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Radiolytic Transformation of TiO_2 Revisited with High Resolution EELS.

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In 1995 Peter Rez et al. discussed the Radiolytic transformation of TiO_2 to TiO under high flux electron irradiation (~$10^8 A/m^2$) as observed from the fine structure changes in Electron Energy Loss Spectra (EELS) [1]. We would like to revisit this topic with the specific focus of High resolution EELS of this transformation and general cautionary commentary on STEM work in nanostructures.

Fig 1 shows the nanoparticle sample of study. It consists of ~7 nm nanoparticles of TiO2 anatase that have conglomerated into larger nano-porous structures of ~70 nm in size. This image is taken in STEM mode with a monochromated beam. The resulting probe is several nanometers in diameter. If the beam is rapidly scanned over a region such as a line or square (as indicated in Fig 1), the observed spectra (Fig 2) is typical of anatase TiO_2 with the B peak split into B_1 and B_2 and B_1 showing up stronger than B_2 [2]. In Fig 2, this is only seen as the peak at the B_1 position and an asymmetry in the B peak. However, when the beam is stopped at the center of the circle shown in Fig 1, the spectra shifts to lower energy onset and loses the clear A – B set of peaks. This new fine structure appears to be two peaks separated by less than 1 eV. Peak labeling follows the A, B pattern of reference 2.

Both spectra shown in Fig 2 were taken at 6 seconds of integration time. However, the electrons involved in the "area" spectra are spread over a region greater than 100 times as large as the spot spectra with an expected corresponding greater than 100 fold decrease in the damage rate. However, in the case of the stopped beam, the damage rate is significantly faster than that seen by Rez [1]. This difference in damage rate could be attributed to difference in electron dose. However, similar data from single crystal anatase particles of similar overall size (~70-100 nm) show no damage on the six second time scale. This indicates a significant enhancement of the damage rate due to the small size and resulting large surface of the fundamental constituent particles.

This underscores and illustrates that we must be careful to both minimize and understand the role of beam damage when using the extremely high electron density probes seen in STEM work [3].

References

[1] P. Rez, J.K. Weiss, D.L. Medlin, D.G. Howitt, *Microsc. Microanal. Microstruct.* **6** (1995) 433-440

[2] R. Brydson, H. Sauer, W. Engle, J.M. Thomas, E. Zeitler, N Kosugi, and H. Kuroda. *J. Phys.: Condens, Matter* **1** (1989) 797-812.

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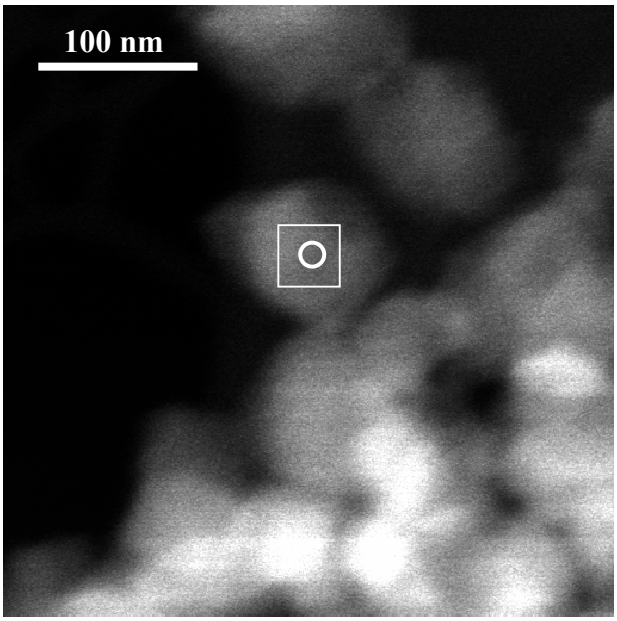

FIG. 1. STEM ADF image with Monochromator on. White areas are conglomerates of TiO2 nanoparticles (~7 nm each). Square and circle show EELS collection regions. See Fig 2 and text.

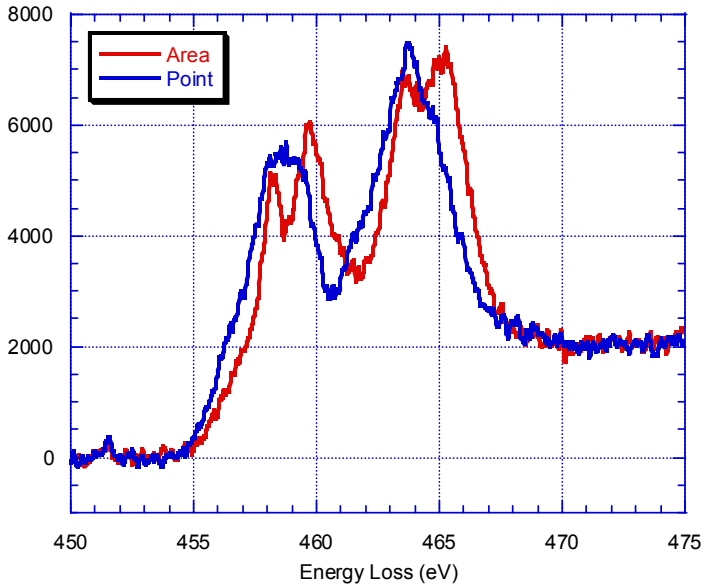

FIG. 2. EELS spectra (~ 0.4 eV resolution in this case) of the two regions in Fig 1. The shift of edge onset and loss of well-separated peak structure illustrates the beam damage transformation.

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