

Size-dependent mechanical deformation mechanisms in sub-20 nm lead crystals

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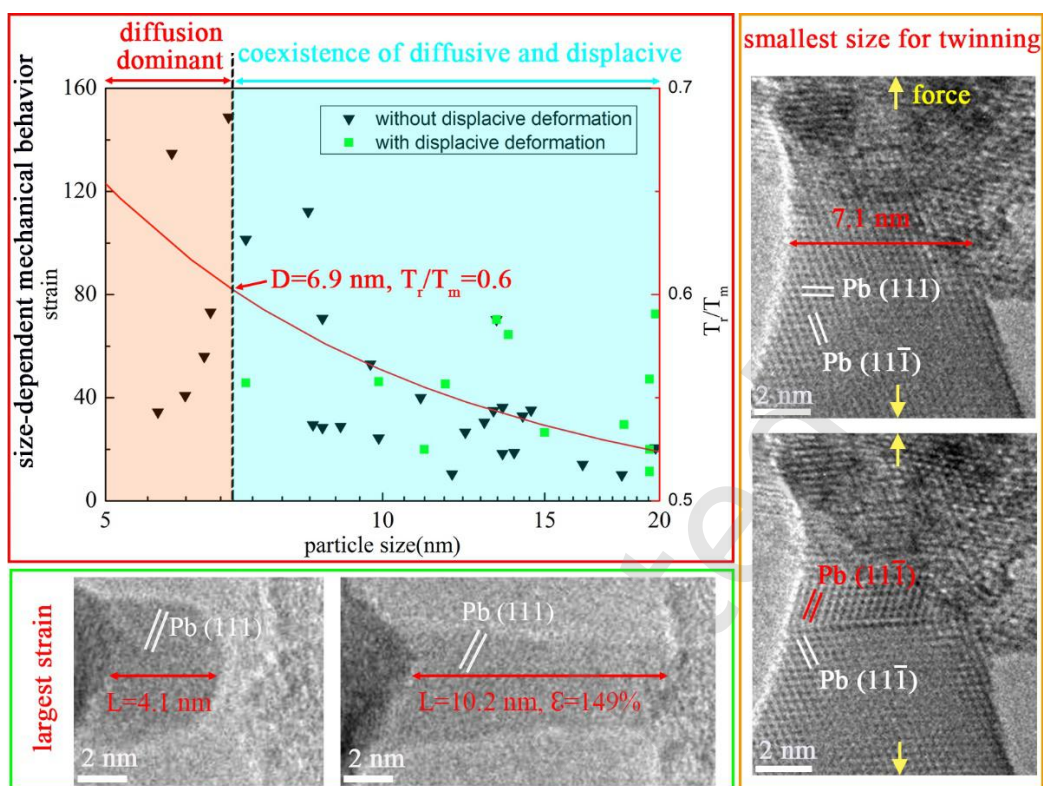
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As size decreases, the atomic surface diffusion gradually dominates the deformation process of Pb nano-particles while the critical size for dislocation dynamics of Pb is determined to be 7.1 nm.

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ABSTRACT: Mechanical properties of small-volume metals critically affect the reliability and performance of nano-devices. Under mechanical forces, behavior of small-volume metals differs considerably from that of their bulks, but the knowledge of how the feature size give rise to the unique characteristics is currently insufficient, particularly in sub-20 nm regime. In this study, we investigate the influence of feature size on mechanical behaviors in sub-20 nm Pb crystals via performing in situ mechanical deformation tests inside TEM. Diffusion-induced pseudo-elastic deformation and dislocation-triggered plastic deformation processes were observed at atomic precision in 5-20 nm Pb particles. As size decreases, surface diffusion gradually dominates the deformation process while smallest size for twinning of Pb is determined to be 7.1 nm. Moreover, surface layers with thickness 1-6 nm are found to diffuse readily, playing a decisive role in the deformation of all Pb particles. Minimization of surface energy provides driving force for both the diffusion and size-dependent spherical surface morphology after deformation. This research directly reveals the dramatic impact of feature size on the deformation mechanisms of metallic nanocrystals, which provides significant implications for property tuning of advanced nano-devices.

KEYWORDS: deformation, surface diffusion, size effect, *in situ*

1 Introduction

Mechanical properties of nano-sized metallic crystals have attracted interest as the feature size of electrical-devices have gradually decreased to sub-20 nm scale[1-4]. Previous studies have shown that mechanical behavior of nano-metals differs from their bulks[5-15]. On one hand, dislocations nucleate at truncated source instead of traditional Frank-Read source and annihilate at surface after slip, leading to a “dislocation starvation” state and “smaller is stronger” characteristic of nano-metals[16-21]. On the other hand, the atomic diffusion rate increases with decreasing feature size as: $r \propto s^{-3}$ [22, 23], resulting in “smaller is weaker” characteristic and inducing novel mechanical deformation phenomena such as self-healing[24, 25], super-plasticity[26], and pseudo-elasticity of nano-metals[27, 28]. The competition between dislocation dynamics and atomic diffusion processes dominates the mechanical properties and behavior of metallic nanocrystals[21, 29].

Multiple evidences have proved that the competition varies with the feature size of metals[28, 30-34]. In general, the deformation mechanism transitions from dislocation-

dominant into diffusion-controlled as feature size decreases to nano-sized scale, although the critical size is not universal across different metals. Numerous studies have focused on metallic crystals with high thermal stability such as Au, Pt or Ag[9, 16, 17, 24, 27, 30-36]. For inert Au and Pt, the critical size is found to be <3 nm[5, 9, 17, 24, 34]. Since the diffusivity of Ag is much higher than them, the diffusion becomes dominant mechanism at 3-10 nm[27, 33, 34, 36]. However, we notice that few studies have focused on low-melting-point metals (such as Pb, Bi, Sn or In) and thus, there is still lack of conclusion regarding their critical sizes[37-39].

The low-melting-point Pb is one of the earliest metals that have been widely applied in numerous fields including glasses, alloys, lead-acid batteries and photovoltaic devices[40-43]. Mechanical behavior of large-sized Pb under various conditions has been studied since the mechanical stability of Pb can significantly influence the performance of devices[28, 40, 41, 44]. Nevertheless, there is a lack of direct and systematic evidence on the deformation of Pb nanocrystals and the evolution from dislocation-dominant into diffusion-controlled deformation has not yet been fully clarified. Thus, it is necessary to provide direct and real-time observation of their deformation processes with different

crystal sizes with atomic precision to address this gap.

In this work, in situ mechanical deformation experiments were conducted on Pb particles with various feature sizes (5-20 nm) in an aberration-corrected Titan TEM/STEM. Size-dependent pseudo-elastic deformation and plastic deformation processes were observed. As size decreases, the atomic surface diffusion becomes prevailing and the critical size for dislocation dynamics is 7.1 nm. Even for large-sized Pb particles, their deformation processes are still significantly influenced by diffusion of surface atoms with layer approximately 1-6 nm thick. Tendency to minimize the surface energy via atomic diffusion is responsible for the size-dependent spherical morphology resulting from the spontaneous shrinkage after deformation.

2 Results and Discussion

Preparation of Pb particles with distinct particle sizes is

shown in Materials and Methods. Typical results are shown in Figure S1. More details can be found in our previous research[45].

In-situ mechanical deformation tests were conducted on pure Pb particles with different sizes, and the liquid-like pseudo-elastic deformation process has been captured on some particles, as shown in Figure 1 and Figure S2. Initially, a Pb particle (6 nm) was supported on the W tip surface, where Pb(111) lattice fringes can be clearly identified (Figure 1(a)). Subsequently, W tip moved upward to compress the Pb particle (Figures 1(b)-(c)). As the W tip moved, the particle was gradually compressed into flattened morphology in Figure 1(d). The width increased to 7.6 nm and thickness decreased to 3.5 nm. Then the W tip moved downward to release the particle in Figures 1(e)-(f) and the particle was even stretched to 8.5 nm in Figure 1(g) owing to the van der Waals forces. As the W tip continued to move downward, the

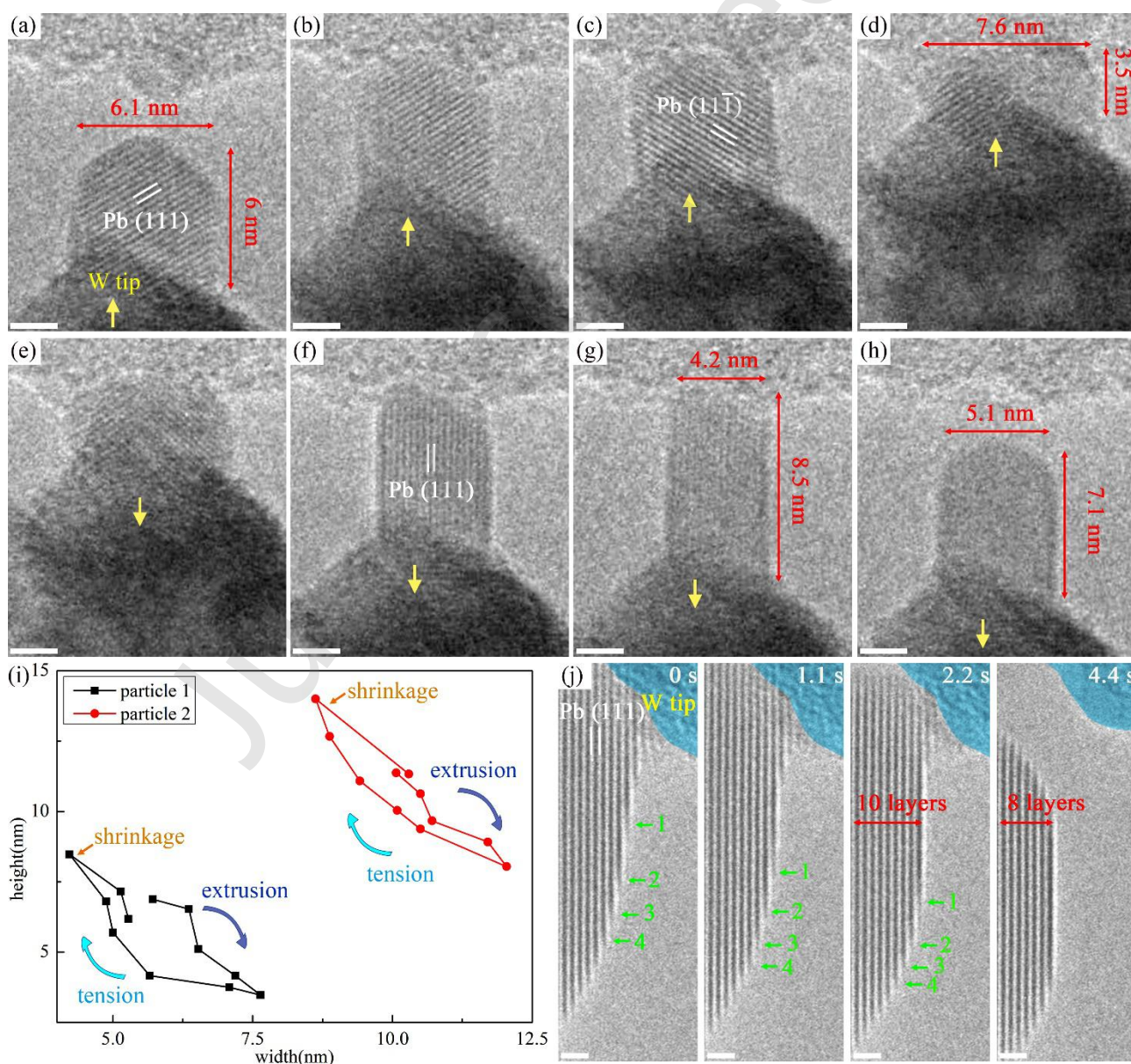


Figure 1 Diffusive deformation processes of Pb crystals. (a)-(h) Liquid-like pseudo-elasticity deformation of Pb particle. (a) Initial morphology of Pb particle before deformation. (b)- (d) Shape evolution of the Pb particle during extrusion. (e)- (g) Shape evolution of the Pb particle during tension. (h) Final morphology of the Pb particle after deformation. (i) Evolution of particle height as function with particle width of two Pb particles (Figure 1 and

Figure S2). (j) Surface evolution of Pb crystal under tensile. Scale bars: (a)-(h): 2 nm; (j): 1 nm.

van der Waals forces became too weak and the Pb particle lost contact with the tip. Meanwhile as shown in Figure 1(h), the Pb particle rapidly shrank into a morphology similar to its initial shape in Figure 1(a). Similar deformation process is also observed on larger particle (10 nm), as presented in Figure S2. Variation of particle height with width is shown in Figure 1(i). For both particles, the tendency to recover their original shapes and liquid-like shrinkage processes were observed. These results clearly demonstrate pseudo-elastic deformation which has been proved to originate from diffusion of surface atoms[27, 28]. Direct evidence of atomic diffusion is presented in Figure 1(j). Atomic steps (green arrows) are formed on the Pb particle surface under tension from W tip. Pb atoms tended to diffuse along the surface from upper region to the bottom, driving migration of atomic steps. After 4.4 s, since sufficient atoms had diffused away from the contact region, the tip lost connection with the particle. Consequently, the spontaneous shrinkage happens and leads to a reduction of atomic layers.

In addition to the diffusive pseudo-elastic deformation in Figure 1, displacive plasticity induced by dislocation dynamics was also observed during the similar in situ compression and stretching experiments on other Pb particles. As shown in Figure 2(a), two full dislocations were observed near a twin boundary in the Pb crystal. As the W tip stretched the particle in Figure 2(b), a new full dislocation was nucleated and formed “tail-to-tail” configuration within the green rectangle. Under sustained tensile stress, all these dislocations slipped and were annihilated at the twin boundary, as shown in Figure 2(c). Gradual formation and disappearance of stacking faults are shown in Figures 2(d)-(f), which are induced by emission and migration of partial dislocations. In previous study, we have observed stacking faults in surface-oxidized Pb particles[28]. Here, we further present the evolution of stacking faults in clean Pb particle under shear stress. In addition, displacive twinning process

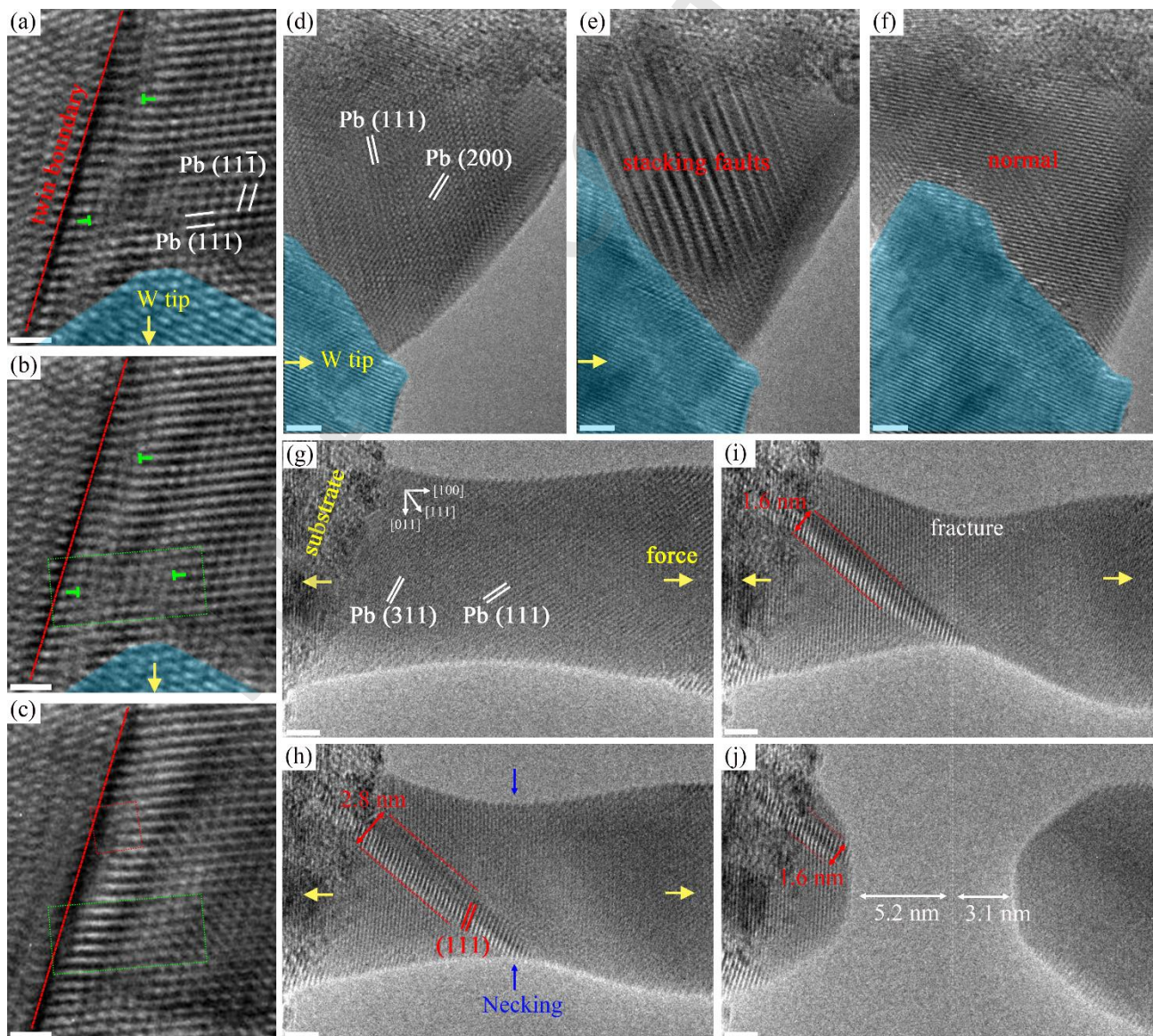


Figure 2 Displacive deformation processes of Pb crystals. (a)-(c) Dislocation dynamics of Pb crystal under tension. All dislocations have been marked

as green “T”. (d)- (f) Evolution of stacking faults of Pb particle under shear stress. (g)- (j) Twinning process of Pb particle under tension. For better view, W tips have been painted blue. All yellow arrows indicate the force direction. The red dotted lines show the twin boundary. Scale bars: (a)- (c): 1 nm; (d)- (j): 2 nm.

was also captured during in-situ stretching of Pb particles. As shown in Figure 2(g), the Pb particle was stretched along [100]. Under the continuing tension, necking of the crystal was captured. Meanwhile, a twinning band with width =2.8 nm was formed from the substrate toward the necking region, as shown in Figure 2(h). As the necking proceeded, width of the twinning band decreased to 1.8 nm in Figure 2(i). Subsequently, the fracture happened at the necking region and the particle broke into two parts. After fracture, similar to Figure 1, the diffusion-induced liquid-like spontaneous shrinkage was observed for both fragments, with shrinkage lengths of 5.2 nm and 3.1 nm, respectively. After the fracture, the twinning band still exist inside the particle.

Based on above results, both atomic diffusion and dislocation dynamics can induce the deformation processes in Pb crystals. A half-quantitative analysis, similar to previous study on Ag nano-particles, was performed by comparing the diffusive and displacive thinning rate of pure Pb particles with different sizes during tensile deformation [28, 30], as shown in Figure S3(a). For Pb particles <20 nm, the diffusive thinning rate is significantly higher than thinning by dislocations. Thus, we classify the deformation processes as displacive only when clear dislocations are observed, such as Figure 2(i). In previous study, we have qualitatively shown that as particle size decreases, the surface diffusion gradually becomes dominant compared with the dislocation dynamics[28]. Here, we performed further statistical analysis on ~40 Pb particles with similar morphology to reveal the size-dependence of the deformation processes, as shown in Figures 3-4. We measured the maximum tensile strain of all Pb particles before fracture (stretch limit) and the scatterplot is presented in Figure 3(a).

During all deformation processes, the Pb particles are attached to W tip and substrate just by van der Waals forces and they are strongly affected by surface state of these materials. For instance, the W tip is prepared by electrochemically etching (Materials and Methods 4.2) and the W-Pb interfaces depends on the etching processes.

Meanwhile, the irradiation induced growth of Pb particle may also result in different Pb surfaces[28]. Thus, the tensile stress is not strictly uniform across all Pb particles and these contribute to the scatter of measurement in Figure 3(a). Nevertheless, the maximum strain generally exhibits a weak decreasing trend with increasing particle. In Figure 3(a), the largest measured strain of Pb was measured to be ~149% and the corresponding particle is shown in Figures 3(b)-(c). Moreover, all the displacive deformation processes were observed only in Pb particles with feature size >7 nm and the smallest particle (7.1 nm) exhibiting twinning is shown in Figures 3(d)-(e). We propose 7.1 nm to be critical size between diffusive and displacive deformation processes and related this to the size-dependent melting point of crystals.

In contrast to the weak temperature sensitivity of dislocation dynamics, the atomic diffusion processes are suppressed at low temperature and enhanced at high temperature[12, 23, 29]. Previous studies have shown that displacive deformation and diffusive deformation are dominant at temperature <0.3T_m, >0.6T_m respectively (T_m: melting temperature of metals)[37, 44, 46, 47]. Meanwhile, the T_m decreases with decreasing particle size as:[48]

$$T_m = T_0 \left(1 - \frac{1}{\frac{2D}{h} - 1}\right) e^{-\frac{2S_{b0}}{3R} * \frac{1}{\frac{2D}{h} - 1}}.$$

Here T₀ represents the T_m of bulk Pb (600.65 K), D is particle size, h denotes atomic diameter, R is the ideal gas constant, and S_{b0}=ΔH_{b0}/T_{b0} is the bulk solid-vapor transition entropy with ΔH_{b0} and T_{b0} being the bulk enthalpy of vaporization and the bulk boiling temperature, respectively. Based on this, the variation of T_r/T_m (T_r: room temperature) with particle size is plotted as the red line in Figure 3(a). At particle size <6.9 nm, T_r >0.6T_m. Thus, the atomic diffusion dominates deformation of all Pb particles with size <6.9 nm and this is in excellent agreement with our experimental results of 7.1 nm in Figures 3(d)-(e). On the other hand, this result also is consistent with the size-dependent competition between elastic strain energy and dislocation formation energy[49, 50]. Dislocation activity can only occur at ΔE_{strain}>ΔE_{dislocation}, which is derived to be >5.1 nm, as shown in Figure S3(b).

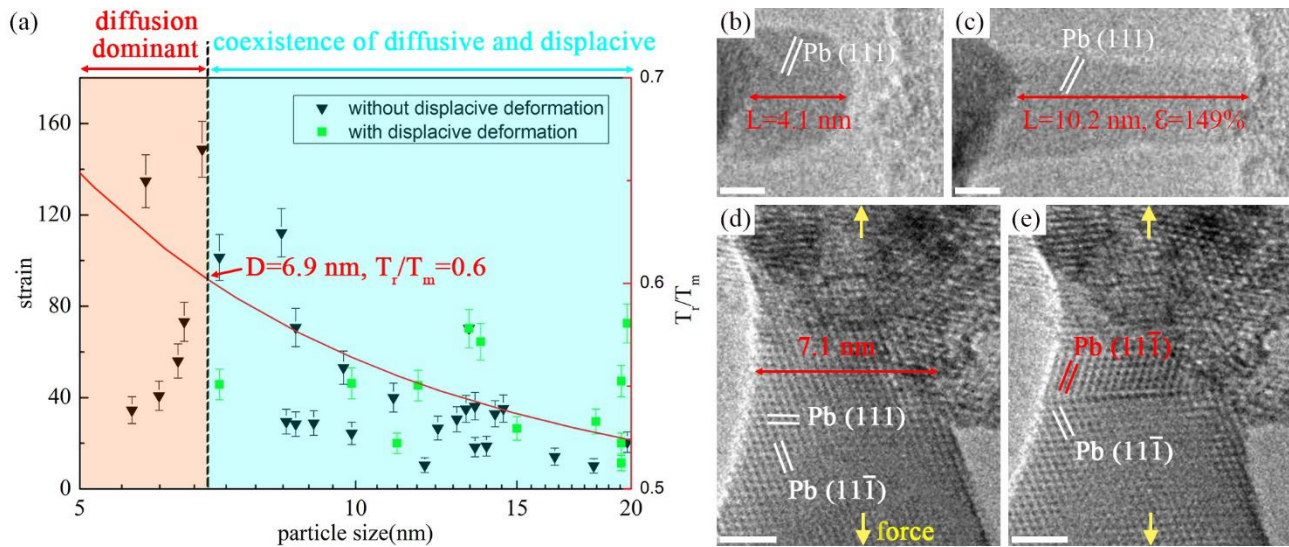


Figure 3 Size-dependent tensile deformation of sub-20 nm Pb crystals. (a) Largest strain (left y axis) and melting point (right y axis) of Pb particles as function with particle size. (b)-(c) TEM images of Pb particle with the maximum strain. (d)-(e) TEM images of smallest Pb particle that experience displacive deformation under tension. Scale bars: 2 nm.

Meanwhile, for all Pb particles with size >6.9 nm, there is $0.3T_m < T_t < 0.6T_m$. Thus, neither displacive nor diffusive deformation is solely dominant during the deformation process. In other words, the diffusive deformation is a universal phenomenon for all Pb crystals (including large-sized crystals). Typical diffusive tensile-deformation process of large-sized crystal (~ 20 nm) is shown in Figures 4(a)-(d). Initially, the surface of the particle is smooth (Figure 4(a)). Under tension from W tip, the surface tends to adopt a straight-arc-straight profile. Both the upper surface (away from tip) and the front side (near the tip) remain smooth, as shown in Figure 4(b). Under continued tension in Figure 4(c), rapid thinning occurs at the front side (near the tip) while no obvious change is observed on the upper surface. Figures 4(b)-(c) indicate that rapid thinning occurs only in narrow region (near the tip) and thus, leads to limited tensile strain of the crystal ($\sim 20\%$ in Figure 3(a)). Subsequently, the fracture happens at the Pb-W interface, followed by rapid spontaneous shrinkage of the particle in Figure 4(d). The surface morphology shrinks to a circular shape with radius of 10.5 nm, corresponding to a shrinkage length of 3.9 nm.

According to Figures 1-4, the spontaneous shrinkage is a common phenomenon for Pb particles after fracture. Since it is a typical process driven by atomic diffusion[27, 31, 51], this behavior was systematically investigated across different Pb particles, and the statistical results are plotted in Figures 4(e)-(f). In contrast to tensile strain in Figure 3(a), the shrinkage length of all sub-20 nm Pb particles is in the range

of 1-6 nm and exhibits no obvious size-dependent increasing or decreasing trend. The average of shrinkage length across all particles is measured to be 3.1 nm. In addition, we notice that stable front shape of the obtained Pb crystals after tensile fracture all tend to be nearly circular in Figures 1 and 2. Statistical analysis of the size-dependent morphology is presented in Figure 4(f). The circular shape can form on all the Pb particles and generally, curvature radius of the Pb crystals varies linearly with the particle size. These results indicate the spontaneous atomic diffusion is a universal behavior for all Pb particles. Meanwhile, according to classical theory of atom-density-driven surface diffusion[22, 27], Figure 4(e) suggests that the effective surface thickness for diffusion in Pb nano-crystals is ~ 3 nm. This is also consistent with the results in Figure 3(a) since for particles <6.9 nm, nearly all the Pb atoms can be considered to reside within the surface region. Moreover, the atomic diffusivity D_s of Pb particles can also be estimated based on these. According to previous studies[30, 38], there is:

$$D_s \sim \frac{h_0 R_0^3 k_B T}{\Delta t \gamma \Omega X_s \delta_s}$$

Here k_B is Boltzmann constant, T is temperature, γ is surface energy, Ω is atomic volume, X_s (≈ 1) is solubility of diffusing atom in surface, δ_s is surface layer thickness, h_0 is shrinkage height, R_0 is radius of curvature, and Δt (~ 0.1 s) is shrinkage time. As an order-of-magnitude estimate, we get $D_s \sim 10^{-14}$ m²/s, which is consistent with results in previous studies[38, 41, 52].

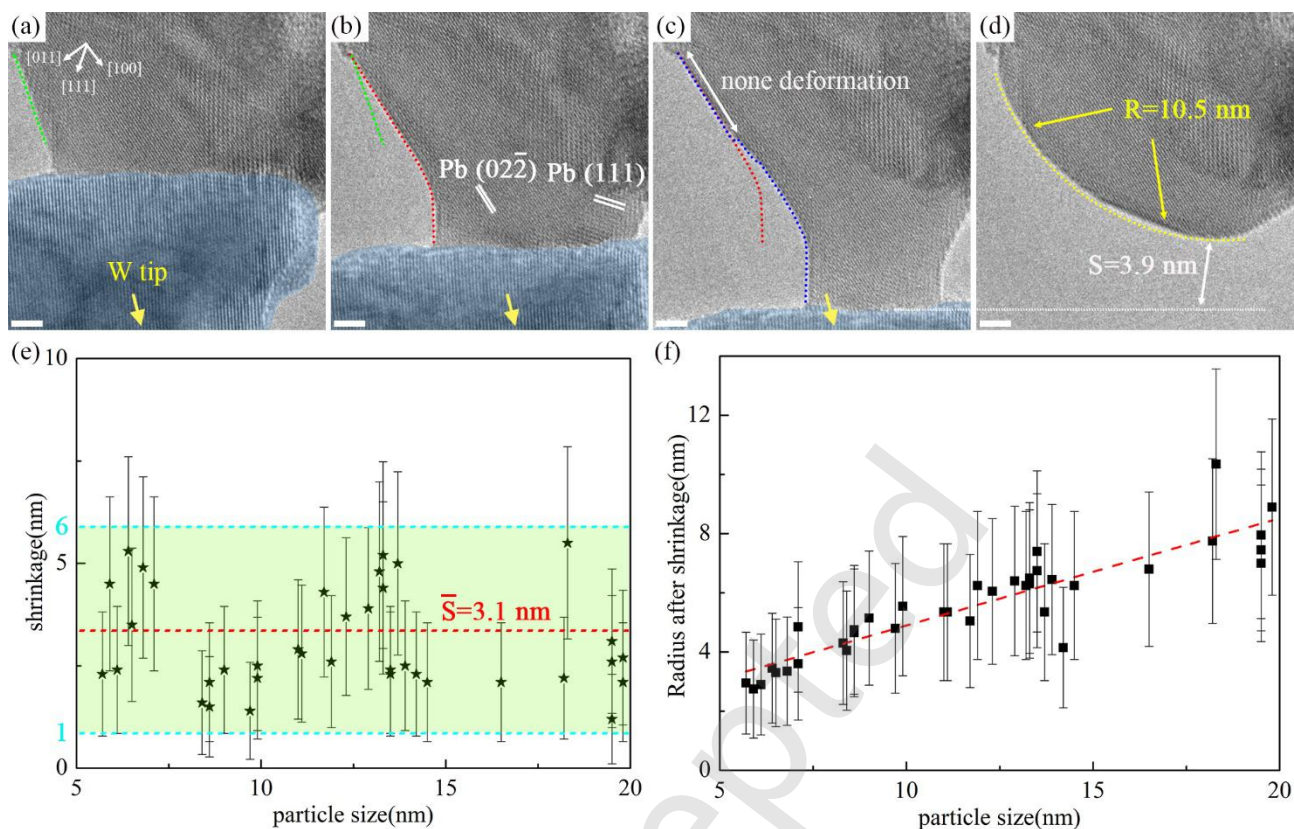


Figure 4 Size-dependent shrinkage of sub-20 nm Pb crystals after tensile-fracture. (a)- (d) Shape evolution of a 19.8 nm Pb particle during tensile deformation and after fracture. Dotted lines in (a)- (c) show the surface shape of Pb particle during tensile deformation. For better view, W tips have been painted blue in (a)- (c). All yellow arrows indicate the force direction. (e) Shrinkage length of Pb particles as function with particle size. (f) Curvature-radius of Pb particle surface as function with particle size. Scale bars: 2 nm.

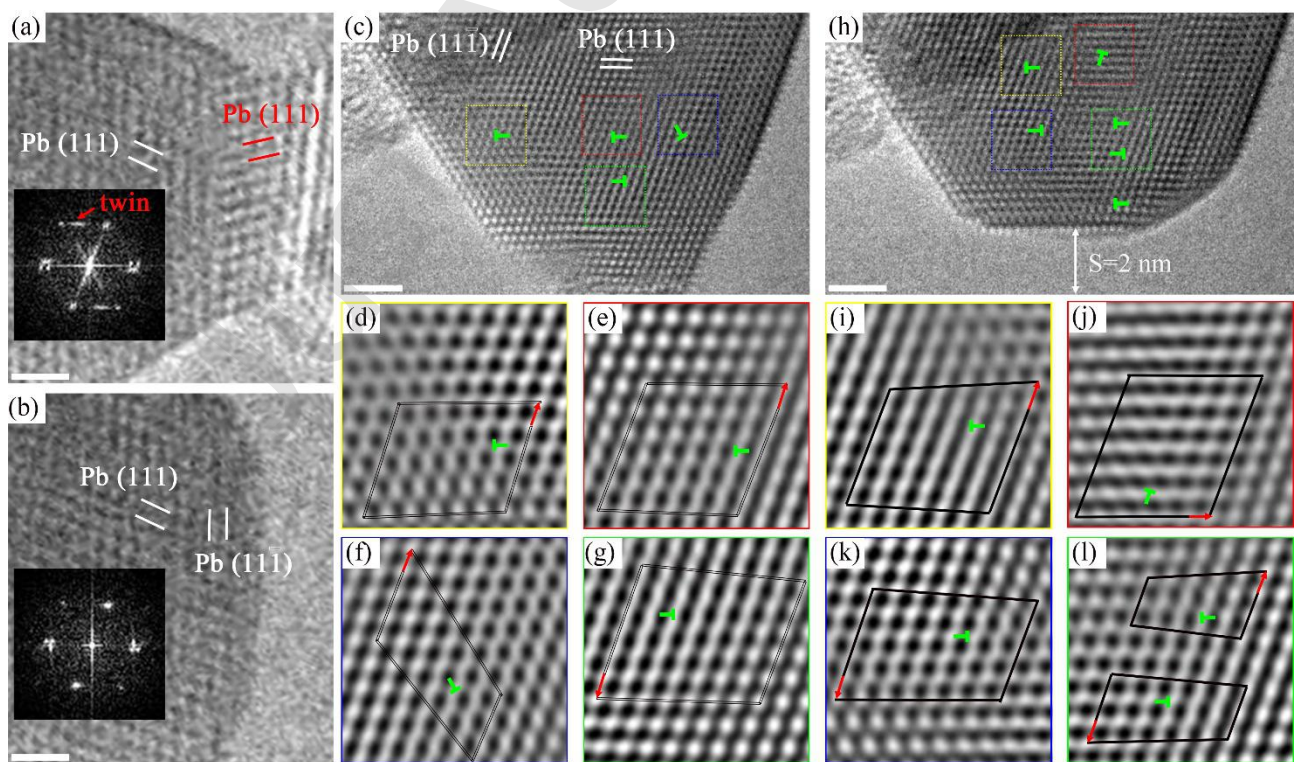


Figure 5 Diffusion-driven displacive mechanical behavior of Pb crystals during tensile-fracture. (a)- (b) Diffusion-driven detwinning process of Pb particle. (c)- (l) Dislocation dynamics of Pb particle (c-g) before and (h-l) after fracture. (d)- (g) and (i)- (l) are Filtered-TEM images of corresponding colored-squares in (c) and (h), respectively. All dislocations have been marked as green "T". Scale bars: (a) and (b): 1 nm; (c) and (h): 2 nm.

Further evidence is presented in Figures 5(a)-(b). Under tension, a twinning band (width ~ 3 nm) was formed in the Pb particle. After fracture, the spontaneous shrinkage occurred and led to disappearance of the twinning band. Notably, since the twinning band was nearly perpendicular to the loading direction, it could be considered to lie on the particle surface after the fracture, allowing all the Pb atoms to diffuse from the twinning region toward the side faces, thereby inducing detwinning. In contrast, in Figure 2, the twinning band extended through the fracture surface into interior of the particle (length ~ 8 nm) and only the front portion was exposed on the surface and underwent diffusion after fracture. Consequently, the twinning band remained present after the diffusive shrinkage.

Since twinning is induced by migration of partial dislocations, Figures 5(a)-(b) also suggest that atomic diffusion can trigger movement of dislocations. Direct observation of the diffusion-driven dislocation activities is shown in Figures 5(c)-(l). In Figure 5(c), four dislocations are captured inside the Pb particle before fracture and the corresponding filtered images are shown in Figure 5(d)-(g). Then the fracture happened and the spontaneous shrinkage was observed in Figure 5(h). Meanwhile, the dislocation structure also changed. Some dislocations disappeared and some slipped while additional new dislocations formed within the particle, as shown in Figures 5(i)-(l). This indicates that the diffusive shrinkage process altered the internal stress state of the Pb particle.

Here, the diffusion-driven dislocation activities can be rationalized by the minimization of surface energy which generates surface pressure inside the crystals[7, 27]. The surface pressure induced by surface energy of an ideal spherical surface can be calculated as: $P=2\gamma/R$, where γ is surface energy and R is the curvature radius of the surface[31]. The corresponding variation is shown in Figure S4(a). As the curvature radius decreases, the surface pressure accordingly increases. If the crystal diameter was small enough, the surface pressure would be large enough to activate the dislocation dynamics. As an order-of-magnitude estimate, taking γ of Pb as ~ 500 mJ/m²[52], the surface pressure in this study is at the range of 50-200 MPa which exceeds elasticity limit of Pb[41, 52]. Thus, the high surface pressure not only drives the atomic diffusion but also induces the dislocation activities.

On the other hand, the critical size 7.1 nm of transition from dislocation-dominated to diffusion-dominated deformation can also be explained based on the competition between surface energy and dislocation formation energy. Since the driving force for deformation originates from the elastic strain energy, the process that requires less energy will preferentially occur. As shown in Supplementary section 1, the energy of surface diffusion of a particle with size D increases as $E_{\text{diffuse}} \propto \gamma D^2$, while the energy for dislocation scales as $E_{\text{dislocation}} \propto D \ln(D)$ [49, 50]. Considering the shape evolution during deformation (quantified as a geometric factor α), the critical size for surface diffusion to prevail is estimated to be 3-9 nm at $\alpha \sim (0.05, 0.1)$, as shown in Figure S4 (b). Since α is typically small during most mechanical deformation processes[12, 21, 23], this estimate is consistent with our experimental observation of 7.1 nm

within the same order of magnitude.

In previous study, the surface energy driven partial dislocation activities were observed in ultra small Au nanocrystals (~ 1 nm)[31]. The melting point of Au is 1337 K, considerably higher than Pb. Therefore, much smaller size of Au is necessary for diffusion to be dominant over dislocations. Since the T_m of other low-melting-point metals (including Bi, Sn and In) is even lower than Pb, it is reasonable to expect that this phenomenon may occur at larger feature sizes and the size-dependent deformation process in this study may also be applicable for these metals.

The size-dependent deformation mechanisms in this study have direct implications for the reliability and performance of metallic nanodevices at sub-20 nm dimensions. In this regime, the competition between dislocation and diffusion influences not only the mechanical response but also the long-term stability of device components under service conditions[1, 2]. For Pb-based nanostructures smaller than critical size (~ 7.1 nm), the prevailing surface diffusion enables spontaneous shape recovery and stress relaxation without causing permanent crystallographic damage, which could be beneficial for applications requiring high cyclic stability or self-healing capability[43]. Conversely, for larger structures where dislocation activity becomes significant, irreversible plastic deformation may accumulate under continuing loading, which may induce fatigue failure[41]. Moreover, the surface layer of 1-6 nm identified in this work suggests that the outside atomic layers play a dominant role in determining the mechanical behavior of sub-20 nm devices. Therefore, surface engineering strategies including coating, alloying, or controlling surface chemistry, could be effective routes to tune the mechanical stability of nanodevices[40-42, 47]. These findings provide a mechanistic basis for predicting and optimizing the service life of nanoscale metallic components in next-generation electronic, optoelectronic, and sensing devices.

3 Conclusions

In this research, the mechanical deformation process of Pb nanoparticles with different feature sizes (5-20 nm) were investigated via in situ experiments inside an aberration-corrected Titan TEM/STEM. We found that 7.1 nm is the critical size for dislocation dynamics. For Pb particles < 7.1 nm, surface diffusion prevails and leads to pseudo-elasticity, whereas for particles > 7.1 nm, dislocations become active and dominate plastic deformation accompanied by surface diffusion from atomic layers 1-6 nm thick. All Pb crystals exhibit tendency to minimize the surface energy through atomic diffusion, which induces spontaneous shrinkage after deformation and results in both size-dependent spherical morphology and dislocation activities. This research directly reveals the size-dependent deformation mechanisms of metallic nanocrystals and provides implications for developing new advanced nano-devices in the future.

4 Materials and Methods

4.1 Synthesis of Pb particles.

The Pb particles are obtained based on in situ heat treatment of PX phase PbTiO_3 nanowires. The PX- PbTiO_3 nanowires are prepared in a hydrothermal method: Firstly, 4 mmol $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved in 8 mL of ethanol and then, the transparent solution was hydrolyzed in 8 mL of deionized H_2O . Next, 20 mmol KOH, 5.2 mmol $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and 0.050 g polyvinyl alcohol (PVA) were added into the solution and mixed under stirring. The feedstock was transferred to a 50 mL Teflon-lined autoclave and held at 200 °C for 3.5 h after adjusted to 40 mL with deionized H_2O . The obtained products were washed with deionized H_2O and 10 wt% CH_3COOH solution repeatedly until the remnant PbO was totally removed. Finally, after dried at 60 °C in air, the pure PX-phase nanowires were obtained.

Then to prepare the Pb particles, firstly the PX- PbTiO_3 nanowires were dissolved in ethanol by ultrasonic dispersion. Then the suspension was dropped onto a half Cu grid and dried in air for 5 min. The Cu grid was put on a TEM-thermal holder (Gatan 628 Single Tilt Heating Holder) and heated at 350 °C at the highest heating rate under the radiation of electron beams with the beam density of about $4 \times 10^4 \text{ A/m}^2$. Both the clean Pb particles and the surface-passivated Pb particles can be obtained during the heat treatment. The particle size can also be adjusted by controlling the heating time. All the TEM characterization and the in situ experiments were carried out inside the aberration-corrected TEM (FEI Titan 80-300). More details of the preparation can be found in our previous research[28].

4.2 In situ mechanical tests.

As for the in situ mechanical tests, after the Pb particles were prepared on the half Cu grid, the grid was fast transferred to a TEM-scanning tunneling microscopic holder by glued onto a gold wire with conductive epoxy. Then the in situ mechanical experiments on the Pb particles were conducted using some tungsten tips as prepared by electrochemically etching: 2 mol/L NaOH was used for the etching and the etching voltage was 2.5 V with a compliant current of 20 mA. All W tips were cleaned by plasma cleaning for 5 minutes for the in situ TEM experiments. The in situ compression and stretching process of the Pb particles were conducted at a speed approximate 0.3 nm/s.

Electronic Supplementary Material: Supplementary material (Figure S1: Preparation of Pb nano-particles. Figure S2: Liquid-like pseudo-elasticity deformation of 10 nm Pb particle. Figure S3: Variation of surface pressure as function with particle size.) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909186>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Hongtao Zhang: Conceptualization, Investigation, Funding acquisition, Formal analysis, Writing - original draft, Writing - review & editing, Project administration, Validation. Chongyang Zhu: Methodology, Formal analysis, Validation. Yuwei Xiong: Data curation. Wen Wang: Conceptualization, Writing - original draft. Hui Zhang: Funding acquisition, Project administration. Jun Sun: Methodology. Li Zhong: Methodology. Xing Li: Software, Funding acquisition. Xiaohui Wu: Software, Funding acquisition. Litao Sun: Supervision, Writing - review & editing, Project administration.

Informed consent

None.

Ethics statement

None.

Use of AI statement

None.

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Electronic Supplementary Material

Size-dependent mechanical deformation mechanisms in sub-20 nm lead crystals

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1. Theoretical analysis of deformation processes of Pb particles.

(1) Comparison of thinning rates between diffusive and displacive deformation of Pb particles with different feature sizes.

According to our previous studies[1, 2], the thinning rate due to dislocation slip should be:

$$\frac{dD_{\text{slip}}}{dt} = \frac{\epsilon L D \sin \alpha}{D \cos \alpha - \epsilon_0 L \sin \alpha} \quad (\text{S1})$$

Meanwhile thinning rate by diffusion is:

$$\frac{dD_{\text{diffuse}}}{dt} = \frac{\Omega \delta_s D_s}{k_B T} \left(\frac{4\gamma}{L^2 D} + \frac{15E\epsilon_0^2}{16L^2} \right) \quad (\text{S2})$$

Here, ϵ is deformation rate, L is length of Pb particle, D is diameter, α is the projected angle with respect to the $\langle 112 \rangle$ loading direction of the $\langle 110 \rangle$ slip, ϵ_0 is elastic limit, Ω is atomic volume, δ_s is atomic diameter, k_B is Boltzmann constant, T is temperature, γ is surface energy, and E is Young modulus. Comparison of Equations S1 and S2 is shown in Figure S3(a).

(2) Theoretical analysis of energy evolution during deformation of Pb particles.

During deformation under stress, extra energy would be stored in Pb particles as[3, 4]:

$$\Delta E_{\text{strain}} = \frac{\sigma^2}{2E} * \frac{\pi D^3}{6} \quad (\text{S3})$$

Here, σ is stress, E is Yang's modulus, and D is diameter.

When Pb particle deforms by dislocation dynamics, the energy for dislocation formation is:

$$\Delta E_{\text{disl}} = \frac{Gb^2}{4\pi} * D * \ln \left(\frac{D}{b} \right) \quad (\text{S4})$$

Here, G is shear modulus and b is Burgers vector.

When Pb particle deforms by surface diffusion, the energy change associated with surface diffusion is:

$$\Delta E_{\text{diff}} = \alpha \gamma \frac{1}{4} \pi D^2 \quad (\text{S5})$$

Here, α is a shape-dependent constant and γ is surface energy.

The dislocation dynamic happens as: $\frac{\sigma^2}{2E} * \frac{\pi D^3}{6} > \frac{Gb^2}{4\pi} * D * \ln \left(\frac{D}{b} \right)$, as shown in Figure S3(b).

Compared with dislocations, the surface diffusion prevails when: $\alpha \gamma \frac{1}{4} \pi D^2 - \frac{Gb^2}{4\pi} * D * \ln \left(\frac{D}{b} \right) < 0$, as shown in Figure S4(b).

2. Supplementary Figures

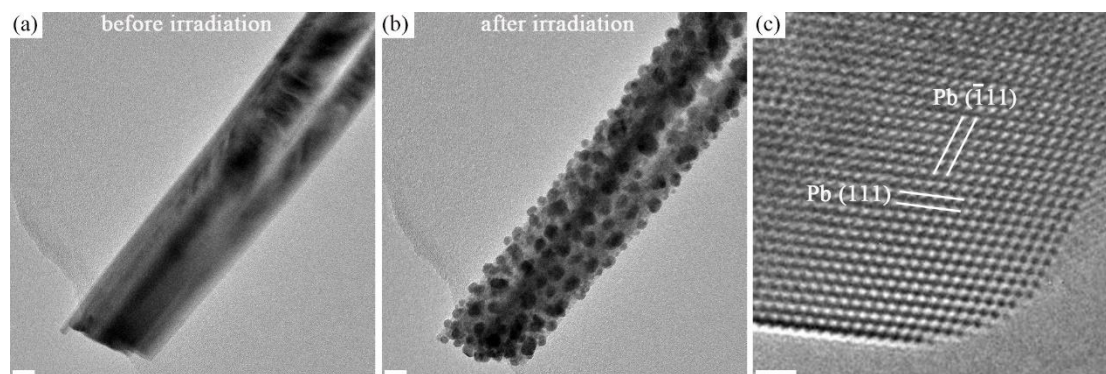


Figure S1 Preparation of Pb nano-particles. (a)- (b) Morphology (a) before and (b) after in-situ heat treatment of a PX-PbTiO₃ nanowire under irradiation. (c) HR-TEM image of a Pb particle. Scale bars: (a) and (b): 20 nm; (c): 1 nm.

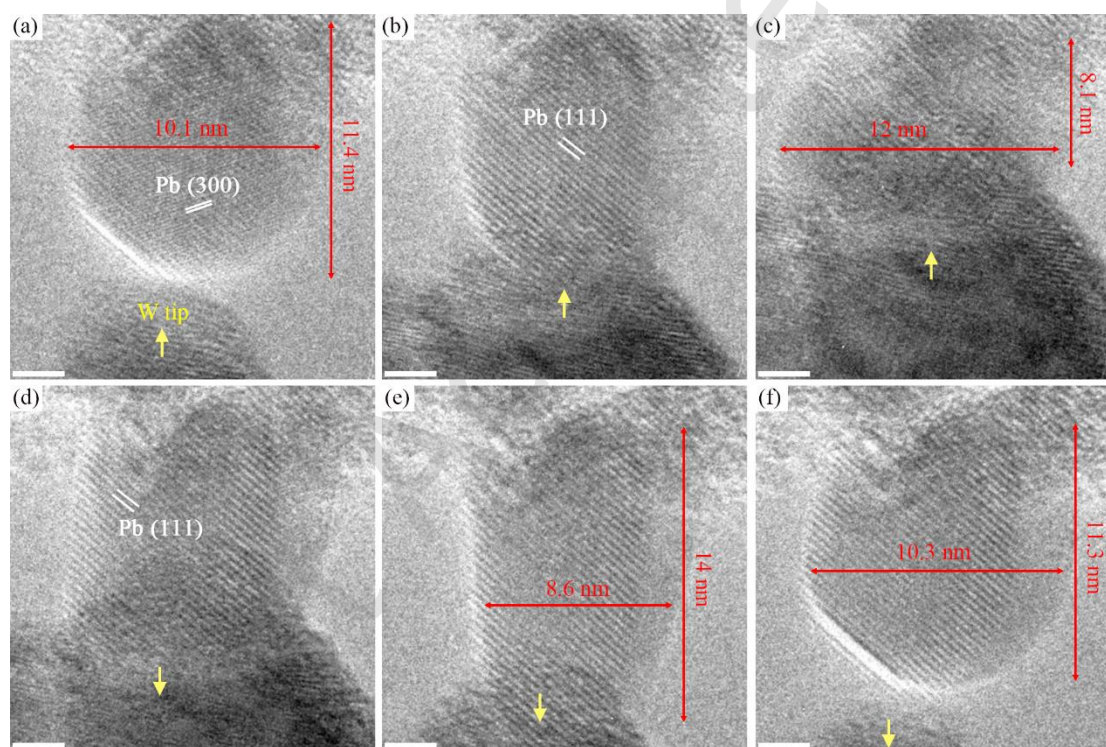


Figure S2 Liquid-like pseudo-elasticity deformation of 10 nm Pb particle. (a) Initial morphology of Pb particle before deformation. (b)- (c) Shape evolution of the Pb particle during extrusion. (d)- (e) Shape evolution of the Pb particle during tension. (f) Final morphology of the Pb particle after deformation. Scale bars: 2 nm.

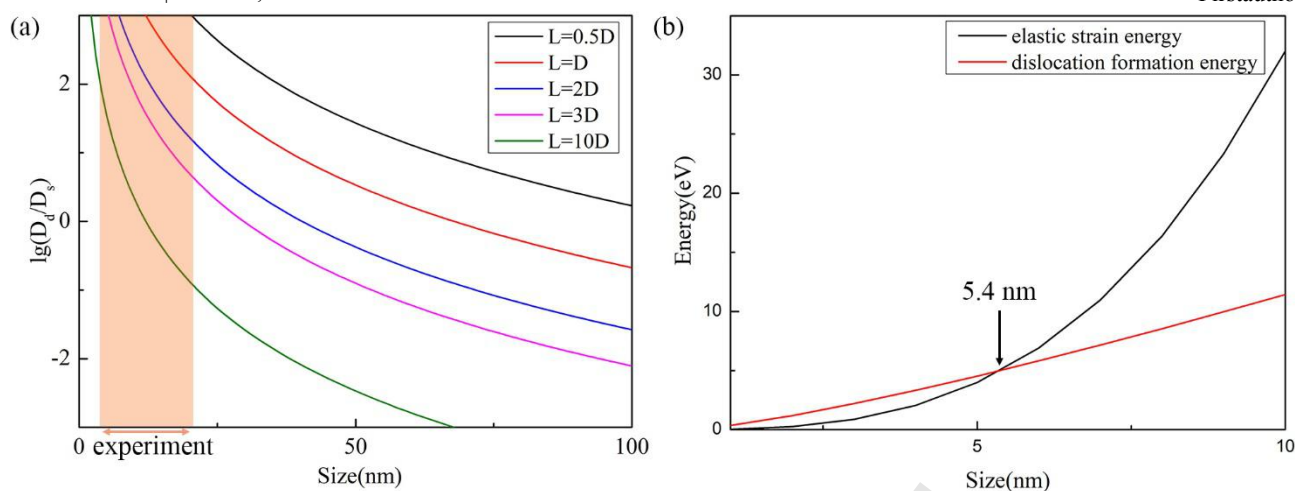


Figure S3 Theoretical comparison of diffusion and dislocation dynamics in sub-20 nm Pb particles. (a). Comparison of diffusive and dislocation deformation rate of Pb particles with different sizes. (b) Evolution of elastic strain energy and dislocation formation energy as a function of feature size of Pb particles.

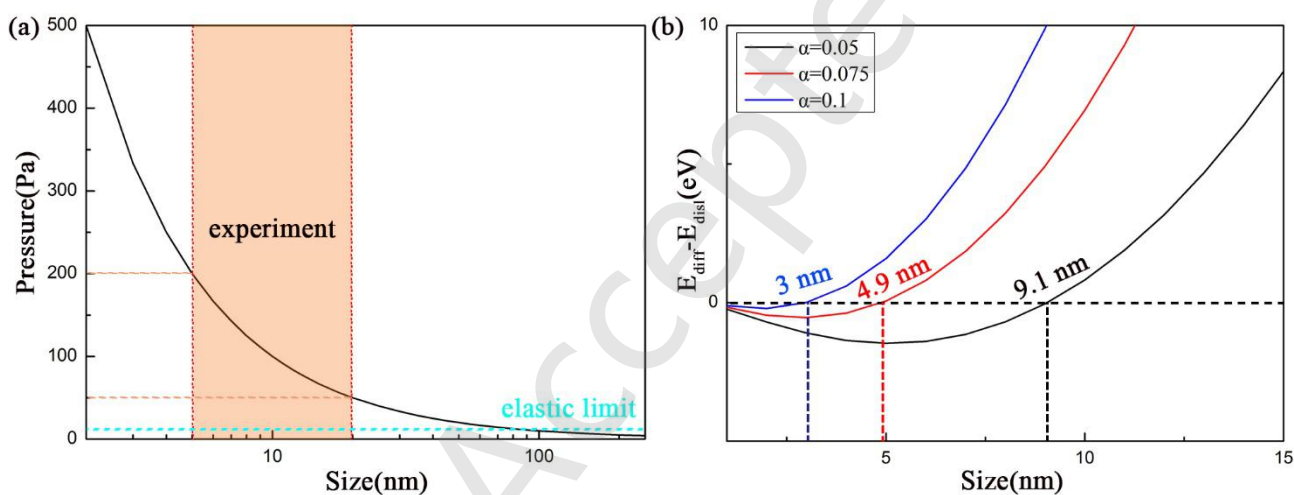


Figure S4 (a) Variation of surface pressure as function of particle size. (b) Energy difference between atomic diffusion barrier and dislocation formation energy of different Pb particles.

3. Supplementary Table

Parameters used in calculation

Physical quantity	Value
Melting point of bulk: T_0	600.65 K
atomic diameter of Pb atom: h	3.5×10^{-10} m
bulk solid-vapor transition entropy: Sb_0	$88 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
surface energy of Pb: γ	$0.5 \text{ J} \cdot \text{m}^{-2}$
atomic volume: Ω	$2.24 \times 10^{-29} \text{ m}^3$
elastic limit: ε_0	0.000147
Young modulus of Pb: E	16×10^9 Pa
shear modulus: G	5.6×10^9 Pa
Burgers vector: b	3.5×10^{-10} m
Boltzmann constant: k_B	$1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
ideal gas constant: R	$8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

4. Supplementary References

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