Supporting Information for

Atomistic manipulation of reversible oxidation and reduction in Ag by electron beam

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Table S1 Projected area of the Ag_2O grain in Figure 2.

Status	Growing					Decomposing				
E-beam dose rate ($e\ Å^{-2}\ s^{-1}$)	10^5					10^6				
Irradiation time t (s)	0	13	27	40	55	60	71	87	95	104
Projected area of the grain S (nm^2)	11	25	49	71	90	79	55	30	16	5

Table S2 Change of the projected area of the Ag_2O grain at different electron beam dose rate, 8 sets of data.

Video No.	1	2	3	4	5	6	7	8
e-beam dose rate ($e\ Å^{-2}\ s^{-1}$)	1.7×10^4	2.7×10^4	4.6×10^4	8.1×10^4	2.5×10^5	4.3×10^5	9.5×10^5	1.0×10^6
Total irradiation time Δt (s)	105	168	105	168	128	128	48	39
Change of the projected area of the grain ΔS (nm^2)	247	272	159	205	74	5	-56	-83
Growth rate $\Delta S/\Delta t$ ($nm^2\ s^{-1}$)	2.35	1.62	1.51	1.22	0.58	0.04	-1.17	-2.13

Equilibrium flux between oxidation and reduction

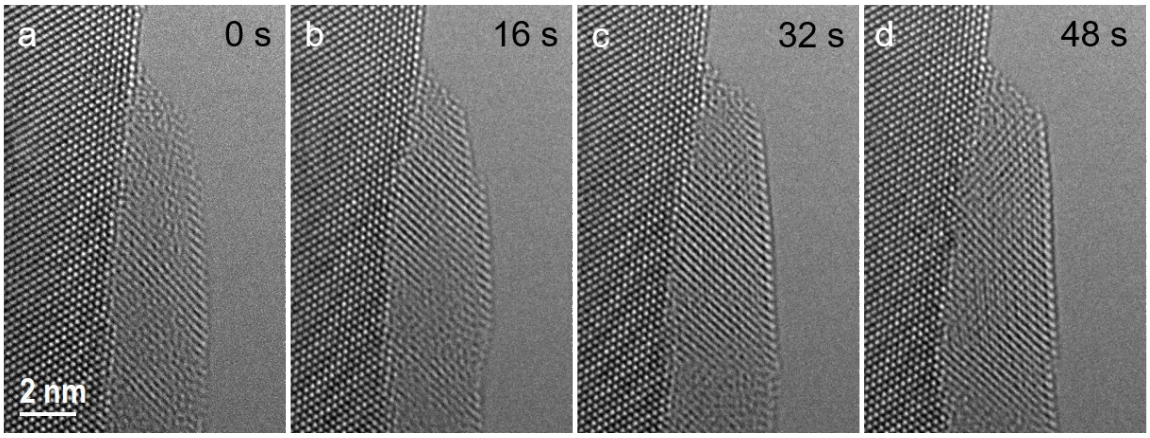


Fig. S1 Snapshots images taken from video No. 6 (Video S4 in below) as listed in Table S2. At the dose rate of 4.3×10^5 e $Å^{-2}$ s^{-1}, the projected area of the Ag_2O grain barely changed, indicating an almost equilibrium state between oxidation and reduction.

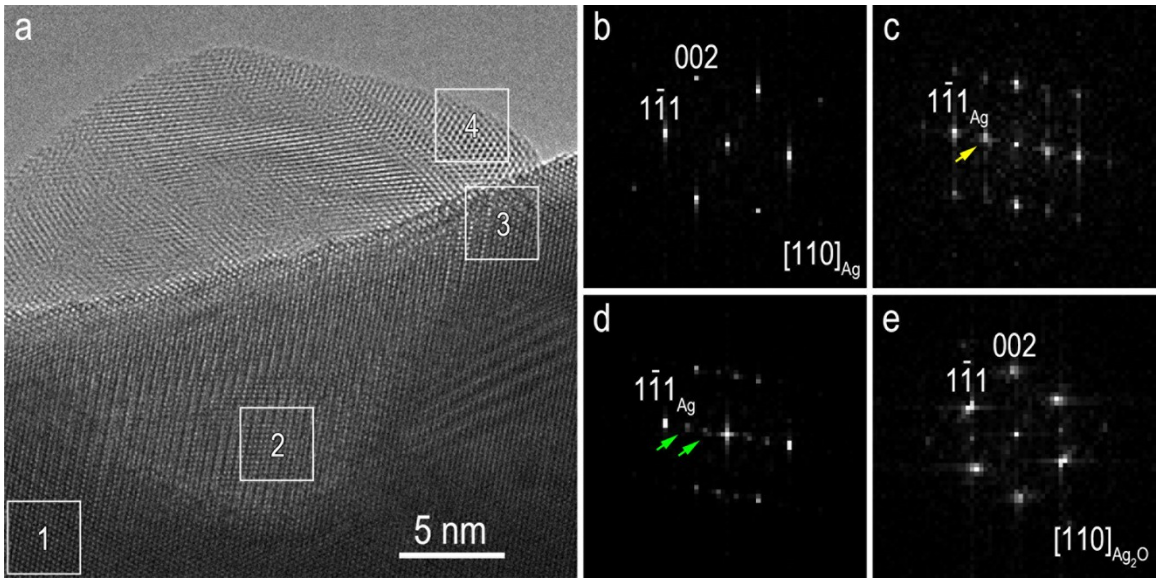


Fig. S2 (a) High resolution image showing the atomic details of an Ag-Ag_2O interface. (b-d) FFT images of the squared area 1-4 in (a), mapping relations: figure (b) corresponds to square 1, (c) to 2, (d) to 3, and (e) to 4. The $\frac{1}{2}(1\bar{1}1)$ diffraction spots (as pointed by a yellow arrow) in (c) indicate a twice modulation of the lattice and the $\frac{1}{3}(1\bar{1}1)$ diffraction spot (as pointed by two green arrows) in (d) indicates a three times modulation of the lattice. (e) FFT image proves that the attached grain is Ag_2O.

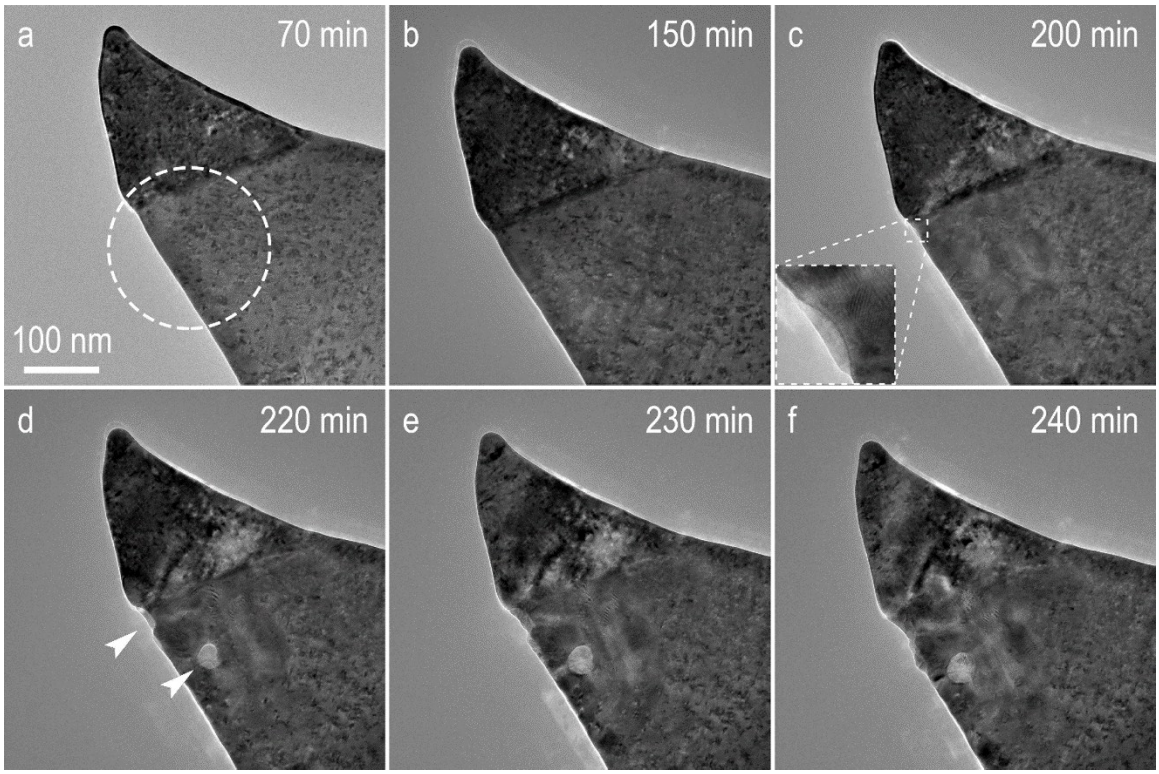


Fig. S3 (a-f) Time elapsed images showing the evolution of the specimen under e-beam irradiation. The specimen had been hold in TEM for more than 12 hours before introducing irradiation to the circled area. No oxidation was observed after the holding time (a) until the irradiation time reached 200 min (c). Oxidation only occurred within the irradiated area (d-f).

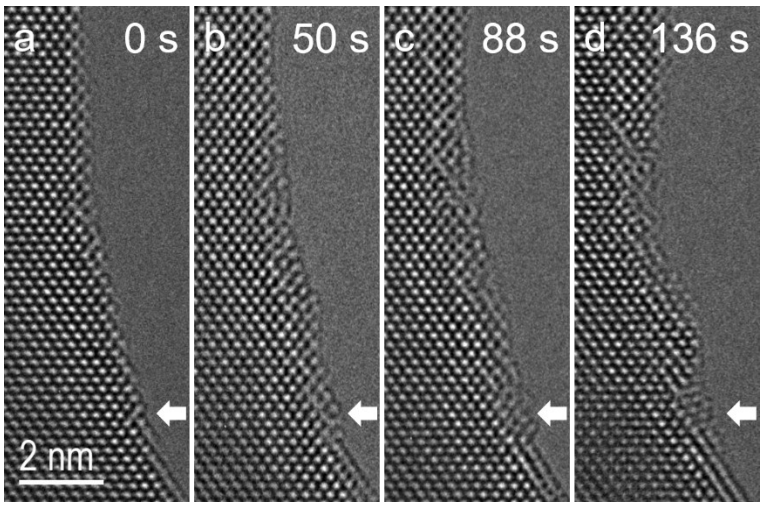


Fig. S4 The nucleation of a Ag_2O grain at the step edge of the Ag surface.

Ag_2O nanodots formation under various spot sizes

At each spot size, the probe size is minimized and HRTEM image for the change of atomic structure at the probe is recorded. As shown in Fig. S5, using spot 3 combined with a 70 micrometer C2 aperture, a nanodot of Ag_2O is formed around 300 seconds of e-beam illumination (Fig. S5 a-d). When using a spot size 2, a nanopore is drilled around 5 minutes e-beam irradiation (Fig. S5 e-h). When using spot size 3 or higher, no nanodots are formed after 8 minutes e-beam irradiation (Fig. S5 i-l).

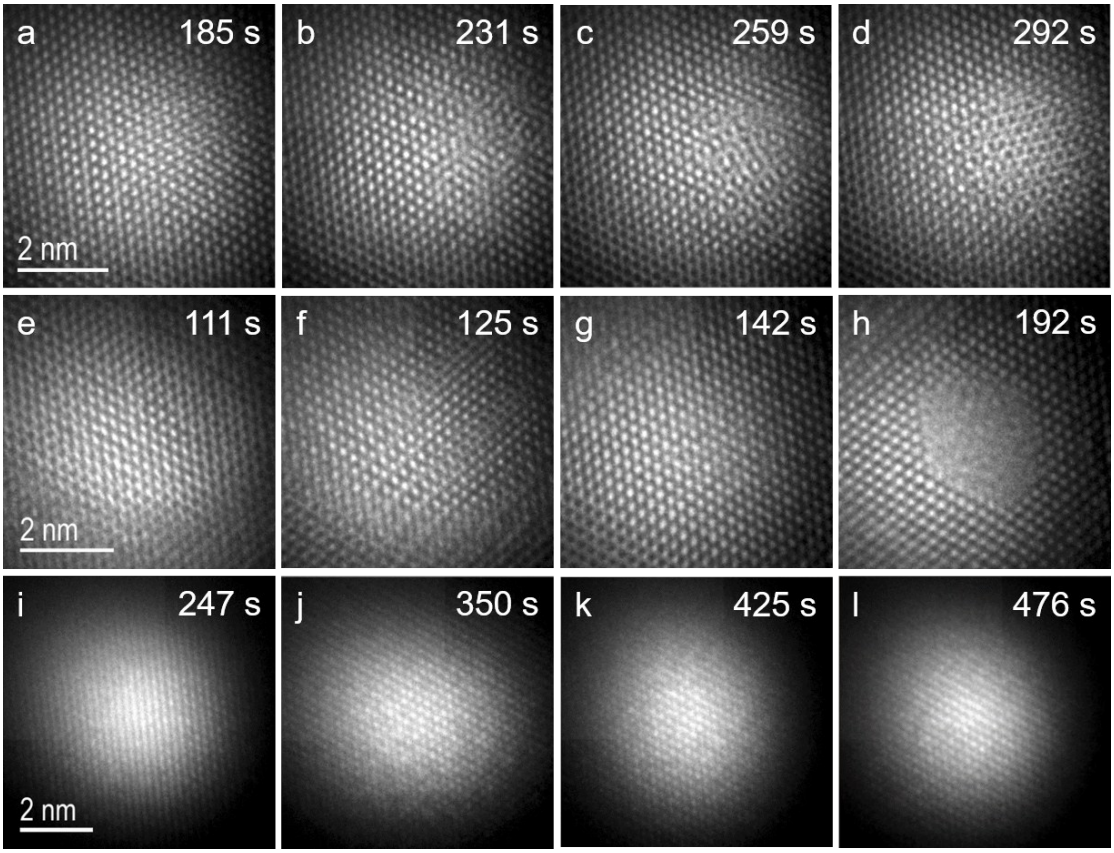
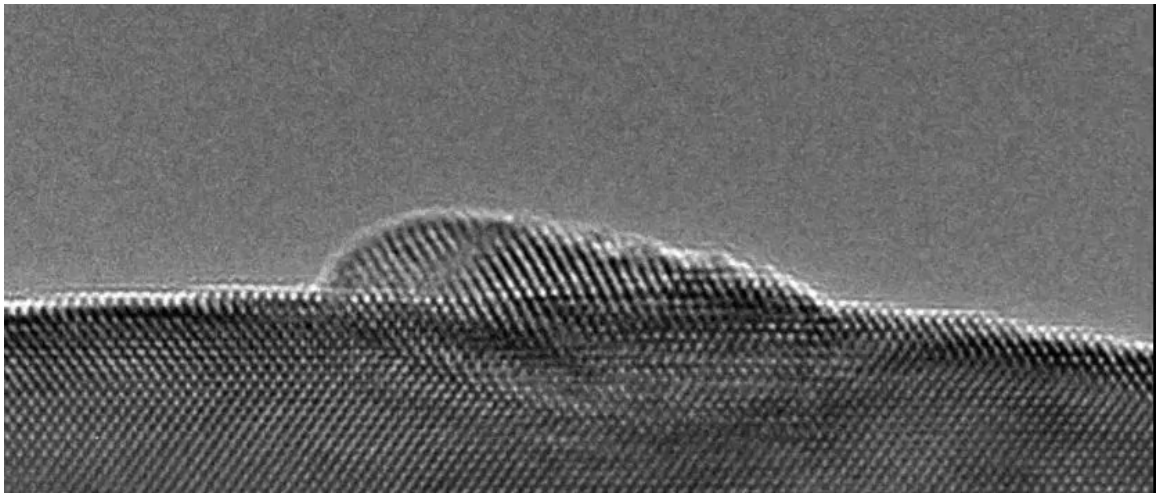
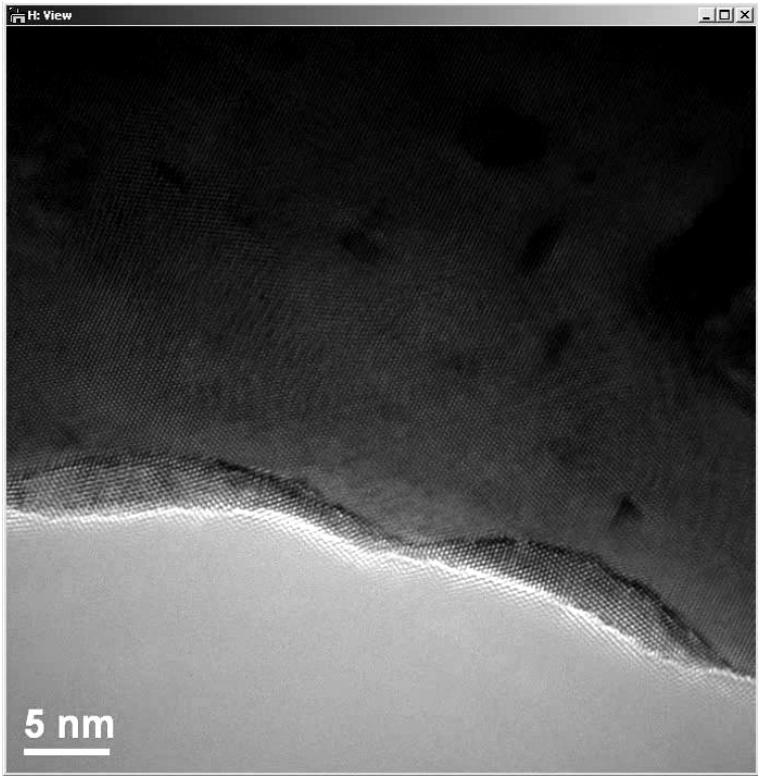


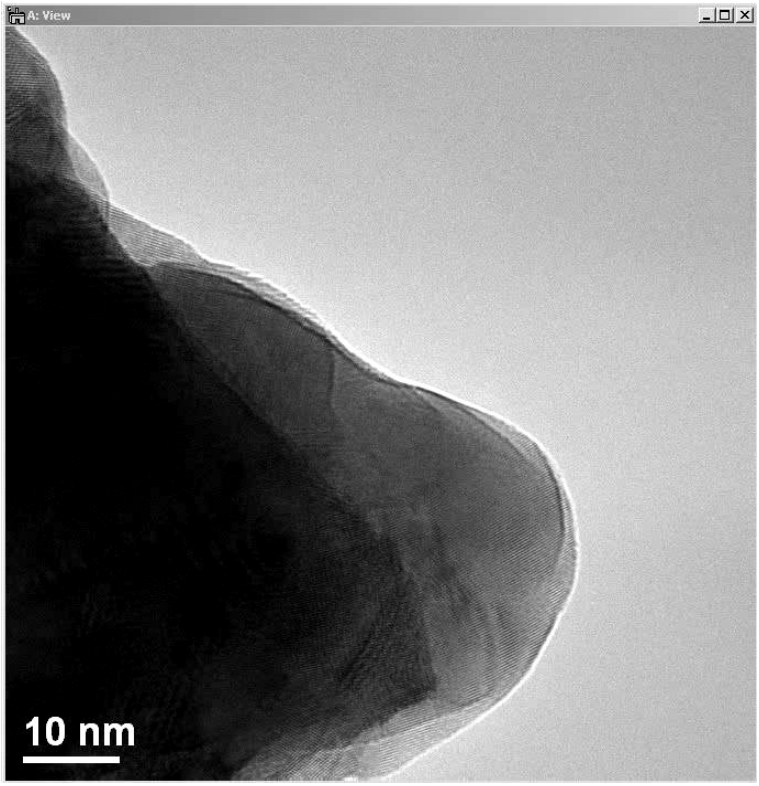
Fig. S5 Parameter study of the patterning. (a-d) With spot size 3 of the microscope, an oxide formed within the irradiated area after 5 min. (e-h) With spot size 2, a hole showed up after 3 min's irradiation. (i-l) With spot size 4, no obvious change was observed after 8 min's irradiation. More dedicated parameter study regarding the patterning experiment is still in need.



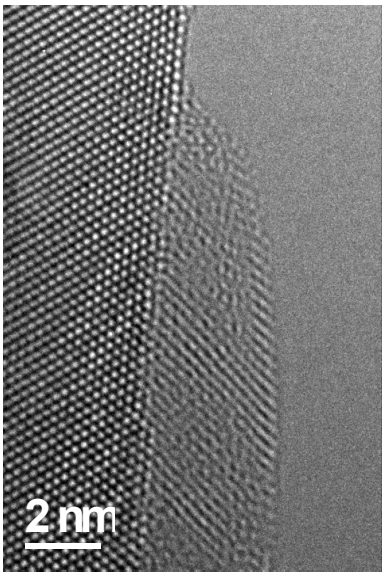
Video S1 Growth-decomposition cycles of a Ag_2O grain attached on the Ag substrate. The dose rate of the e-beam irradiation was switched from ~10^5 e $Å^{-2}$ s^{-1} to of ~10^6 e $Å^{-2}$ s^{-1} back and forth. The Ag_2O grain would grow when the dose rate is ~10^5 e $Å^{-2}$ s^{-1} (darker contrast) and would decompose back to Ag when the dose rate is ~10^6 e $Å^{-2}$ s^{-1} (brighter contrast). Play rate, ×20.



Video S2 The decomposition process of surface attached Ag_2O grains with electron beam focused on the Ag substrate region adjacent to the oxide. The inward contraction of the oxide grain indicates that the reduction happens at the surface of the oxide, i.e., oxide-vacuum interface and oxide-metal interface. Play rate, ×5.



Video S3 The furious oxidation process of the Ag specimen. When the microscope is operated without adding liquid nitrogen to the Dewar cooling trap, Ag specimen oxidizes in a very furious way. The outward expansion of the oxide and the inward contraction of the Ag metal are clearly observed. Play rate, ×25.



Video S4 At the dose rate of 4.3×10^{5} e $Å^{-2}$ s^{-1}, the morphology change of the oxide attached to the Ag surface remains very small, indicating an almost equilibrium state between the oxidation and reduction. Play rate, ×1.6.