Ordered water inside carbon nanotubes: formation of pentagonal to octagonal ice-nanotubes

Yutaka Maniwa a,d,*, Hiromichi Kataura b, Masatoshi Abe a, Akiko Udaka a, Shinzo Suzuki c, Yohji Achiba c, Hiroshi Kira a, Kazuyuki Matsuda a, Hiroaki Kadowaki a, Yutaka Okabe a

a Department of Physics, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachi-oji, Tokyo 192-0397, Japan
b Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 4, Higashi 1-I-1, Tsukuba, Ibaraki 305-8562, Japan
c Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachi-oji, Tokyo 192-0397, Japan
d CREST, Japan Science and Technology Corporation (JST), Japan

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Abstract

We report on a systematic X-ray diffraction analysis for the ordered water inside single-walled carbon nanotubes (SWNTs) with diameters of 10.9–15.2 Å. Four distinct ordered structures identified in this diameter range were assigned to polygonal ice-nanotubes predicted by molecular dynamics (MD) calculations. The ordering transition temperature rose from 190 K of octagonal ice-nanotubes to 300 K of pentagonal ice-nanotubes without applying high pressure when the SWNT diameter decreased. The results indicate a crossover from bulk to atomic scale phenomena with decreasing SWNT diameter.

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1. Introduction

Confined water [1–5] within restricted spaces is expected to show unusual properties that cannot be observed in bulk water [6]. Such water actually exists in our surroundings, and even within our bodies. However, knowledge about its physical properties is rather limited. This is partly due to the limited number of well-defined containers in which systematic studies can be performed. Advanced methods of preparing high-purity and diameter-controlled single-walled carbon nanotubes (SWNTs) [7,8] provide quasi-one-dimensional (quasi-1D) cavities of nano- or subnanometers in diameter and micrometers in length made up of graphene sheets. Theoretical works based on computer simulations have already predicted several characteristic properties of water inside and outside SWNT bundles [3,5,9,10], such as phase transitional behavior. It has been observed [11,12] that heat-treated SWNTs with an average diameter of 13.6 Å can adsorb water molecules inside the SWNTs and that the adsorbed water exhibits liquid-solid phase transition at 235 K. The authors [12] have also demonstrated that the low-temperature phase is polygonal ice-nanotubes predicted by MD calculations [3]. These findings and theoretical predictions have stimulated us to carry out further systematic investigations on the confined water inside SWNTs as a function of the SWNT diameter. We report here on our powder X-ray diffraction (XRD) experiments on high-quality SWNTs [8] exposed to water vapor.
2. Experimental

SWNTs were crystallized into close-packed bundles with a 2D hexagonal (triangular) lattice [13]. XRD experiments were made to gain information on the density profile of water adsorbed inside SWNTs, distinct from molecules on the bundle surfaces and in contaminant phases such as amorphous carbons and nanographites [11–17]. Powder XRD data for six purified SWNT samples were collected using synchrotron radiation with 1.00 Å at beam-line BL1B in the Photon Factory, KEK, Japan. The average diameters of SWNTs were $2R = 11.7, 13.0, 13.4, 13.5, 13.8$ and $14.4$ Å. The diameter distribution of each sample was $1.6$ Å as the full width at half maximum (FWHM) of Gaussian distribution function, roughly covering $10.9–15.2$ Å. A typical diameter of the SWNT bundle was $180$ Å.

The SWNTs were sealed into a quartz glass tube with a thickness of $0.01$ mm with water vapor of the saturated pressure at $300$ K for the XRD experiments, after well degassed [11,14]. The small volume of the sealed tube, whose dimension was typically $0.7$ mm $\times$ $20$ mm, ensured to minimize the amount of excess water in the glass tubes. The temperature $(T)$ in the range of $90$ and $360$ K was controlled with a cryostat of N$_2$ gas-flow type. Because one end of the glass tube was kept at room temperature (RT: $300$ K), the water pressure for $T > 300$ K was set equal to the saturated vapor at RT, $27$ Torr.

3. Results and discussions

3.1. Adsorption of water molecules inside SWNTs

Fig. 1 shows the XRD patterns taken at $330$, $300$ and $100$ K in the SWNT sample with an average diameter of $2R = 13.5$ Å. $Q$ is the amplitude of the scattering vector. The observed peaks are indexed on the basis of the 2D triangular lattice of SWNTs [13]. The inset of Fig. 1 is the $T$-dependence of the 10 peak intensity at $Q/\sqrt{3} = 0.43$ Å$^{-1}$ along with that for the $11.7$ Å SWNT sample. We find that the patterns exhibit drastic changes at $\approx 315$ K. Because the XRD profiles for $T > 330$ K were identical to that of the pristine (empty) SWNTs, the sudden changes can be assigned to water-adsorption (desorption) into (from) SWNT bundles with decreasing (increasing) temperature. The reduction in the 10 peak intensity from that of the empty SWNTs implies that the dominant adsorption site is inside the SWNTs [11,12,15,16]. Similar features, observed in all the SWNT samples studied, confirm that water adsorption occurs irrespective of the SWNT diameter in the range of $11–15$ Å. The narrowness of transition suggests that water exhibits a liquid–gas like phase transition around $315–330$ K. This temperature is slightly higher than $300$ K of bulk water at $27$ Torr.

3.2. Ordering of water molecules inside SWNTs

As already mentioned, all the XRD peaks observed at RT are indexed on the basis of the 2D triangular lattice with the same lattice parameter as in the pristine SWNTs, and no new peak appears on the water adsorption. This implies that there is no long-range order of water molecules inside SWNTs at RT. With lowering $T$, however, sharp Bragg peaks are newly observed at $Q \approx 2.2$ Å$^{-1}$ in all the samples, indicating the development of long range ordering of water molecules. (These peaks are called ice peaks in what follows.) The $T$-dependences of the ice peaks are shown in Fig. 2a for three SWNT samples with average diameters of $11.7, 13.5$ and $13.8$ Å. The second-order reflection is also observed at $4.4$ Å$^{-1}$ in the best-quality sample with an average diameter of $11.7$ Å, as shown in Fig. 3b. The corresponding lattice spacing is estimated to be $2.8–2.9$ Å. The size of crystalline domain $N$ in the $11.7$ Å SWNTs is also estimated from the peak broadening as shown in Fig. 2b. The $N$ develops below $300$ K and reaches $140$ Å of nearly $50$ 1D unit cells at $100$ K. Such a long-range order indicates the occurrence of phase transitions with lowering $T$.

Here, an important feature of the ice peaks is a sawtooth shape tailed to the high-$Q$ side. Such a feature is caused by 1D characteristics of the ordered water...
[15,18,19]; there is no inter-tube correlation among the 1D ordered structures in different SWNTs. Further detailed inspection has identified a two-peaked structure for SWNTs with intermediate diameters, as shown by A and B in Fig. 2a. When $T$ decreases, peak A appears first and then peak B develops at slightly lower $Q$. This $T$-dependence of the intensities of peaks A and B is summarized in Fig. 2c for the six SWNT samples. The peak intensities change reversibly within 3 K in all of the samples. We find from Fig. 2c that there are four transition
temperatures, \( T_m \), 190 ± 5, 280 ± 5 and 300 ± 5 K from the onset of the ice peak and 220 ± 5 K from the kinks observed for peak A.

Since the observed ice peak profile can be assigned to a superposition of those from the 1D-ordered water within different SWNTs, we ascribe the observed four transition temperatures to water in different SWNTs, but not to the same water that exhibits successive structural conversion with \( T \). In the latter case, peak A should disappear or diminish when peak B develops below its onset temperature, being contradictory to the observed features. The coexistence of peaks A and B at slightly different \( Q \) values simply indicates that there are two 1D-ordered structures with different lattice constants. This argument is also applicable to the apparent successive transitions in peak A observed as kinks.

On the other hand, a detailed fitting of calculated XRD patterns to the observed ones below \( Q = 2.0 \text{ Å}^{-1} \) has shown that the water density averaged along the SWNT axis changes to a tube-like profile at low temperatures, as reported [12]. For example, the water of an average content of \( C_\text{H}_2\text{O} \) is confined in the range of 3.2 Å < \( r \) < 9.0 Å at 100 K for the 13.5 Å SWNTs, as shown in Fig. 1.

### 3.3. Low-temperature ordered structures

The features of the low-\( T \) structures clarified so far can be summarized as follows: (1) The density profile of water inside SWNTs is tube-like. (2) The 1D periodicity of 2.8–2.9 Å with a long-range order develops. (3) Four distinct transition temperatures in the diameter range of 11–15 Å. (4) The average content of water, \( C_\text{H}_2\text{O} \) for the typical SWNT sample, implies 6.5 water molecules for a 1D unit cell. These features impose strong restrictions on the possible low-\( T \) structures. With provision of the structures based on the hydrogen bonding of water, we are naturally led to the model of polygonal ice-nanotubes [3], whose presence was first predicted by MD calculations under axial pressures of 50–500 MPa inside SWNTs and was actually observed in the SWNT sample with an average diameter of \( \approx 13.6 \text{ Å} \) without application of pressure [12].

The possible forms of 1D polygonal ice-nanotube structures are illustrated in Fig. 3a. The \( n \)-water molecules (with integer \( n \)) form a polygon \((n\text{-gonal ring})\) through hydrogen bonds and then stacked one-dimensionally. In ideal ice-nanotubes, each water molecule is bonded to the four nearest-neighbor water molecules through a hydrogen bond, as in bulk ice. Therefore, the 1D lattice constant along the tube axis is determined by the hydrogen bond length in this direction [3], \( d \approx 2.8 \text{ Å} \). This is close to the observed 1D lattice constants, 2.8–2.9 Å.

On the other hand, the diameter of ice-nanotubes is given by \( n \) and the hydrogen bond length within the ring, \( d_{\text{OO}} \approx 2.8 \text{ Å} \). If the ice-nanotube diameters can be approximated by that of a circle connecting the oxygen nuclei in the \( n \)-gonal ring, they are given by \( d_{\text{OO}}/\sin(\pi/n) \). Thus, the difference in the ice-nanotube diameters between \( n \) and \( n + 1 \) is estimated to be 0.85 Å for \( n = 4 \)–8 (for the possible ice-nanotubes inside the present SWNTs). Therefore, we expect that there are four or five possible polygonal ice-nanotubes in the diameter range of 11–15 Å, as actually observed.

The above ice-nanotube structures are confirmed by further detailed calculations of the XRD profiles of ice peaks. The experimental observation for the 2\( R = 11.7 \) Å SWNTs is compared in Fig. 3b with the calculated patterns. In the 1D system, the diffraction appears at \( Q \sim 2\pi/\text{d} \), and its high-\( Q \) tail is modulated by the structural factor of the 1D unit cell [18], water ring in the present case. Therefore, the ring diameter 2\( r \) can be sensitively determined from an analysis of the 1D peak profile, as demonstrated by comparison of the calculated patterns for \( n = 5 \) (2\( r = 4.76 \) Å) and 6 (5.6 Å) with the observed patterns in Fig. 3b. The best fit was obtained for a mixture of pentagonal \((n = 5)\) and hexagonal \((n = 6)\) ice-nanotubes with small traces of square \((n = 4)\) and heptagonal \((n = 7)\) ice-nanotubes. The nearest-inter-polygon distance (1D lattice constant) is estimated to be \( d = 2.88 \) Å for both \( n = 5 \) and 6 at 100 K. A similar analysis has been made for the thicker SWNT samples with average diameters of 13.0, 13.5 and 13.8 Å. The profile for the 13.8 Å SWNTs, shown in Fig. 3c, is well reproduced as a superposition of three ice-nanotubes with \( n = 6, 7 \) and 8, consistently with the observed three transition temperatures of 280, 220 and 190 K. The 1D lattice constant is \( d = 2.88, 2.90 \) and 2.94 Å for \( n = 6, 7 \), and 8, respectively. In all the samples analyzed, the mean distance between the ice-nanotube and the SWNT wall, 3.5 ± 0.2 Å, agrees well with the result of MD calculations [3].

### 3.4. Transition temperature vs. SWNT diameter

The relationship between the cavity diameter \( D \) of SWNT and \( T_m \) is estimated in Fig. 4, where \( D \) is assumed
to be 3.5 Å larger than the ice-nanotube diameters. The $T_m$ in a glass capillary is also shown by the dotted line [2], where the $T_m$ depression from the bulk value is extrapolated down to $D \approx 2$ nm from the measurement range of $6 < D < 175$ μm using a well-established relationship, $\propto 1/D$. Although this relationship roughly predicts the magnitude of $T_m$ in the 14.4 Å SWNTs, the diameter dependence in SWNTs opposes this relationship. This suggests a cross-over from bulk to atomic-scale phenomena. It should also be noted that the $T_m$ above 273 K has never been observed except under high pressure. Because the quasi-1D nature usually destroys ordered structures [20], understanding of these observations requires a new mechanism for stabilization of ordered water molecules in the nano-space of SWNTs.

Now we briefly discuss the stability of ice-nanotubes. Many theoretical and experimental studies have reported [21–23] on the stability of ring structures in small isolated water clusters (H$_2$O)$_n$ with $n = 3, 4$ and 5. In bulk water, no specific isolated ring structures are stable, but many kinds of networks, including ring structures with $n = 5$ as well as 4, 6 and 7 are formed and dynamically convert to one another [6]. From this structural point of view, the proposed ice-nanotubes can be placed between the bulk water networks, and the interaction among the water molecules with the SWNT wall stabilize the polygonal ring structures inside SWNTs. The SWNT wall would cut out the bulk water networks, and the interaction among the water molecules with the SWNT wall stabilize the 1D lattice constant on $n$ with $n = 3, 4$ and 5. In bulk water, no specific isolated ring structures are stable, but many kinds of networks, including ring structures with $n = 5$ as well as 4, 6 and 7 are formed and dynamically convert to one another [6]. From this structural point of view, the proposed ice-nanotubes can be placed between the bulk water networks, and the interaction among the water molecules with the SWNT wall stabilize the polygonal ring structures inside SWNTs. Within such a model of ring stacking structures for ice-nanotubes, the stability may be related to that of isolated water ring clusters [21–23]. The observed small dependence of the 1D lattice constant on $n$ may be ascribed to that of the inter-ring interactions. In summary, consistency of the results of theoretical calculations [3,24] and the observed trends of the melting transition of ice-nanotubes inside SWNT is still qualitative, and further detailed consideration is needed for full understanding of their stabilities.

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