Supporting information:

Surface premelting/recrystallization governing collapse of open-cell nanoporous Cu via thermal annealing

L. Wang, ¹ X. M. Zhang, ¹ L. Deng, ^{1, *} J. F. Tang, ^{1, †} S. F. Xiao, ² H. Q. Deng, ² and W. Y. Hu³

 ¹College of Science, Hunan Agriculture University, Changsha 410128, People's Republic of China
 ²Department of Applied Physics, Hunan University, Changsha 410001, People's Republic of China
 ³College of Material Science and Engineering, Hunan University, Changsha 410001, People's Republic of China

Table S I. Characteristics and surface collapse temperatures for two groups of np-Cu samples with different system sizes. ρ_r (%): relative mass density; A_{solid} (× 10⁴ nm²): surface area; V_{solid} (× 10⁴ nm³): solid volume; γ (nm⁻¹): specific surface area; T_{C} : collapse temperature of np-Cu; T_{M} : equilibrium melting temperature for defect-free bulk Cu.

| | # | k | $ ho_r$ | $A_{\rm solid}$ | $V_{\rm solid}$ | γ | $T_{\rm C}/T_{\rm M}$ | Dimension (nm^3) |
|----------|-----|----|---------|-----------------|-----------------|----------|-----------------------|-----------------------------------|
| | A1 | 1 | 58.19 | 0.45 | 2.44 | 0.18 | 1.00 | |
| Group I | A2 | 2 | 58.22 | 0.91 | 2.45 | 0.37 | 0.96 | |
| | A3 | 4 | 58.11 | 1.89 | 2.42 | 0.78 | 0.93 | |
| | A4 | 6 | 58.22 | 2.92 | 2.43 | 1.20 | 0.89 | |
| | A5 | 8 | 58.07 | 4.08 | 2.45 | 1.67 | 0.81 | |
| | A6 | 10 | 58.70 | 5.11 | 2.40 | 2.13 | 0.70 | $36.15 \times 36.15 \times 36.15$ |
| | A7 | 11 | 58.19 | 5.77 | 2.40 | 2.38 | 0.67 | |
| | A8 | 12 | 58.18 | 6.36 | 2.42 | 2.63 | 0.59 | |
| | A9 | 13 | 58.19 | 6.99 | 2.40 | 2.94 | 0.52 | |
| | A10 | 14 | 58.22 | 7.58 | 2.42 | 3.13 | 0.48 | |
| Group II | B1 | 1 | 58.22 | 0.12 | 0.32 | 0.37 | 0.96 | |
| | B2 | 2 | 58.68 | 0.25 | 0.32 | 0.77 | 0.93 | |
| | B3 | 3 | 58.22 | 0.38 | 0.31 | 1.20 | 0.81 | |
| | B4 | 4 | 58.07 | 0.51 | 0.31 | 1.67 | 0.78 | $18.08 \times 18.08 \times 18.08$ |
| | B5 | 5 | 58.70 | 0.64 | 0.30 | 2.13 | 0.67 | |
| | B6 | 6 | 58.11 | 0.80 | 0.30 | 2.67 | 0.59 | |
| | B7 | 7 | 58.22 | 0.95 | 0.30 | 3.14 | 0.52 | |



FIG. S1. (a) Temporal evolution of volume for np-Cu (#A1) at 1350 K and 1300 K (inset I) and(b) np-Cu (#A10) at 800 K and 750 K (inset I).



FIG. S2. The function of temperature for np-Cu collapse, $T_{\rm C}/T_{\rm M}$, of nanoporous Cu (Group I and II) and Cu nanoparticles [1] in the simulations, and specific surface area, γ . The red solid line denotes the function of $T_{\rm M}$ and γ according to Eq. S11, respectively. The dotted and dash lines denote the limit temperature of supercooling liquid and equilibrium melting temperature, respectively.



FIG. S3. Snapshots of dislocation structures in np-Cu #A8 before its collapse, during thermal annealing.



FIG. S4. The surface reconstruction for np-Cu #A8 during incremental heating. (a) Evolution of surface atoms with different CN; and (b)–(e) Local surface configuration at (I) 300 K, (II) 500 K, (III) 750 K, and (IV) 800 K (before melting), respectively.

ANALYSIS OF MELTING IN NANOPOROUS CU BASED ON CLASSICAL NU-CLEATION THEORY

To describe the nucleation of melting in nanostructures, the Gibbs-Thomson equation, derived from classical nucleation theory (CNT) [2], is used. For a solid spherical nanoparticle with the size of d, the change of Gibbs free energy during melting is expressed as [3, 4]

$$\Delta G = -\pi d^3 \Delta G_{\rm V} / 6 + \pi d^2 \sigma_{\rm sl},\tag{S1}$$

where $\sigma_{\rm sl}$ is the solid-liquid interfacial energy; $\Delta G_{\rm V}$ is Gibbs free energy difference per unit volume between solid and liquid phase, and

$$\Delta G_{\rm V} = (1 - T_{\rm M,np}/T_{\rm M}) \,\Delta H_{\rm f}/V_{\rm s},\tag{S2}$$

where $T_{\rm M,np}$ is the melting point of nanoparticle, $T_{\rm M}$ is melting temperature of defect-free bulk metals, ΔH_f is the latent heat of fusion, and $V_{\rm s}$ is the molar volume of solid phase. When maximizing ΔG , Gibbs-Thomson equation, describing the relation of particle size and corresponding melting temperature, is obtained [5, 6]

$$T_{\rm M,np} = T_{\rm M} \left(1 - \frac{\zeta}{d} \right), \tag{S3}$$

and

$$\zeta = 4\sigma_{\rm sl} V_{\rm s} / \Delta H_f. \tag{S4}$$

For a nanoparticle, $\sigma_{\rm sl}$ is size dependent [7, 8], and

$$\sigma_{\rm sl}(d) = \frac{2S_{\rm vib}(d)\Delta H_f(d)h}{3V_{\rm s}R}.$$
(S5)

Here R is the ideal gas constant, ~8.314 J mol⁻¹ K⁻¹; h is the atomic diameter, ~0.256 nm for Cu; and $S_{\rm vib}$ is the vibrational contribution of overall melting entropy of bulk crystals, which is a weak function of d, and could be ignored as a first-order approximation [9], that $S_{\rm vib}(d) \approx S_{\rm vib}(\infty) \approx 7.85 \text{ J mol}^{-1} \text{ K}^{-1}$ [1]. Substituting $\sigma_{\rm sl}(d)$ and $S_{\rm vib}(d)$ into Eq. S4, we have

$$\zeta = 8hS_{\rm vib}(\infty)/3R.\tag{S6}$$

It reasonably matches the experimental data with $d \ge 10$ nm [10, 11] as the crystal retains its bulk values of $\sigma_{\rm sl}$, ΔH_f and $S_{\rm vib}$ [5, 12]. However, it fails for small-sized nanoparticles, adopting nonspherical shapes [13–15] with a large γ . Here, a shape factor [16, 17], $\delta = A_{\rm NP}/A_{\rm SN}$, where $A_{\rm SN}$ is the surface area for a spherical nanoparticle and $A_{\rm NP}$ is the surface area of a nonspherical nanoparticle with the same volume as spherical nanoparticle, is used to describe the shape effect of nanoparticles. For a solid nonspherical particle with size of d and shape factor of δ , its surface area $A_{\rm solid} = \delta \pi d^2$. Combined with Eqs. S1–S4, the melting temperature of nonspherical nanoparticle is

$$T_{\rm M,np} = T_{\rm M} \left(1 - \frac{\delta \zeta}{d} \right). \tag{S7}$$

The melting temperature of np-Cu with the identical sized nanopores, should be equal to that for the nanoparticle with the same size and shape. For a closed-cell np-Cu containing N spherical nanopores with an identical size, d, we assume that $V_{\rm sp,unit}$ and $A_{\rm sp,unit}$ are the volume and surface area of a spherical nanopore, respectively. The system volume, solid volume and total surface area of sphere-shaped nanopores in the samples are denoted as $V_{\rm sys}$, $V_{\rm solid}$, and $A_{\rm sp}$, respectively. Here $NV_{\rm sp,unit} = V_{\rm sys} - V_{\rm solid}$, and $NA_{\rm sp,unit} = A_{\rm sp}$. It is noted that $A_{\rm sp} = A_{\rm solid}$, the surface area of solid, for the np-Cu with sphere-shaped nanopores. Consequently, the size of spherical nanopore is

$$d = \frac{6V_{\rm sp,unit}}{A_{\rm sp,unit}} = \frac{6(V_{\rm sys} - V_{\rm solid})}{A_{\rm sp}}.$$
(S8)

As $\gamma = S_{\text{solid}}/V_{\text{solid}}$, $\rho_r = V_{\text{solid}}/V_{\text{sys}}$, and $A_{\text{sp}} = A_{\text{solid}}$, Eq. S8 can be rewritten as

$$d = \mu/\gamma, \tag{S9}$$

where $\mu = 6(1 - \rho_r)/\rho_r$. For np-Cu containing N nonspherical nanopores, $A_{\rm sp} < A_{\rm solid} = NA_{\rm np,unit}$, where $A_{\rm np,unit}$ is the surface area of a nonspherical nanopore. Then Eq. S9 can be rewritten as

$$d = \delta \mu / \gamma, \tag{S10}$$

here δ is the shape factor, and $\delta = A_{\text{solid}}/A_{\text{sp}}$. For an open-cell np-Cu, it can be considered to contain a nonspherical nanopore, whose size is $d = \sqrt[3]{6(V_{\text{sys}} - V_{\text{solid}})/\pi}$. Thus the melting temperature of open-cell np-Cu foams $(T_{\text{M,np}})$ can be obtained

$$T_{\rm M,np} = T_{\rm M} \left(1 - \zeta \gamma / \mu \right), \tag{S11}$$

indicating that the melt of nanoporous is the function of specific surface area (γ), liquid-solid interfacial energy ($\sigma_{\rm sl}$ in ζ), and mass density (ρ_r in μ). For our constructed np-Cu, ρ_r are almost constant, ~ 58.20%; and their sizes are almost the same, $d \approx 35.0$ nm > 10 nm, implying $\sigma_{\rm sl}$ is the bulk values.

SUPPLEMENTARY ANIMATIONS (MOVIES S1-S4)

Movie S1 Dynamic processes of melting and collapse in nanoporous Cu #A1 during thermal-annealing.

Movie S2 Evolution of surface melting and collapse in nanoporous Cu #A1 at 1350 K.

Movie S3 Dynamic processes of surface melting, collapse, recrystallization, and bulk melting in nanoporous Cu #A8 during thermal-annealing.

Movie S4 Evolution of surface melting, collapse and recrystallization in nanoporous Cu #A8 at 800 K.

* leideng@hunau.edu.cn

[†] jftang@hunau.edu.cn

- [1] Y. F. Zhu, J. S. Lian, and Q. Jiang, J. Phys. Chem. C 113, 16896 (2009).
- [2] D. A. Porter and K. E. Easterling, *Phase transformations in metals and alloys, 2nd Ed.* (Chapman & Hall, London, 1992).
- [3] D. Kashchiev, Nucleation: Basic theory with applications (Butterworth-Heinemann, Oxford, 2000).
- [4] L. K. Wu, Q. L. Li, B. Xu, and W. Liu, J. Mater. Res. **31**, 3649 (2016).
- [5] C. L. Jackson and G. B. Mckenna, J. Chem. Phys. **93**, 9002 (1990).
- [6] D. Jones, J. Mater. Sci. 9, 1974 (1974).
- [7] X. M. Bai and M. Li, Phys. Rev. B **72**, 052108 (2005).
- [8] L. H. Liang, M. Zhao, and Q. Jiang, J. Mater. Sci. Lett. 21, 1843 (2002).
- [9] G. Guisbiers and L. Buchaillot, J. Phys. Chem. C 113, 3566 (2009).
- [10] T. Castro, R. Reifenberger, E. Choi, and R. Andres, Phys. Rev. B 42, 8548 (1990).
- [11] K. Dick, T. Dhanasekaran, Z. Zhang, and D. Meisel, J. Am. Chem. Soc. 124, 2312 (2002).
- [12] K. F. Peters, J. B. Cohen, and Y.-W. Chung, Phys. Rev. B 57, 13430 (1998).
- [13] Y. Sun and Y. Xia, Science **298**, 2176 (2002).
- [14] A. S. Barnard, N. P. Young, A. I. Kirkland, M. A. Van Huis, and H. Xu, ACS Nano 3, 1431 (2009).

- [15] Y. Xia, Y. Xiong, B. Lim, and S. E. Skrabalak, Angew. Chem. Inter. Ed. 48, 60 (2009).
- [16] W. H. Qi and M. P. Wang, Mater. Chem. Phys 88, 280 (2004).
- [17] W. H. Qi, Acc. Chem. Res. 49, 1587 (2016).