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Antifreezing Gold Colloids

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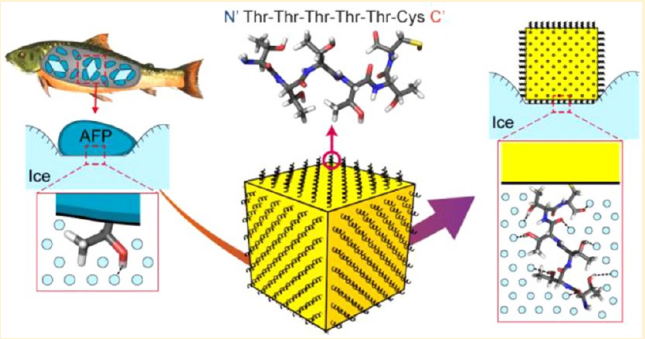
Supporting Information

ABSTRACT: Gold (Au) colloids are becoming ubiquitous across biomedical engineering, solar energy conversion, and nano-optics. Such universality has originated from the exotic plasmonic effect of Au colloids (i.e., localized surface plasmon resonance (LSPRs)) in conjunction with the versatile access to their synthetic routes. Herein, we introduce a previously undiscovered usage of Au colloids for advancing cryoprotectants with significant ice recrystallization inhibition (IRI). Oligopeptides inspired by the antifreeze protein (AFP) and antifreeze glycoprotein (AFGP) are attached onto the surface of well-defined Au colloids with the same sizes but different shapes. These AF(G)P-inspired Au colloids can directly adsorb onto a growing ice crystal via the synergistic interplay between hydrogen bonding and hydrophobic groups, in stark contrast to their bare Au counterparts. Dark-field optical microscopy analyses, benefiting from LSPR, allow us to individually trace the in situ movement of the antifreezing Au colloids during ice growth/recrystallization and clearly evidence their direct adsorption onto the growing ice crystal, which is consistent with theoretical predictions. With the assistance of molecular dynamics (MD) simulations, we evidently attribute the IRI of AF(G)P-inspired Au colloids to the Kelvin effect. We also exploit the IRI dependence on the Au colloidal shapes; indeed, the facet contacts between ice and Au colloids can be better than the point-like counterparts in terms of IRI. The design principles and predictive theory outlined in this work will be of broad interest not only for the fundamental exploration of the inhibition of ice growth but also for enriching the application of Au colloids.



INTRODUCTION

The impressive capabilities of the antifreeze protein (AFP) and antifreeze glycoprotein (AFGP), abbreviated collectively as AF(G)Ps, in inhibiting ice crystal growth have inspired both understanding and harnessing of their mechanism, which can in turn underpin a wide range of transformative applications.[1−11] Regularly arrayed, typically flat assemblies of AF(G)Ps with a specific sequence are believed to adhere to the facet of ice crystals; consequently, micro- or nano-curvatures of a growing ice crystal, formed between the AF(G)P-anchored regions, make it more thermodynamically difficult for water molecules to crystallize.[3−8]

Even if a full rationalization of the underlying mechanism is yet to be addressed, two origins, broadly speaking, are likely involved in the ice adhesion of AF(G)P, as follows. In the initial stage of study, a hydrogen bonding was suggested as the most prevalent rationalization route toward this end.[9−11] This is intuitive because all amino acids within AF(G)Ps can universally form hydrogen bonds with water molecules due to their carbonyl and amine groups. Furthermore, AF(G)Ps and type-I AFP, mainly consisting of threonine (Thr), can facilitate such hydrogen bonding due to their hydroxyl groups in addition to carbonyl and amine groups.[10,11] Artificial cryoprotectants such as poly(vinyl alcohol) (PVA) and graphene oxides (GOs) with a bunch of hydroxyl groups further evidenced the importance of hydrogen bonds in terms of ice crystal inhibitions.[12−15]

However, an approach depending only on hydrogen bonding is found to be inconsistent across AF(G)Ps.[16−24] For example, it empirically turns out that co-oligopeptides consisting of Thr and Serine (Ser) show more efficient inhibition of ice growth as with a higher ratio of Thr to Ser.[17,18] From the point of view of hydrogen bonding, this is counterintuitive because Thr is more hydrophobic as compared to Ser. This result implies that the hydrophobicity of AF(G)Ps also contributes to their ice binding and the resulting inhibition of ice growth. This importance of hydrophilic and hydrophobic duality in ice growth inhibition was also artificially reproduced by using amphipathic glycopolymers.[25] As well as these empirical observations, recent numerical simulations have theoretically supported the above arguments.[26−28] In line with this, both hydrophobic and hydrophilic moieties need to cooperatively interplay to

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