

Supplementary Materials for
**Crystal plane orientation-dependent surface atom diffusion in sub–10-nm
Au nanocrystals**

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Figs. S1 to S13
Legends for movie S1
References

Other Supplementary Material for this manuscript includes the following:

Movie S1

Supplementary Text

Surface pressure and curvature radius calculation

Surface atom diffusion of the hill-like structure can be driven by the surface pressure. The surface pressure P can be calculated by the Laplace pressure equation: $p = \frac{\gamma}{R_1} + \frac{\gamma}{R_2}$, where γ is the surface energy, R_1 and R_2 are the main curvature radius of the hill-like structure as shown in **Fig. S2A**. Since the surface of the hill-like structure is approximately semispherical (11), R_1 and R_2 can be considered equal. Hence, the above equation can be rewritten as: $p = \frac{2\gamma}{R}$. The surface energy of (001) plane for Au is 0.864 J/m² (37). In **Fig. S2B**, at the initial moment of the Au ligament fracture, the curvature radius of the newly formed hill-like structure is 0.90 nm. Thus, the surface pressure is calculated to be 1.91 GPa. This value is comparable to the ideal yield strengths of Au and is sufficiently high to break the atomic bonds and lead to surface atom diffusion (46). The changes in the curvature radius and the surface pressure against time are plotted in **Fig. S2C**. As diffusion proceeded, the curvature radius of the hill-like structure gradually increased to ~3.63 nm and the surface pressure decreased to 0.48 GPa. Correspondingly, the atom diffusion gradually slowed down and eventually stopped.

In accordance with the aforementioned calculation method, we determine the curvature radius of layer “5” during diffusion process as shown in **Fig. S4**. The topmost atomic layer can also be conceptualized as a semispherical surface, denoted by a blue arc defined by three red points. Similar to **Fig. S2A**, we can express the curvature radius of semispherical in terms of the curvature radius of a two-dimensional blue arc. Therefore, the radius of the outer circle of the purple triangle, determined by three red points (i.e., the radius of the blue arc) is denoted as R , calculated as $R = \frac{abc}{S}$, where a , b and c are the lengths of the sides of the triangle, and S is the area of the triangle as indicated in **Fig. S4A**. The side length and area of the triangle can be defined by the number of atomic columns and the radius of the Au atom. Therefore, the curvature radius of the topmost atomic layer can be derived by the number of atomic columns and the radius of one Au atom.

Consequently, the formula is given by $R = \frac{(4+N^2)r}{4}$, where R is the curvature radius, N is the number of atomic columns, and r is Au atomic radius (0.139nm) (47). As atom diffusion on the topmost layer, the height of the topmost atomic layer remains constant, while the number of atomic columns gradually decreases, leading to increase in curvature.

Atomic stress calculation

To calculate atomic stress near the surface dislocation, we constructed an atomistic model using the coordinate extracted from the atomic tracking program, where the length per pixel is 0.018 nm. As the view direction is along $\langle 110 \rangle$, the out-of-plane coordinate of each atom column has two possibilities. Then, the in-plane scaled coordinates s_x , s_y of each atom are fixed, because the relative positions of atom columns are considered accurate from experiments. The unknown out-of-plane coordinates s_z and simulation cell are optimized to minimize the total energy. In the final equilibrated configuration, we calculate the atomic stress tensor using the “compute stress/atom” command in LAMMPS, where the interatomic potential is EAM/alloy (48). This command computes the stress tensor times the atomic volume for each atom. The final stress tensor is obtained by dividing the quantity by the equilibrium atomic volume of FCC Au. Atomic stress near the surface dislocation is shown in **Fig. S8**.

A surface dislocation annihilation

Figure S10 presents a time series of HRTEM images, showing the annihilation of a surface dislocation on layer “6”. We extracted the intensity profiles across layer “6” enclosed by the white rectangle areas in **Fig. S10A-C**, as shown in **Fig. S10D**. Since the white spots in the HRTEM images represent Au atomic columns while the dark spots represent channels between atomic columns, the peaks on the profiles correspond to the atomic columns and the valleys correspond to the channels. From 0 s to 0.05 s, the two atomic columns at the core of the dislocation began to merge. At 0.1 s, the two atomic columns completed the merging. As shown in **Fig. S10D**, two atomic columns of the dislocation core in profile A transformed into one atomic column in profile C, implying the rearrangement of the atomic columns and the annihilation of a surface dislocation.

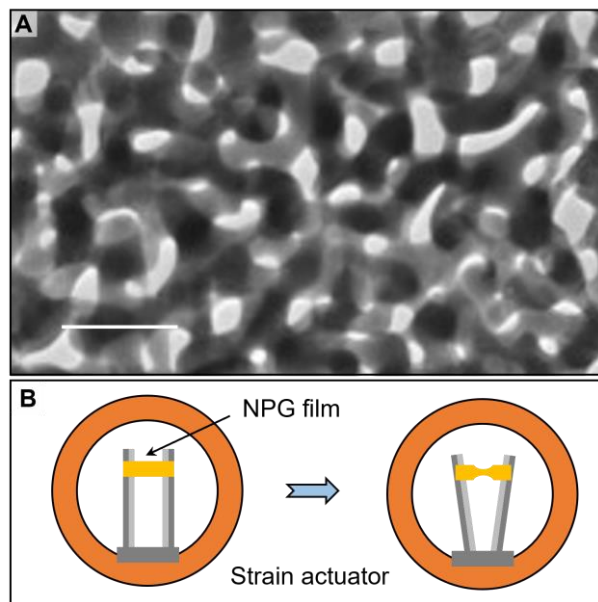


Fig. S1. Microstructure of the nanoporous gold and the schematic illustration of tensile test. (A) A typical bright-field TEM image of the as-prepared NPG film. Scale bar: 100 nm. (B) Schematic illustration showing in situ TEM tensile tests with the homemade strain actuator.

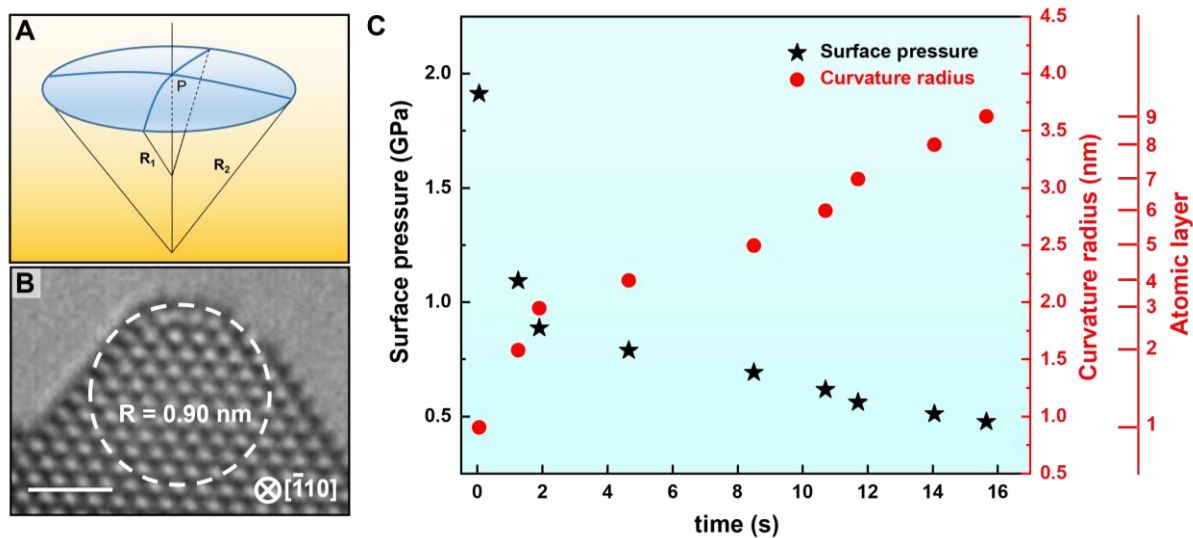


Fig. S2. Surface pressure calculation of the hill-like structure. (A) A schematic illustration of the curvature radius of a surface. (B) HRTEM images showing the hill-like structure of the fractured Au ligament with curvature radius. Scale bar: 1 nm. (C) The change of the surface pressure and curvature radius of the hill-like structure as a function of time.

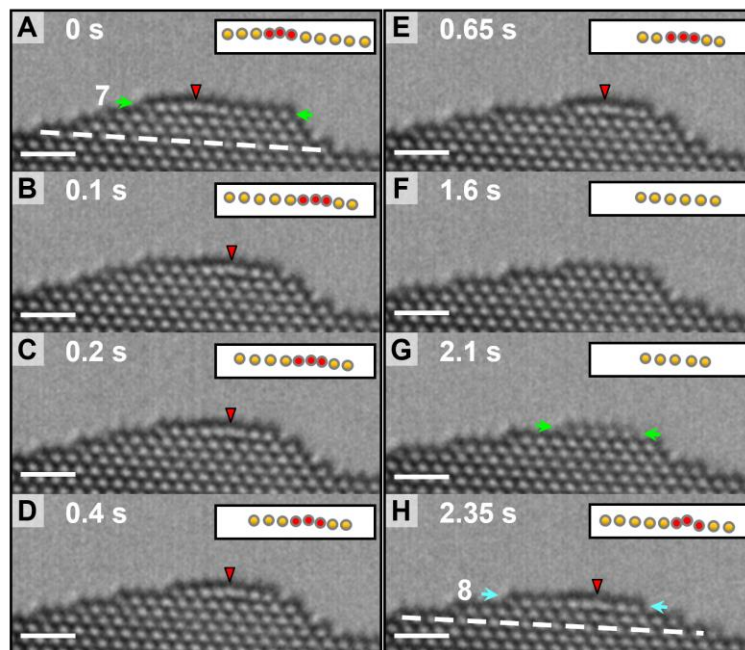


Fig. S3. Surface atom diffusion on (001) plane. (A to H) Time series of HRTEM images showing the surface atom diffusion on layer “7”. The surface dislocation core is denoted by the red triangles. The insets on the top right represent the schematic illustrations of the atom configurations on the topmost layer. Scale bars: 1 nm.

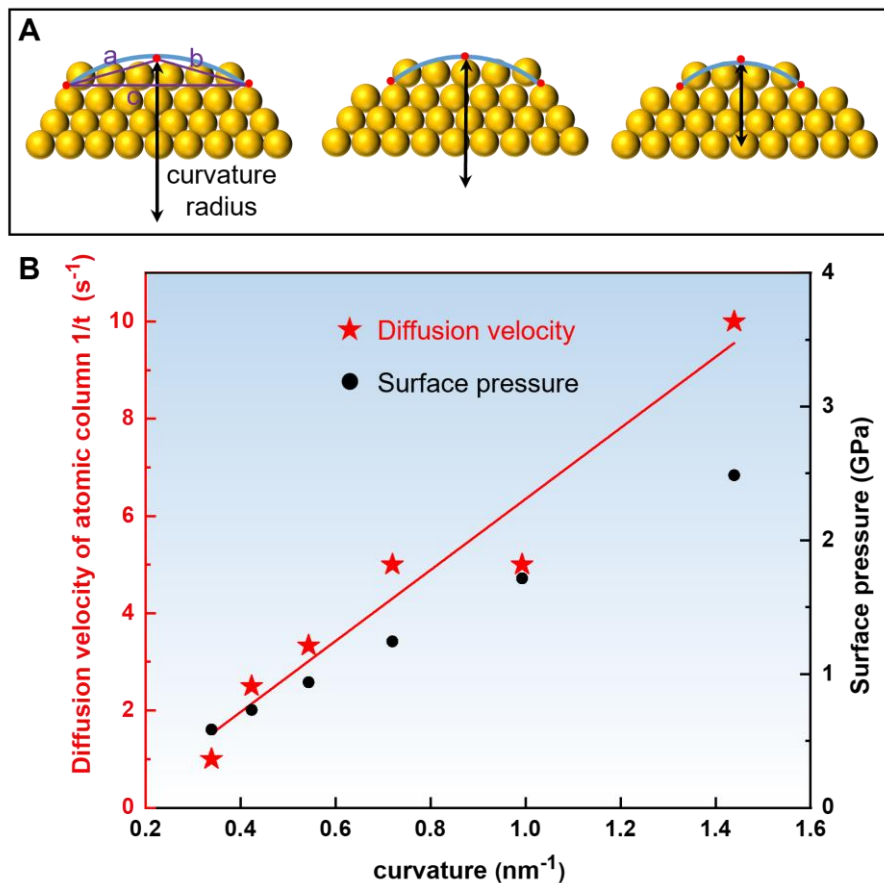


Fig. S4. The relationship between curvature and diffusion velocity. (A) A schematic illustration for calculating the curvature of the topmost atomic layer. The blue curve and the black double arrow are the curvature arc and radius of the topmost atomic layer, respectively. (B) The measured diffusion velocity of atomic column ($1/t$) and surface pressure versus curvature of layer “5”.

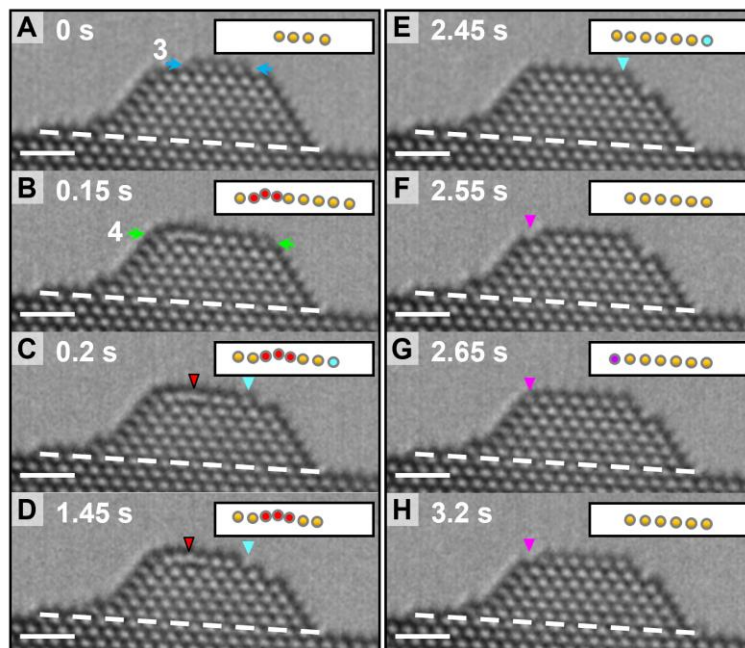


Fig. S5. Surface atom diffusion on (001) plane. (A to H) Time series of HRTEM images showing the surface atom diffusion on layer “4”. The surface dislocation core is denoted by the red triangles. The cyan and purple triangles indicate the removal and adding back of atomic columns. The insets on the top right represent the schematic illustrations of the atom configurations on the topmost layer. Scale bars: 1 nm.

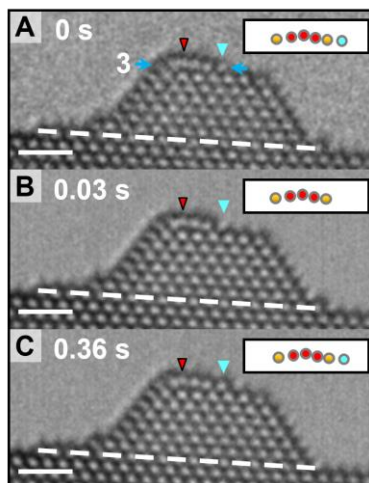


Fig. S6. Surface atom diffusion on (001) plane. (A to C) Time series of HRTEM images showing the surface atom diffusion on layer “4”. The surface dislocation core is denoted by the red triangles. The cyan triangles indicate the removal and adding back of atomic columns. The insets on the top right represent the schematic illustrations of the atom configurations on the topmost layer. Scale bars: 1 nm.

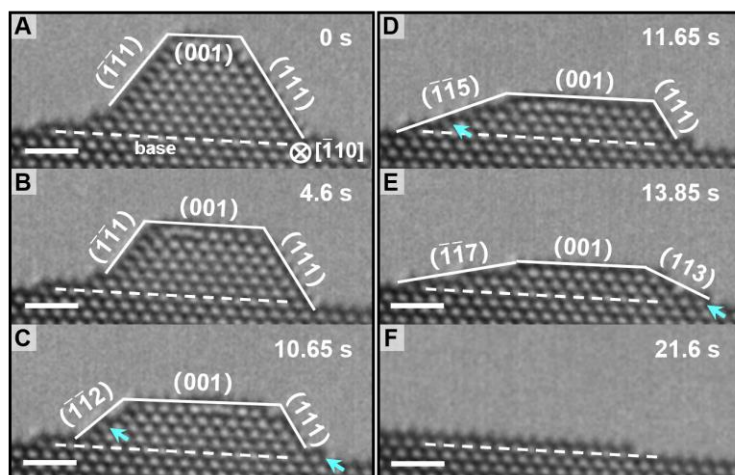


Fig. S7. Temporal dynamic change of the hill-like structure. (A to F) Successive Fourier-filtered HRTEM images show that the crystal plane orientation of side plane undergoes dynamic changes. Scale bars: 1 nm.

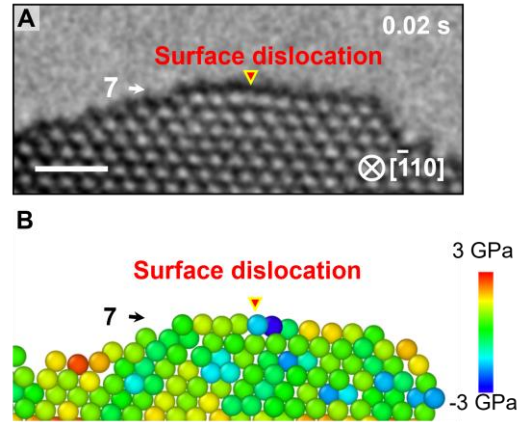


Fig. S8. Atomic stress calculation of surface dislocation. (A) The HRTEM image captures the nucleation of surface dislocation, corresponding to **Fig. 3(C)**. (B) Evaluation of atomic stress in distinct regions of the hill-like structure reveals substantial compressive stress at the dislocation core, suggesting the induction of local drastic compressive strain by the surface dislocation.

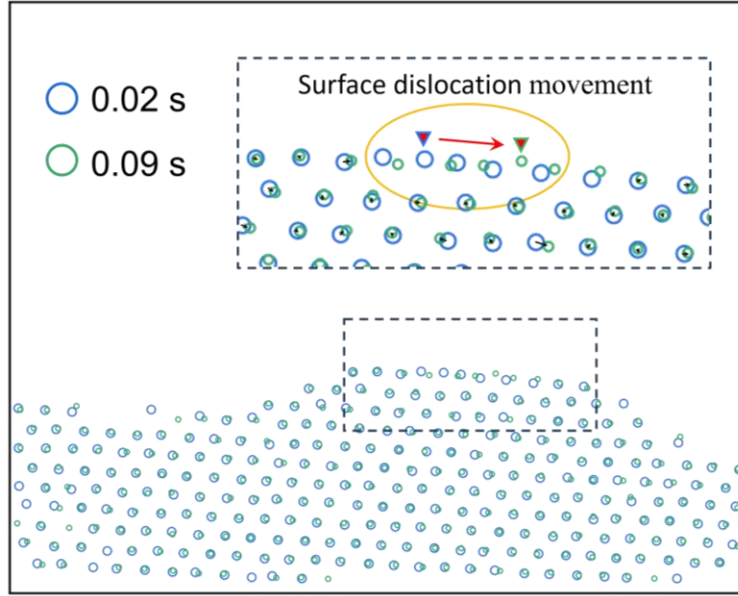


Fig. S9. Atomic columns trajectories of surface dislocation movement. Atomic column trajectories and associated atomic displacement map extracted from **Fig. 3(C to D)** from automated analysis. The upper right image is an enlarged view within the dotted box. The red triangles with different edge colors indicate the location of the surface dislocation at different time, and the red arrow indicates the surface dislocation movement.

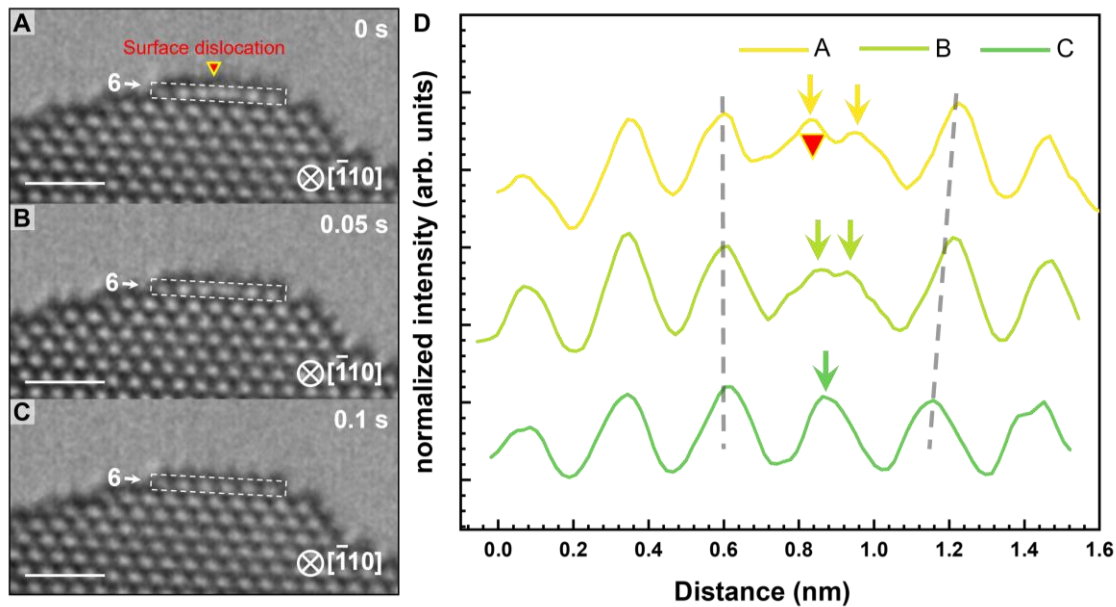


Fig. S10. A surface dislocation annihilation. (A to C) A time-series of Fourier-filtered HRTEM images showing the annihilation of a surface dislocation by the merging of two adjacent atomic columns at the core of the surface dislocation. Scale bars: 1 nm. (D) Intensity profiles extracted along the white dotted rectangle areas in (A to C).

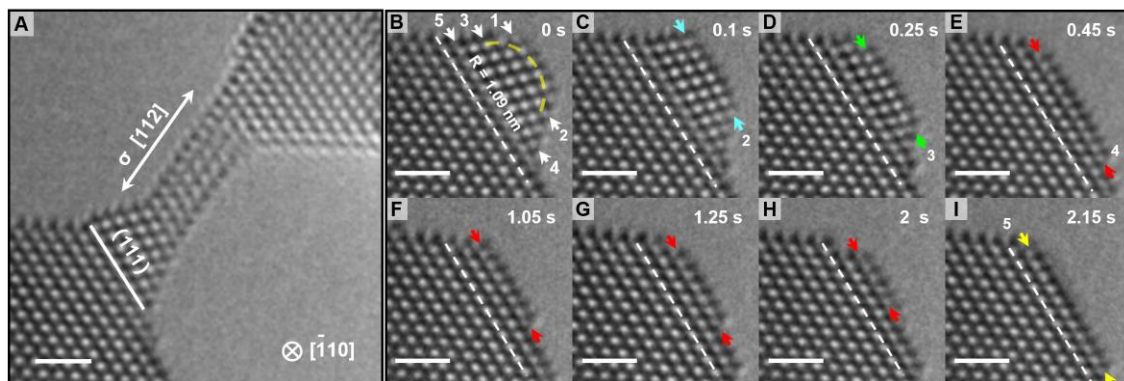


Fig. S11. Surface atom diffusion on (111) plane of a hill-like structure with initial 1.09 nm curvature radius. (A) Fourier-filtered HRTEM image of an Au nanowire. (B to I) Successive Fourier-filtered HRTEM images showing layer-by-layer diffusion on (111) plane, acquired from Fig. 4. Scale bars: 1 nm.

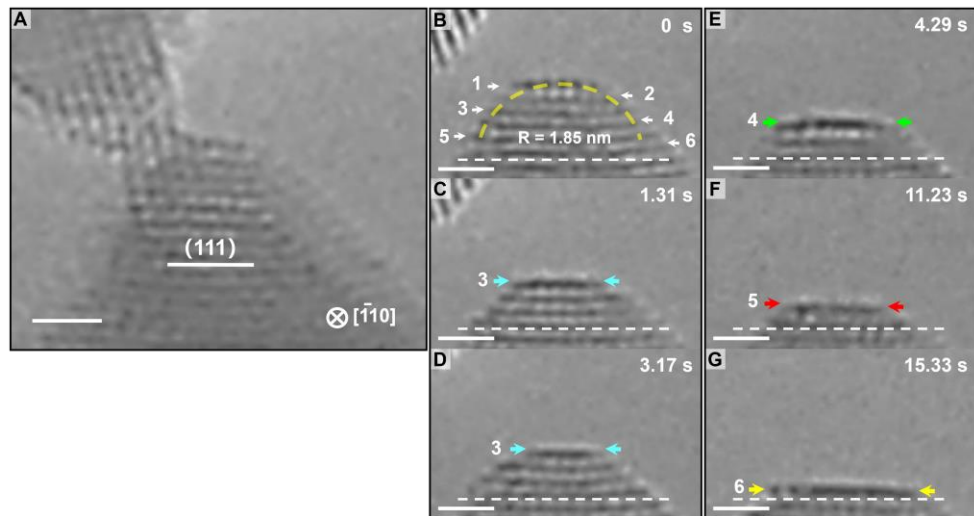


Fig. S12. Surface atom diffusion on (111) plane of a hill-like structure with initial 1.85 nm curvature radius. (A) Fourier-filtered HRTEM image of an Au nanowire. (B to G) Successive Fourier-filtered HRTEM images showing layer-by-layer diffusion on (111) plane. Scale bars: 1 nm.

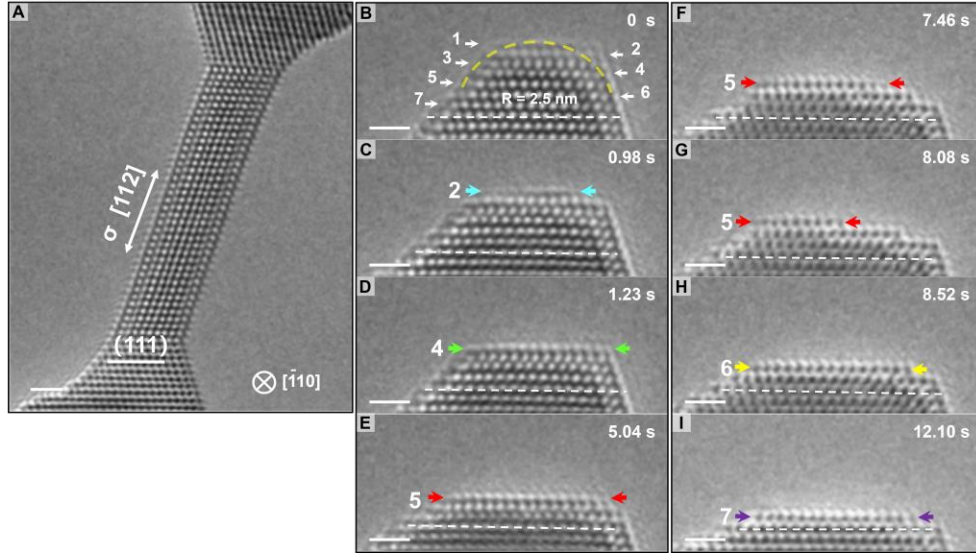


Fig. S13. Surface atom diffusion on (111) plane of a hill-like structure with initial 2.5 nm curvature radius. (A) Fourier-filtered HRTEM image of an Au nanowire. (B to I) Successive Fourier-filtered HRTEM images showing layer-by-layer diffusion on (111) plane. Scale bars: 1 nm.

Movie S1.

Surface atoms layer-by-layer diffusion process of fractured Au ligament, recorded at a rate of 100 frames per second and played at 1x speed.

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