Responses to Reviewers

We appreciate all reviewers for the comments.

Reviewer #1 commented *"This paper reported the observation about the moment of initial crystallization captured on functionalized nanoparticles and found that silver nanoparticles accelerate the formation of clusters but noble metals palladium, gold and iridium likewise form nanoparticles do not promote crystallization. Nanoparticles as nucleating agents to suppress supercooling has been reported widely, this paper does not provide new ideas to solve the problem of supercooling. Also, the expression of this paper is not clear and the presentation need improvement."*

Authors' reply

In the manuscript, we suggest the reason why only Ag nanoparticles are effective in diminishing supercooling compared to Pd, Ir, and Au nanoparticles, not the general theory that nanoparticles are effective in diminishing supercooling. We were able to take a snapshot of the moment when a Ag nanoparticle is enveloped by a cluster in initial crystallization of phase change materials. Through XAS, moreover, we have clarified the mechanism that the coexistence of silver nanoparticle and F anion promotes the cluster formation and the subsequent nucleation.

Reviewer #2 commented *"**What are the major claims of the paper?***

Study on clathrate hydrate but potential broad applications: fundamental to understanding of heterogeneous nucleation mechanism and applied to the control of supercooling (or metastability) by seeding with nanoparticles.

Are they novel and will they be of interest to others in the community and the wider field?

This paper is in the continuity of the work previously published by the authors. They applied their knowledge of nanoparticles synthesis, crystallization of clathrate and direct observation of solution structure by electronic microscopy to the field of nucleation. The community of nucleation studies will be interested by this paper.

***Is the work convincing, and if not, what further evidence would be required to strengthen the conclusions**?*

Mostly yes. I had some comments on that point hereafter.

On a more subjective note, do you feel that the paper will influence thinking in the field?

It confirms some old assumption (see reference 1 in 1956) on heterogeneous nucleation and proposes some possible synergic effect of additives as promoters of nucleation.

***We would also be grateful if you could comment on the appropriateness and validity of any statistical analysis, as well the ability of a researcher to reproduce the work, given the level of detail provided**.*

Supercooling measurements were repeated 14 times. No information on the repetition of the electronic microscopy observation (how many samples and how many zones)."

Authors' reply

According to the reviewer's suggestion, we have added the sentence on the SEM observation to "Structural observation in aqueous solution" of the "Methods".

"We prepared at least two replica films under a condition. For each, more than 10 fields were observed using a SEM", instead of "It was observed using a SEM".

Reviewer #2 commented *"**More specific comments:***

Page 2 line 27 / Page 4 line 66 /Page 4 line 78/ Page 5 line 97/ Page 5 line 104/ Page 9 line 184 and 189: I think the word diminish supercooling is more appropriated than suppress supercooling."

Authors' reply

According to the reviewer's suggestions, we have changed the word "suppress" to "diminish" in the relevant parts.

Reviewer #2 commented *"Page 4 lines 76-77: The authors wrote "It is thought that silver iodide has close to the same crystal structure as ice, which is why silver iodide works as a nucleus1" (which is not exactly what it is written in reference 1) In reference 1 it is written "The success of silver iodide, which was chosen originally because the lattice constants of the hexagonal form are very similar to those of ice". I suggest using the same phrasing or maybe more precisely to reformulate as a possible heteroepitaxy to explain how crystallization seeds diminish supercooling."*

Authors' reply

According to the reviewer's suggestions, we have corrected the sentence to "It is thought that the lattice constants of the hexagonal form of silver iodide are very similar to those of ice, which is why silver iodide works as a nucleus."

Reviewer #2 commented *"Page 4: TBAF with Ag carboxylate have a synergic effect, it is not explain where does the idea to use TBAF as additive, in this paper, come from? What is the role of TBAF? The authors probably refer to reference 28 for the use of TBAF?"*

Authors' reply

In the present study, TBAF has two crucial roles. As described in reference 28, one of the important roles of TBAF is to improve the solubility of Ag-PA. Otherwise, Ag nanoparticles are not effectively formed. We have added the sentence to "Methods".

In addition, as mentioned in the original manuscript, TBAF forms a semiclathrate hydrate, which has a melting point of 300 K higher than that (278.1 K) of TBA-3MP. The formation of TBAF (or TBAF+TBA-3MP mixed) semiclathrate hydrate around Ag nanoparticles plays a role of further diminishing supercooling in the TBA-3MP semiclathrate hydrate formation.

Reviewer #2 commented *"Page 5 line 94 and Extended Data Fig. 3: How do the authors measure the time for crystallization to be completed?"*

Authors' reply

According to the reviewer's suggestion, we have added the description on how we determined the time for crystallization to be completed.

"The onset temperature and offset time of the exothermic peak derived from crystallization were determined as the crystallization temperature and the time for crystallization to be completed, respectively."

Reviewer #2 commented *"Page 5 line 96 : It is written that "Whereas their amounts are almost independent of the degree of supercooling" What does it means and where are the data to support this affirmation?"*

Authors' reply

We have corrected the sentence "the degree of supercooling is almost independent of their amounts (**Extended Data Fig. 3a**)". According to the reviewer's suggestions, we have added the panel a) to extended data Fig.3.

Reviewer #2 commented *"Pages 7 and 8: XANES spectra of Ag-PA +TBAF+TBA-3MP are provided and showed similarities with AgF. This is used to explain why did only Ag, but not Pd, Ir, or Au nanoparticles diminish supercooling. It explains why did only Ag carboxylate associated to TBAF diminish supercooling but not the specific role of Ag compared to other metals."*
"Page 8 lines 169-171: the explanation given for the specific role of Ag (its monovalence) requires more data. For instance, how do compare XANES spectra of Ag-PA +TBA-3MP (not shown or measured) with Ag-PA +TBAF+TBA-3MP of figure 3? Moreover, I understand that it is difficult to have XANES data (access to synchrotron), the authors should justify their choice of temperatures (293 and 273K) and why not perform experiments at 281K. Here again, XANES of Ag without TBAF would have been complimentary to observations of figure 2."

Authors' reply

As mentioned in the original manuscript (Extended Data Fig. 4), XANES spectra of Pd, Ir, and Au are almost the same as each metal acetate. Thus, there is little or no interaction between a metal cation (Pd, Ir, and Au) and F anion. On the other hand, XANES spectrum of Ag at 273 K, similar to that of AgF, clearly changed from that of Ag pentanoate. We believe, as mentioned in the original manuscript, the locally concentrated F anion around Ag increases the probability of TBAF (or TBAF+TBP-3MP mixed) semiclathrate hydrate formation.

According to the reviewer's suggestions, we considered an additional XAS measurement to compare XANES spectra of Ag-PA +TBA-3MP with Ag-PA +TBAF+TBA-3MP at 273 and 293 K, but could not secure beam time. Without TBAF, due to small solubility of Ag-PA, the XANES spectrum of solid Ag-PA should be dominant. The results the reviewer imaged could not be given. Since there was no suitable temperature controller at the beamlines in the large synchrotron

radiation facilities, it was not possible to measure at various temperatures. The measurement at 293 K was performed at room temperature, and, in the measurement at 273 K, ice packs were used to keep the sample cool.

Reviewer #2 commented *"Page 9 line 180: The authors refer to the similarity of the 2 crystal structures of TBA-3MP semiclathrate hydrate and TBAF semiclathrate hydrate. They probably mean the lattice constants of the hexagonal form are very similar (epitaxy?), they should add the crystallographic data of TBAF semiclathrate hydrate to extended data figure 6."*

Authors' reply

According to the reviewer's suggestions, we have added the crystallographic data of TBAF semiclathrate hydrate to extended data figure 6.

Reviewer #2 commented *"Page 9 line 185: The authors wrote: " To summarize the present study: we have reported that Ag nanoparticles act to suppress supercooling during the formation of TBA-3MP semiclathrate hydrate and have elucidated the mechanism, which is the promotion of formation of 10-30 nm clusters around Ag nanoparticles, through STEM observation using the freeze-fracture replica method and XAS." I think it is clearly shown by the experiment the effect of Ag nanoparticles in the diminution of supercooling. Moreover, the TBAF alone has no effect (sample #2) but associated to Ag it forms 10-30 nm TBAF semiclathrate hydrate clusters around Ag nanoparticles at 281 K and in the experiments presented in this paper there are no evidence of the existence of such cluster without TBAF added. The conclusion should be written in that direction."*

Authors' reply

According to the reviewer's suggestions, we have corrected the conclusion as follows.

"To summarize the present study: we have reported that Ag nanoparticles act to diminish supercooling under the coexistence of TBAF during the formation of TBA-3MP semiclathrate hydrate and have elucidated the mechanism, which is the promotion of formation of 10-30 nm clusters around Ag nanoparticles, through STEM observation using the freeze-fracture replica method and XAS. Furthermore, neither Ag nanoparticles nor TBAF has effect on diminishing supercooling alone."

Reviewer #2 commented *"Captions of figure 1 and extended data figure 2: X and O to be explained.*

To conclude, I think this paper deserve to be published after corrections according to my comments.

I will be available for a rereading after corrections."

Authors' reply

We apologize that the missing of the description. According to the reviewer's suggestions, we have added the description of symbols (O and X) to figure 1 and extended data figure 2.

Reviewer #3 commented "*Active centres (foreign particles, ions, point defects, etc.) decrease the nucleation barrier and thus promote the crystallization process (crystallization occurs under lower supercooling, or supersaturation). In many cases, the origin of the active centres is not known (e. g. the role of pollutants in the atmospheric aerosol formation). On the other hand, the influence of the nucleation centre (or nucleation agent) on heterogeneous nucleation and crystallization is systematically studied (see e. g. [H. Kumomi, F. G. Shi, Phys. Rev. Lett. 82 (1999) 2717; K. Okada et al., Polymer 48 (2007) 1116.]).*

This paper is focused on the influence of various metal additives on the clathrate hydrate crystallization from an aqueous solution. Authors showed that Ag nanoparticles reduce supercooling during the formation of the tetra-n-butylammonium 3-methylpentanoate (TBA-3MP) semiclathrate hydrate. The mechanism of the cluster formation around Ag nanoparticles is proposed.

The conclusions of the paper are well presented and supported by the experimental data. The paper is valuable to the readers of the Communications Materials.
However, the several sentences are a little bit confusing. The revisions are necessary.

I have the following comments on the paper:

Abstract, the sentences 3-6: In the first sentences the freezing, i. e. the liquid-solid transition is considered. However, the next sentence considers artificial rainfall, i. e. the vapour-liquid transition. Moreover, it seems that the processes of the formation of ice and snowflakes are mixed together."

Authors' reply

According to the literature on artificial rainfall, there are two kinds of artificial rainfalls. One is in a cold cloud and the other is in a warm cloud. In a cold cloud (at high altitude), for rain to fall, ice grains need to be present in a low-temperature cloud. Around Japan, most of rainy clouds are such cold clouds. On the other hand, in a warm cloud, the aggregation of tiny droplets results in rainfall. In the present manuscript, we considered such a cold cloud only in the original manuscript. To avoid misunderstanding, we have modified the sentence and changed the literature (Ref. 1) below. Due to the word limitation in abstract, the details have been added in introduction zone around page 4.

"For rain to fall in cold clouds below 273 K, ice grains need to be present in a low-temperature

cloud, but if supercooled water injected into the cloud remains as water droplets, it does not rain." Mason, B. J. Design and evaluation of large-scale rain-making experiments, *Nature* **175**, 448–451 (1955).

Reviewer #3 commented *"Similarly, the artificial rainfall is discussed in the middle of p. 4: "Artificial rainfall ... it is necessary to form ice crystallites in a supercooled cloud". I understand rainfall as the formation of droplets from a liquid phase. However, the authors write about the formation of ice crystallites. It is confusing."*

Authors' reply

As mentioned in the response above, there are two kinds of artificial rainfalls. We considered only a cold cloud in the original manuscript. To avoid misunderstanding, we have added some sentences on two types of clouds.

"One example of the prevention of supercooling is seen with artificial rainfall. There are two kinds of rainy clouds: a cold cloud below 273 K and a warm cloud above 273 K[1]. To make it rain artificially in cold clouds, it is necessary to form ice crystallites in a supercooled cloud."

Reviewer #3 commented *"In the extended data Fig. 3 is shown that the crystallization is faster for the higher ratio of tetra-n-butylammonim fluoride (TBAF). In Fig. 1, I did not find information about the amount of the metal species added to the aqueous solution."*

Authors' reply

We described it on the 7th line from the bottom of the "Samples" section of the "Methods". For readers' convenience, we have added the ratio in the captions of Figure 1 and Extended Data Figure 2.