

Surface Dynamics Associated with Redox Processes on TiO₂ Nanoparticles

Qianlang Liu¹, Shery Chang² and Peter A. Crozier¹

¹ School for the Engineering of Matter, Transport and Energy, Arizona State University, 501 E. Tyler Mall, Tempe, AZ 85287-6106, USA.

² LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704, USA.

TiO₂ anatase nanoparticles have shown interesting properties as ultraviolet (UV) light photocatalysts for water and air remediation as well as solar water splitting. The surface of the nanoparticle plays a vital role in controlling the catalytic reactivity. For example, reactant adsorption, breaking/forming of chemical bonds, and product desorption all take place on the surface. *In situ* observations of such catalysts at the atomic level is required to follow structural transformations under near-reaction conditions thus elucidating the reaction and deactivation mechanisms. An optical fiber based *in situ* illumination system has been built and installed on an aberration-corrected environmental transmission electron microscope (TEM), allowing the sample to be illuminated with a broadband light source (200-800 nm in wavelength) while exposing to heat and gases such as water vapor. Negative spherical aberration imaging (NCSI) was used to enhance the contrast from oxygen and titanium columns to allow observation of structural dynamics induced by the light and water [1].

Anatase nanoparticles were hydrothermally synthesized. An aberration-corrected FEI Titan 80-300 was employed at 300 kV to image the particles with a single-electron-detection K2 camera operated in the counted mode. In our initial work, we used the electron beam to simulate the effect of light illumination. Moderate and controlled electron dose may be used to simulate the light illumination effect [2]. The K2 camera allows high quality electron imaging to be performed with a dose rate <10 e⁻/pixel/s (<150 e⁻/Å/s for high-resolution).

Fig. 1a demonstrates that oxygen columns at the thin region of an anatase particle close to [010] zone axis (ZA) can be imaged and resolved. Because of the Cs value of -20 μm and positive defocus, the Ti and O dumbbells in the anatase unit cell structure (Fig. 1c) appear as a pair of bright dots and the oxygen atoms appear as less bright individual dots between dumbbells. The intensity profile across a subsurface layer of atoms (Fig. 1b) clearly shows signals from the oxygen atomic columns. Fig. 1d-f shows an example of electron beam induced structural evolution taking place on a {001} nanofacet of this particle. Initially the image from the top surface layer terminated mostly with a row of dumbbells representing column pairs containing Ti cations. During irradiation, the initial terrace width of 5 column pairs changed to a wider terrace consisting of 8 individual columns. Simultaneously, the layers below the {001} surface became wider and the intensities of edge columns increased. Bridging oxygens will be preferentially removed during electron beam irradiation leading to a partial reduction of the surface. The cations on the reduced surface are de-stabilized and become mobile and migrate to the high energy edge sites thus widening the {001} terrace as illustrated in Fig 1g. *In situ* experiments will be performed in the presence of ultraviolet light and are likely to show similar changes in surface structure. In the presence of water vapor, we hypothesize that the cations will be pinned and a different hydroxylated structure will be formed. These results will be discussed during the presentation.

References:

[1] C. Jia et al., *Microscopy and Microanalysis* **10** (2004) p. 174.

[2] L. Zhang et al. *Nano Letters* **13** (2013) p.679.

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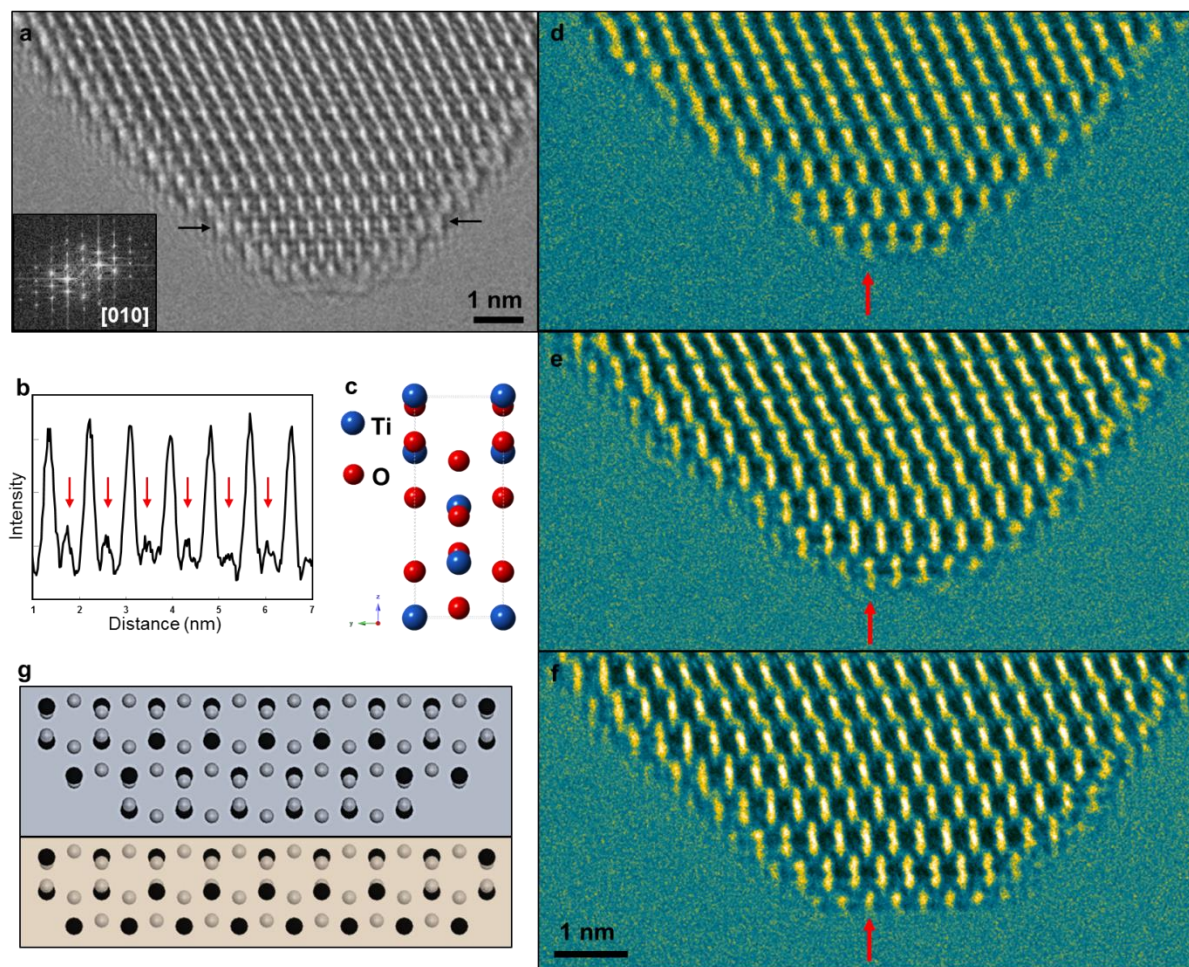


Figure 1. (a) NCSI image of an anatase particle at [010] ZA with $\sim 150 e^-/\text{\AA}^2/\text{s}$ showing the oxygen columns between the dumbbells. Insert is the fast Fourier transform (FFT) from the area shown. (b) Intensity profile extracted from the row of atoms indicated with the black arrows in (a). The red arrows indicate the same position on the terrace in each frame. (c) An anatase unit cell model from the [010] ZA. (d-f) time sequence images at the same magnification of the {001} surface from this particle. (g) Model structures of {001} surfaces illustrating removal of one layer of atoms from the surface breaking dumbbell pairs.