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Response to Comment on “Reversible disorder-order transitions in atomic crystal nucleation”

Sungho Jeon^{1†}, Sang-Yeon Hwang^{2‡}, Jim Ciston³, Karen C. Bustillo³, Bryan W. Reed⁴, Sukjoon Hong¹, Alex Zettl^{5,6,7}, Woo Youn Kim², Peter Ercius^{3*}, Jungwon Park^{8,9*}, Won Chul Lee^{1*}

¹Department of Mechanical Engineering, BK21FOUR ERICA-ACE Center, Hanyang University, Ansan, Gyeonggi 15588, Republic of Korea. ²Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea. ³National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. ⁴Integrated Dynamic Electron Solutions Inc., Pleasanton, CA 94588, USA. ⁵Department of Physics, University of California, Berkeley, CA 94720, USA. ⁶Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. ⁷Kavli Energy NanoSciences Institute, Berkeley, CA 94720, USA. ⁸School of Chemical and Biological Engineering and Institute of Chemical Process, Seoul National University, Seoul 08826, Republic of Korea. ⁹Center for Nanoparticle Research, Institute for Basic Science, Seoul 08826, Republic of Korea.

*Corresponding author. Email: wonchullee@hanyang.ac.kr (W.C.L.); jungwonpark@snu.ac.kr (J.P.); percus@lbl.gov (P.E.)

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

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

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

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 figure 3A of our original report (2) should be improved to precisely calculate size ranges. Second, in the small-cluster case in figure 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 three assessments, although 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 figures 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 size. The three parts in our report are divided by ~ 1.0 nm² and ~ 3.0 nm² not according to physical principles, but rather to represent a size-dependent evolution of structural behaviors occurring within the continuous growth of nanoclusters. The fitting function in figure 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 the data points of figure 3A

and then performing curve fitting (their figure 1B)—because this method gives inconsistent weightings to the data points. Whereas each point in figure 3A is measured from a uniform length of time periods, the data points in their figure 1B 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 1, obviously obtained by reducing the scatteredness of data points by averaging, do not imply true statistical improvement. In particular, presenting their figure 1B as an alternative to figure 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 figure 3B) in such a way that the disordered state is more stable than the crystalline state in small nanoclusters (their figure 1F). Although this claim has been presented in many previous studies (6–10), a general consensus about this fundamental issue has not yet been reached. 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 figure 3A can provide an answer to this controversial problem as follows: Because temporal fractions of the crystalline state (TFCSSs), indicating the probability of observing the crystalline state (P_c), are less than

0.5 in the small-nanocluster case of figure 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 the TFCs in our figure 3A 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 TFCs. The observation that presynthesized 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 TFCs 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 aforementioned 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 figure 3B. The diagrams further presenting a lower free-energy level of the disordered state than that of the crystalline state in small nanoclusters (their figure 1F) are an overinterpretation of our data. An alternative set of free-energy diagrams without the overinterpretation (Fig. 2) was 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 figure 1F, 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 does not mean that we have experimentally verified 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 that the shape effect is a main cause of the data scatteredness in original figure 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 transmission electron microscopy movies, but this claim has no detailed explanation and is incorrect. Most important, 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 nonhemispherical shapes in the calculation reduces the 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.

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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.
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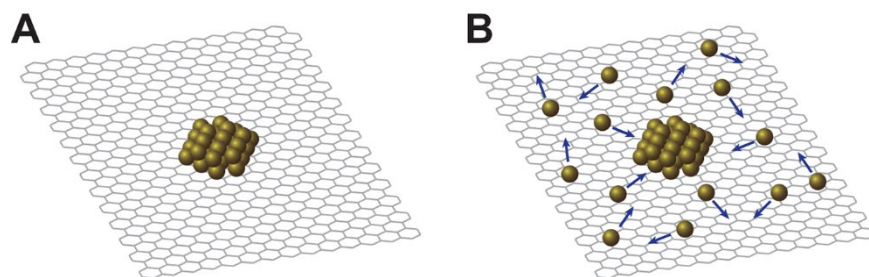


Fig. 1. Schematic models of nanoclusters. (A) A sole nanocluster on a graphene surface. (B) A nanocluster surrounded by mobile adatoms on a graphene surface. The system observed in the original report is not (A) but rather (B).

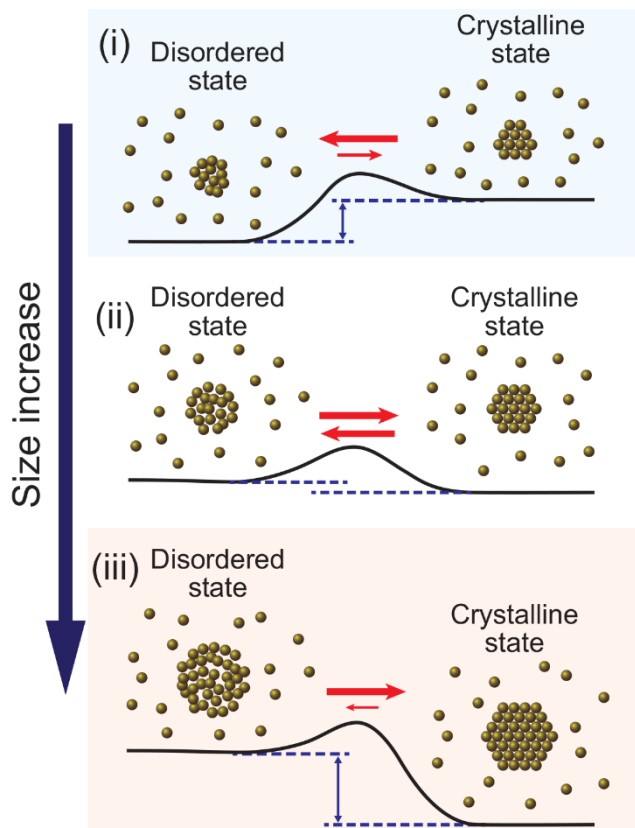


Fig. 2. Schematic energy diagrams about a system composed of a nanocluster and surrounding atoms during the nucleation process. The free-energy diagrams show size-dependent thermodynamic characteristics of nanoclusters during the nucleation process. This alternative candidate for figure 3B was considered during the revision of the original report, but we discarded it because interactions between a nanocluster and surrounding atoms are unclearly presented.

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