Nanoscale NEXAFS for Probing TiO$_2$-B Nanoribbons.

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TiO$_2$ nanostructures exist in different crystallographic phases including brookite, anatase, rutile, and TiO$_2$−B (bronze). Among these, due to its open channel-like crystal structure which can enhance ion mobility, the TiO$_2$−B phase has been reported as an optimal anode material for lithium ion batteries, particularly in the form of nanowires [1]. In view of device applications, where different phases may coexist and TiO$_2$−B particles may transform to the thermodynamically stable anatase phase, it is important to identify and understand the structural and electronic differences between these two phases. Here we have studied the electronic structure of TiO$_2$ nanoribbons in TiO$_2$−B and anatase phases using polarization dependent near-edge X-ray absorption fine structure spectroscopy (NEXAFS) in the transmission X-ray microscope (TXM) and density functional theory (DFT) [2,3]. NEXAFS at both the O K-edge and the Ti L-edge is very sensitive to the local bonding environment in TiO$_2$-based materials and thus provides diagnostic information about the crystal structures and oxidation states. We report the observation of strong linear dichroism in the O K-edge spectra of single TiO$_2$−B nanoribbons. Using DFT calculations we show that the dichroism is a consequence of the directional Ti−O bonding in the monoclinic crystal structure.

Figure. 1. TEM and SEM images of a typical TiO$_2$−B sample.

TiO$_2$-B nanoribbons were obtained by calcining the H$_2$Ti$_3$O$_7$ nanoribbons precursor in static air at 450 °C [4]. The morphology of the samples was studied using electron microscopy (**Fig. 1**) revealing its characteristic porous surface, the lateral dimension from 30 to 250 nm and length 1 to 4 µm. The crystal structure was determined using powder X-ray diffraction. The Ti atoms sit at the centers of distorted TiO$_6$ octahedra, there are four inequivalent O sites, with Ti-coordination between two and four. To understand the electronic structure, we have recorded linear polarized NEXAFS with the TXM [2] at the new U41-XM beamline of the BESSY II synchrotron, Berlin [P. Guttmann *et al* at this conference]. The spectra were normalized using the signal intensity in the proximity of the sample to correct for intensity variations with the photon energy. The polarization dependence was controlled by rotating the sample in the plane perpendicular to the beam direction; the spectra acquired at four different angles are shown in **Fig. 2**. The polarization dependence of the Ti L-edge is very weak, thus we focus on the O K-edge where we can observe a strong variation in the peak A:B intensity ratio. The measured polarization dependence of the O K-edge is in accordance with our DFT calculations for each of the inequivalent O sites in TiO$_2$-B showing that the A:B
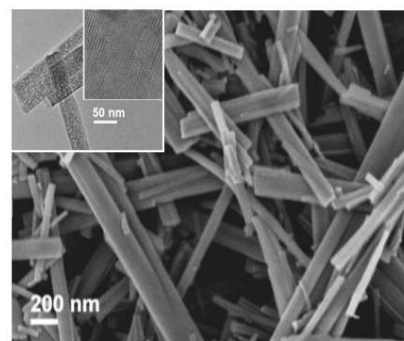
Figure. 2. TXM-NEXAFS of a single TiO₂-B nanoribbon.
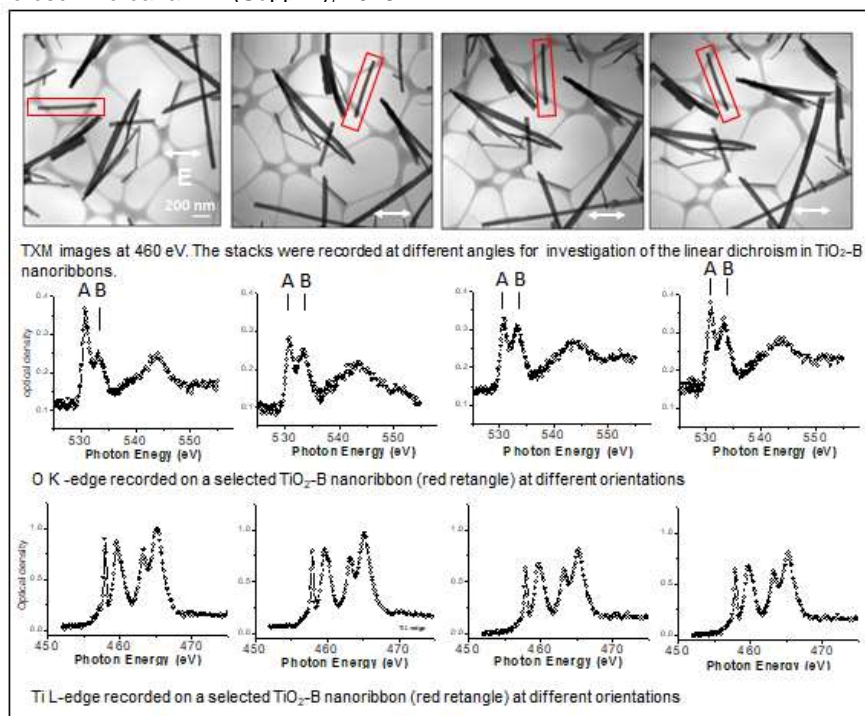
ratio is strongly polarization and site dependent reflecting the directional O-2p to Ti-3d bonding of the different O sites.

Figure 3 shows the calculated O K-edge spectra as a function of the angle θ between the X-ray polarization and the longest nanoribbon axis. θ is varied from 0° (parallel) to 90° (perpendicular) in steps of 15°. The spectra are computed as $I(\theta)= I(b)\ \cos^2(\theta)+ I(a)\ \sin^2(\theta)$, where I(b) and I(a) correspond to the polarization vector aligned with the b- and a-axis of the TiO₂-B crystal, respectively [3]. It can be seen that the A:B intensity ratio is progressively reduced when going from parallel to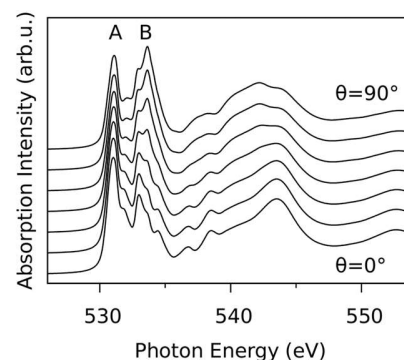 perpendicular alignment, in good agreement with the experimental O K-edge spectra (**Fig.2**). In our previous calculations [3], core-hole effects had been neglected. While good agreement with experiment was obtained, the A peak displayed fine structure not observed in experiment. Here, the core-hole effect has been taken into account in a supercell calculation with 4 primitive cells. The core-hole was put on a single O site of the 48 atom cell and the spectra obtained for different core-hole sites were summed. As a result, the line shape in the A-B region is much improved, with a sharply rising A peak in agreement with experiment. The A:B branching ratio is, however, hardly affected by the core-hole and thus our analysis of the X-ray linear dichroism in TiO2-B remains unchanged [3].

In conclusion, we have shown that TXM-NEXAFS combined with DFT calculations is a valuable tool to study titania nanostructures. The O K-edge spectra of individual nanoribbons show strong X-ray linear dichroism which reflects the anisotropic electronic structure around the O sites. The agreement with experiment has been improved by taking account of the core-hole effect in the calculation.

Figure. 3. Calculated O K-edge for different angles θ between the X-ray polarization and the longest nanoribbon axis.

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