small science
www.small-science-journal.com

Plasmonic Observation of High-Density Nanoclustering in Low-Temperature H_2O

Nu-Ri Park, Yedam Lee, Sang Yup Lee, Han-Na Kim, Myung-Ki Kim, and Dong June Ahn**

There has been considerable scientific interest in comprehending the behavior and phase transitions of H_2O at the nanoscale in low temperatures. Herein, a highly sensitive and nondestructive surface plasmonic detection system operated at low temperatures to investigate the real-time nanoscale variation in H_2O density from a rapidly cooled thin ice layer formed at 77 K is employed. The nanoslit device exhibits a distinct plasmonic response at 180–250 K, correlated to an increase in the local density of H_2O at the nanometer scale. Along with theoretical analyses, it is revealed that high-density H_2O clusters form by vigorous aggregation of H_2O molecules within the interphase liquid region between polymorphic ice crystals. The utilization of ice-active materials, known to inhibit ice growth, suppresses the initiation of such high-density nanoclustering at 180 K. These results contribute to the comprehension of the interplay between polymorphic crystals and density-variant interphases in low-temperature H_2O systems.

1. Introduction

Understanding the intricate behavior and phase transitions of water (H_2O) at various scales—from molecular to macroscopic—is fundamental to many scientific disciplines.[1–3] Ice, the solid phase of water, exhibits diverse polymorphic forms, including but not limited to hexagonal ice (Ice Ih) and cubic ice (Ice Ic), each characterized by unique structural and thermodynamic properties.[4,5] Beyond these well-documented phases, amorphous ice forms and a multitude of crystalline structures present a complex landscape of ice's physical state, particularly under varying environmental conditions such as temperature and pressure.[6,7]

Advancements in analytical techniques, including Raman spectroscopy,[8–11] X-ray diffraction,[12,13] neutron scattering,[14,15] and cryogenic electron microscopy,[16–18] have significantly enhanced our understanding of ice at the angstrom scale.[19,20] These methods have provided detailed insights into the phases, structures, molecular motions, and energy states of H_2O under various conditions.[21–26] Recent studies highlight the significance of refractive index measurements in supercooled water, showing that liquid-like phases can exist under specific conditions.[27] However, despite these technological advances, understanding ice remains challenging due to the complex scenarios in phase transition that occur as it thaws from cryogenic conditions to ambient temperature.

This complexity is evident in the various ice dynamics through nucleation, growth, and recrystallization, manifesting in diverse states such as amorphous, cubic, and hexagonal ice. These transitions are intricately influenced by the presence of complex structures where supercooled liquid water exists at grain boundaries between ice crystals. As these structures pass through the temperature range known as "no man's land" between 150 and 235 K, the impact of this liquid water on the phase transitions of ice crystals remains largely unexplored. Predictive models have identified the presence of both high-density (HDL) and low-density (LDL) liquid water phases within this temperature range,[28,29] which are believed to play significant roles in the dynamics of the transition between ice and liquid water.[30] The experimental observation of these interactions is challenging due to the highly sensitive and transient nature of these states in response to temperature changes.

In this report, we utilized a plasmonic sensor that effectively detects subtle fluctuations in the refractive index at the nanometer

N.-R. Park, S. Y. Lee, H.-N. Kim, M.-K. Kim, D. J. Ahn
KU-KIST Graduate School of Converging Science and Technology
Korea University
Seoul 02841, Republic of Korea
E-mail: rokmk@korea.ac.kr; ahn@korea.ac.kr

Y. Lee, S. Y. Lee, D. J. Ahn
Department of Chemical and Biological Engineering
Korea University
Seoul 02841, Republic of Korea

Y. Lee, S. Y. Lee, D. J. Ahn
W:I Interface Augmentation Center
Korea University
Seoul 02841, Republic of Korea

M.-K. Kim
Center for Quantum Information
Korea Institute of Science and Technology
Seoul 02792, Republic of Korea

D. J. Ahn
Center for Theragnosis
Korea Institute of Science and Technology (KIST)
Seoul 02792, Republic of Korea

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smsc.202400427.

DOI: 10.1002/smsc.202400427