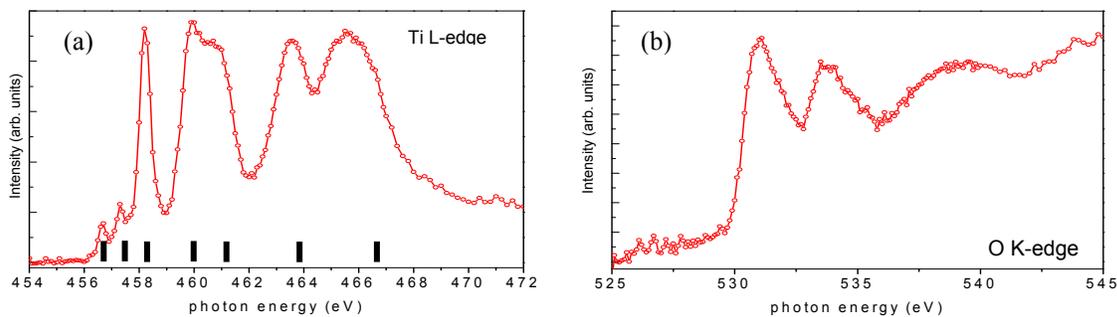


FIGURE 3. TXM-NEXAFS spectra recorded on TiO₂ anatase particles powder: (a) Ti L-edge, (b) O K-edge.

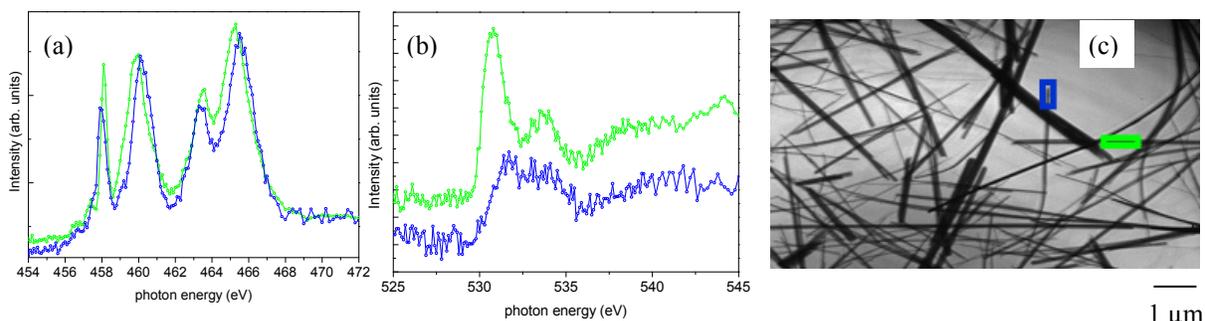


FIGURE 4. TXM-NEXAFS spectra recorded on a single TiO_x-nanoribbon: (a) Ti L-edge, (b) O K-edge, (c) TXM - image at $h\nu = 464$ eV showing the two experimental geometries used to record the spectra.

CONCLUSIONS

This work shows the high potential for using TXM-NEXAFS to study the electronic states of isolated low-dimensional nanostructures with high spatial resolution in the 20-nm range and short exposure times.

The Ti-O bond directionality was probed varying the angle between the electric field vector of the x-rays and the principal axis of the TiO_x-nanoribbons. The O 1s spectra suggest anisotropic distribution of O sites, whereas no strong evidence for anisotropic distribution of Ti sites was observed. A more detailed description of the reported results is submitted for publication [8].

ACKNOWLEDGMENTS

This work is financially supported by the Belgian Program on Interuniversity Attraction Pole (PAI 6/08) and by the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH and the European Commission under contract RII3-CT 2004-506008 (IASFS). The authors thank the COST Action MP901 NanoTP for creating new opportunities for scientific discussions.

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