Structural analysis of artificial nanoparticle formation in *Listeria innocua* Dps

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Abstract

Biomineralization is an essential phenomenon in our nature, which leads to the formation of inorganic structures such as bone, tooth and so on. One of the cage shaped proteins, ferritin, has a pivotal role to maintain the iron concentration in living. Ferritin can form iron oxide nanoparticles (NP: 7 nm) through biomineralization at the center of their cavity (8 nm). As the size of NPs is regulated by protein shell, researchers have fabricated of artificial NPs, such as Fe_3O_4, Co_3O_4, In_2O_3 or CdSe [1,2], in the ferritin cavity to use them for electrical and magnetic applications [3, 4]. In order to minimize the structures, smaller cage shaped protein has been paid attention of. Dps (**D**NA-binding **p**rotein from **s**tarved cells) has a spherical form with a cavity at the center. Since the diameter of the cavity is 4.5 nm, the size of NPs can be regulated within less then 4.5 nm. Recent literature reports the production of artificial NPs in Dps proteins, however, the mechanism of NPs formation in Dps is still not clear.

Iron oxide mineralization in *Listeria innocua* Dps has been reported to occur through ions translocated through ion channels (IC) of Dps and are gathered at feroxidase centers (FOC). This site can potentially induce nucleation and iron oxide NPs formation. Through those sites on the Dps, Iron oxide NPs can be formed through oxidation of divalent iron ions in the Dps *in vivo* and *in vitro*. The reason of the preference and ease is unknown part on the formation of iron oxide NP. Especially, the characteristic of iron ions states including divalent and trivalent states makes it difficult to understand the phenomena. In this work, we analyzed the structures of *Listeria innocua* Dps including metal ions such as Fe, divalent Co and trivalent Yb ions using synchrotron radiation. As Co and Yb ions are redox-stable in neutral solutions, the positions of metal ions can be analyzed by X-ray analysis without oxidation.

At the ICs, the number of the metals ions were different depending on ion species and the conformation of the Glutamic acids were changed from that in apo-Dps (without metal ions). These results indicate that the conformational change would assist the uptake of metals ions into the Dps cavity. FOC had all metals ions regardless of the difference of charge state. On the other hand, the conformations of negative charged amino acid are changed from the positions in apo-Dps, suggesting that the FOC can act for nucleation center for artificial NPs formations and the conformation change would encourage to form nuclei of NPs.

References

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