

Anomalous Phase Behavior of Water Confined in Single-Walled Carbon Nanotubes

Haruka KYAKUNO¹, Kazuyuki MATSUDA¹, Hitomi YAHIRO¹, Tomoko FUKUOKA¹, Yasumitsu MIYATA¹, Kazuhiro YANAGI¹, Yutaka MANIWA^{1,2}, Hiromichi KATAURA^{3,2}, Takeshi SAITO⁴, Motoo YUMURA⁴, and Sumio IIJIMA⁴

¹Department of Physics, Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan.

²JST, CREST, Kawaguchi 332-0012, Japan.

³NRI, AIST, Central 4, Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan.

⁴Nanotube Research Center, AIST, Tsukuba 305-8565, Japan.

Water confined within restricted spaces shows unusual properties that cannot be observed in the bulk. A greatly suitable model for such a system is a single-walled carbon nanotube (SWCNT) filled with water. Theoretical studies predicted that water filling narrow SWCNTs undergoes liquid-solid like transition at low temperature and forms ordered tubular ice structures, so-called ice nanotubes (ice-NTs). The formation of ice-NTs inside SWCNTs with diameters between 1.17 and 1.44 nm was proved experimentally by our previous studies. Although computational studies with larger-diameter SWCNTs have been performed recently, few experimental studies have been conducted.

In this work, we aimed at water-filled SWCNTs with a diameter range of 1.46 to 2.4 nm to clarify nano-ice structures and also establish the global phase diagram of water confined in SWCNTs. Employing a combination of X-ray diffraction (XRD) and nuclear magnetic resonance (NMR), we found that water confined in SWCNTs with $D > 1.6$ nm undergoes a wet-dry transition at low temperature. Moreover we found the formation of an ice-NT containing a one-dimensional water chain inside SWCNTs with $D \sim 1.5$ nm by molecular dynamics (MD) calculations and XRD experiments.

(Powder XRD experiments were performed at the BL1B and BL8B stations in the Photon Factory, KEK, Japan.)

[References]

1. H. Kyakuno *et al.*, JPSJ **79** (2010) 083802
2. D. Takaiwa *et al.*, PNAS **105** (2008) 39

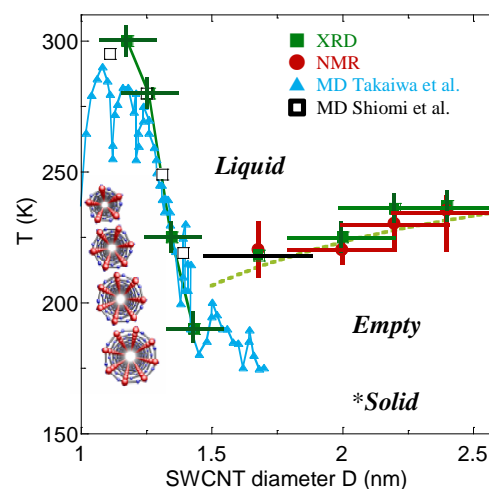


Figure Global temperature-diameter (T-D) phase diagram of water inside SWCNTs. The left insets are schematic illustrations of the ice NTs.