Quantifying Structural Transformations from Redox Reactions in TiO_2

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TiO_2 anatase nanoparticles have shown interesting properties as ultraviolet (UV) light photocatalysts for water and air remediation as well as for solar water splitting. Understanding the structural changes that take place during photocatalysis is critical to developing structure-reactivity relations for these applications. Oxygen vacancies are believed to play an important role in surface reactivity. The structure of TiO_2 nanoparticles has been investigated with *in situ* atomic resolution transmission electron microscopy (TEM) [1,2]. In these experiments, a low electron flux was used to prevent structural damage, however, this results in a poor signal-to-noise ratio. Differentiating intensity fluctuations due to shot noise from fluctuations associated with defect-induced structural changes is crucial and challenging, and the interpretation of the point defect structure can only be accomplished through a detailed comparison with theory. Here, computational methods based on molecular dynamics (MD) and density functional theory (DFT) are employed to construct defect models of TiO_2, which are employed in image simulations to interpret experimental observations.

Experimental images of TiO_2 anatase nanoparticles were acquired using negative C_s imaging in an aberration-corrected FEI Titan environmental TEM equipped with a single-electron-detection K2 camera operated in the counting mode. The K2 camera allowed high quality electron imaging to be performed with an electron flux <10 e-/pixel/s (<250 e-/Å^2/s for high-resolution). For MD simulations, a reactive forcefield developed for modeling interactions between water and titania was used, with DFT+U serving to benchmark selected simulations [3]. TEM image simulations were performed on the benchmarked structures, and oxygen vacancy fingerprints were generated for a variety of defect configurations to compare with the experimental images.

Figure 1 shows an atomic-resolution image from a thin region of anatase recorded with an electron flux of 250 e/Å^2/s. The image is a sum of 20 frames (each of 0.1 s) and has been filtered using a 1-pixel Gaussian blur. The Ti-O dumbbells and O columns appear with differing intensities, and show bright contrast from the choice of -C_s. Figure 2 shows the relaxed structures of anatase with one (a) and two (b) oxygen vacancies, which are located in the squared columns. These structures were used in TEM image simulations, shown in Figure 2(c) and 2(d), respectively. The structural relaxations from oxygen vacancies are clear when overlaying the defect-free image (blue) on the image with vacancies (red). Oxygen vacancies (marked by stars) are seen to displace the Ti cations, as seen by the red-shift in intensity near the vacancies. Interestingly, the resultant displacement induced in the O columns appears much less pronounced. We are currently quantifying the position and intensity fluctuations in experimental images and comparing them to simulations. Figure 3 shows two consecutive frames from the experimental image series. Approaches to differentiate fluctuations due to shot noise from those due to defects will be discussed during the presentation.

References:

[1] Liu, Qianlang, *et al*., Microscopy and Microanalysis **23.S1** (2017), p. 906-907.
[2] Zhang, L., *et al*., Nano Letters **13** (2013), p. 679.
[3] Kim, Sung-Yup, *et al.*, "Development of a ReaxFF Reactive Force Field for Titanium Dioxide/Water Systems." Langmuir, **29**, (2013), p. 7838-7846.
[4] The authors acknowledge support from NSF DMR-1308085 and DOE (DE-SC0004954). The authors acknowledge John M. Cowley Center for High Resolution Microscopy at ASU and Gatan for the loan of the K2 camera.

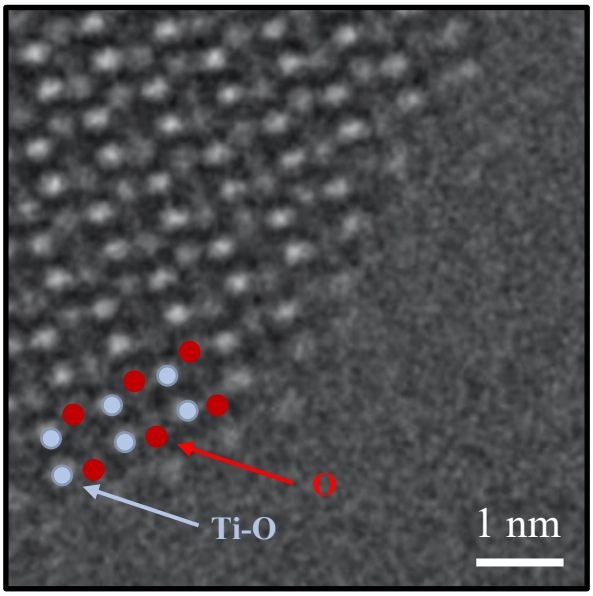

Figure 1: TiO_2 anatase nanoparticle in the [100] zone axis showing clearly resolved O and Ti-O columns. The image is a sum of 20 individual frames taken with 0.1 second exposure and a fluence rate of 250 e/Å^2/s. The 20-frame summed image has been filtered with a 1-pixel Gaussian blur for clarity.

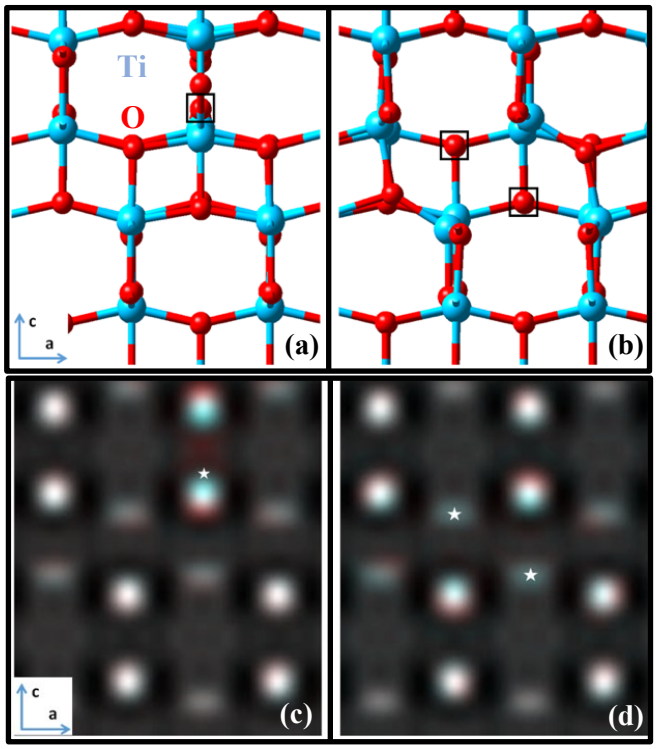

Figure 2: Relaxed anatase with 1 (a) and 2 (b) O vacancies, marked by squares. The corresponding simulated images are shown in (c) and (d), where vacancies are starred. Vacancy induced relaxations are seen by overlaying the defect-free image (blue) on the image with the vacancies (red).

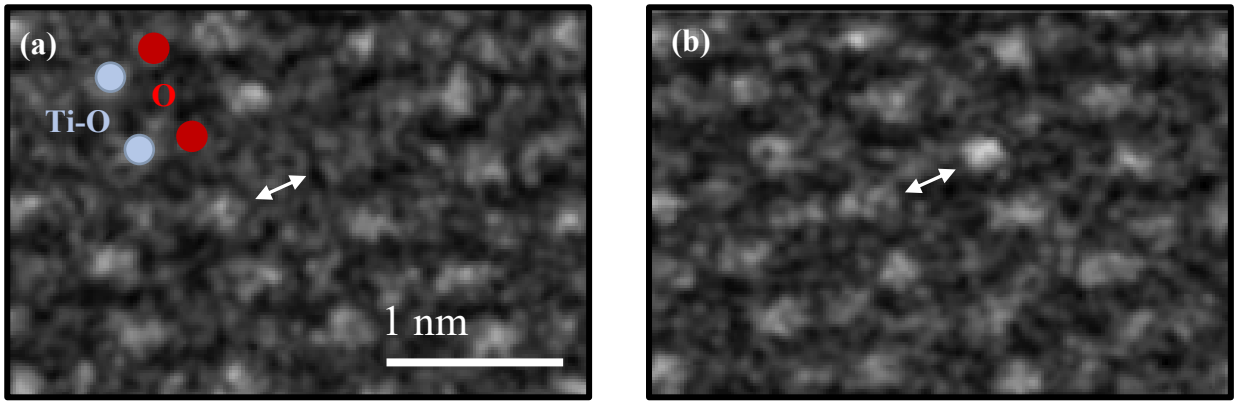

Figure 3: Two consecutive 2-frame images from Figure 1 showing neighboring Ti-O columns that fluctuate in intensity between (a) and (b). Intensity fluctuations may be attributed to shot noise, or to structural reconfigurations from defects present in the anatase structure.