Restructuring Cracks in Rutile TiO_2 with Radiolysis-Driven Rolling of Octahedral Units

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When energetic electrons interact with crystals in transmission electron microscope (TEM), a combination of "knock-on" and radiolysis effects takes place [1]. Radiolysis, in particular, is known to either amorphize or crystalize materials and limit the accuracy of the measurements [2]. However, the precise atomistic mechanisms of these transformations are still under debate. Here, we use scanning TEM (STEM) imaging and electron energy loss spectroscopy (EELS) to study the bond-breakage, atomic movements and crystallization mechanisms in rutile-TiO_2 driven by radiolysis [3].

Thin-film rutile IrO_2 was grown on top of rutile TiO_2, introducing nano-meter width cracks due to an anisotropic epitaxial strain (Figure 1a). To assess the impact of electron beam exposure on the structural healing process of the atomically sharp cracks in rutile-TiO_2, high angle annular dark-field STEM (HAADF-STEM) time-lapse images of the cracks were obtained (Figure 1b). With the accumulation of electron doses, the crack undergoes a self-healing restructuring process. Based on these observations and quantitative EELS analysis, we propose a "2-step rolling" model for the TiO_6 octahedral building blocks located at the crack's edge of rutile-TiO_2 as a possible mechanism for radiolysis-driven atomic migration (Figure 1c and d). With radiolytic bond breakage (Figure 1c), the TiO_6 octahedral units from the edge of the crack can roll and occupy new sites and, in the process, move materials from both sides of the crack into the gap (Figure 1d) [3].

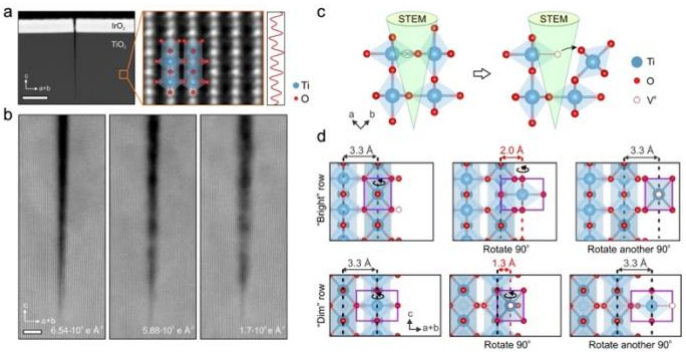
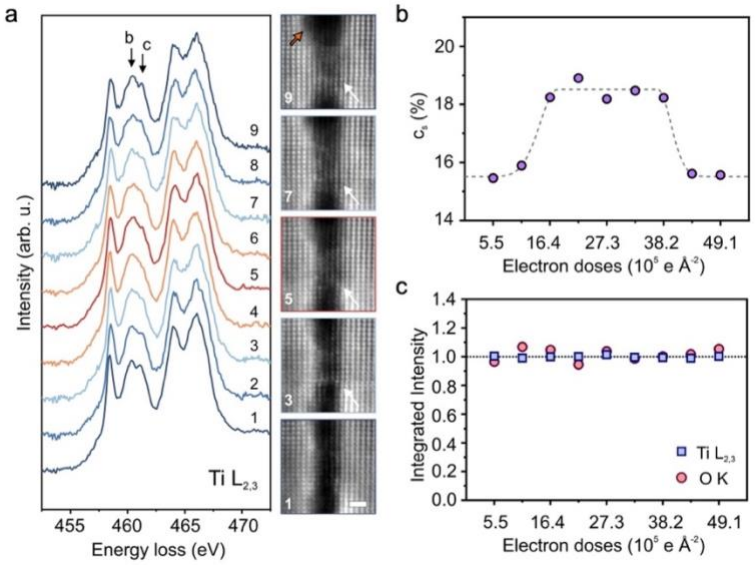


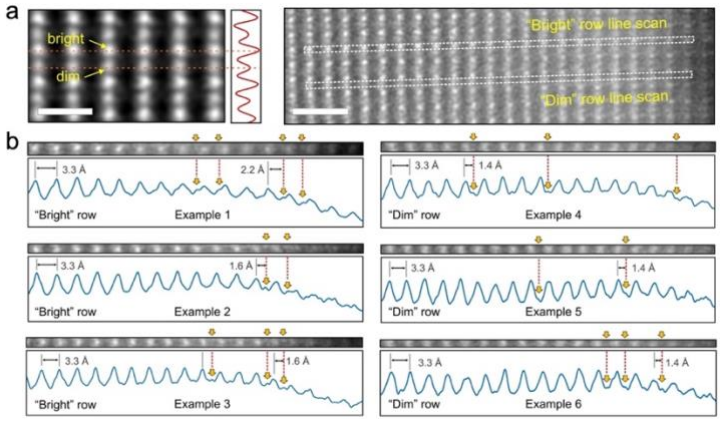
Figure 1. a, A rutile IrO_2/TiO_2 sample with an atomically sharp crack. **b,** A set of HAADF-STEM images showing the self-healing crystallization in the center of the crack with increase of electron doses. Scale bar is 3 nm. **c,** Radiolysis-driven Ti-O bond breakage between two octahedra units in rutile TiO_2. **d,** A "2-step rolling" model for octahedral motion from the "bright" and "dim" row configurations.

[1] L. Reimer and H. Kohl, *Transmission Electron Microscopy: Physics of Image Formation* (Springer, Berlin, 2008), 5th edn.
[2] L. W. Hobbs, *Introduction to Analytical Electron Microscopy*, edited by J. J. Hren, J. I. Goldstein, and D. C. Joy (Scanning Microscopy International, Chicago, 1979), p. 437
[3] S. Guo, H. Yun, S. Nair, B. Jalan and K. A. Mkhoyan (arXiv: 2304.03482)

Supplementary Information



Supplementary Figure 1. a, A set of EELS Ti-$L_{2,3}$-edges as function of electron beam doses from a crack region in rutile TiO_2. Five HAADF-STEM images are acquired in parallel with these EELS measurements showing bridging. Scale bar is 1 nm. The peaks "b" and "c" with most changes are at 460.3 and 461.1 eV, correspondingly. **b,** Concentrations of surface Ti atoms in the exposed crack area (c_s) as a function of electron dose determined from Ti $L_{2,3}$-edge spectra in **a**. **c,** The changes in the number of Ti and O atoms as a function of electron dose in beam-exposed crack area in **a** are evaluated using integrated intensities of Ti $L_{2,3}$- and O K-edge EELS spectra [3].



Supplementary Figure 2. a, Atomic-resolution HAADF-STEM image of [110] rutile TiO_2. Orange dashed lines show the rows of "bright" and "dim" atomic columns. Scale bar is 0.5 nm. On the right, a magnified image from the crack bridging region with dashed rectangle strips indicating where the "Bright" row and "Dim" row line scans are taken. Scale bar is 1 nm. **b,** Six examples of one-atom-width strips of HAADF-STEM images and the corresponding intensity line scans. They show the locations of Ti atoms at interstitial sites with specific 2.2 Å, 1.6 Å and 1.4 Å spacings from the main columns [3].