

Supporting Information

Mending Cracks Atom-by-atom in Rutile TiO₂ with Electron Beam Radiolysis

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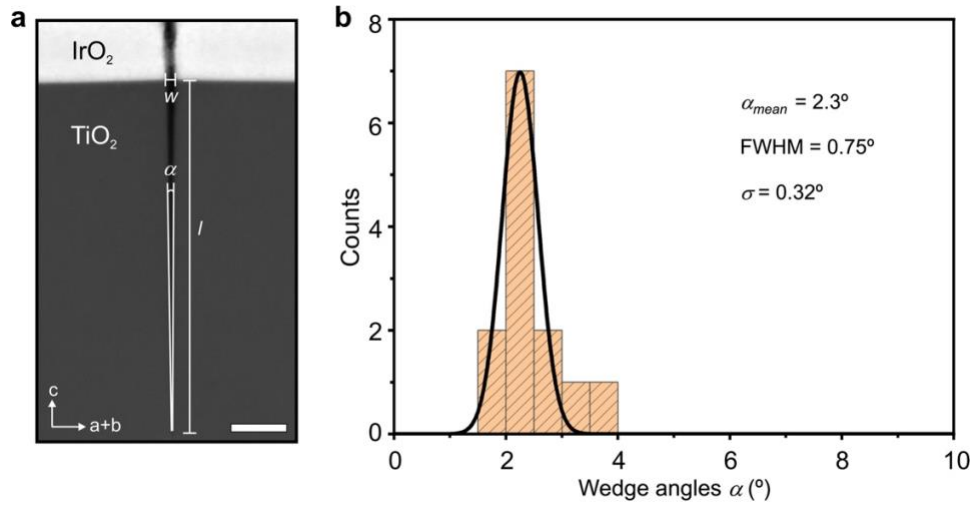
This PDF file includes:

Supplementary Figures 1 to 15

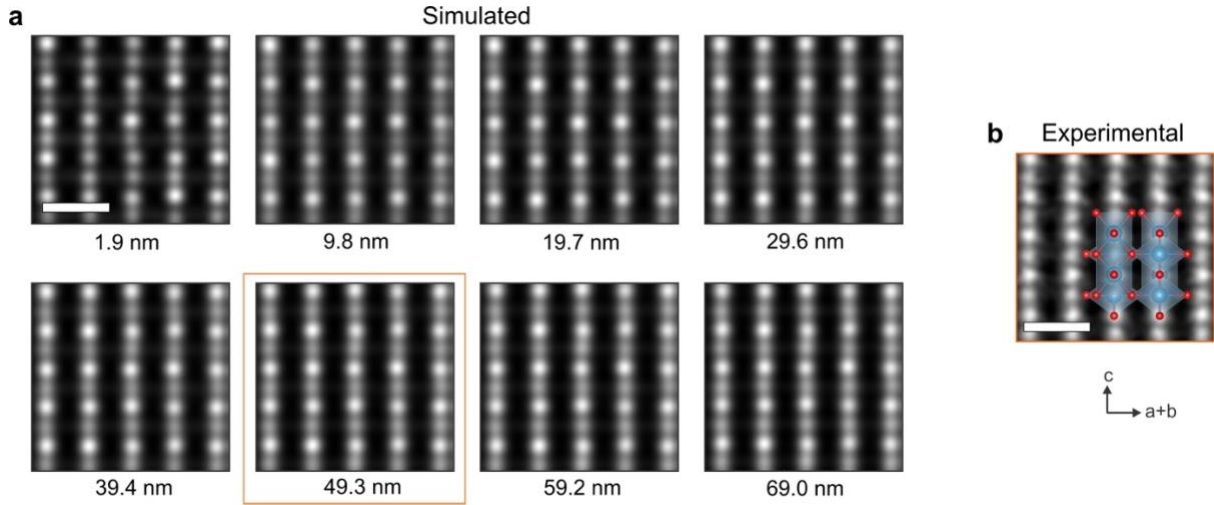
Supplementary Tables 1 and 2

Captions to Supplementary Movies 1 to 3

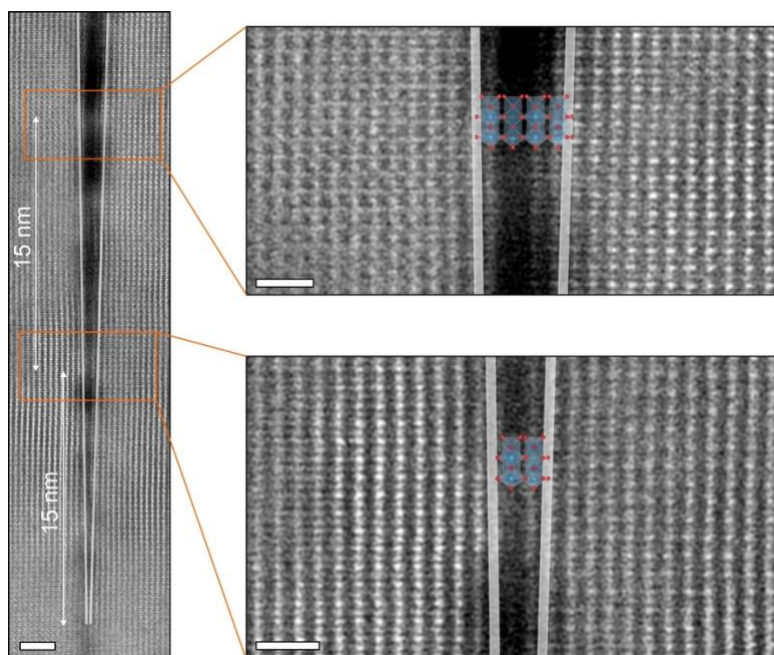
Supplementary references



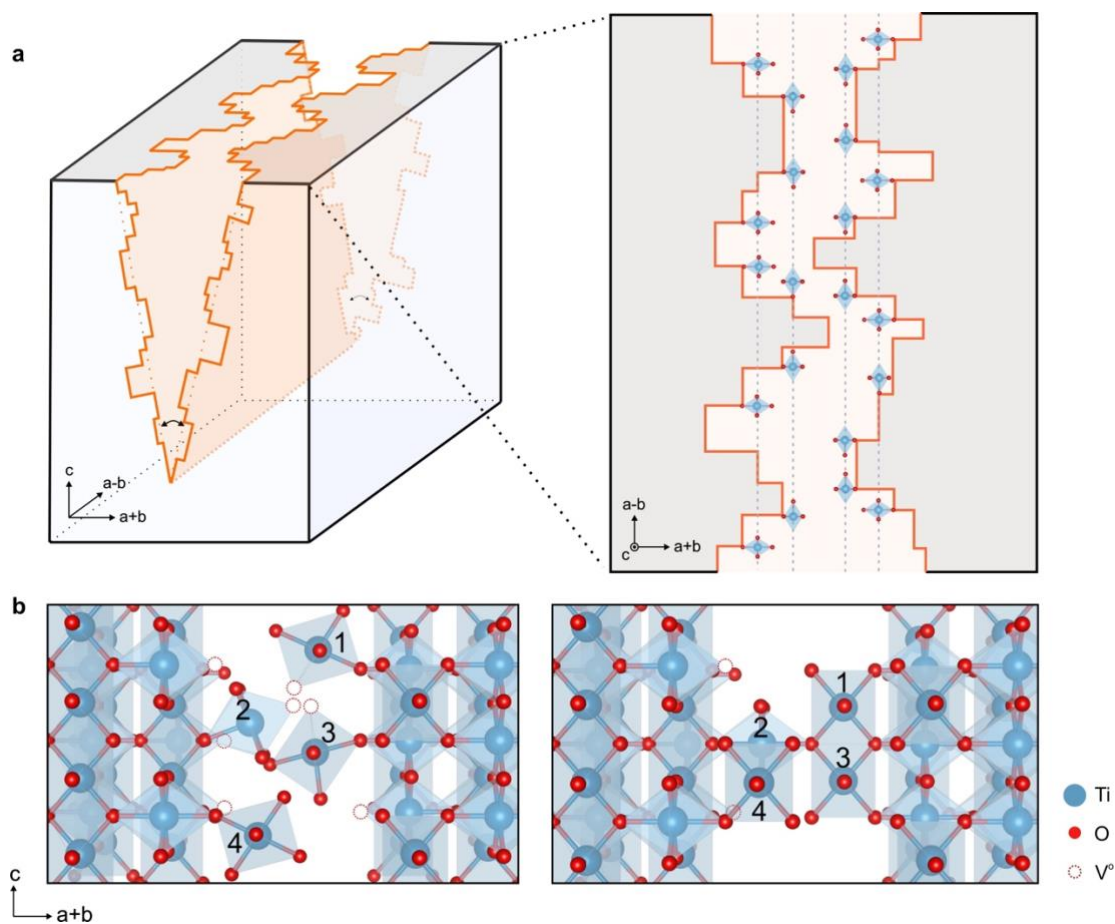
Supplementary Figure 1. Statistics of the crack wedge angles. **a**, HAADF-STEM image of a typical crack in rutile TiO_2 formed due to epitaxial stresses introduced by a rutile- IrO_2 film grown on it by SSMO-MBE. The crack can be described either by length l and width w (measured at the $\text{TiO}_2/\text{IrO}_2$ interface), or by wedge angle α . scale bar = 20 nm. **b**, Histogram of wedge angles based on measurements from 12 cracks. The histogram is fitted with a Gaussian function, which shows a narrow distribution with a peak position at 2.3° . The full width half maximum (FWHM) of the Gaussian function is 0.75° and the standard deviation σ is 0.32° .



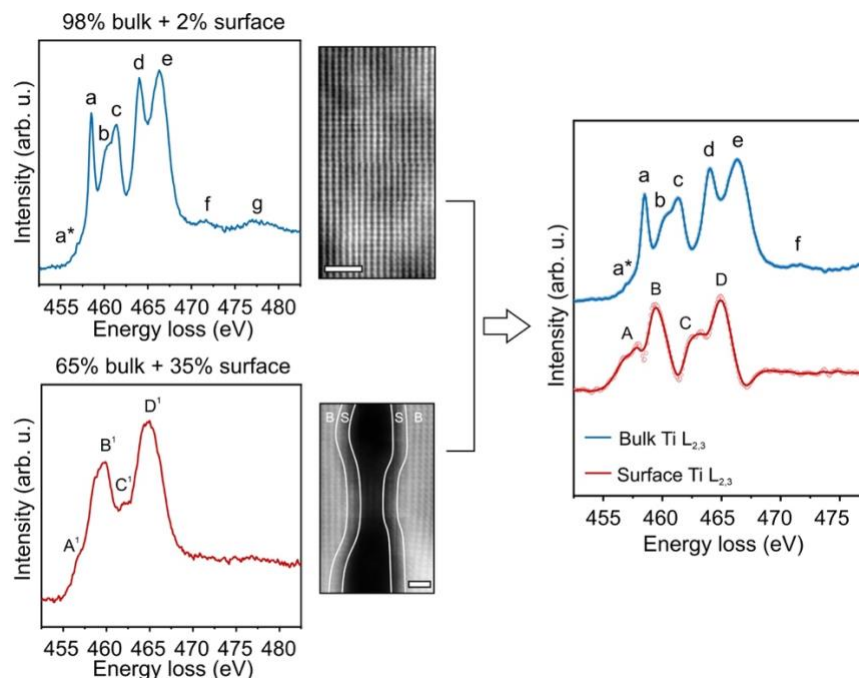
Supplementary Figure 2. Simulated HAADF-STEM images of rutile-TiO₂ crystal viewed in the [110] direction. **a**, Simulated atomic-resolution HAADF-STEM images of rutile-TiO₂. Sample thicknesses ranging from 1.9 nm to 69.0 nm are considered. These images are simulated using *Multislice* method and TEMSIM code developed by Kirkland¹ with following STEM parameters: $E_0 = 200$ keV, $C_{S(3)} = 0$, $\Delta f = 0$, $\alpha_{obj} = 25$ mrad, and HAADF detector inner and outer angles of 50 and 200 mrad. These values are used to mimic the condition of the STEM used for these experiments. Thermal atomic displacement values of 0.075 Å for Ti and 0.110 Å for O atoms are used.^{2,3} Ten frozen phonon configurations are averaged for each image. The final simulated images were convoluted with 2D Gaussian function with the full width at half maximum (FWHM) of 1 Å to incorporate the effects of source size.⁴ Scale bar is 0.5 nm. **b**, Experimental atomic-resolution HAADF-STEM image of rutile-TiO₂ crystal in the same [110] orientation obtained from region next to a crack. Image is low-pass filtered for noise reduction. Atomic model of rutile-TiO₂ is overlaid on the image to show the relationships between columns of Ti atoms and columns of Ti and O atoms and their HAADF “dim” and “bright” intensities, correspondingly. Relative intensity comparison suggests that the experimental image is from about $t = 50$ nm thick region. Scale bar is 0.5 nm.



Supplementary Figure 3. Closer look at the bridging sites of the crack after initial electron beam exposure. HAADF-STEM image taken after $1.5 \times 10^6 \text{ e } \text{\AA}^{-2}$ electron doses. This is the same image shown in Figure 3 of the main text. Scale bar is 2 nm. Two magnified atomic-resolution images of the bridging regions of the crack are also shown. Formation of rutile TiO_2 at these locations, where the gaps are an integer number of crystal unit cells (top region with $2a_{[110]}$ and bottom region with just $a_{[110]}$), can be seen. Scale bars are 1 nm. Atomic models of rutile TiO_2 are overlayed on these images for guidance. Images are low-pass filtered for noise reduction.

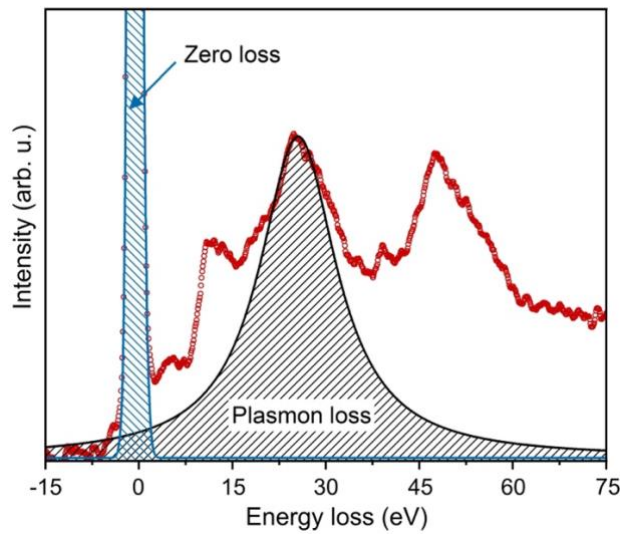


Supplementary Figure 4. Simplified 3D models of the cracks at different stages. a, (left) 3D model and (right) top view of the crack at early stage of mending illustrating initial structural changes with “octahedra” units at the edges and corners. **b**, Simplified 3D schematics showing locking of “octahedra” units from opposite sides of the crack. The dashed open red circles are missing oxygens. After locking “octahedra” 1 shares its left-bottom oxygen with “octahedra” 2 and 3, resulting in all units having 6 oxygens and turning them into true TiO_6 octahedrons.

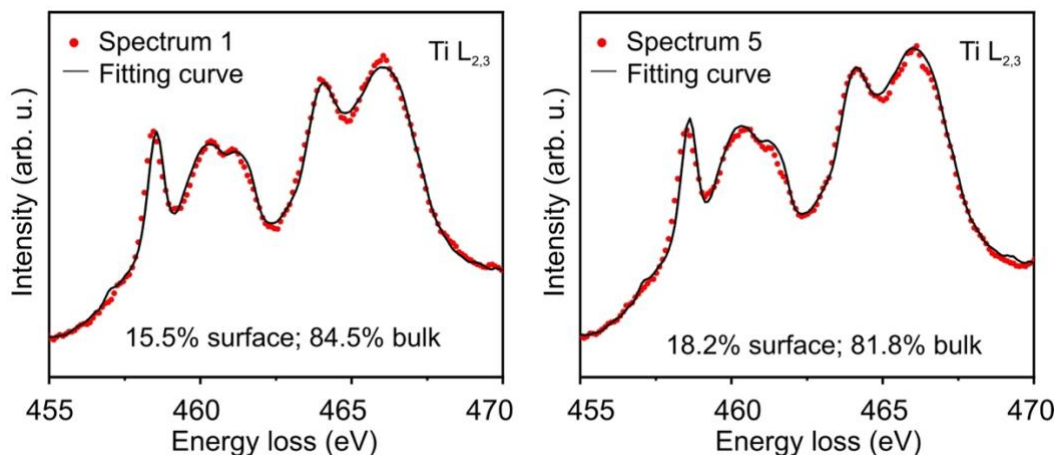


Supplementary Figure 5. Determination of reference bulk and surface EELS Ti L_{2,3}-edges.

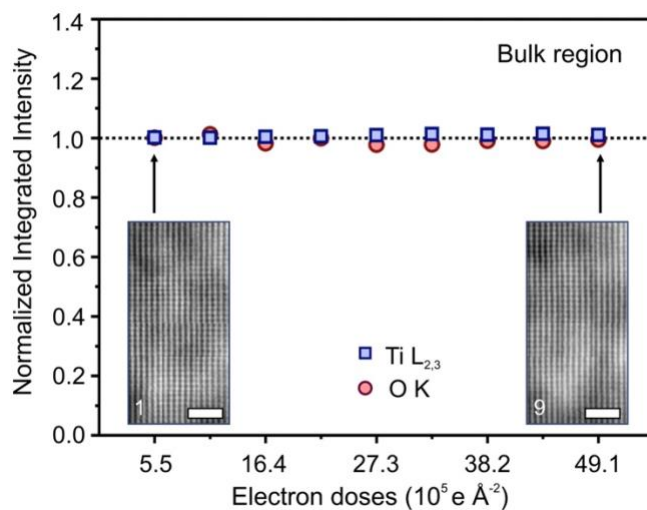
Monochromated EELS Ti L_{2,3}-edges are obtained from two locations of the sample. One from the region in-between the cracks (I_1) and one from the edge region of the crack (I_2). The spectrum I_1 , shown in top left, based on an evaluated thickness of the sample in this region $t = 52$ nm, should consist of 98% bulk and 2% surface Ti L_{2,3}-edges. The spectrum I_2 , shown in bottom left, based on evaluated thickness of the sample in this region $t = 52$ nm and wedge surface fraction relative to bulk as indicated in the HAADF-STEM image on the right (“S” for surface and “B” for bulk), should consist of 65% bulk and 35% surface Ti L_{2,3}-edges. Scale bars are 2 nm and 1 nm, correspondingly. Using these two spectra as a “a system of two equations with two unknowns”, the reference spectra of bulk and surface EELS Ti L_{2,3}-edges were determined. They are shown on the right.



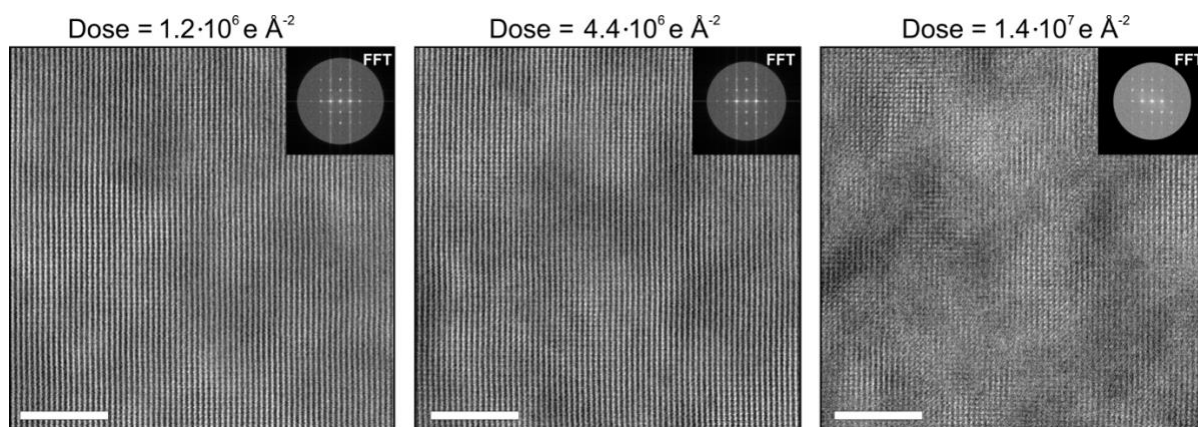
Supplementary Figure 6. Thickness determination using low-loss EELS. For thickness determination of the specific location of the rutile-TiO₂ sample, first, low-loss EELS spectrum was obtained from that region. Then, the “log-ratio” method was applied.⁵ The mean free path of plasmon excitation in rutile TiO₂ is $\lambda_p = 130$ nm.⁶ The zero-loss peak is fitted by a Gaussian function and the plasmon peak is fitted by a Lorentzian function after zero-loss peak was subtracted.⁷ This method was used to evaluate the thickness of the regions discussed in Supplementary Figure 4.



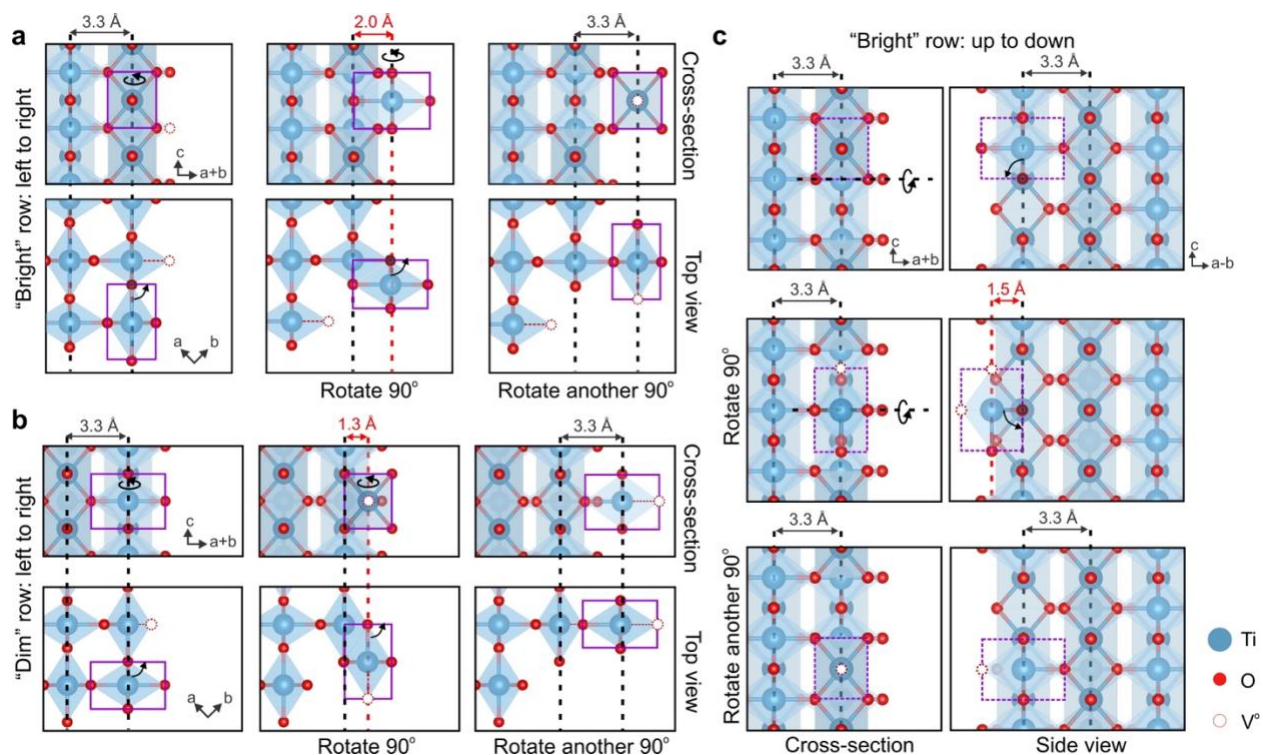
Supplementary Figure 7. Determination of relative fractions of bulk and surface components in measured EELS Ti L_{2,3}-edges. The fractions of surface and bulk components in each EELS Ti L_{2,3}-edge spectrum, discussed in Figure 4a in the main text, are determined by fitting it with a linear superposition of two reference spectra: $I = x \cdot I_s + (1 - x) \cdot I_b$. Here I_b and I_s are the reference spectra of surface and bulk Ti L_{2,3}-edges, respectively, determined earlier (Supplementary Figure 4). Through “least square” fitting algorithm, the normalized fractions of surface and bulk components are identified for each spectrum. Two examples of such analysis performed on Spectrum 1 and Spectrum 5 from Figure 4a in the main text are shown here.



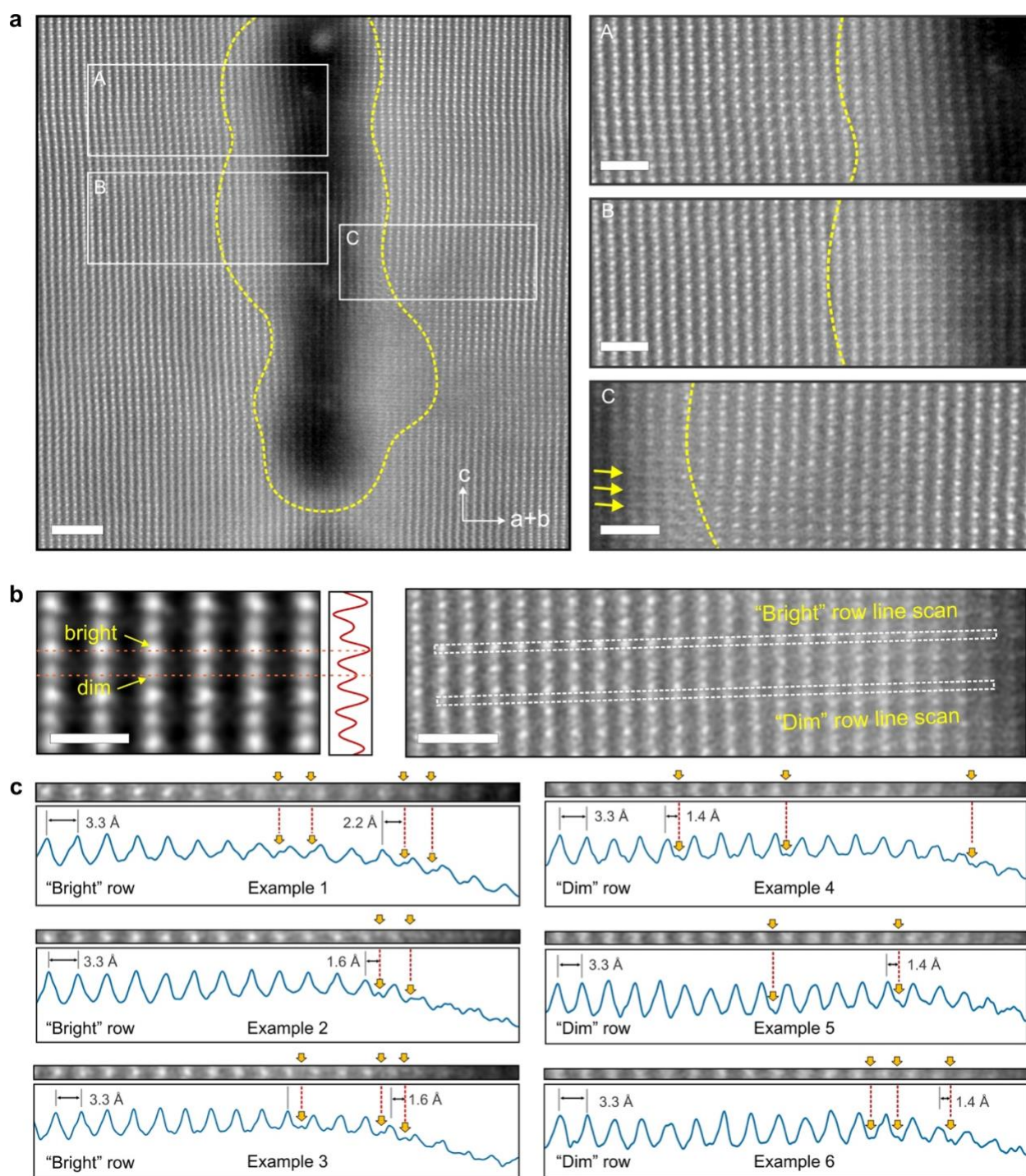
Supplementary Figure 8. EELS analysis of bulk region in rutile TiO_2 . HAADF-STEM images with parallel EELS measurements from bulk region of the rutile TiO_2 showing no identifiable compositional and structural changes. Scale bars are 2 nm. The changes in the number of Ti and O atoms as a function of electron dose in beam-exposed area are evaluated using integrated intensities of Ti $L_{2,3}$ - and O K-edge EELS spectra similar to those discussed in Figure 3d in the main text. The irradiation doses used here are comparable with those used for crack regions (see Figures 3c and 3d in the main text).



Supplementary Figure 9. Effects of the high electron beam doses in bulk region of rutile TiO₂. Atomic-resolution HAADF-STEM images of bulk region of the rutile TiO₂ at three e-beam exposure doses. The FFTs are shown in the upper-right corner. Partial loss of crystallinity is visible in the image at electron doses $1.4 \times 10^7 \text{ e } \text{\AA}^{-2}$. Images are low-pass filtered for noise reduction. Scale bars are 5 nm.

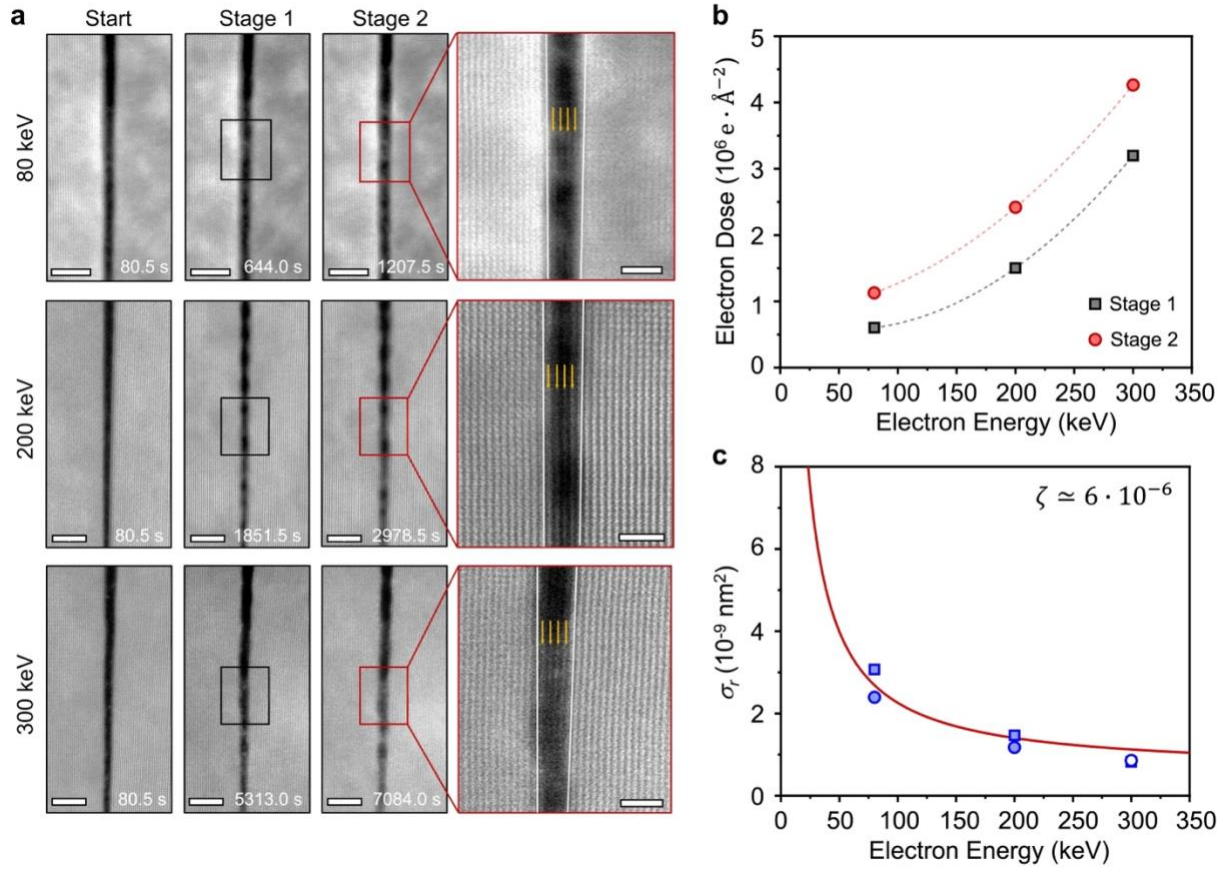


Supplementary Figure 10. A rotational model for TiO_6 octahedral units. **a**, Illustration of the “2-step rolling” model showing how an octahedral unit (highlighted in purple) at the edge of the crack from the “bright” atomic columns can rotate 90° and occupy an interstitial site in first step and then reach its final stable site after another 90° rotation in second step. The axes of rotations are indicated. Both cross-sectional ($[110]$ projection) and top ($[001]$ projection) views are shown. **b**, The “2-step rolling” model now illustrated for octahedral unit from the “dim” atomic columns. Unique interstitial sites occupied by rolling TiO_6 “octahedra” after the first 90° rotation can be characterized by their characteristic distances from the neighboring atomic column (highlighted by the red dashed line). **c**, “2-step rolling” model showing how an octahedral unit (highlighted in purple) at the edge of the crack from the “bright” atomic columns can rotate 90° down (or up) along the crack line and occupy an interstitial site in first step and then reach its final stable site after another 90° rotation in second step. The axes of rotations are indicated. Both cross-sectional ($[110]$ projection) and side ($[1\bar{1}0]$ projection) views are shown. Unique interstitial site occupied by rolling TiO_6 octahedra after first 90° rotation can be characterized by its distance from the neighboring atomic column (highlighted by the red dashed line). The red dashed open circles in models are oxygen vacancies, V^O .

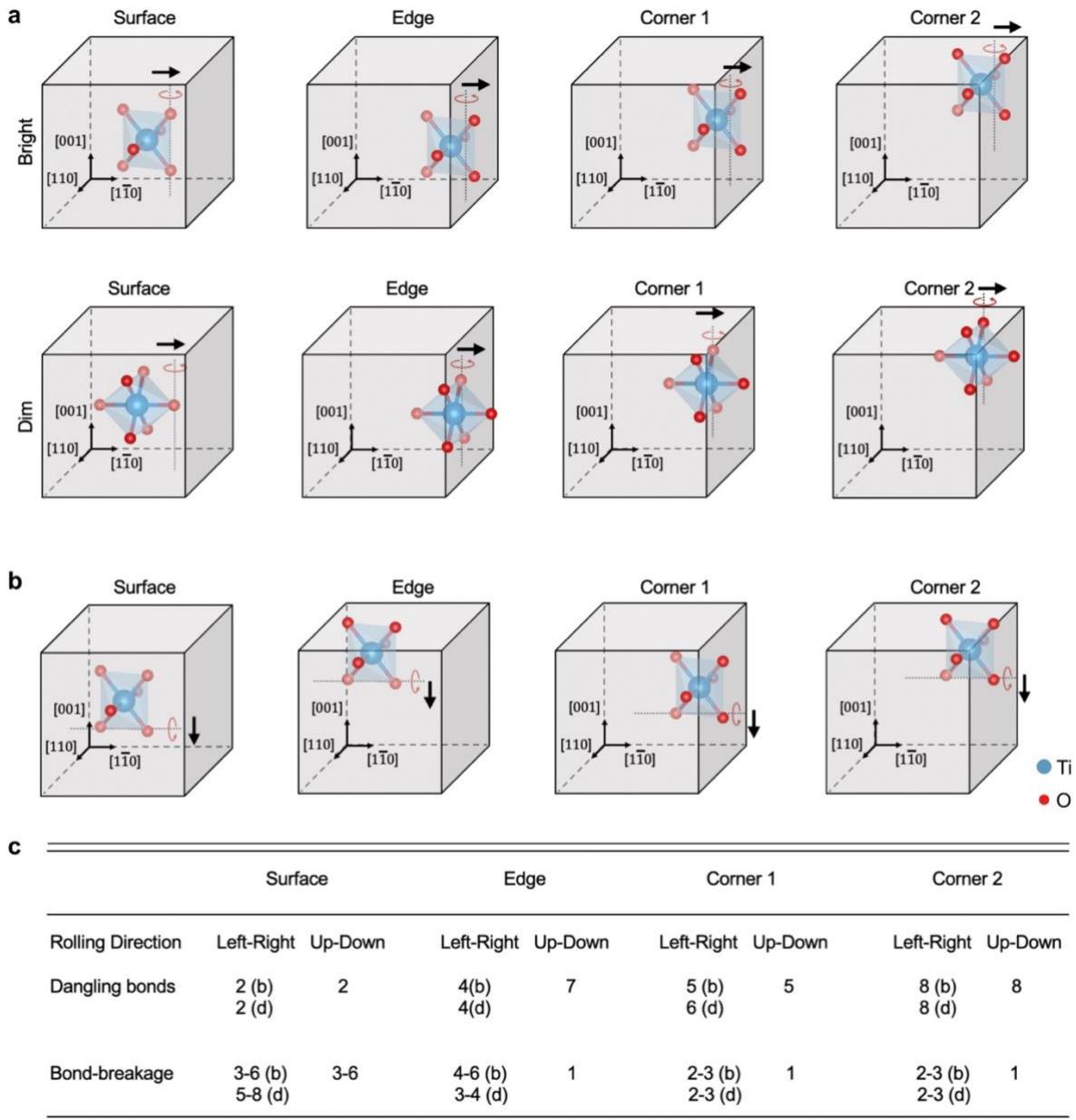


Supplementary Figure 11. HAADF-STEM imaging of a recrystallized crack for interstitial site analysis. **a**, Atomic-resolution HAADF-STEM image of a wider crack region after $4.1 \times 10^6 \text{ e} \text{ \AA}^{-2}$ electron beam exposure. The yellow dashed line indicates the boundary between considerably modified regions next to crack and the rest of the rutile-TiO₂ sample. The modified regions clearly show different lattice contrast compared to original rutile TiO₂. Scale bar is 2 nm. Magnified images from these regions, including bridging and non-bridging sites (labeled A to C), show close-up of these structural modifications. For example, C shows how “bright” rows become less bright

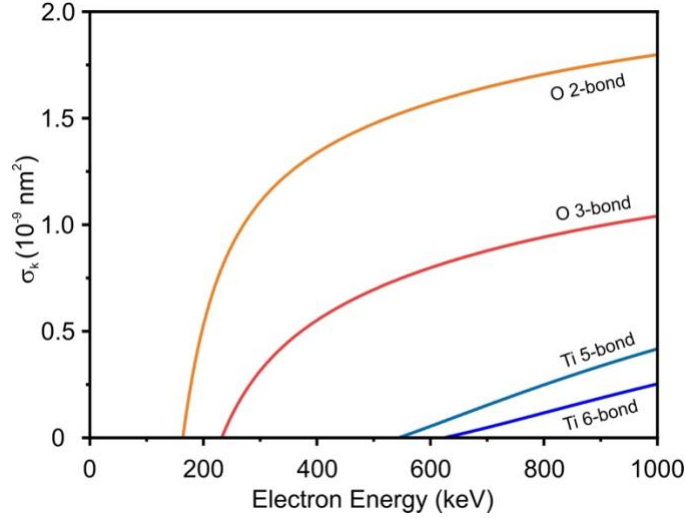
with added intensities between original rutile columns, indicated by yellow arrows. Scale bars are 1 nm in A, B and C. **b**, Atomic-resolution HAADF-STEM image of rutile TiO₂ viewed along [110] direction. Orange dashed lines show the rows of “bright” and “dim” atomic columns. The “bright” spots corresponding to atomic columns with Ti and O atoms and “dim” spots to columns with only Ti atoms. 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. **c**, Six examples of one-atom-width strips of HAADF-STEM images from the larger image shown in **a**, 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. Here “bright” rows are in examples 1 to 3 and “dim” rows in examples 4 to 6. The statistical analysis of these interstitial locations is presented in Figure 4d in the main text. Images are low-pass filtered for noise reduction.



Supplementary Figure 12. Radiolysis under three electron beam energies: 80 keV, 200 keV and 300 keV. a, HAADF-STEM images of three cracks in the same rutile TiO₂ sample. They were exposed to STEM electron probes with beam energies of $E_0 = 80, 200$ and 300 keV, correspondingly. Scale bars are 5 nm. Magnified (in red box) regions show 2 unit-cells-wide rutile TiO₂ is formed in the crack. Scale bars are 2 nm in the magnified regions. The images are low-pass filtered. The exposure times needed for two gap restructuring stages are indicated on the images, respectively. The thickness of the filled region in the gap is estimated to be about 10 nm (stage 1) and 15 nm (stage 2). **b,** Electron doses needed to form the rutile TiO₂ of same thicknesses in the gap (based on HAADF intensity) for both stages are plotted for all three electron beam energies. **c,** The data from panel **b** is converted into probabilities of single radiolysis-driven event (one-step of rolling) and fitted to a function describing the cross-section of radiolysis:⁸ $\sigma_r(E_0) = 8\pi a_0^2 \times \left(Z \frac{U_R}{m_0 c^2}\right) \left(\frac{U_R}{E_{th} \beta^2}\right) \times \zeta$, where a_0 is the Bohr radius, Z is the number of moving unit, U_R is Rydberg energy, m_0 is the rest mass of electron, c is the speed of light, E_{th} is the threshold energy that must be transferred to produce a movement, and $\beta = \frac{v}{c} = \sqrt{1 - \left(1 + \frac{E_0}{m_0 c^2}\right)^{-2}}$. Considering that, for rolling an octahedral unit, it will require breaking about 1 - 3 bonds (see Tables S1 and S2), the efficiency factor is estimated to be $\zeta \simeq 6 \times 10^{-6}$. For more accuracy, the fitting was performed only on results from $E_0 = 80$ and 200 keV probes.

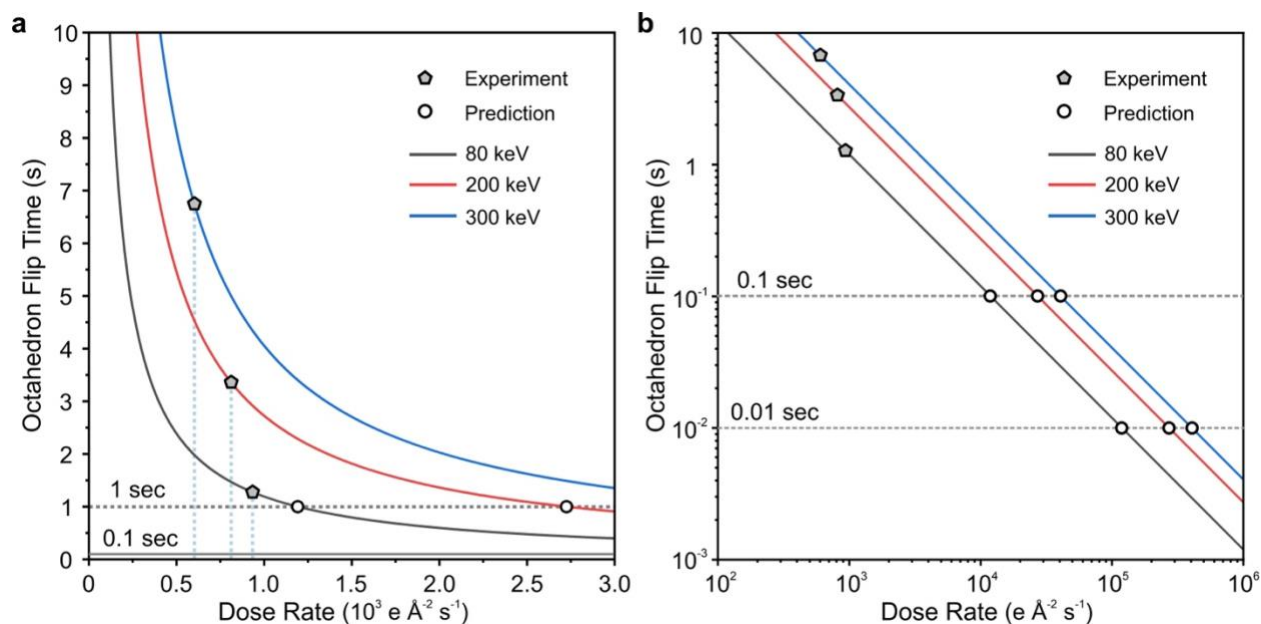


Supplementary Figure 13. Models of possible surface, edge and corner octahedrons rolling. **a**, Models of two types of octahedra rolling from left to right (or from right to left) along $[110]$ direction. The first row corresponds to “bright” row and the second to “dim” row (described in Supplementary Figure 9a). The orientation of these models is the same as the sample with crack. **b**, Models of octahedral unit rolling from up to down (or from down to up). Black arrows indicate octahedron rolling directions. **c**, A summary table of the numbers for the dangling bonds and bond-breakages needed for rolling of the octahedral units shown in panels **a** and **b**. The labels “b” and “d” designate octahedra from “bright” row and “dim” row, respectively.



Supplementary Figure 14. Surface sputtering probabilities for O and Ti atoms in rutile TiO₂.

The knock-on cross-sections were calculated using the Mott cross-section for relativistic incident electron: $\sigma_k(E_0) = 4\pi a_0^2 \left(\frac{Z^2 U_R^2}{(m_0 c^2)^2} \right) \frac{1-\beta^2}{\beta^4} \times [(\xi - 1) - \beta^2 \ln(\xi) + \pi\alpha\beta \{ 2 [\xi^{\frac{1}{2}} - 1] - \ln(\xi - 1) \}]$, where a_0 is the Bohr radius, Z is the number of moving unit, U_R is Rydberg energy, m_0 is the rest mass of electron, c is the speed of light, and $\beta = \frac{v}{c} = \sqrt{1 - \left(1 + \frac{E_0}{m_0 c^2}\right)^{-2}}$, $\alpha = \frac{Z}{137}$, $\xi = E_{max}/E_{th}^{(2)}$, $E_{max} = \frac{2E_0(E_0 + 2m_0 c^2)}{M_0 c^2}$, M_0 is the mass of the atom, $E_{th}^{(2)}$ is the threshold energy that must be transferred to sputter atoms from the surface.^{9,10} Ti 6-bond atomic displacement energy and O 3-bond atomic displacement energy are 47 eV and 39 eV, respectively.^{11,12}



Supplementary Figure 15. Octahedron flip time vs dose rate for electron energies: 80, 200, 300 keV. **a**, Experimental data points are following dose rates: 934, 812, and 602 $\text{e} \text{ \AA}^{-2} \text{ s}^{-1}$ for 80, 200 and 300 keV, respectively, shown with the grey data indicators. The 1-second dashed line shows intersections with the 80 and 200 keV curves at dose rates of 1194 and 2734 $\text{e} \text{ \AA}^{-2} \text{ s}^{-1}$. The 0.1-second horizontal line indicates that the dose rate needs to be very high to achieve “octahedra” flipping. **b**, The octahedron flip time vs dose rate plotted in a wider range. The 0.1 second dashed line shows intersections with the 80, 200, and 300 keV lines at dose rates of 1.1×10^4 , 2.5×10^4 and $3.8 \times 10^4 \text{ e} \text{ \AA}^{-2} \text{ s}^{-1}$. The 0.01 second dashed line shows intersections with the 80, 200, and 300 keV lines at dose rates of 1.2×10^5 , 2.5×10^5 and $3.7 \times 10^5 \text{ e} \text{ \AA}^{-2} \text{ s}^{-1}$.

Supplementary Table 1. Calculation of the cohesive energies for different wide bandgap metal oxides. In these calculations the values of heat of formation, ΔH_f^0 , and heat of atomization (ΔH_M^0 for metal and ΔH_O^0 for oxygen) were used to evaluate the cohesive energies, E_{coh} , for the MO_2 unit and for single M-O bond ¹³⁻¹⁹.

Materials (MO_2)	Heat of formation (ΔH_f^0) (eV/ MO_2)	Heat of atomization (ΔH_M^0) (eV/atom)	Heat of atomization (ΔH_O^0) (eV/atom)	E_{coh} (eV/ MO_2)	E_{coh} (eV/bond)
Rutile- TiO_2	9.79 [13]	4.88 [14]	2.6 [14]	19.9	3.3
Anatase- TiO_2	9.72 [13]	4.88 [14]	2.6 [14]	19.8	3.3
Rutile- GeO_2	5.59 [15]	3.907 [14]	2.6 [14]	14.7	2.5
Rutile- SnO_2	5.98 [16]	3.14 [14]	2.6 [14]	14.3	2.4
Rutile- IrO_2	2.58 [17]	6.954 [14]	2.6 [14]	14.7	2.5
α -quartz GeO_2	5.59 [15]	3.907 [14]	2.6 [14]	14.7	3.7
α -quartz SiO_2	9.44 [18]	4.73 [14]	2.6 [14]	19.7	4.9
α - Al_2O_3 (sapphire)	17.37 (Al_2O_3) [19]	3.39 [14]	2.6 [14]	31.9 (Al_2O_3)	2.7

Supplementary Table 2. Summary of the exciton energies and their lifetimes for different wide bandgap metal oxides. The values of bandgap and cohesive energies, determined theoretically and experimentally (Supplementary Table 1), are also listed for evaluation of viability of radiolysis in these materials.²⁰⁻³⁷

Materials	Building unit	Exciton energy (eV)	Exciton lifetime (τ_{ex})	Band gap (eV)	E _{coh} (eV/bond)	
					Theoretical	Experimental
Rutile-TiO ₂	Octahedral	2.91, 3.05 [20,21]	16 ns [22]	3.0 [22]	3.57 [23]	3.3
Anatase-TiO ₂	Octahedral	2.91, 3.26 [21]	0.1-1 ns [22]	3.2 [22]	3.59 [24]	3.3
Rutile-GeO ₂	Octahedral	4.64, 4.67 [25]	--	4.68 [25]	2.41 [26]	2.5
Rutile-SnO ₂	Octahedral	3.2, 3.6 [27,28]	0.6 ns [28]	3.64 [27]	2.58 [29]	2.4
Rutile-IrO ₂	Octahedral	--	--	Metallic	2.8 [29]	2.5
α -quartz GeO ₂	Tetrahedral	6.6 [30]	--	5.5-6 [30]	3.45 [26]	3.7
α -quartz SiO ₂	Tetrahedral	8-11 [31]	14 ns [32]	7.52-9.6 [31]	5-5.5 [33]	4.9
α -Al ₂ O ₃ (sapphire)	Octahedral	7.6 [34] 9.1[35]	20-150 ns [34] --	8.80 [36]	2.59 [37]	2.7

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