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# Direct observation of autonomous self-healing in silver



By taking advantage of *in situ* transmission electron microscopy, we show that solid-state silver can autonomously self-heal nanoscale damage (both nanopores and nanocracks) at room temperature without any external intervention. Such an autonomous self-healing phenomenon is not observed in gold under equivalent conditions, and our molecular dynamics simulation results well reproduce the experimentally observed different self-healing behaviors of silver and gold. Atomistic dynamics unveil that the surface self-diffusion process constitutes the basis of the observed autonomous self-healing process in nanoscale silver.

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### Highlights

The first *in situ* observation of autonomous self-healing behavior in nanoscale Ag

Theoretical simulation results well reproduce the experimental observations

The self-healing process is accomplished through surfacemediated diffusion



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### Article Direct observation of autonomous self-healing in silver

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### SUMMARY

Although the concept of self-healing has undergone a recent resurgence of interest in polymers and other soft materials, it is extremely rare for metal solids to autonomously self-repair structural damage without any external trigger. Here, we report on the direct in situ observation of such an autonomous solid-state selfhealing behavior in nanoscale silver (Ag) by utilizing atomic-resolution transmission electron microscopy (TEM). Two representative kinds of structural damage—both nanopores and nanocracks—are observed to undergo automatic self-repair at room temperature and well below (down to 173 K) without any external intervention. Importantly, such an autonomous self-healing phenomenon does not occur in gold (Au) at room temperature, as it is hindered by the stronger Au-Au bonding resulting from the known relativistic effect. A combination of atomistic imaging and molecular dynamics simulation unravels that the self-healing process is accomplished through surface-mediated diffusion of Ag atoms as driven by chemical potential imbalance due to the Gibbs-Thomson effect.

### INTRODUCTION

Inspired by nature's living organisms with the capability of damage recovery, selfhealing materials have long been conceptualized and studied. Self-healing of a material refers to the ability to recover from physical or chemical damage. Generally speaking, self-healing phenomena in materials can be classified into two conceptually distinct categories: intrinsic autonomic healing and non-autonomic healing.<sup>1-3</sup> Whereas the occurrence of non-autonomic self-healing normally requires the assistance of an external trigger or additional energy, such as heat, light, or stress, to promote mass transfer, autonomic self-healing obviates the need for any external trigger or intervention.<sup>1</sup> For soft materials such as polymers and their composites, both the autonomous and non-autonomic self-healing processes can be achieved easier owing to the inherent reversibility of dynamic covalent bonds and/or hydrogen bonding or van der Waals (vdW) interactions in polymeric materials.<sup>4-7</sup> In solid-state metals, however, any types of self-healing are fundamentally more challenging to realize due to the crystalline nature of metals and their high melting point, strong cohesive bonding, and slow diffusion kinetics of atoms at ambient temperatures. Some previous studies of self-healing in metallic materials often involve complicated scenarios that require the use of shape memory alloys or the input of external healing agents.<sup>8–10</sup> Thus far, far fewer studies have addressed solid-state self-healing phenomena in pure metals, but the efficient healing of damage can only be achieved with the assistance of external intervention such as heating, 11,12 mechanical

### **PROGRESS AND POTENTIAL**

The conceptual inspiration of selfhealing materials derives from nature's living organisms with intrinsic ability to self-repair injury and damage. Most studies of selfhealing materials have been focused on soft materials such as polymers and their composites. Solid-state metals, by contrast, are much more difficult to selfheal due to the strong, cohesive metallic bonding. Here we present the first direct observation and dynamic characterization of self-healing behavior in nanoscale Ag that occurs autonomously at room temperature and even below without any external intervention. The ability of Ag to spontaneously heal nanoscale damage can be exploited for the development of mechanically stable and damage-tolerant components and devices. In broader terms, the experimental finding of self-healing phenomena in solid metals and atomistic insights into the healing mechanism may provide an inspiration for developing sustainable self-healing metal materials toward green manufacturing.

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assistance, <sup>13–18</sup> and electron beam irradiation.<sup>19</sup> In this work, we present a key observation that straightforward autonomic self-healing behavior can also occur in pure metals such as silver (Ag) at room temperature without any external intervention. Our experiments were performed in situ using atomic-resolution transmission electron microscopy (TEM). We utilized Ag nanosheets as specimens on which two representative kinds of structural damage, namely nanopores and nanocracks, were deliberately fabricated first by focused electron beam (Figure S1). These two kinds of microscopic damage were observed to undergo rapid self-healing autonomously within a practical time period of several to dozens of minutes. Even at a temperature as low as 173 K, self-healing behavior can still take place in Ag. As a comparative study, this autonomous nanoscale self-healing behavior is not readily accessible in gold (Au) under equivalent conditions. The atomic-scale spatial resolution of TEM allows us to track the exact process and mechanistic details of the damage healing. With a combination of atomistic calculations, we identify that the exact process of self-healing involves the surface-mediated spontaneous diffusion of Ag atoms toward the damage sites as driven by surface chemical potential gradient.

### RESULTS

#### Autonomous self-healing phenomenon in nanoscale Ag

Figure 1A presents the sequential high-resolution TEM (HRTEM) images depicting the autonomous self-healing of a representative single damage embedded in a single-crystalline Ag nanosheet sample. This kind of nanocrack damage was purposefully fabricated at the edge site of the Ag nanosheet through in situ TEM electron beam drilling (see section "experimental procedures" for details). To avoid any possible intervention of electron beam to the subsequent healing process, the electron beam was turned off immediately after damage fabrication. This "beam-off" state was kept all through except at the moments to record TEM images in desired time intervals. As can be seen from Figures 1A and S3, the original nanocrack has a smooth negative curvature with concave-down depth of 8.41 nm, along with a small fraction of convex region with positive curvature. After a 06'01" interval, the partial self-repair of the nanocrack damage can be clearly observed. When imaging again after another interval until 13'58", the depth of the nanocrack was observed to be further decreased, nearly restoring the overall shape of original Ag nanosheet. Importantly, it is worth noting that the healed region consists of homogeneous crystal lattice that shows a high degree of consistency to the face-centered cubic (FCC) lattice of surrounding intact Ag regions, as can be seen from HRTEM images (Figure 1A) and the corresponding fast Fourier transform (FFT) patterns (Figure S4A).

A detailed comparison of HRTEM images before and after the healing process (Figure 1A) indicates that the atoms filled into the nanocrack region are mainly those coming from the convex region. This result implies that, from a thermodynamics point of view, the self-healing process is surface-energy dependent and can be rationalized within the framework of Gibbs-Thomson (G-T) effect.<sup>20</sup> More specifically, due to the general curvature dependence of chemical potential, an Ag atom on the concave-up surface (positive curvature) has larger chemical potential than that on the nanocrack surface (negative curvature). With the continuous negative-to-positive variation of surface curvature, a chemical potential gradient will thereby be established along which a net flow of Ag atom diffusion will arise, as shown in Figure S3.

The remarkable observation of automatous healing of nanocrack damage prompts us to examine whether the similar self-healing behavior can also take place in other <sup>1</sup>Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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#### Figure 1. Direct observation of the self-healing processes on nanoscale Ag and Au nanosheets by in situ TEM

(A) Sequential HRTEM images showing the autonomous partial closure of nanocrack on Ag nanosheet at room temperature. The concave-down depth gradually decreases from 8.41 to 6.02 nm.

(B) Sequential HRTEM images showing the self-healing processes of nanopore on Ag nanosheet at room temperature.

(C) The self-healing process of the nanopore on Ag nanosheet at  $\sim$ 173 K.

(D) Sequential HRTEM images showing that the nanopore on Au nanosheet remains frozen and retains its original size over a long period after ~1 h at room temperature.

The yellow dashed lines in (A), (B), and (D) highlight the boundaries of nanocracks and nanopores.

more complex damage structures. To this end, upon the inner region of Ag nanosheets, nanopore damage was fabricated by highly focused electron beam in the same way as that of nanocracks. Shown in Figure 1B are the HRTEM images of nanopore damage that exhibited a faceted octagonal shape with an original area of  $\sim$ 12.1 nm<sup>2</sup>. When imaging at 09'59" (the electron beam was turned off during this time interval), the nanopore was observed to become notably smaller, with the measured area decreasing down to  $\sim$ 8.1 nm<sup>2</sup>. With extended time, the nanopore was found to be self-healed nearly completely when observed at 15'05". Also, as verified by HRTEM imaging and corresponding FFT analysis, the highly crystalline FCC lattice is well restored in the healed region, with no sign of defect formation or amorphization (Figures 1B and S4B). In order to verify the reliability of this observation, we repeated the nanopore forming/healing experiments in multiple Ag nanosheets samples (Figures S5; S6) as well as one-dimensional (1D) Ag nanowires (Figure S7), and we observed the same self-healing behavior.

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Just as in the case of nanocrack, it is the G-T effect that provides a thermodynamic basis for directing the healing processes of nanopore damage. The high-angle annular dark field (HAADF) images and corresponding three-dimensional (3D) intensity profiles of the nanopore (Figures S8A and S8B) suggest that the nanopore can be equivalently treated as a sloped structure (see more details in Note S6). Since the planar basal surface has a zero curvature, whereas the bottom of nanopore has a highly negative curvature, a gradient of chemical potential will naturally be built along the slope due to gradual decease of curvature. That is, the closer the region to the pore bottom, the bigger the negative curvature and the lower the chemical potential of the surface Ag atoms (Figure S8C). As such, the chemical potential will be a continuous function of position and can be described by a modified version of G-T equation<sup>20</sup>:

$$\mu_{hole} = \mu_{\infty} - \frac{\gamma \Omega}{R_{hole}}$$
 (Equation 1)

where  $R_{hole}$  is the radius of curvature,  $\mu_{hole}$  is the chemical potential at the slope surface with radius of curvature  $R_{hole}$ ,  $\mu_{\infty}$  is the chemical potential at a planar surface,  $\gamma$  is the surface-free energy per unit area, and  $\Omega$  is the molecular volume curvature. On this basis, the surface atomic flux J along the slope surface of nanopore can be modeled by<sup>20,21</sup>:

$$J = -\frac{D_s v}{k_B T} \frac{\partial \mu_{hole}}{\partial s} = -\left(\frac{D_0 v}{k_B T} e^{-E_a/k_B T}\right) \frac{\partial \mu_{hole}}{\partial s}$$
(Equation 2)

where  $D_s$  is the coefficient of surface diffusion ( $D_0$  is a pre-factor and has different values according to materials and shapes of the system),  $E_a$  is the activation energy of diffusion, v is the number of atoms per unit area, s is the arc length along the profile,  $k_B$  is Boltzmann constant, and T is temperature. This result implies that the rate of self-healing will be temperature dependent. Keeping this in mind, we have also repeated the experiments at low temperatures by employing cryo-TEM observation (see section "experimental procedures" for more details). It was striking to find that, when the temperature is lowered to 173 K, the nanopore on Ag nanosheets could still exhibit self-healing capabilities, although it takes much longer than that at room temperature (Figure 1C). When the temperature is further lowered to 106 K, it appears that the self-healing of Ag nanosheet is frozen and the nanopore retains its original shape over a long period of time (Figure S9).

In the periodic table, Au is the most relevant element to Ag, sharing many similarities in physical and chemical properties. In our present work, we have performed detailed comparative studies by utilizing Au nanosheets as control specimens under otherwise identical experimental conditions. Figure 1D shows the results of control experiments performed on Au nanosheet with a nanopore damage. It can be seen that the nanopore retains its original size over a long period up to  $\sim 1$  h, even though some surface reconstruction around the nanopore that may be caused by the electron beam during imaging can be observed. Furthermore, the nanopore on Au nanosheet did not shrink over a period of 7 h but instead the nanopore may even expand in size to some extent (Figure S10). In other words, Au nanosheets do not exhibit obvious self-healing behavior at room temperature. This difference between Ag and Au is somewhat not surprising when considering the distinct relativistic effect of Au.<sup>22-24</sup> To be specific, due to the stronger atomic bonding of Au, the resultant higher cohesion energy gives rise to the lower diffusivity of surface Au atoms as compared to that of surface Ag atoms.<sup>25-27</sup> To compare the differences in diffusion behavior between Ag and Au, we calculated the diffusion barrier and diffusion coefficients for Ag and Au atoms on the (110) surface by using the nudged elastic band



### Matter Article

(NEB) method.<sup>28,29</sup> Our results show that the diffusion barriers for Ag atoms along different directions on the (110) surface are consistently smaller than those for Au atoms. Notably, at room temperature, the diffusion coefficients of Ag atoms via different pathways on the (110) surface are higher than those of Au atoms by more than four orders of magnitude (see Note S2 and Table S1 for more details). The substantially different diffusion coefficients are consistent with the typical behavior of Ag and Au and align with numerous computational studies.<sup>25–27,30,31</sup> In fact, the ease of the surface-mediated diffusion process of Ag shows strong consistency with the several recent experimental observations that highlight that the surface atoms of Ag nanocrystals possess high mobility and low activation energy barrier for self-diffusion,<sup>17,32–35</sup> which results in a variety of extraordinary phenomena in nanostructured Ag, such as unusual wettability,<sup>34</sup> pseudoelasticity,<sup>33</sup> super-elongation,<sup>17</sup> and softening.<sup>35</sup>

#### Atomistic process of Ag self-healing

To depict the atomistic details and dynamic evolution of the automatous self-healing process, we show in Figures 2A-2D the sequential HAADF images and corresponding geometric phase analysis (GPA) of another representative nanopore damage over the course of the healing process. The as-fabricated nanopore, as observed along the [110] zone axis, exhibits a well-faceted vacant bottom with octagonal configuration enclosed by three sets of low-index facets corresponding to the  $\{1\overline{10}\}, \{001\}, \text{ and } \{1\overline{1}, 1\} \text{ planes. With the proceeding of self-healing process under } \{1\overline{10}\}, \{001\}, 1000 \text{ m}$ the beam-off condition and when observed in separate time intervals at 05'56", 08'52", 13'43", and 18'29", respectively, it can be seen that the size of the vacant bottom area gradually decreases while retaining the original faceted configuration, as shown in Figure 2A. This implies that, on the whole, the shrinkage of nanopore is accomplished through a layer-by-layer growth manner that occurs evenly in all eight directions. At 23'23", the vacant bottom of the nanopore has been integrally filled, but, as can be discerned from the variation of image contrast and the corresponding 3D intensity profile (Figures 2A and S11), the healed bottom region remains fairly thin. The 3D intensity profile of the HAADF image at 23'23" also clearly showcases that the partially healed nanopore is analogous to a "basin-like" structure. As the self-healing process further propagates to 30'22", a distinct increase of image contrast of the healed region can be observed, indicating that, after the closure of vacant bottom area, the subsequent atom diffusion leads to the thickening of the healed region. Taken together, it is evident that the healing of nanopore damage involves a two-step process-the initial gradual shrinking of the nanopore area and the subsequent thickening growth. Here it is emphasized that, throughout the process, the slope structure remains present, allowing the chemical potential gradient to be consistently maintained. This is deemed to be the reason for the sustained persistence of self-healing in Ag nanostructures.

Shown in Figure 2C are the magnified atomic-scale HAADF images that depict one corner of the nanopore with adjacent  $(1 \ \overline{1} \ 1)$  and (001) facets (see zoom-in relation in Figure S12). From a frame-by-frame comparison of the time-lapse HAADF images, it can be seen that the adjacent  $(1 \ \overline{1} \ 1)$  and (001) facets are actually not perfectly flat but are instead slightly concave at the atomic scale, with slightly more Ag atoms being accumulated at the inward corner. This result is also a consequence of G-T effect in that the diffusive adatoms are more preferentially attached to the corner sites where the chemical potential is lower as compared to that at the facet center. However, note that this concave tendency will not keep increasing all through the healing process. Specifically, with the accumulation of Ag adatoms at the corner site, the asformed terrace steps will competitively absorb the diffusive Ag adatoms such that



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#### Figure 2. Atomistic dynamics of nanopore healing on Ag nanosheet

(A) Sequential low-magnification HAADF images showing an overall self-healing process of nanopore. The nanopores exhibit an octagonal shape enclosed by  $\{1\overline{1}0\}$ ,  $\{001\}$ , and  $\{1\overline{1}1\}$  crystal planes, as observed along [110] zone axis, with the inset yellow dashed lines depicting the octagonal boundaries.

(B) The left four panels are 3D intensity profiles extracted from the corresponding HAADF images in (A); the right panel is a schematic illustration showing the distribution of surface curvature and chemical potential around the nanopore. Note that the 3D intensity profiles obtained from HAADF images do not directly represent the actual morphology of the nanopores but can accurately depict the thickness of the sample. (C) Enlarged HAADF images of a nanopore corner from (A).

(D) GPA of the images shown in (A) for determining the strain maps of  $\varepsilon_{xx}$ . The color scale is shown on the right and ranges from -0.15 (blue) to 0.25 (red). (E) HAADF images and corresponding strain maps of  $\varepsilon_{xx}$  showing the self-healing process of nanopore accompanying a stacking fault.

(F–I) Enlarged HAADF images (F and G) from the regions marked by red rectangles in (E) and the corresponding atom arrangements (G and I) showing the propagation process of stacking fault and the alteration from FCC to HCP stacking order.

the steps will grow inward toward the facet centers. It is a subtle self-regulating growth manner that gives rise to the appearance of the slightly concave facet shape. From the direct atomic-scale HAADF imaging, it is also evident that the healed

### Matter Article



region nearly perfectly restores the FCC lattice of Ag, with only the outmost one to two atomic layers being a little distorted. The result is in good agreement with the GPA mapping results shown in Figure 2D, where only near the peripheral rim of nanopore is the localized strain concentration apparent. Since the Ag nanosheets are single crystalline in nature, there are no grain boundaries or structural defects such as dislocations and stacking faults. This indicates that surface-mediated diffusion should be the only possible pathway for Ag atom transport to accomplish the healing process.

Occasionally, we also found the formation of stacking faults during the healing process. Shown in Figure 2E is such a defect-forming event accompanying the self-healing process of nanopore damage. From the sequential HAADF images and the corresponding strain maps by GPA (Figure 2E), it can be seen that a stacking fault forms and propagates during the self-healing process. For the FCC metals, stacking faults normally originate from the nucleation and propagation of a leading partial dislocation.<sup>36–39</sup> For the specific Ag nanosheet shown in Figure 2E, it seems that the presence of local strain concentrated near the peripheral rim of the nanopore leads to the generation of a leading partial dislocation to nucleate at first. Then, with the slide of this leading partial dislocation across the {111} planes, a stacking fault will be left behind. After the closure of nanopore bottom, the stacking fault then stays at the interior of the Ag nanosheet, and the partial dislocation evolves into the full dislocation with Burgers vector of  $\frac{1}{2}$  [112] (Figures 2F–2I). According to the established knowledge in the field of metal materials, the emergence of planar defects or line defects could be a favorable factor for atomic diffusion.<sup>17,35</sup> On one hand, it reduces the energy barrier for surface atomic diffusion, and, on the other hand, it can establish a pathway for the diffusion of atoms. Here it is worth noting that this kind of defect-forming event was seldom observed in our experiments, and, in most cases, the atomic surface diffusion and self-healing processes were not necessarily accompanied by the formation of any structural defects.

To further develop mechanistic insight into the healing process, we also performed *in situ* kinetic measurements regarding the evolution trajectories of the slope structure during nanopore healing. Figure 3A displays an enlargement of the slope region acquired crossing nanopore bottom from the sequential HAADF images shown in Figure 2A (see zoom-in relation in Figure S12). By measuring the corresponding line profiles of the atomic column intensity (Figure 3B), we were able to quantify the slope angle of the partially healed nanopore at each time interval. Notably, during the initial "shrinking" stage, the slope angle around the nanopore remained almost constant. By contrast, after the closure of the nanopore bottom, the slope angle started to decrease, which is a natural consequence of the thickening of the healed region. The fact that the slope angles are constant during the shrinking stage means that the chemical potential gradient remains invariant, such that the diffusion flux will also remain constant. Keeping this in mind, we also measured the variation of vacant area as a function of healing time (Figure 3C), and, as expected, an approximately linear relationship can be deduced.

In view of the fact that the across-the-step diffusion of Ag atoms is a critical step for nanopore healing, we further investigated the atomistic dynamics of this key process by using the NEB method. Figures 3D, S16A, and S16B show the schematic diagrams of the model for our calculations. On the (110) surface, we constructed both single step and double step along two distinct  $[1\ \overline{1}\ 0]$  and [001] directions, respectively. It is well known that the (110) surface of FCC Ag is highly anisotropic,<sup>30,31</sup> with the so-called in-channel hopping path where the atom moves along the atomic valley

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#### Figure 3. Diffusion kinetics of Ag atoms on the slope structure during self-healing

(A and B) A close-up view of the evolution of slope structure across nanopore (A), as enlarged from the HAADF images in Figure 2A and the corresponding line profiles (B) extracted from the regions marked by red dotted rectangles in (A). The insets in (B) depict the proposed evolution of the slope structure.

(C) The slope angle (top) and the vacant area of nanopore (bottom) as a function of time.

(D) Schematic diagram for diffusion paths of Ag atoms on Ag nanosheet across single step and double step along [001] and  $[1 \overline{1} 0]$  directions on (110) surface.

(E) The activation energy barrier of Ag atoms descending across the steps in terms of MEPs and activation energy barriers.

to the  $[1\ \overline{1}\ 0]$  direction, and the so-called out-channel hopping path, in which the atom climbs over the atomic mountains to the [001] direction, as shown in Figure S16A. Our calculation results show that the in-channel hopping (0.52 eV) along the  $[1\ \overline{1}\ 0]$  direction on the planar (110) surface has a much lower barrier than out-channel hopping (0.72 eV) along the [001] direction (Table S1). From a structural viewpoint, since the presence of nanopore damage can be regarded as the clusters of vacancies, during the self-healing process of a nanopore damage, the directed diffusion of Ag atoms toward the nanopore region is equivalent to the reverse diffusion of vacancies away from the nanopore. Hence, the calculation of activation energy barriers of Ag diffusion is deduced via that of the vacancy diffusion. Based on the calculation results, the diffusion paths with the lowest barriers for Ag atoms across the single step and double step along [001] and  $[1\ \overline{1}\ 0]$  directions are shown in Figure 3E (see Table S2 and Note S1 for more details), respectively. As expected, for both steps along the [001] direction and  $[1\ \overline{1}\ 0]$  direction, the diffusion barriers

### Matter Article

across the single step are smaller than those across the double step. This result is not surprising considering the fact that the diffusion barrier increases with the thickness of steps for FCC metals.<sup>30</sup> For the across-the-step diffusion, the so-called Ehrlich-Schwoebel (ES) barrier<sup>30,40,41</sup> is a factor that has to be taken into account. Our calculation results show that the ES barrier for Ag atoms descending across a single step along the [1 1 0] direction is only 0.038 eV. This suggests that the ES barrier does not pose a significant obstacle to the across-the-step diffusion of Ag atoms, which is in line with the conclusions drawn in the literature.<sup>30</sup> Moreover, along the in-channel [1 1 0] direction, the kinetic barrier of Ag atom ascending diffusion is significantly higher than that of descending diffusion for both single and double steps, indicating that the net diffusion will be the diffusion of Ag atoms descending toward the nanopore.

### Molecular dynamics simulations of healing processes

To support our TEM observations, we carried out atomistic molecular dynamics (MD) simulations of the healing processes for nanoscale Ag and Au, respectively (see section "experimental procedures"). The MD simulations were performed on 12-layer slabs for both Ag and Au, in which the faceted octagonal nanopores are embedded, with crystallographic orientation in line with the experimental observations. The temperature for simulation was set at 650 K to accelerate the calculation, given the limited accessible timescale of MD simulations. For the simulated Ag slab shown in Figure 4A, it can be seen that the nanopore shrinks rapidly and gets cured after  $\sim$ 10 ns. In the subsequent  $\sim$ 90 ns, Ag atoms continue to diffuse toward the healed region uninterruptedly, with the thickness of the healed region being gradually increased (Figures 4A and S17A; Video S1). The plot of nanopore area vs. time (Figure S18A) shows that the nanopore area on the Ag slab decreases almost linearly with time, similar to the area-time relationship measured experimentally (the bottom chart in Figure 3C). In contrast, for the Au slab, although the nanopore shrinks slightly due to some surface relaxation in the first  $\sim$ 40 ns, its size and shape remain invariant in the subsequent  $\sim$ 60 ns, as shown in Figures 4B and S17B and Video S1.

These MD simulation results well reproduce the experimental observations regarding the difference in the healing behavior between Ag and Au. Importantly, our MD simulations also clearly manifested that surface diffusion plays a crucial role in the self-healing process of Ag. As shown in Figure S18B, the atomic diffusion mobility is quantitatively analyzed by the time evolution of the mean square displacement (MSD) along the  $<1\overline{10}>$  and  $<00\overline{1}>$  directions. Based on the statistical analysis of all surface atoms, the corresponding MSD curves show that the diffusivity (diffusion coefficient; i.e., the slope of the MSD curves) of Ag surface atoms is more than twice of that of Au surface atoms. This means that Ag has a much stronger tendency for surface diffusion than Au, a result that is well consistent with the diffusion barrier E<sub>a</sub> calculated by the NEB method and diffusion coefficients D<sub>s</sub>. Our calculations indicate that the diffusion barrier of Ag on the flat (110) surface is notably lower than that of Au, and the diffusion coefficient of Ag is much higher than that of Au (see Note S2 and Table S1 for additional details). Further, we also tracked the diffusion trajectory of the atoms filled into the nanopores. As discerned from the color labeling of atoms in the healed region from cross-section side views (FigureS17A), it can be seen that the majority of the Ag atoms filled into nanopores come from the top or bottom surface. Notably, MSD curves (Figure 4D) reveal that the diffusivity of Ag atoms along the in-channel direction ( $<1\overline{10}>$ ) is much stronger than the out-channel direction ( $< 00\overline{1} >$ ). This result correlates well with the above NEB calculation results (the blue curves in Figure 4E) that the diffusion barrier of Ag atoms along in-channel direction is much lower than that along out-channel





Figure 4. MD simulations of the healing process of nanopore damage in Ag and Au nanosheets, respectively

(A and B) Sequential top-view snapshots from MD simulations for Ag (A) and Au (B) slabs. The atoms are colored according to the value of  $|Z - Z_{center}|$ and atoms located away from the slab center are labeled with light colors. The rims of nanopores are highlighted by the red dashed line. (C) Schematic diagram showing the in-channel ([1  $\overline{1}$  0]) and out-channel ([00 $\overline{1}$ ]) directions on flat (110) plane.

(D) MSD of Ag atoms filling the nanopores along in-channel and out-channel directions, respectively, showing that the diffusivity along the in-channel direction is much stronger than that along the out-channel direction.

(E) Diffusion barriers of Ag atoms hopping along in-channel (left curves) and out-channel (right curves) directions with/without stacking fault calculated by the NEB methods. With stacking fault, the diffusion barriers are significantly reduced for the in-channel direction. See also Videos S1 and S2.

direction on flat (110) facet, indicating the in-channel hopping mechanism is energetically preferred.

As shown from the MD simulation results shown in Figures 4A, 4B, and S19A–S19D, stacking faults are observed to form in both Ag and Au. The stacking fault nucleates at the rim of the nanopore, propagates on {111} facets, and grows rapidly. For the Ag slab, the stacking fault remains even after the completion of healing of the nanopore. These results correlate well with our experimental observations (Figure 2E). We also investigated the formation energy barriers of stacking faults (in a hexagonal close-packed [HCP] structure) and their stability in Ag and Au, respectively. It turns out that stacking faults are energetically favorable and more stable in Ag (see Note S3 for more details). As mentioned above, experimentally, Ag nanosheets exhibit self-healing behavior with or without defects such as stacking faults (Figures 2A and 2E). This implies that the self-healing behavior is not necessarily related to stacking faults. Nevertheless, the presence of stacking faults is believed to facilitate

Matter Article



atomic diffusion and thereby promote the self-diffusion of Ag atoms. Specifically, with the stacking faults, the diffusion barrier of Ag atoms along the dominant inchannel direction is significantly reduced, as shown in Figure 4E and Table S3.

### DISCUSSION

Metals are one of the most important classes of materials for engineering structures. The inevitable occurrence and accumulation of microscopic mechanical damage (e.g., cracks, pores) in solid metals will reduce safety and service life cycle. The exploration of self-healing concepts in metallic systems has a great potential to enhance the structural reliability and sustainability for material engineering, which has evoked ever-increasing interest in recent years. By utilizing in situ TEM, we present direct observation on the autonomous self-healing behavior of nanoscale Ag metal in representative damage (nanopores and nanocracks) on an atomic scale. The selfhealing process in nanoscale Ag occurs autonomously both at room temperature as well as under low temperature of 173 K. The combination of atomic imaging and MD simulations of the dynamic self-healing process elucidates that it is the surface-mediated self-diffusion of Ag atoms that prompts the occurrence/proceeding of self-healing in Ag nanostructures. On the other hand, thermodynamically, the driving force for self-healing in Ag metal originates from the chemical potential imbalance (G-T effect). Once a damage structure (either nanopore or nanocrack) forms, there will arise a chemical potential imbalance due to the local curvature at the damage sites relative to the main part of the nanosheet. As a comparative study, this autonomous nanoscale self-healing behavior is not readily accessible in Au at room temperature.

To date, the concept of self-healing in solid metals is still in a very early stage of development. One of the key obstacles is the strong metallic bonding and therefore the low mobility of atoms at room temperature. This key difference indicates that Ag is a rare case in the metal family that has sufficiently high mobility of surface diffusion for accomplishing self-healing. In fact, regarding the ease of surface self-diffusion, several recent studies have reported it is a general property of Ag under a broad range of imposed conditions, especially for experiential testing with mechanical loading. However, it is the first time that our work unveils a previously unseen connection between the surface self-diffusion and self-healing behavior in Ag. Perhaps most importantly, in a broader term, our unusual experimental finding of the self-healing phenomena in Ag and the atomistic insights into healing mechanism are potentially applicable to some other metals provided the surface self-diffusion is promoted under certain conditions. For instance, with a reminiscence of the wellknown "Sn whisker" phenomenon widely reported in previous literature, where it is the ease of surface self-diffusion of Sn atoms that plays a key role for facilitating the spontaneous whisker growth in Sn-based solders at ambient temperature,<sup>42–44</sup> Sn may be expected as a possible candidate for exhibiting such autonomous selfhealing behavior as Ag.

For greater utilization of practical materials with effective autonomous self-healing functionality, the repeatability is particularly important.<sup>2,45</sup> In our present work, we have also observed the repeated reversible healing behavior of nanopore damage on Ag nanosheets. Shown in Figure 5 is a representative result of such multiple damage-forming/healing events. Following the initial nanopore self-repair, the second and third cycles of damage-forming and -healing tests were performed over the same region. It is evident that the second and third runs of healing can occur as fast as the first run without reducing the self-healing efficiency. The repeatable,

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**Figure 5.** The repeated reversible self-healing behaviors in Ag nanosheets Three runs of nanopore damage forming/healing are conducted over the same region.

on-site self-healing and elimination of incipient defects have significant influence on long-term persistence of metal materials, especially for potentially life-limiting material failure processes. This encouraging result further establishes that Ag can be exploited for the design and development of mechanically stable and damage-tolerant components and devices. On this basis, this work may serve as an inspiration for developing sustainable self-healing metal materials toward green manufacturing.

### **EXPERIMENTAL PROCEDURES**

### **Resource** availability

#### Lead contact

More information and requests for resources should be directed to and will be fulfilled by the lead contact, Wenlong Wang (wwl@iphy.ac.cn).

#### Materials availability

This study did not generate new unique reagents.

#### Data and code availability

All data reported in the manuscript or the supplemental information are available upon reasonable request.

### Sample preparation

The commercial Ag nanosheets, Ag nanowires, and Au nanosheets were purchased from Nanjing XFNANO Materials Tech. The thicknesses of Ag nanosheets and Au nanosheets were appropriately 30–60 nm and ~10 nm, respectively. The samples were first dispersed into ethyl alcohol by ultrasonic dispersion and then transferred to TEM grids. We also performed the nanopore fabrication and the observation of nanopore evolution on the Ag nanosheet prepared from bulk Ag. The bulk Ag was first thinned by mechanical grinding and dimpling and then we performed Arion milling in a Gatan precision ion polishing system. The morphologic low-magnification TEM images and selected area electron diffraction (SAED) patterns of all Ag and Au samples are shown in Figure S2.

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#### Fabrication of nanopore and nanocrack

The nanopore or nanocrack damage was fabricated by using highly focused electron beam (TEM mode) or scanning transmission electron microscopy (STEM) convergent beam on Ag and Au materials. The resulting knock-on effect caused the formation of nanopores and nanocracks on the surface of the Ag nanosheets.<sup>46–48</sup> In the TEM model, the total electron dose that we used was as low as  $\sim$ 2.77 nA. However, it should be emphasized that the fabrication of nanopores or nanocracks depends upon current density instead of the total electron dose. When the electron beam was focused with a diameter of  $\sim$ 5 nm, its current density reached  $8.8 \times 10^8 \text{ e/nm}^2 \cdot \text{s}$  (1.41  $\times 10^4 \text{ A/cm}^2$ ) and was strong enough to induce the nanopore or nanocrack damage. Under STEM mode, by adjusting the height of specimen to achieve focus in Ronchigram, the processes of the fabrication of nanopore or nanocrack can be visualized directly. Depending on the thickness of the sample (10-60 nm), the fabrication time varies from 20 to 60 s. Generally, the thicker samples require longer fabrication times, and the fabrication time for Au is slightly longer than that for Ag with similar thickness. After fabrication, the areas of the as-formed nanopores range from 13 to 53 nm<sup>2</sup>.

### **TEM and STEM characterization**

The TEM and STEM imaging were carried out in an aberration-corrected (S)TEM (JEM-ARM300F, JEOL.) operated at 300 kV acceleration voltage with a cold fieldemission gun and double dodeca-poles Cs correctors. The TEM images were recorded by a complementary metal-oxide semiconductor (CMOS) camera (4k × 4k, Gatan OneView camera) with an exposure time of 0.25–1 s. For HAADF imaging, we adopted a convergence angle and an angular range of collected electrons of 22 mrad and 54–220 mrad, respectively. The pixel time used to acquire HAADF-STEM images with the size of 1,024 × 1,024 was 19  $\mu$ s.

### **Cryo-TEM**

Cryo-TEM experiments were performed using a single-tilt liquid-nitrogen cooling holder provided by ZepTools Technology Company. The TEM samples were loaded onto the holder and transferred to the TEM column at room temperature. Then, liquid nitrogen was added to the dewar of the cooling holder. It took about 30 min for the samples to stabilize at a temperature of 106 K ( $-167.15^{\circ}$ C). In addition, the cooling holder was equipped with a heating unit, allowing for continuous temperature adjustment and stabilization ranging from 106 K to  $\sim$ 363 K ( $\sim$ 90.15°C). At the reduced temperature (106 K and 173 K), the nanopore was fabricated and its evolution process was recorded as described above.

### **GPA**

In this work, GPA was performed using the FRWR tools plugin for the Digital Micrograph software, which is based on the methods of Hytch et al.<sup>49,50</sup>

The strain and rotation fields were calculated from the local distortion of the lattice from the gradient of the displacement field. The plane strain can be written as<sup>49,50</sup>

$$\begin{cases} \varepsilon_{xx} = \frac{\partial u_x}{\partial x} \\ \varepsilon_{yy} = \frac{\partial u_y}{\partial y} \\ \varepsilon_{xy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) \end{cases}$$

and rigid rotation (in radians) can be written as





$$\omega_{xy} = \frac{1}{2} \left( \frac{\partial u_y}{\partial x} - \frac{\partial u_x}{\partial y} \right)$$

where  $u_x$  and  $u_y$  are the x and y components of the displacement field at the position (x, y) in the HAADF images. We first applied Fourier transform on the atomic-resolution HAADF images. In the FFT images, we placed circular Gaussian masks on two non-collinear reciprocal lattice vectors  $\mathbf{g}_1$  and  $\mathbf{g}_2$  along <002> and <1  $\overline{1}$  1>, respectively, to calculate the displacement field  $u_x$  and  $u_y$ . Then, the strain maps  $\varepsilon_{xx}$ ,  $\varepsilon_{yy}$ , and  $\varepsilon_{xy}$  and rigid rotation  $\omega_{xy}$  can be obtained. Note that the GPA parameters used for the whole HAADF image of Ag are the same and all the strain calculations utilized the Ag lattice far from the nanopore as a reference.

#### **MD** simulations

Classical MD simulations were carried out by Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program,<sup>51</sup> and visualizations were performed with the aid of OVITO package.<sup>52</sup> The embedded atom method (EAM) potential<sup>25,53</sup> was applied to describe the interactions between metal atoms. A flat (110) slab model with size of 15 × 15 × 1.7 nm (12 layers) was used in MD simulations combined with periodic boundary conditions along x and y axes. Meanwhile, an octagonal nanopore with diameter about 1 nm was located at the center of the slab. In order to provide a particle reservoir for self-healing, we randomly deleted 10% of surface atoms. The Nose-Hoover canonical (NVT) ensemble<sup>54</sup> was employed and the temperature was set to be 650 K (much lower than the melting point) to accelerate MD simulations. The timestep of simulation was set as 1.0 fs, and the total simulation time was 100 ns.

### **DFT** calculation

In this work, all static calculations, including NEB calculation and formation barrier of stacking faults, were performed within the framework of density functional theory (DFT). DFT calculations were carried out with Vienna Ab Initio Simulation Package (VASP)<sup>55</sup> using the projector augmented wave (PAW)<sup>56</sup> method and Perdew-Burke-Ernzerhof (PBE) for exchange-correlation energy. The energy cutoffs were set at 250 eV for Ag and 230 eV for Au. The Brillouin zone was sampled with 3 × 3 × 1 k points using the Monkhorst-Pack scheme. Geometrical optimization was fully achieved with force converge within 0.01 eV/Å.

#### **NEB** calculation

In order to determine the minimum-energy path (MEP) for diffusion, NEB calculation was performed.<sup>28,29</sup> The initial configurations of three intermediate replicas were interpolated in a linear fashion between the first and last replicas. At the first stage of NEB calculation, the set of replicas converged toward an MEP roughly with force converge within 0.01 eV/Å. Next, at the second stage, the replica with the highest energy was selected and driven to the saddle point of the barrier through barrier-climbing calculation with the same criteria for convergence. After that, we obtained the energy barrier for different diffusion paths.

#### **Common neighbor analysis**

In order to recognize the defects such as stacking faults in MD simulation, common neighbor analysis<sup>57</sup> was applied. In this method, four indexes are used to distinguish different structures starting with a pair of atoms,  $\alpha$  and  $\beta$ :

- (1) Values 1 or 2 indicate that  $\alpha$  and  $\beta$  are nearest neighbors (*i* = 1) or not (*i* = 2)
- (2) Indicates the number of nearest neighbors shared by the (α,β) pair (common neighbors)





- (3) Indicates the number of bonds among the common neighbors
- (4) Differentiates diagrams with same (i), (ii), and (iii) indexes and different bonding among common neighbors

The method performs well to distinguish FCC, body-centered cubic (BCC), HCP structures for monoatomic system.

### Formation barrier of stacking faults

Two slabs with FCC-structured Ag and Au, respectively, modeled by 18 sequentially stacked close-packed (111) atomic planes (1,008 atoms), were used to calculate the formation barriers of stacking faults. In the slabs, the vacuum layers with thickness of ~6 nm were built in the direction perpendicular to the slab (z direction) to separate each slab from the adjacent ones in the next periodic cell, thus minimizing the interaction of the slabs. Next, along the MEP ( $\langle 11\overline{2} \rangle$  direction), the top eight atomic layers were shifted by the Burgers vector of the Shockley partial  $b_s = a/6 \langle 11\overline{2} \rangle$  (a is the lattice parameter) to create stacking faults with an artificial stacking sequence ABCABC| BCABC, as shown in Figures S19E and S19F. During the NEB simulation, the top three layers and the bottom three layers are fixed, and the remaining atomic configurations of the slabs are geometrically relaxed to the MEPs in the three directions until the force on each atom becomes smaller than 0.01 eV/Å. Finally, the formation barriers of the stacking faults in Ag and Au are obtained by the energy difference of the two optimized structures normalized by the area of the stacking faults, as shown in Figure S19G.

### SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.matt. 2024.07.009.

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#### **AUTHOR CONTRIBUTIONS**

J.W., W.W., and X.B. conceived the idea and designed the experiments. W.W., S.M., and X.B. supervised the research. J.W. performed the TEM and STEM measurements. Q.X. and S.M. conducted the MD simulation and DFT calculation. All authors participated in analyzing the experimental results. J.W., M.S., and W.W. wrote this manuscript with the input of all authors.

### **DECLARATION OF INTERESTS**

The authors declare no competing interests.

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#### REFERENCES

- Hager, M.D., Greil, P., Leyens, C., van der Zwaag, S., and Schubert, U.S. (2010). Self-Healing Materials. Adv. Mater. 22, 5424–5430. https://doi.org/10.1002/adma.201003036.
- Blaiszik, B.J., Kramer, S., Olugebefola, S.C., Moore, J.S., Sottos, N.R., and White, S.R. (2010). Self-healing polymers and composites. Annu. Rev. Mater. Res. 40, 179–211. https://doi. org/10.1146/annurev-matsci-070909-104532.
- Yang, Y., and Urban, M.W. (2013). Self-healing polymeric materials. Chem. Soc. Rev. 42, 7446– 7467. https://doi.org/10.1039/c3cs60109a.
- Cordier, P., Tournilhac, F., Soulié-Ziakovic, C., and Leibler, L. (2008). Self-healing and thermoreversible rubber from supramolecular assembly. Nature 451, 977–980. https://doi. org/10.1038/nature06669.
- Burnworth, M., Tang, L., Kumpfer, J.R., Duncan, A.J., Beyer, F.L., Fiore, G.L., Rowan, S.J., and Weder, C. (2011). Optically healable supramolecular polymers. Nature 472, 334–337. https://doi.org/10.1038/nature09963.
- Urban, M.W., Davydovich, D., Yang, Y., Demir, T., Zhang, Y., and Casabianca, L. (2018). Keyand-lock commodity self-healing copolymers. Science 362, 220–225. https://doi.org/10.1126/ science.aat2975.
- Pena-Francesch, A., Jung, H., Demirel, M.C., and Sitti, M. (2020). Biosynthetic self-healing materials for soft machines. Nat. Mater. 19, 1230–1235. https://doi.org/10.1038/s41563-020-0736-2.
- Manuel, M.V., and Olson, G.B. (2007). Biomimetic self-healing metals. In Proceedings of the 1st International Conference on Self-Healing Materials held in Noordwijik aan Zee, The Netherlands, pp. 18–20.
- Rohatgi, P. (2014). Al-shape memory alloy selfhealing metal matrix composite. Materials Science & Engineering: A 619, 73–76. https:// doi.org/10.1016/j.msea.2014.09.050.
- Zhang, S., Kwakernaak, C., Sloof, W., Brück, E., van der Zwaag, S., and van Dijk, N. (2015). Self Healing of Creep Damage by Gold Precipitation in Iron Alloys. Adv. Eng. Mater. 17, 598–603. https://doi.org/10.1002/adem. 201400511.
- Gao, K., Qiao, L., and Chu, W. (2001). In situ TEM observation of crack healing in α-Fe. Scripta Mater. 44, 1055–1059. https://doi.org/ 10.1016/S1359-6462(01)00671-6.
- Kovalenko, O., Brandl, C., Klinger, L., and Rabkin, E. (2017). Self-Healing and Shape Memory Effects in Gold Microparticles through the Defects-Mediated Diffusion. Adv. Sci. 4, 1700159. https://doi.org/10.1002/advs. 201700159.
- Gao, K.W., Qiao, L.J., and Chu, W.Y. (2002). Molecular dynamics simulation and in situ TEM study of crack healing. Mater. Sci. Technol. 18, 1109–1114. https://doi.org/10.1179/ 026708302225006133.
- Xu, G.Q., and Demkowicz, M.J. (2013). Healing of Nanocracks by Disclinations. Phys. Rev. Lett. 111, 145501. https://doi.org/10.1103/ PhysRevLett.111.145501.

- Wang, B., Han, Y., Xu, S., Qiu, L., Ding, F., Lou, J., and Lu, Y. (2018). Mechanically Assisted Self-Healing of Ultrathin Gold Nanowires. Small 14, 1704085. https://doi.org/10.1002/smll. 201704085.
- Barr, C.M., Duong, T., Bufford, D.C., Milne, Z., Molkeri, A., Heckman, N.M., Adams, D.P., Srivastava, A., Hattar, K., Demkowicz, M.J., and Boyce, B.L. (2023). Autonomous healing of fatigue cracks via cold welding. Nature 620, 552–556. https://doi.org/10.1038/s41586-023-06223-0.
- Zhong, L., Sansoz, F., He, Y., Wang, C., Zhang, Z., and Mao, S.X. (2017). Slip-activated surface creep with room-temperature superelongation in metallic nanocrystals. Nat. Mater. 16, 439–445. https://doi.org/10.1038/ nmat4813.
- Gwak, E.-J., Jeon, H., Song, E., and Kim, J.-Y. (2020). Self-Healing of Nanoporous Gold Under Ambient Conditions. Nano Lett. 20, 6706–6711. https://doi.org/10.1021/acs. nanolett.0c02551.
- Zheng, H., Liu, Y., Cao, F., Wu, S., Jia, S., Cao, A., Zhao, D., and Wang, J. (2013). Electron beam-assisted healing of nanopores in magnesium alloys. Sci. Rep. 3, 1920. https:// doi.org/10.1038/srep01920.
- Mullins, W.W. (1957). Theory of Thermal Grooving. J. Appl. Phys. 28, 333–339. https:// doi.org/10.1063/1.1722742.
- Jost, W. (1952). Diffusion in solids, liquids, gases. Z. Phys. Chem. 201, 319–320. https:// doi.org/10.1515/zpch-1952-2011-229.
- Koelling, D.D., and Harmon, B.N. (1977). A technique for relativistic spin-polarised calculations. J. Phys. C Solid State Phys. 10, 3107–3114. https://doi.org/10.1088/0022-3719/10/16/019.
- Fiorentini, V., Methfessel, M., and Scheffler, M. (1993). Reconstruction mechanism of fcc transition metal (001) surfaces. Phys. Rev. Lett. 71, 1051–1054. https://doi.org/10.1103/ PhysRevLett.71.1051.
- Yu, B.D., and Scheffler, M. (1997). Physical origin of exchange diffusion on fcc(100) metal surfaces. Phys. Rev. B 56, R15569–R15572. https://doi.org/10.1103/PhysRevB.56.R15569.
- Liu, C.L., Cohen, J.M., Adams, J.B., and Voter, A.F. (1991). EAM study of surface self-diffusion of single adatoms of fee metals Ni, Cu, Al, Ag, Au, Pd, and Pt. Surf. Sci. 253, 334–344. https:// doi.org/10.1016/0039-6028(91)90604-q.
- Montalenti, F., and Ferrando, R. (1999). Jumps and concerted moves in Cu, Ag, and Au(110) adatom self-diffusion. Phys. Rev. B 59, 5881– 5891. https://doi.org/10.1103/PhysRevB. 59.5881.
- Agrawal, P.M., Rice, B.M., and Thompson, D.L. (2002). Predicting trends in rate parameters for self-diffusion on FCC metal surfaces. Surf. Sci. 515, 21–35. https://doi.org/10.1016/s0039-6028(02)01916-7.
- Jónsson, H., Mills, G., and Jacobsen, K.W. (1998). Nudged elastic band method for finding minimum energy paths of transitions. In Classical and quantum dynamics in condensed

phase simulations (World Scientific)), pp. 385–404.

- Henkelman, G., Uberuaga, B.P., and Jónsson, H. (2000). A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901–9904. https://doi. org/10.1063/1.1329672.
- Kim, S.Y., Lee, I.-H., and Jun, S. (2007). Transition-pathway models of atomic diffusion on fcc metal surfaces. II. Stepped surfaces. Phys. Rev. B 76, 245408. https://doi.org/10. 1103/PhysRevB.76.245408.
- Kim, S.Y., Lee, I.-H., and Jun, S. (2007). Transition-pathway models of atomic diffusion on fcc metal surfaces. I. Flat surfaces. Phys. Rev. B 76, 245407. https://doi.org/10.1103/ PhysRevB.76.245407.
- Wang, W., Wang, M., Ambrosi, E., Bricalli, A., Laudato, M., Sun, Z., Chen, X., and lelmini, D. (2019). Surface diffusion-limited lifetime of silver and copper nanofilaments in resistive switching devices. Nat. Commun. 10, 81. https://doi.org/10.1038/s41467-018-07979-0.
- Sun, J., He, L., Lo, Y.-C., Xu, T., Bi, H., Sun, L., Zhang, Z., Mao, S.X., and Li, J. (2014). Liquidlike pseudoelasticity of sub-10-nm crystalline silver particles. Nat. Mater. 13, 1007–1012. https://doi.org/10.1038/nmat4105.
- Grouchko, M., Roitman, P., Zhu, X., Popov, I., Kamyshny, A., Su, H., and Magdassi, S. (2014). Merging of metal nanoparticles driven by selective wettability of silver nanostructures. Nat. Commun. 5, 2994. https://doi.org/10. 1038/ncomms3994.
- Wang, X., Zheng, S., Shinzato, S., Fang, Z., He, Y., Zhong, L., Wang, C., Ogata, S., and Mao, S.X. (2021). Atomistic processes of surfacediffusion-induced abnormal softening in nanoscale metallic crystals. Nat. Commun. 12, 5237. https://doi.org/10.1038/s41467-021-25542-2.
- Oh, S.H., Legros, M., Kiener, D., and Dehm, G. (2009). In situ observation of dislocation nucleation and escape in a submicrometre aluminium single crystal. Nat. Mater. 8, 95–100. https://doi.org/10.1038/nmat2370.
- Zheng, H., Cao, A., Weinberger, C.R., Huang, J.Y., Du, K., Wang, J., Ma, Y., Xia, Y., and Mao, S.X. (2010). Discrete plasticity in sub-10-nmsized gold crystals. Nat. Commun. 1, 144. https://doi.org/10.1038/ncomms1149.
- Zou, L., Yang, C., Lei, Y., Zakharov, D., Wiezorek, J.M.K., Su, D., Yin, Q., Li, J., Liu, Z., Stach, E.A., et al. (2018). Dislocation nucleation facilitated by atomic segregation. Nat. Mater. 17, 56–63. https://doi.org/10.1038/nmat5034.
- George, E.P., Raabe, D., and Ritchie, R.O. (2019). High-entropy alloys. Nat. Rev. Mater. 4, 515–534. https://doi.org/10.1038/s41578-019-0121-4.
- Ehrlich, G., and Hudda, F.G. (1966). Atomic View of Surface Self-Diffusion: Tungsten on Tungsten. J. Chem. Phys. 44, 1039–1049. https://doi.org/10.1063/1.1726787.



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- Schwoebel, R.L., and Shipsey, E.J. (1966). Step Motion on Crystal Surfaces. J. Appl. Phys. 37, 3682–3686. https://doi.org/10.1063/1.1707904.
- 42. Lee, B.Z., and Lee, D.N. (1998). Spontaneous growth mechanism of tin whiskers. Acta Mater. 46, 3701–3714. https://doi.org/10.1016/s1359-6454(98)00045-7.
- Galyon, G.T. (2005). Annotated tin whisker bibliography and anthology. IEEE Trans. Electron. Packag. Manuf. 28, 94–122. https:// doi.org/10.1109/tepm.2005.847440.
- He, A., and Ivey, D.G. (2015). Microstructural study of Sn films electrodeposited on Cu substrates: Sn whiskers and Cu6Sn5 precipitates. J. Mater. Sci. 50, 2944–2959. https://doi.org/10.1007/s10853-015-8859-6.
- Hager, M.D., Sybrand, V.D.Z., and Schubert, U.S. (2016). Self-healing Materials (Springer), pp. 387–408. https://doi.org/10.1007/978-3-319-32778-5.
- Vajda, P. (1977). Anisotropy of electron radiation damage in metal crystals. Rev. Mod. Phys. 49, 481–521. https://doi.org/10.1103/ RevModPhys.49.481.

- Egerton, R.F., Li, P., and Malac, M. (2004). Radiation damage in the TEM and SEM. Micron 35, 399–409. https://doi.org/10.1016/j.micron. 2004.02.003.
- Egerton, R.F., McLeod, R., Wang, F., and Malac, M. (2010). Basic questions related to electron-induced sputtering in the TEM. Ultramicroscopy 110, 991–997. https://doi.org/ 10.1016/j.ultramic.2009.11.003.
- Hÿtch, M.J., Snoeck, E., and Kilaas, R. (1998). Quantitative measurement of displacement and strain fields from HREM micrographs. Ultramicroscopy 74, 131–146. https://doi.org/ 10.1016/s0304-3991(98)00035-7.
- Hÿtch, M.J., Putaux, J.L., and Penisson, J.M. (2003). Measurement of the displacement field of dislocations to 0.03 angstrom by electron microscopy. Nature 423, 270–273. https://doi. org/10.1038/nature01638.
- Plimpton, S. (1995). Fast parallel algorithms for short-range molecular dynamics. J. Comput. Phys. 117, 1–19. https://doi.org/10.1006/jcph. 1995.1039.
- 52. Stukowski, A. (2010). Visualization and analysis of atomistic simulation data with OVITO-the

Open Visualization Tool. Model. Simulat. Mater. Sci. Eng. 18, 015012. https://doi.org/10. 1088/0965-0393/18/1/015012.

- Foiles, S.M., Baskes, M.I., and Daw, M.S. (1986). Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys. Phys. Rev. B 33, 7983–7991. https://doi.org/10. 1103/physrevb.33.7983.
- Evans, D.J., and Holian, B.L. (1985). The nose– hoover thermostat. J. Chem. Phys. 83, 4069– 4074. https://doi.org/10.1063/1.449071.
- Kresse, G., and Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186. https://doi.org/10. 1103/PhysRevB.54.11169.
- Blöchl, P.E. (1994). Projector augmented-wave method. Phys. Rev. B 50, 17953–17979. https:// doi.org/10.1103/PhysRevB.50.17953.
- Tsuzuki, H., Branicio, P.S., and Rino, J.P. (2007). Structural characterization of deformed crystals by analysis of common atomic neighborhood. Comput. Phys. Commun. 177, 518–523. https://doi.org/10. 1016/j.cpc.2007.05.018.

