Title
Response to Comment on "Reversible disorder-order transitions in atomic crystal nucleation"

Permalink
https://escholarship.org/uc/item/6gq6n0q9

Journal
Science, 375(6587)

ISSN
0036-8075

Authors
Jeon, Sungho
Hwang, Sang-Yeon
Ciston, Jim
et al.

Publication Date
2022-03-25

DOI
10.1126/science.abj3683

Peer reviewed

Title: Response to Comment on "Reversible disorder-order transitions in atomic crystal nucleation"

Authors: Sungho Jeon[1]†, Sang-Yeon Hwang[2]‡, Jim Ciston[3], Karen C. Bustillo[3], Bryan W. Reed[4], Sukjoon Hong[1], Alex Zettl[5,6,7], Woo Youn Kim[2], Peter Ercius[3]*, Jungwon Park[8,9]*, Won Chul Lee[1]*

Affiliations:

[1]Department of Mechanical Engineering, BK21FOUR ERICA-ACE Center, Hanyang University, Ansan, Gyeonggi 15588, Republic of Korea.

[2]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea.

[3]National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory (LBNL), Berkeley, California 94720, United States.

[4]Integrated Dynamic Electron Solutions, Inc., Pleasanton, California 94588, United States.

[5]Department of Physics, University of California, Berkeley, California 94720, United States.

[6]Materials Sciences Division, LBNL, Berkeley, California 94720, United States.

[7]Kavli Energy NanoSciences Institute, Berkeley, California 94720, United States.

[8]School of Chemical and Biological Engineering, and Institute of Chemical Process, Seoul National University, Seoul 08826, Republic of Korea.

[9]Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea.

*Correspondence to: wonchullee@hanyang.ac.kr (W.C.L.), jungwonpark@snu.ac.kr (J.P.), or percius@lbl.gov (P.E.).

†Present address: Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia 19104, United States.

‡Present address: HITS incorporation, Seoul 06234, Republic of Korea.

Abstract (58 words)**:**

Yu *et al.* suggested calculating precisely size ranges of the three parts in Fig. 3A, adjusting the free-energy levels in Fig. 3B, and considering the shape effect in the first-principles calculation. The first and second suggestions raise strong concerns for misinterpretations and overinterpretations of our experiments. The original calculation is sufficient to support our claim about crystalline-to-disordered transformations.

Main Text (1,000 words)**:**

We appreciate the interest in our work by Yu *et al.* (*1*), who claimed the following three assessments. First, the analysis of the fitting curve in Fig. 3A of our original report (*2*) should be improved to precisely calculate size ranges. Second, in the small cluster case in Fig. 3B, the disordered state must have a lower free-energy level than the crystalline state has. Third, the shape effect of nanoclusters needs to be considered in the first-principles calculation. We respectfully disagree with all the three assessments, but we believe that the second assessment regarding structural states of small nanoclusters could be developed into a future in-depth study.

Their first assessment is to precisely calculate size ranges of the three parts in original Figs. 3A and 3B. However, emphasizing the size ranges (named "magic numbers" by Yu *et al.*) as they suggested may lead to misunderstanding our claim, which is that thermodynamic characteristics of growing nanoclusters change "gradually" depending on their sizes. The three parts in our report are divided by ~1.0 nm^2 and ~3.0 nm^2, not based on physical principles, but to represent a size-dependent evolution of structural behaviors occurring within the continuous growth of nanoclusters. The fitting function in Fig. 3A is entirely empirical and meant as a guide to the eye. Precisely analyzing the function has no physical meaning, and the result from this analysis (discrete size ranges) obscures the concept of gradual changes. We also disagree with their method, averaging data points of Fig. 3A and then performing curve fitting (their Fig. C1B), because this method gives inconsistent weightings to the data points. While each point in Fig. 3A is measured from a uniform length of time periods, the data points in their Fig. C1B are obtained by averaging variable numbers (*n* varies from 1 to ~10) of the original points. Curve fitting with inequivalently obtained data is problematic, as explained by Simpson's paradox ("The average of averages is not the average.") in statistics (*3-5*). The increased Adj. R^2 values in their Table C1, obviously obtained by reducing the scatteredness of data points by averaging, don't imply true statistical improvement. In particular, presenting their Fig. C1B instead of Fig. 3A should be avoided because readers need to check deviations, not just general trends, of measured data.

Their second assessment suggests that we revise the free-energy diagrams (original Fig. 3B) in a way that the disordered state is more stable than the crystalline state in small nanoclusters (their Fig. C1F). Although this claim has been presented in many previous studies (*6-10*), a general consensus about this fundamental issue has not been reached yet. A traditional and presumably dominant idea is that small nanoclusters have ordered (crystalline or icosahedral) atomic structures (*11-15*). Yu *et al.* claimed that our data in Fig. 3A can provide an answer to this controversial problem as follows: Because temporal fractions of the crystalline state (TFCSs), indicating the probability of observing the crystalline state (P_c), are less than 0.5 in the small nanocluster case of Fig. 3A, the disordered state has a lower free-energy level than the crystalline state.

We claim that the second assessment is an overinterpretation of our results, mainly because of the invalid assumption that TFCSs in Fig. 3A of our report indicate absolute values of P_c. The observed system is not a sole nanocluster (Fig. 1A) but rather a nanocluster surrounded by mobile adatoms (Fig. 1B). Interactions between the nanocluster and adatoms induce crystalline-to-disordered transformations (*2*), significantly reducing TFCSs. The observation that pre-

synthesized nanoclusters without surrounding adatoms spend a much larger fraction of their time in the crystalline state supports this statement. In addition, the possibility of missing short-lived crystalline states in the observations (shorter than the temporal resolution, 10 ms) makes TFCSs underestimated. Therefore, it is impossible to claim that our experimental result verifies that the absolute value of P_c is less than 0.5 in small nanoclusters. Fortunately, a relative comparison of P_c is possible because the two fore-mentioned sources of the underestimation similarly affect the measurements. An exact description of this relative comparison in thermodynamics is the set of free-energy diagrams in original Fig. 3B. The diagrams further presenting a lower free-energy level of the disordered state than that of the crystalline state in small nanoclusters (their Fig. C1F) are an overinterpretation of our data. An alternative set of free-energy diagrams without the overinterpretation (Fig. 2) has been considered during the revision of the original report, but we discarded it because interactions between a nanocluster and surrounding atoms are unclearly presented. Despite its similarity to their Fig. C1F, the physical meaning of Fig. 2 (free-energy diagrams about a system composed of a nanocluster and surrounding atoms) is distinct from what Yu *et al*. wanted to claim. We do agree that our result "eventually (with extrapolation)" suggests that the disordered state is more stable in small nanoclusters, but it doesn't mean that we experimentally verify this statement at the current stage.

Their third assessment is to consider the shape effect of nanoclusters in the first-principles calculation for making our model more realistic. They suspected the shape effect is a main cause of the data scatteredness in original Fig. 3A, but a more straightforward reason for this is the stochastic nature of nucleation and early-stage growth. They also claimed that all the crystals during collapse and recrystallization along with {111} have polyhedral shapes in our TEM movies, but this claim has no detailed explanation and is incorrect. Most importantly, the original calculation successfully supports the claim that adatom binding can provide sufficient energy to small nanoclusters to induce the crystalline-to-disordered transformation. Adopting non-hemispherical shapes in the calculation reduces energy levels required for the transformation, thus further strengthening our claim. Therefore, we believe that the more complex calculation is not required at this moment.

In conclusion, what Yu *et al*. suggested can be summarized as finding additional information and meanings from our experimental results. We respectfully disagree with them, because the suggestions raise strong concerns for misinterpretations and overinterpretations of our experiments.

References and Notes

1. C. L. Yu *et al.*, Comment on "Reversible disorder-order transitions in atomic crystal nucleation". *Science* XXX, XXX (2021).

2. S. Jeon *et al.*, Reversible disorder-order transitions in atomic crystal nucleation. *Science* **371**, 498-503 (2021).

3. The simplest instance of Simpson's paradox is that the average of averages is not the average. For example, the average of {1, 1, 1} is 1 ($n = 3$), and the average of {5} is 5 ($n = 1$). The average of the two averages is $6/2 = 3$, but the average of all numbers is $8/4 = 2$. What Yu *et al.* performed is to average variable numbers of data points and then to apply curve fitting to the averages, which has the mathematically equivalent problem as this example has.

4. E. H. Simpson, The interpretation of interaction in contingency tables. *J. R. Stat. Soc. Series B Stat. Methodol.* **13**, 238-241 (1951).

5. S. Stevens, *Introduction to Statistics: Think & Do* (Worldwide Center of Mathematics, ver. 4.1, 2019), chap. 2.5.

6. I. L. Garzon *et al.*, Lowest energy structures of gold nanoclusters. *Phys. Rev. Lett.* **81**, 1600-1603 (1998).

7. Z. W. Wang, R. E. Palmer, Experimental evidence for fluctuating, chiral-type Au-55 clusters by direct atomic imaging. *Nano Lett.* **12**, 5510-5514 (2012).

8. V. Petkov *et al.*, Periodicity and atomic ordering in nanosized particles of crystals. *J. Phys. Chem. C* **112**, 8907-8911 (2008).

9. L. Li *et al.*, Noncrystalline-to-crystalline transformations in Pt nanoparticles. *J. Am. Chem. Soc.* **135**, 13062-13072 (2013).

10. Y. Sun, L. Zhuang, J. Lu, X. Hong, P. Liu, Collapse in crystalline structure and decline in catalytic activity of Pt nanoparticles on reducing particle size to 1 nm. *J. Am. Chem. Soc.* **129**, 15465-15467 (2007).

11. A. S. Barnard, N. P. Young, A. I. Kirkland, M. A. van Huis, H. F. Xu, Nanogold: A quantitative phase map. *ACS Nano* **3**, 1431-1436 (2009).

12. I. Chakraborty, T. Pradeep, Atomically precise clusters of noble metals: Emerging link between atoms and nanoparticles. *Chem. Rev.* **117**, 8208-8271 (2017).

13. J. D. Aiken, R. G. Finke, A review of modern transition-metal nanoclusters: Their synthesis, characterization, and applications in catalysis. *J. Mol. Catal. A* **145**, 1-44 (1999).

14. P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell, R. D. Kornberg, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science* **318**, 430-433 (2007).

15. M. Azubel *et al.*, Electron microscopy of gold nanoparticles at atomic resolution. *Science* **345**, 909-912 (2014).
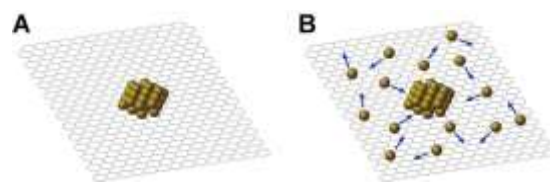
Fig. 1. Schematic models of nanoclusters. (**A**) A sole nanocluster on a graphene surface. (**B**) A nanocluster surrounded by mobile adatoms on a graphene surface. The system observed in the original report is not (A) but rather (B).
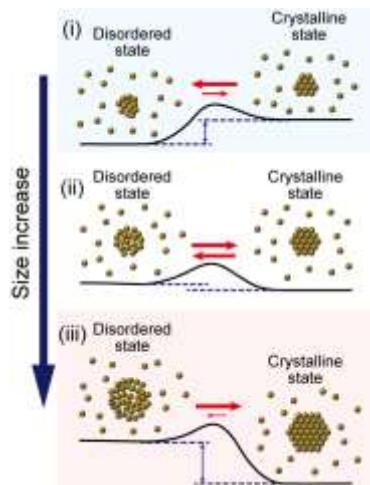

Fig. 2. Schematic energy diagrams about a system composed of a nanocluster and surrounding atoms during the nucleation process. The free-energy diagrams show size-dependent thermodynamic characteristics of nanoclusters during the nucleation process. This alternative candidate of Fig. 3B has been considered during the revision of the original report,

but we discarded it because interactions between a nanocluster and surrounding atoms are unclearly presented.