NANO LETTERS

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Letter

Self-Assembled Nanostructures of Homo-Oligopeptide as a Potent Ice Growth Inhibitor

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Cite This: *Nano Lett.* 2023, 23, 9500−9507

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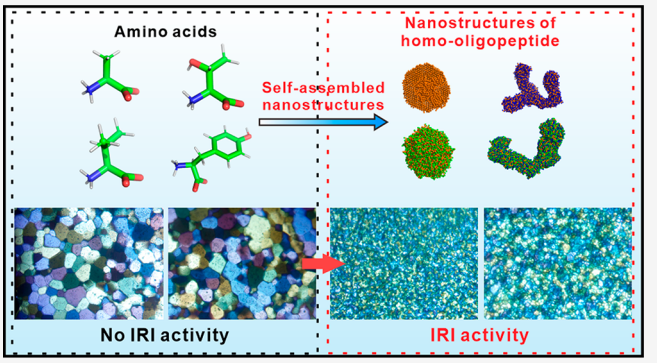
ABSTRACT: This study reports the formation of self-assembled nanostructures with homo-oligopeptides consisting of amino acids (i.e., alanine, threonine, valine, and tyrosine), the resulting morphologies (i.e., spherical shape, layered structure, and wire structure) in aqueous solution, and their potential as ice growth inhibitors. Among the homo-oligopeptides investigated, an alanine homo-oligopeptide (n = 5) with a spherical nanostructure showed the highest ice recrystallization inhibition (IRI) activity without showing a burst ice growth property and with low ice nucleation activity. The presence of nanoscale self-assembled structures in the solution showed superior IRI activity compared to an amino acid monomer because of the higher binding affinity of structures on the growing ice crystal plane. Simulation results revealed that the presence of nanostructures induced a significant inhibition of ice growth and increased lifetime of hydrogen bonding compared with unassembled homo-oligopeptide. These results envision extraordinary performance for self-assembled nanostructures as a desirable and potent ice growth inhibitor.



KEYWORDS: *biomimicry, antifreeze protein, homo-oligopeptide nanostructure, ice recrystallization inhibition, self-assembly*

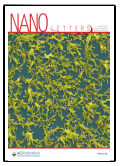
Organisms living in the polar regions have antifreeze proteins (AFPs) that allow them to survive, even at extremely low temperatures (−2.0 to −20 °C).[1] AFPs inhibit the formation of ice crystals and prevent the growth of ice that is fatal to cells.[2] So far, four different types of AFPs (I, II, III, and IV) have been identified.[3] The antifreezing activity mainly relies on the presence of specific amino acids such as alanine (Ala), threonine (Thr), and their aligned structures on the α-helix or β-sheet structure.[4,5] AFP type I has a high Ala ratio and an α-helical structure containing Thr residues.[4] Hydrogen bonding with water molecules during ice growth and hydrophobic interactions also play an important role.[6]

Mimicking the functions of AFPs with materials has been a promising strategy to obtain an improved antifreezing performance and eventually replace AFPs, which have limited scalability for practical applications.[7,8] Materials including an L-proline oligomer (n = 3, 8, and 15),[8,9] 2D materials such as graphene oxides,[10] synthetic polymer (i.e., poly(vinyl alcohol) [PVA]),[11] and hydrogel[12] have been investigated for their antifreezing activity. In addition to the types of materials, nanoscale design is also considered to be critical.[13] A recent study showed the importance of size and surface structure for the presentation of amino acids, to increase ice growth inhibition activity, as demonstrated by the use of spherical or cube-shaped gold nanoparticles.[14] In addition, the self-assembled nanoparticles composed of "non-IRI active" polymers (i.e., poly[vinylpyrrolidone], poly[ethylene glycol]) showed significant IRI activity.[15]

In this regard, self-assembled nanostructures composed of oligopeptides with Ala or Thr are promising antifreezing materials because of the intrinsic biocompatibility and functionality of the amino acids. Although the recent focus on the self-assembled structure for diverse applications,[16] the antifreezing activity of the homo-oligopeptide in nanoscale structures has not been investigated.[17] In this study, we designed four different homo-oligopeptides composed of Ala, Thr, valine (Val), and tyrosine (Tyr) to prepare the self-assembled nanostructures. The antifreezing properties of the self-assembled nanostructures were compared with that of an amino acid monomer, including the simulation studies with a coarse-grained model and an all-atom simulation model.

First, to examine the formation of self-assembled nanostructures, each homo-oligopeptide (n = 3, 5, and 7) composed of Ala, Thr, Val, and Tyr was completely dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which can completely destroy

Received: August 15, 2023
Revised: September 15, 2023
Published: October 16, 2023



https://doi.org/10.1021/acs.nanolett.3c03059
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