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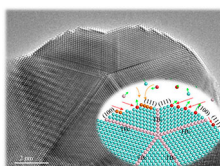
Anomalous sublimation passivation of nanotwinned silver particles

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ABSTRACT

Metal sublimation plays a crucial role in understanding natural phenomena, purification and advanced manufacturing. Herein, we report anomalous sublimation passivation of nanotwinned silver particles under e-beam irradiation through *in situ* transmission electron microscopy, wherein the sublimation velocity is reduced by three-quarters due to the formation of five-fold twins. Theoretical calculations reveal that this sublimation passivation mechanism is mainly related to the increment in sublimation energy by the presence of twin boundaries.



IMPACT STATEMENT

Differing from traditional cognition of defect-assisted sublimation, anomalous sublimation passivation of nanotwinned silver particles under e-beam irradiation has firstly been identified in terms of TEM observations and DFT calculations.

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KEYWORDS

Sliver; TEM; DFT; sublimation

Sublimation is a first-order phase transition in which atoms break away from their neighbors in the crystal lattice and are transformed into the gas phase. Understanding sublimation mechanisms could impose great influences not only on scientific advances but also on a variety of technological applications including purification [1], sublimation deposition [2] and machining MEMS devices [3]. Due to its high chemical stability and low sublimation temperature, silver (Ag) nanocrystal with a face-centered cubic structure has been deemed as an ideal model material to exploit metal sublimation procedures. However, a majority of previous work relative to sublimation was associated with equilibrium thermodynamic parameters (vapor pressure, size-dependence, free energy) in vaporization reactions. For example, Mori et al. confirmed that no occurrence of nanoparticle melting during Ag sublimation by using conventional transmission electron microscopy [4]. Subsequently, the

sublimation of Ag nanoparticles was carried out under heating condition in the vacuum chamber of a transmission electron microscopy, in which a particle size-dependent sublimation phenomenon was revealed [5]. More recently, a new sublimation experiment on carbon-covered Ag cubes has been performed at the nano-scale [6]. Comparatively, the information on the kinetics of vaporization in real materials, where defects significantly matter, is limited owing to the shortage of sound technique.

Basically, crystal defects alter the bonding environments of local atoms, which remarkably influence the de-bonding sequences. For instance, a high density of screw dislocations will accelerate the sublimation velocity of pure Mg [7]. Herein, the effects of defects (twin boundaries: TBs) on the sublimation of Ag nanoparticles are investigated on an atomic scale for the first time. The *in situ* phase transition method for sample preparation

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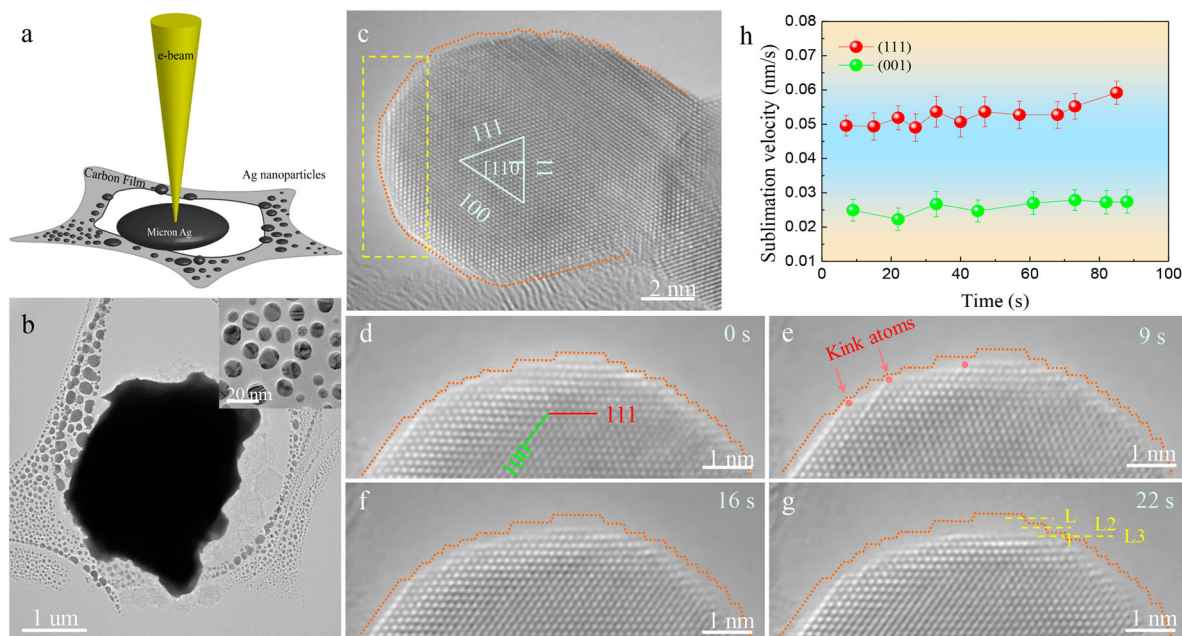


Figure 1. Schematic process (a) and TEM image (b) of SC-Ag and 5FT-Ag nanoparticles by e-beam irradiating on Ag powders. (c) The HRTEM image of SC-Ag particle with a dimension of ~ 12 nm. (d–g) A series of HRTEM images illustrating the sublimation of SC-Ag particle. The transient structural transformation is highlighted corresponding to $\{111\}$ and $\{001\}$ planes, respectively. (h) The sublimation velocity of $\{111\}$ and $\{001\}$ planes as a function of time, respectively.

provides a prerequisite to attain the same-sized single crystal silver (SC-Ag) and five-fold twinned silver (5FT-Ag) particles, which can effectively eliminate the effects of size and impurity. Simultaneously, the sublimation process was carried out at low temperatures with aberration-corrected transmission electron microscopy (AC-TEM), allowing us to directly resolve small nanostructures that are not clearly visible by a conventional TEM.

High-purity Ag powder with an average dimension of $1 \sim 2 \mu\text{m}$ was purchased from Sigma-Aldrich company. The Ag powder was dispersed in a mixed organic solution of dodecanethiol and acetone. And this mixed solution was dropped on the copper grid for AC-TEM observation. The organic solvent was decomposed to form a carbon film under the e-beam irradiation of $15000 \text{ e/nm}^2\cdot\text{s}$, which provides a substrate to collect nanoscale Ag sublimation products. The TEM experiments were conducted in a high-resolution AC-TEM (FEI Titan ETEM G2, acceleration voltage 300 kV). The pressure was about 10^{-3} Pa . The intensity of e-beam remained at the dose range of $1800 \sim 4200 \text{ e/nm}^2\cdot\text{s}$ (Movies 1–3).

All calculations were performed using the projector augmented wave (PAW) method, as implemented in the Vienna *ab initio* simulation package. The detailed calculation process has been reported previously [8]. Briefly, the cutoff energy of the plane wave basis was set to 500 eV. The electronic structures, including density of states

(DOS) of single-crystal Ag and twinned structure sublimation on $\{001\}$ and $\{111\}$ surfaces, were obtained using k point of $2 \times 2 \times 3$ and $2 \times 2 \times 1$ Gamma-centered Monkhorst–Pack k-point grid, respectively. A large vacuum space of $20 \text{ \AA}$ was used to avoid the interaction between slabs.

The sublimation energy (E_{sub}) for hydrogen is calculated as [7]

$$E_{\text{sub}} = E_{\text{total}} - E_{\text{atom}} \quad (1)$$

where E_{total} is the total energy of Ag surface, E_{atom} is the total energy after removing an Ag atom on $\{001\}$ or $\{111\}$ surface.

As shown in Figure 1(a), Ag nanoparticles were directly fabricated by irradiating the mixed solution containing Ag powder by a high e-beam dose irradiation on the copper grid in a vacuum system for about 2 min, which effectively avoids the disturbance of unwanted solvents. During the decomposition process, a thin carbon film was formed, and the sublimated Ag powder was collected on the carbon film, resulting in the concentric rings of Ag nanoparticles (Figure 1(b) and Movie 1). Principally, the dimension of Ag nanoparticles was reduced by increasing the distance. Also, both SC-Ag nanoparticles and 5FT-Ag nanoparticles were detected during the same process. According to the previous results [9], the increment in temperature under this e-beam dose is below 10 K. Therefore, these concentric

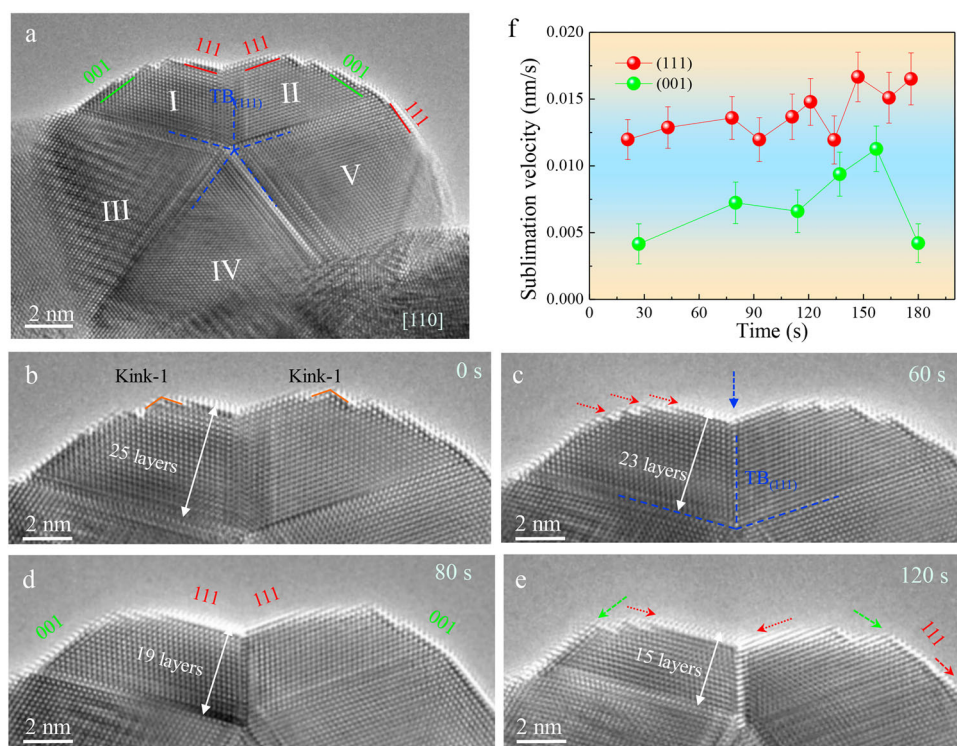


Figure 2. (a) HRTEM image of the 5FT-Ag particle with a dimension of ~ 15 nm. (b–e) A series of HRTEM images illustrating the sublimation of 5FT-Ag particle. The transient structural transformation is highlighted corresponding to $\{111\}$ and $\{001\}$ planes, respectively. (f) Plots of sublimation velocity of $\{111\}$ and $\{001\}$ planes as a function of time, respectively.

rings provided an ideal mode to investigate the effect of twins on sublimation under e-beam irradiation condition at low temperature. Figure 1(c) shows a typical sublimation process of SC-Ag nanoparticles under the exposure at a low e-beam dose. The particle dimension is about 12 nm and it is projected along the cubic $[110]$ axis of the Ag lattice. In addition, based on the time-sequential HRTEM images (Figure 1(d–g)), it can be seen that the sublimation-induced stable surfaces in the Ag nanocrystal are $\{111\}$ and $\{100\}$ planes, which is in agreement with the low-energy surfaces in face-centered cubic noble metals, $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$. It is consistent with the results of the sublimation of Ag_2WO_4 at 650 °C [10], whereas it differs from the reported $\{110\}$ plane for carbon-covered Ag cubes [5]. The sublimation of SC-Ag nanoparticles features three main characteristics. Firstly, a typical symmetric layer-by-layer sublimation mode occurs (marked by yellow dashed lines) continuously. By contrast, the common atomic rearrangement in the surface reported by other groups at elevated temperatures [10] has been hardly detected in our low temperature sublimation. Secondly, the initial sublimation site starts at individual atoms of kink sites located at the junction of $\{111\}$ and $\{001\}$ planes and removed along $\{111\}$ planes. The sublimation-induced stable surface is the $\{111\}$ plane by forming the steps

during the whole process. Finally, the sublimation velocity along $\{111\}$ plane (~ 0.054 nm/s) is higher than that along $\{100\}$ plane (~ 0.024 nm/s), revealing a typical anisotropic sublimation feature (Figure 1(h)). Note that the sublimation velocity is nearly irrelevant with the irradiation time (reducing the dimension of the particles). This anisotropic sublimation of nanoparticles has also been reported in semiconductor PbSe [11] and Bi_2Te_3 [12].

To investigate the effect of twins on the sublimation behavior of Ag nanoparticles, the *in situ* sublimation process of 5FT-Ag with a dimension of ~ 15 nm along a $[110]$ projection was examined under the exposure at a low e-beam dose (Figure 2(a)). Compared with the commonly assumed five-fold twinned structure that consists of 10 $\{111\}$ ‘end’ facets and five $\{100\}$ ‘side’ facets [13], this 5FT-Ag nanoparticle consists of many steps on its surface, forming ‘zig-zag’ edges. Analogous to SC-Ag nanoparticle, 5FT-Ag nanoparticle also shows the same three characteristics as mentioned above: layer-by-layer sublimation, kink-initial sublimation and anisotropic sublimation. Additionally, differing from SC-Ag nanoparticle, there are four unique sublimation characteristics on 5FT-Ag nanoparticle. Firstly, 5FT-Ag nanocrystals show a preferential sublimation in the regions I and II at the initial stage rather than regions

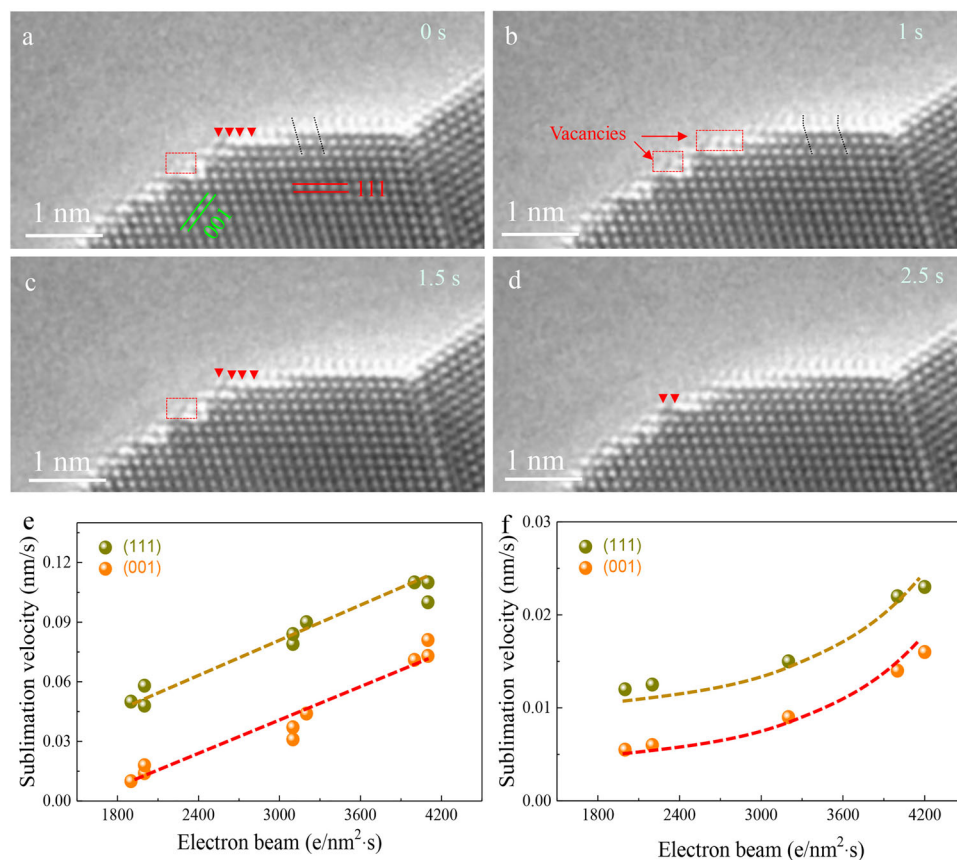


Figure 3. (a–d) A series of HRTEM images illustrating the {111} plane restructure of 5FT-Ag particle. The red inverted triangular marks atom, red rectangle box marks the vacancy. The black dash and broken line in (a) and (b) indicate rearrangement of atoms on the surface. The atom deviates from equilibrium positions. The effects of e-beam dose on sublimation velocity of SC-Ag (e) and 5FT-Ag (f) nanoparticles, respectively.

III, IV and V. Moreover, with retarding sublimation process, the atoms in regions I and II sublime continuously, whereas atoms in the other three regions remain stable. Secondly, although the initial sublimation site is also related to the kinks site (step tip), atoms in the TBs are always the later ones to sublime compared with the atoms in the same-layer surface. Thirdly, the sublimation velocity is remarkably reduced in contrast to that of SC-Ag nanoparticle. For example, the sublimation velocity along {111} plane of 5FT-Ag is ~ 0.013 nm/s, which is 25% than that of SC-Ag. It demonstrates that the formation of 5FT reduces sublimation velocity, which is different from the cognition that defects accelerate the metallic sublimation. Finally, as shown in Figure 2(e), the sublimation velocity fluctuates with reducing dimension, which might be related to the nonuniform sublimation pathway.

To reveal the fluctuated sublimation velocity of 5FT-Ag, interface structural variation was analyzed in detail (Figure 3(a–d)). Except for layer-by-layer sublimation, the rearrangement of outer layer atoms was observed

during the sublimation of 5FT-Ag nanoparticle. When Ag–Ag bonding was broken, the atoms on surfaces (Figure 3(a), the black dashed lines) moved toward new positions (Figure 3(b), the black broken lines), in which the energy to eliminate neighbor atoms from the equilibrium position was significantly reduced. Moreover, as shown in Figure 3(c–d), four and two Ag atoms reappeared in the vacancies of layer 3 and layer 5, respectively. In this regard, the violent fluctuated sublimation velocity was associated with the co-existence of layer-by-layer sublimation and atomic rearrangement.

In addition, to probe e-beam dose on the sublimation behavior of Ag nanoparticles, sublimation processes of both SC-Ag and 5FT-Ag particles were studied at different e-beam doses. Figure 3(e–f) shows the sublimation velocity evolution of {111} and {001} planes of SC-Ag and 5FT-Ag particles under different e-beam doses, respectively. In general, with increasing e-beam doses, the sublimation velocity of both {111} and {001} planes was increased. It is believed that a large number of kink sites or steps were introduced on the surface

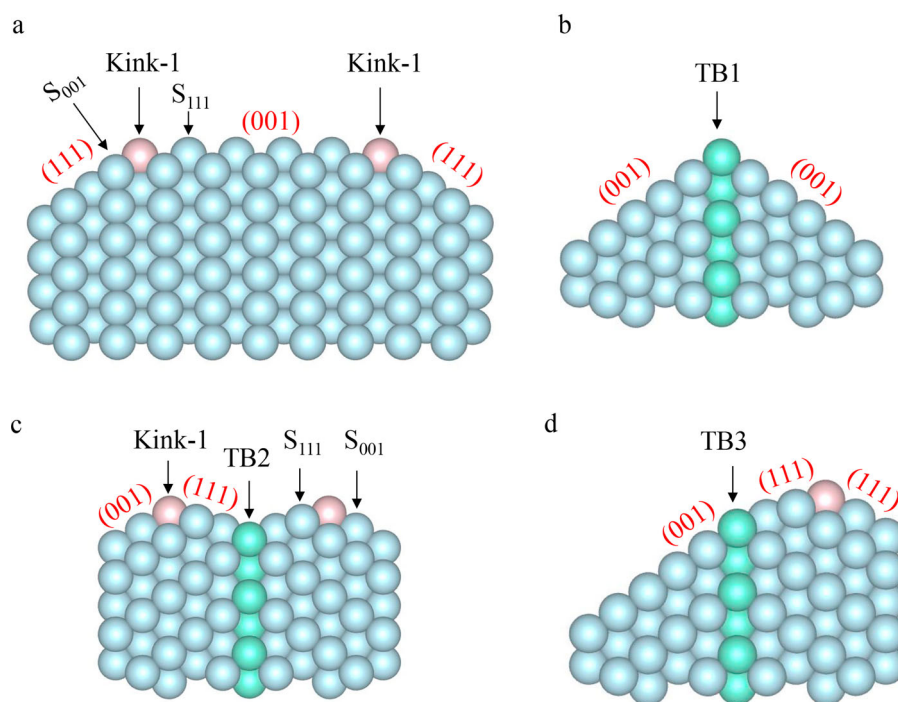


Figure 4. (a) The model used to calculate the sublimation energy of SC-Ag nanoparticle. (b–d) The models used to calculate the sublimation energy of 5FT-Ag nanoparticle-containing different kink sites and TBs, respectively.

of Ag particles with the increment in e-beam doses and irradiation time, resulting in the escape of surface atoms easier. Noteworthy, a linear trend of sublimation velocity depending on e-beam dose was evident in SC-Ag sample, which is consistent with the uniform layer-by-layer sublimation mechanism. In contrast, the non-linear fitting curves were induced in 5FT-Ag sample, revealing that the nonuniform sublimation pathway-sublimation and rearrangement dominates during sublimation processes.

To elucidate the sublimation mechanisms, first-principles calculations were performed on the surface models of both SC-Ag and 5FT-Ag. As shown in Figure 4, the different kink sites on $\{111\}$ and $\{001\}$ planes were denoted, and the energy required for the kink atom and adjacent atoms to leave the surface was calculated. Regarding SC-Ag nanoparticle (Figure 4(a), Table 1), the sublimation energy of the kink-1 site was the lowest (2.621 eV), and the energy of S_{111} and S_{001} site was 2.644 and 2.653 eV, respectively. It indicates that SC-Ag started to sublime from the kink-1 sites, and the atomic sublimation from the $\{111\}$ layers was faster than that along the atomic layers of the $\{001\}$ surfaces. In comparison, the sublimation energies of both $\{111\}$ and $\{001\}$ planes in 5FT-Ag were remarkably increased compared with those of SC-Ag nanoparticle, which was consistent with the lower sublimation velocity. In addition, the kink-1 position had the lowest energy for 5FT-Ag, indicating that 5FT-Ag sample also sublimated from the kink site.

Table 1. Sublimation energies of different sites on the surfaces of the $\{111\}$ and $\{001\}$ planes.

Surface sites	S_{111} (eV)	S_{001} (eV)	Kink1 (eV)	TB1 (eV)	TB2 (eV)	TB3 (eV)
SC-Ag	2.644	2.653	2.621	–	–	–
5FT-Ag	3.016	3.025	3.002	3.118	3.264	3.109

Importantly, when the atoms lay in TBs (Figure 4(b–d)), their sublimation energies are sharply increased, demonstrating that the atom sublimation in TBs requires higher sublimation energy.

In summary, the sublimation dynamics of SC-Ag and 5FT-Ag nanoparticles at low temperature were observed through *in situ* AC-TEM. This first-order phase transition occurs layer-by-layer uniform sublimation in SC-Ag sample. In contrast, in the case of 5FT-Ag sample, this process takes place through nonuniform sublimation pathway-sublimation and rearrangement. Additionally, unlike in SC-Ag sample, an obvious sublimation passivation phenomenon was confirmed in 5FT-Ag sample, which stems from the increment in sublimation energy by forming TBs in terms of DFT calculations.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

- [1] Montag BW, Reichenberger MA, Edwards NS, et al. Static sublimation purification process and characterization of LiZnAs semiconductor material. *J Crystal Growth*. 2016;438:99–103.
- [2] Tung HY, Guan ZY, Liu TY, et al. Vapor sublimation and deposition to build porous particles and composites. *Nat Commun*. 2018;9:2564.
- [3] Kahn H, Heuer AH, Jacobs SJ. Materials issues in MEMS. *Mater Today*. 1999;2:3–7.
- [4] Lee JG, Lee J, Tanaka T, et al. *In-situ* HREM observation of crystalline-to-gas transition in nanometer-sized Ag particles. *Phys Rev Lett*. 2006;96:075504.
- [5] Asoro MA, Kovar D, Ferreira PJ. In situ transmission electron microscopy observations of sublimation in silver nanoparticles. *ACS Nano*. 2013;7:7844–7852.
- [6] Wang Y, Xu D, Gao H, et al. Twisted donor–acceptor cruciform luminophores possessing substituent-dependent properties of aggregation-induced emission and mechanofluorochromism. *J Phys Chem C*. 2018;122:2297–2306.
- [7] Yu Q, Mao MM, Li QJ, et al. *In-situ* observation on dislocation-controlled sublimation of Mg nanoparticles. *Nano Lett*. 2016;16:1156–1160.
- [8] Sun Y, Zhang H, Wang J, et al. Atomic-scale imaging of incipient interval-layered hydrogenation of single crystal magnesium. *Scr Mater*. 2020;174:77–79.
- [9] Zheng H, Liu Y, Cao F, et al. Electron beam-assisted healing of nanopores in magnesium alloys. *Sci Reports*. 2013;3:1920.
- [10] Li J, Wang Z, Li Y, et al. In situ atomic-scale observation of kinetic pathways of sublimation in silver nanoparticles. *Adv Sci*. 2019;6:1802131.
- [11] Maier H, Daniel DR, Preier H. Sublimation growth of PbSe crystals with controlled carrier concentration. *J Crystal Growth*. 1976;35:121–126.
- [12] Buha J, Gaspari R, Del Rio Castillo AE, et al. Thermal stability and anisotropic sublimation of two-dimensional colloidal Bi₂Te₃ and Bi₂Se₃ nanocrystals. *Nano Lett*. 2016;16:4217–4223.
- [13] Narayanan S, Cheng G, Zeng Z, et al. Strain hardening and size effect in five-fold twinned Ag nanowires. *Nano Lett*. 2015;15:4037–4044.