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Electron Radiation Damage in TiOx Nanobelts

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Titania-based nanostructures can exist as nanotubes and nanobelts and these forms show a high photocatalytic activity, making them good candidates for a number of applications in numerous fields as environmental decontamination, photocatalysis, etc. [1-3]. Titania nanotubes and nanobelts are found to be beam sensitive materials and the aim of this work is to characterize the damage to nanobelts in the TEM.

The TiOx nanobelts were obtained using a one-step thermal treatment of TiO_2 in an aqueous solution of NaOH 10M at temperatures above 150 C. The electron irradiation damage was studied in a Hitachi HF3300 microscope at 300 kV. Spatially resolved electron energy-loss spectroscopy (SREELS) and parallel nanobeam diffraction (NBD) were used to study changes *in situ* in the TEM, as a function of the electron dose supplied to the sample. In order to reduce the dose rate, some NBD patterns were acquired over areas up to 120 nm across. For SREELS studies we used current densities ranging between 0.0046 and 0.25 A/cm^2. Absolute thickness was obtained after estimating the inelastic mean free path to be 152 nm by using equations in [4].

Figure 1 shows diffraction patterns obtained at 300 kV using a beam of diameter 120 nm giving a dose rate of about 0.1 A/cm^2. Clearly observed is a progressive appearance of streaking along some reciprocal-lattice directions and at higher doses a fading of higher order Bragg reflections. Figure 2 shows a high resolution image obtained at an early stage of damage: a finely divided mottle contrast can be observed (left). These white nanometer-sized regions exhibit no contrast. At higher doses, these contrastless regions increases in size (right). Other HRTEM observations (not shown) indicate a change in shape at the edges of the nanobelts, suggesting that the damage can proceed with mass loss.
Figure 3 shows low-loss EEL spectra (left) as a function of dose. A smearing of the peaks at 14 eV and 19 eV (marked with arrows) is apparent. No other changes were observed at higher doses or dose rate. Thickness mapping (right) revealed changes in the irradiated areas, confirming that the damage is accompanied of mass loss.

Our results show that the nanobelts damage at relatively low dose, indicating the material is more sensitive than most inorganic compounds (oxides, etc.) but less sensitive than organic materials. Such sensitivity may be related to an initial H loss with subsequent structural rearrangement. After further irradiation mass loss occurs, as shown by our thickness profiles.

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[2] W.-Q.Han, et al., Adv. Mat., 19 (2007) 2525.
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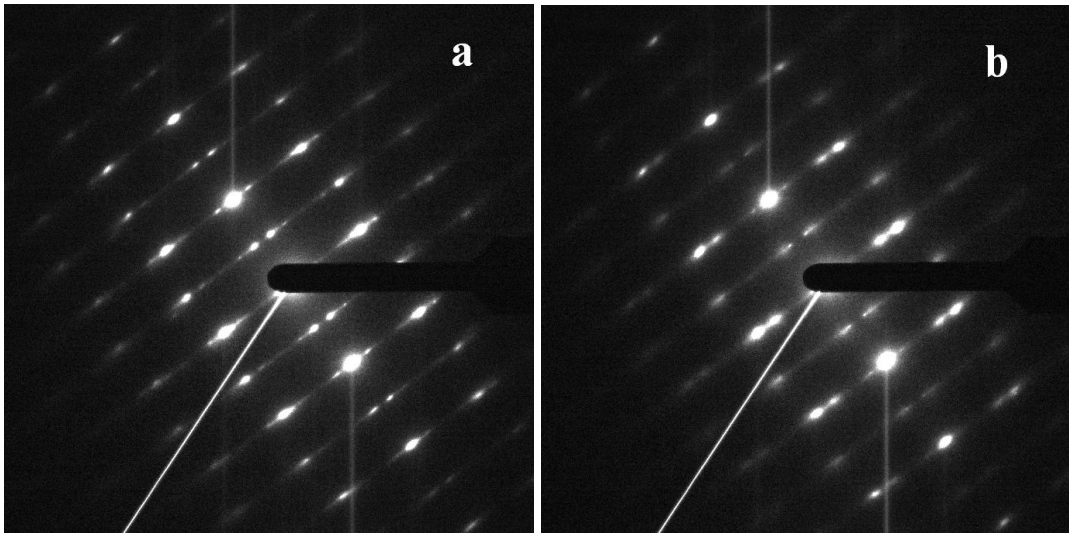

Figure 1. NBD patterns obtained at 0 C/cm^2 (left) and 200 C/cm^2 (right).

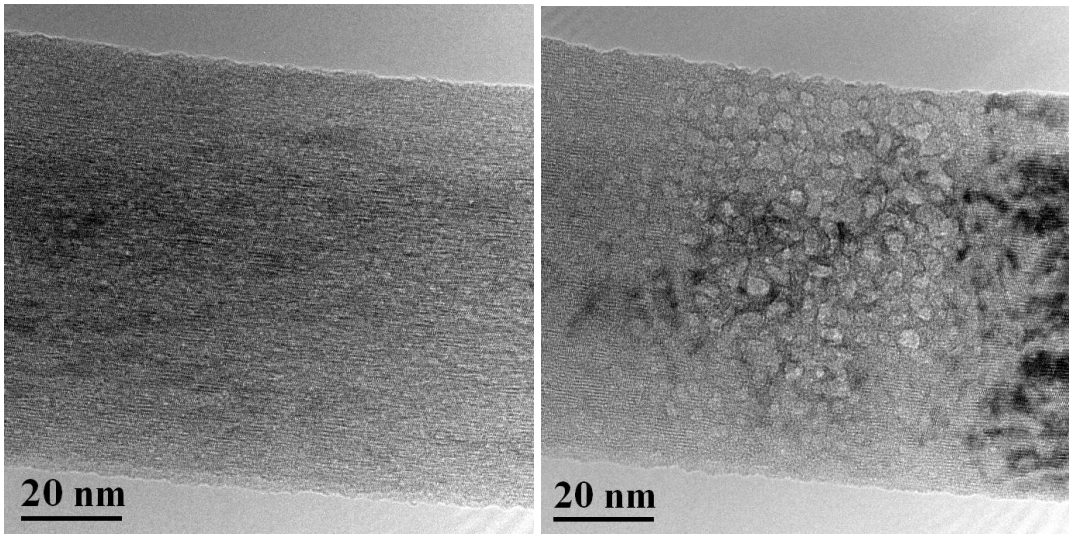

Figure 2. Bright-field images at an early stage of damage (left) and after localized heavy irradiation (right)

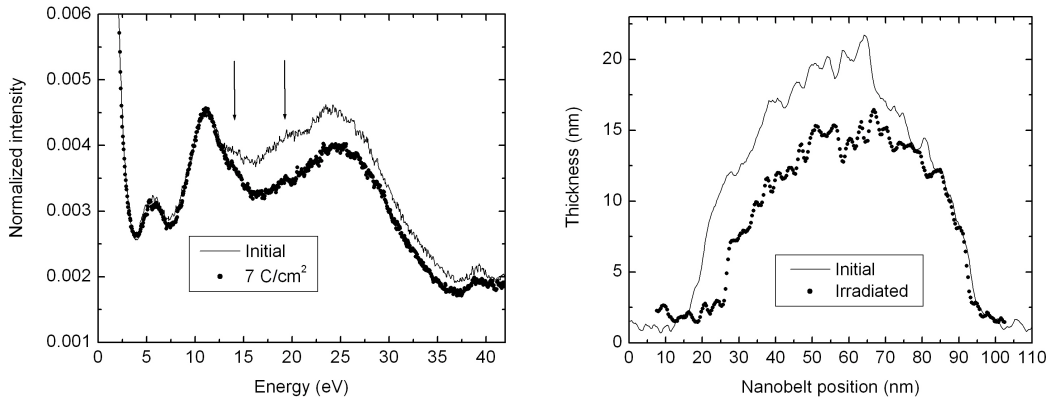

Figure 3. EEL spectra as a function of dose (left). The arrows point to changes in the spectra. Thickness profile for initial and irradiated samples (right).

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