First-Principles Study of Water Nanotubes Captured Inside Carbon/Boron Nitride Nanotubes

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Supporting Information

ABSTRACT: Water confined to nanopores such as carbon nanotubes (CNTs) exhibits different states, enabling the study of solidlike water nanotubes (WNTs) and the potential application of their properties due to confined effects. Herein, we report the interfacial interaction and particular stabilized boundaries of confined WNTs within CNTs and boron nitride nanotubes (BNNTs) using first-principles calculations. We demonstrate that the intermolecular potential of nanotube walls exerts diameter-dependent additive or subtractive van der Waals (vdW) pressure on the WNTs, altering the phase boundaries. Our results reveal that the most stable WNT@CNT is associated with a CNT diameter of 10.5 Å. By correlating the stability of WNTs with interfacial properties such as the vdW pressure and vibrational phonon modes of confined WNTs, we decode and compare various synergies in water interaction and stabilized states within the CNTs and BNNTs, including interfacial properties of WNT@BNNTs that are more significant than those of WNT@CNTs. Our results suggest that the transition of a water tube to an ice tube is strongly dependent on the diameter of the confining CNT or BNNT, providing new insights on leveraging the interfacial interaction mechanism of confined WNTs and their potential application for fabricating nanochannels and nanocapacitors.

1. INTRODUCTION

The unique properties of water, a ubiquitous medium and exible hydrogen network, strongly depend on intermolecular interactions.1 The dipolar and hydrogen bonding interactions due to polar OH bonds are responsible for the phase behavior of water and also play a great role in supramolecular processes.1 Strong confinement of water leads to a modified hydrogen network, exhibiting unusual dynamic and structural properties.2 Scientists have proposed some ways to better understand interactions in water when it is confined to nanoscopic spaces.3,4 For instance, Kurotobi and Murata recently captured a single molecule of water inside a cage of buckminsterfullerene.5 Moreover, Thilgen studied a single water molecule trapped inside hydrophobic C60. Shultz et al. elucidated the local water structure by investigating local- and long-range responses of the hydrogen bond network that exists in water with the C60 surface. Intermolecular coupling and cooperative motion of water are indicative of hydrogen bond potential.6−10 Recent observation of a unique phase transition in water when confined to isolated carbon nanotubes (CNTs) provides evidence for ice nanotubes (INTs).11 However, interpretation of the experimental data requires quantum computational modeling. When water is confined to nanometer-sized channels and pores, such as graphene layers and CNTs, the intermolecular energy of the CNT wall exerts van der Waals (vdW) pressure on square-tube water, which is estimated to be in the gigapascal (GPa) range.12

Some computational techniques such as ab initio methods based on density functional theory (DFT)13 and quantum Monte Carlo have recently been used to investigate experimental results of two-dimensional ice.12,14 For instance, by DFT, Chen et al.13,15 found that at high pressure, square ice exhibited the lowest enthalpy phase, supporting the experimental claim. Moreover, at lower pressures, a “pentagonal ice” phase had the lowest enthalpy, while a “hexagonal ice” phase dominated a previous phase at ambient pressure.13

Using molecular dynamic simulation, Chakraborty et al.2 studied the diffusion of single water molecules confined to narrow CNTs, which exhibited solidlike ordering due to strong hydrogen bonding between nearest-neighbor molecules. Moreover, Sahu and Musharaf Ali investigated the behaviors of both polar and nonpolar fluid molecules within a CNT at the molecular level, reflecting the transport behavior of fluid molecules.16

In this paper, we employed first-principles calculations based on density functional theory (DFT) to probe the electronic properties of water nanotube (WNT) and to determine whether WNT stability, when confined inside CNTs and boron nitride nanotubes (BNNTs), was diameter dependent over a vast diameter range of 8−12 Å. Ab initio techniques
revealed that vdW pressure and phonon dispersion were the key features for phase behavior of a WNT inside either a CNT or a BNNT. It is worth noting that vdW interactions affected the interfacial behavior of the confined WNT, that is, encapsulated in CNT(BNNT) near the vdW boundary (hence the name vdW pressure). Moreover, the WNT had stronger interactions inside BNNTs than inside CNTs likely because of the polarizable structure of BN. Studies of local WNT interactions within nanotubes suggest that a picture of the state diagram for a WNT can be deduced from the vibrational spectrum of WNT. The interaction properties of water and carbon nanomaterials introduce practical applications in water desalination and treatment and in hydrogen storage.

2. COMPUTATIONAL METHODS

To study the structural and interfacial properties of WNT@CNTs and WNT@BNNTs, we carried out ab initio computation based on a density functional theory (DFT) technique implemented in the SIESTA package. The initial geometry optimization of DFT calculations was acquired using periodic boundary conditions (PBCs) within the generalized gradient approximation (PBE+D). The norm-conserving approach was used for Trouillier–Martins pseudopotentials and double-polarized atomic basis sets.

Figure 1. Optimized WNT@CNTs for (a) CNT(10,0), (b) CNT(13,0), and (c) CNT(14,0). (d) Total density of states (DOS) for semiconductor CNTs, that is, CNT(10,0), (11,0), (13,0), and (14,0). (e) Total DOS for metallic CNTs, that is, CNT(12,0) and (15,0).
al.12,13 reported the formation of double-layer ice in a nanoconfinement array, which is in agreement with monolayer and multilayer square ice observed by transmission electron microscopy experiments.14 Chen’s group carried out computations on randomly oriented water molecule structures, starting with pentagonal, hexagonal, square, and hexagonal-close-packed (HCP), in which the structures were nonconfined (ambient) and confined (high pressure).12

Table 1. Structural Analysis of Optimized Confined WNT@CNTs

<table>
<thead>
<tr>
<th>WNT@CNT</th>
<th>(10,0)</th>
<th>(11,0)</th>
<th>(12,0)</th>
<th>(13,0)</th>
<th>(14,0)</th>
<th>(15,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{inter}}$ (eV)</td>
<td>5.63(3.64)</td>
<td>−1.19(−4.45)</td>
<td>−2.93(−6.05)</td>
<td>−5.83(−12.02)</td>
<td>−2.01(−5.61)</td>
<td>−1.68(−5.38)</td>
</tr>
<tr>
<td>opt diameter (Å)</td>
<td>8</td>
<td>8.9</td>
<td>9.5</td>
<td>10.5</td>
<td>11</td>
<td>12.2</td>
</tr>
<tr>
<td>hydrogen bond (Å)</td>
<td>1.45</td>
<td>1.6</td>
<td>1.67</td>
<td>1.75</td>
<td>1.78</td>
<td>1.82</td>
</tr>
<tr>
<td>WNT net charge (e)</td>
<td>−0.28</td>
<td>−0.35</td>
<td>−0.14</td>
<td>−0.23</td>
<td>−0.18</td>
<td>−0.07</td>
</tr>
<tr>
<td>pressure (GPa)</td>
<td>0.13(0.28)</td>
<td>0.11(0.23)</td>
<td>0.09(0.20)</td>
<td>0.06(0.09)</td>
<td>0.07(0.11)</td>
<td>0.05(0.08)</td>
</tr>
<tr>
<td>band gap (eV)</td>
<td>0.61</td>
<td>1.02</td>
<td>0.1</td>
<td>0.53</td>
<td>0.74</td>
<td>0.09</td>
</tr>
<tr>
<td>pristine gap (eV)</td>
<td>0.82</td>
<td>1.11</td>
<td>0</td>
<td>0.53</td>
<td>0.74</td>
<td>0</td>
</tr>
</tbody>
</table>

“aThe numbers inside the parentheses were calculated by vdW-DF.

Table 2. Structural Analysis of Optimized Confined WNT@BNNTs

<table>
<thead>
<tr>
<th>WNT@BNNT</th>
<th>(10,0)</th>
<th>(11,0)</th>
<th>(12,0)</th>
<th>(13,0)</th>
<th>(14,0)</th>
<th>(15,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{inter}}$ (eV)</td>
<td>11.28(8.32)</td>
<td>0.68(−3.7)</td>
<td>−3.83(−9.36)</td>
<td>−4.6(−10.48)</td>
<td>−3.38(−8.77)</td>
<td>−2.13(−4.8)</td>
</tr>
<tr>
<td>opt diameter (Å)</td>
<td>8.26</td>
<td>8.76</td>
<td>9.5</td>
<td>10.52</td>
<td>11.21</td>
<td>12.2</td>
</tr>
<tr>
<td>hydrogen bond (Å)</td>
<td>1.42</td>
<td>1.48</td>
<td>1.62</td>
<td>1.72</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>electrical dipole ($p_x$)</td>
<td>0.09</td>
<td>0.18</td>
<td>0.08</td>
<td>0.04</td>
<td>0.2</td>
<td>0.42</td>
</tr>
<tr>
<td>TMA net charge ($</td>
<td>e</td>
<td>$)</td>
<td>−0.1</td>
<td>−0.07</td>
<td>−0.11</td>
<td>−0.15</td>
</tr>
<tr>
<td>pressure (GPa)</td>
<td>0.35(0.511)</td>
<td>0.243(0.396)</td>
<td>0.136(0.201)</td>
<td>0.081(0.125)</td>
<td>0.101(0.184)</td>
<td>0.077(0.11)</td>
</tr>
<tr>
<td>band gap (eV)</td>
<td>3.94</td>
<td>4.01</td>
<td>4.04</td>
<td>4.21</td>
<td>4.25</td>
<td>4.3</td>
</tr>
</tbody>
</table>

“aThe numbers inside parentheses were calculated by vdW-DF.

Figure 2. Variation of DOS for different CNTs in pristine and WNT@CNTs, that is, (a) CNT(10,0), (b) CNT(11,0), (c) CNT(12,0), (d) CNT(13,0), (e) CNT(14,0), and (f) CNT(15,0).
The phase diagram indicates that double-layer ice favors square-tube (interlayer hydrogen bonding) as the stable structure in the GPa regime. Moreover, Kumar et al. investigated the structural stability of one-dimensional ice nanotubes (INTs) using DFT. They considered four different INTs, namely, (4,0)-INT (square-tube), (5,0)-INT (pentagonal), (6,0)-INT (hexagonal), and (8,0)-INT (octagonal), with different lengths. They found that increasing the size of the ice tube enhanced the stabilization energy (SE). The calculated SE/H-bond was greater for (4,0)-INT (5.8 kcal/mol) than for (5,0)-INT (5.5 kcal/mol), indicating (4,0)-INT or square-tube water is the most stable structure.

Among the hexagonal, pentagonal, square-tube, and HCP structures, a square-tube structure creates interlayer hydrogen bonding (no lateral hydrogen bonding between tubes) in an AA stacking arrangement, as reported by Chen et al. Our goal was to investigate interfacial interactions and in particular the stability state of water within CNT/BNNTs and compare with the results reported by Agrawal et al. Their findings show that the single-walled carbon nanotubes with diameters 1.05 and 1.06 nm have a reversible freezing transition to $105 - 151$ and $87 - 117$ °C, respectively. However, interpretation of the experimental data requires quantum computation.

3. RESULTS AND DISCUSSION

Experimental observation that a unique phase transition of water occurs when confined to isolated CNTs provides evidence for ice nanotubes, predicting to be extremely sensitive to the diameter of the CNT confining the water. Agrawal et al. studied the phase boundaries of water when confined to several isolated carbon nanotubes of different diameters using Raman spectroscopy. Their findings show that the single-walled carbon nanotubes with diameters 1.05 and 1.06 nm have a reversible freezing transition to 105–151 and 87–117 °C, respectively. However, interpretation of the experimental data requires quantum computation.
Our goal in this paper was to correlate the relative stability and vdW pressure of confined WNTs and compare with previous experimental observations. In this regard, we started with square-tube water, which is the most stable structure in the GPa regime.\textsuperscript{12,24} The CNTs investigated in this study were zigzag by their chiral indices $(n,0)$ for the following reasons. First, Liu et al.\textsuperscript{25} reported the effect of CNT topology on the diffusion dynamics of water confined in zigzag and armchair CNTs. They found that the diffusion of water molecules was slower in zigzag CNTs than in armchair CNTs, consequently causing the water to behave in a solidlike phase.\textsuperscript{25} Second, Liu et al.\textsuperscript{26} investigated the transport properties (diffusivity, thermal conductivity, and shear viscosity) and molecular distribution of water molecules confined in CNTs. The pore diameter, the potential of the confining wall, and the helicity of CNTs significantly affected the state of water. The structure of water, the ordered layer of water, and the solidlike behavior of water in CNTs were dominant in zigzag CNTs.\textsuperscript{26,27} Third, we performed periodic boundary calculation (PBC) for infinite WNTs and CNTs, in which the periodic bond length of the WNT matches well with that of the zigzag CNT, as long as the armchair chirality did not commensurate with infinite WNT geometry.

Square-tube water or WNT not only has the proper geometry relevant to CNT, but also has a larger number of interlayer hydrogen bonding; therefore, WNT offers the perfect starting point. WNT as an exclusive water structure is an insulator, indicating a band gap of $E_g \approx 6$ eV with a 1.72 Å hydrogen bond length. In the Supporting Information, we carried out first-principles calculation on armchair CNTs, comparing with zigzag CNTs. Since no covalent bonding between WNTs and CNTs is established for a physisorbed
3.1. WNT@CNT. We first examined WNTs located inside different CNTs by using ab initio computations. We focused on the interfacial properties of WNTs trapped inside CNTs of different diameters, starting with a detailed description of the optimized structures for the square-tube WNT@CNT (Figure 1).

For the intermolecular energy of WNT@CNTs, we used supercells in which CNT(10,0) contained 160 C atoms; CNT(11,0) 176 C atoms; CNT(12,0) 192 C atoms; CNT(13,0) 208 C atoms; CNT(14,0) 224 C atoms; and CNT(15,0) 240 C atoms. Then, 24 water molecules (72 atoms) were inserted inside each CNT. Table 1 shows the DFT results in terms of the intermolecular energy ($E_{\text{inter}}$), the optimized CNT diameter ($d$), the hydrogen bond length, the net Mulliken charge on water, and the intermediate pressure ($P = \frac{\sum F_{ij}}{A}$, in which $F_{ij}$ is the force on the $i$th atom of the adsorbate due to the $j$th atom of the substrate and $A$ is the substrate area) exerted on the WNT by the CNT. With regard to evaluating the adsorption energy and the relative stability of the different CNTs, we performed vDW-DF by considering dispersion into the DFT calculations (Tables 1 and 2). It is
also well known that this correction will mainly affect the total energy (increased total energy and band gap) but that the electronic structure of the system will remain essentially intact. In addition, a previous comparison between local density approximation (LDA) and GW approaches on graphene clearly showed that the band structures were similar except for an energy shift in GW with respect to LDA.

The trends presented in Table 1 are straightforward: (i) CNT(13,0) is the most stable structure, followed by CNT(12,0), (14,0), (15,0), and (11,0), whereas CNT(10,0) is unstable with positive energy adsorption; (ii) the hydrogen bond length increases from CNT(10,0) to (15,0); (iii) intermediate pressure peaks on the WNT by unstable CNT(10,0) (\( P = \sum F_{ij} / A \)), in which \( F_{ij} \) is the force on the \( i \)th atom due to the \( j \)th atom in the WNT and \( A \) is the WNT area), whereas it decreases for the most stable WNT@CNT(13,0); and (iv) the net charge is more important for the unstable case, that is, CNT(10,0), and for the metastable case, that is, CNT(11,0).

To summarize the data presented in Table 1, the most stable WNT is CNT(13,0), in which the vdW pressure on the water tube is less important. Furthermore, such a vdW pressure breaks WNT hydrogen bonds (1.45 Å) and facilitates an overlap (donation) between oxygen atoms and CNTs, making the WNT more polarized. However, the inverse mechanism, in which the vdW pressure is smaller for CNT(12,0) and (13,0) than for unstable (11,0) and metastable (10,0), facilitates the intramolecular energy of the WNT to create hydrogen bonds (1.75 Å) and exhibit a stabilized solidlike state. Consequently, this mechanism would also be consistent for larger CNTs such as (14,0) and (15,0). We analyzed the phonon dispersion as well as electronic structure properties of a water tube within CNTs in the following section.

### 3.1.1. Electronic Properties

We calculated a small charge transfer from CNTs to WNTs, confirming that no covalent bonding exists between the two species. To clarify the influence of WNTs on the electronic structure of CNTs, we present the total density of states (DOS) of WNT@CNT.
compared with the DOS of a pristine CNT (Figure 2). First, the direct comparison of DOS for WNT@CNT with that for a pristine CNT shows that CNT(10,0) and (11,0) are more affected by the water tube when it is around the Fermi level than other CNTs. Intermolecular interactions of the water tube perturbed the electronic states of CNT(10,0) and (11,0); for example, electron-withdrawing oxygen atoms of water result in the transfer of some electrons from the valence band of the CNT to the water tube. Hence, the DOS of the WNT@CNT system is slightly shifted below the Fermi energy of an isolated CNT as a reference. This Fermi energy shifting (Figure 1, panels d and e) proves p-doping of the CNT, confirming charge transfer from the CNT to the WNT by values shown in Table 1. The electronic properties of WNT@CNT(12,0), (13,0), (14,0), and (15,0) are also consistent with the results obtained for the intermolecular energy reported in Table 1, revealing that the formation of highly directional hydrogen bonds makes the WNT the most stabilized state.

To check and compare electronic properties of our model, we calculated band structures of the six systems with respect to a pure CNT, shown in Figure 3. A small but systematic band gap closing in the CNT is observed for semiconductor CNTs such as CNT(10,0), (11,0), (13,0), and (14,0), and band gap opening is observed in metallic CNTs such as CNT(12,0) and (15,0) (Figure 3). The latter results suggest that such an intermolecular interaction between water and the CNT improves the overlap and mixing between O (water) and C atoms (CNT) states, to finally introduce a band gap in the CNT through a local electronic perturbation by O atoms.29−31

To calculate phonon dispersion at points of high symmetry in the Brillouin zone, we performed lattice dynamics to consider phonon frequency modes. Phonon dispersion plots of WNTs within CNTs are depicted in Figure 4, where an isolated WNT is plotted for comparison. The calculated phonon of an isolated WNT is in good agreement with the experimental phonon band dispersion reported by Lyo and co-workers.32 Figure 4 shows variation of the vibrational phonon modes for WNTs inside CNTs, giving additional details on the intermolecular interaction. Concerning stability, existence of negative phonon vibrations for both CNT(10,0)—the most
unstable system—and CNT(11,0) for the metastable system supports our DFT results presented in Table 1. Second, we observed that splitting occurs for low frequency (long wavelengths, acoustic modes) for almost all WNTs inside the CNTs. WNT can be considered a polar structure (see Figure S2), which affects its interfacial properties inside a CNT, creating an interior electrical field and broken symmetry. The long range of Coulomb interactions between the water tube (a square bonded polar system) with the CNT causes splitting of the long wavelength. The origin of the splitting is the interior electrical field created by the natural polarity existing in the WNT, in line with previous reports for ice systems.33

Third, there are some band gaps or stop bands in the frequency spectra due to the nonunity mass ratio of water tubes.33 The dispersion of bands is strongly influenced by the intermolecular interaction of WNTs trapped inside CNTs, while the stop bands (band gap) are being shifted. The phonon group velocity related to the slope of dispersion curves in the phonon spectrum gives information about atomic mobility. For instance, flat bands lead to slower group velocity and atomic mobility, while dispersed bands cause higher atomic mobility (orientational mobility).

These plots inform the fact that dispersed bands lead to higher atomic mobility (orientational mobility), while flat bands indicate more localized carriers.30 Analysis of these phonon spectra shows that the lower frequency or acoustic phonons for all WNT@CNTs include more dispersed bands or higher atomic mobility than what appears in the phonon spectrum for isolated WNTs. This finding suggests that confined WNTs within CNTs can modulate the electronic properties of the CNT due to the intermolecular interaction between them, improving the correlation between electrons and confirming our DFT results about band gap closing in the system. However, larger frequency or optical phonons belong to both isolated WNTs and WNT@CNTs, considering the low phonon group velocity or atomic mobility. Therefore, these phonon bands support the notion that isolated and
confined WNTs exhibit localized, slow electron mobility or, in other words, behave solidlike, in close agreement with previous observations.\textsuperscript{1,2,14}

Figure 5 is a schematic of the state diagram vs intermolecular energy of WNT@CNTs and the interfacial pressure for CNTs of different diameters. The blue diamonds plot the intermolecular energies of different systems, showing WNT@CNT(10,0) is unstable, WNT@CNT(11,0) is metastable, and WNT@CNT(13,0) is the most stable structure. In this regard, black triangles plot the vdW pressure exerted on a WNT in different CNTs, showing how the pressure varies with CNT diameter. The unstable system, that is, WNT@CNT(10,0), suffers from high pressure (∼0.3 GPa), while for the most stable system, that is, WNT@CNT(13,0), the pressure is decreased to ∼0.1 GPa.

3.2. WNT@BNNT. Encouraged by our results described above and in order to evaluate the influence of a WNT confined within a BNNT, we constructed a system with square-tube water (WNT) inside a BNNT. BNNTs are promising candidates for water desalination\textsuperscript{34} and biological nanochannels due to their wettability character.\textsuperscript{35} Hence, we compared interfacial properties of WNTs confined in CNTs or in BNNTs, which are of extreme interest from both scientific and technological standpoints. To compare results from BNNTs with those from CNTs, we chose the same supercell used to study CNTs for BNNTs. For the intermolecular energy of WNT@BNNTs, we used supercells in which the BNNT(10,0) contained 160 B,N atoms; BNNT(11,0) 176 B,N atoms; BNNT(12,0) 192 B,N atoms; BNNT(13,0) 208 B,N atoms; BNNT(14,0) 224 B,N atoms; and BNNT(15,0) 240 B,N atoms, in which 24 water molecules (72 atoms) had been inserted inside each BNNT (Figure 6). The first interesting properties to compare between WNT@CNTs and WNT@BNNTs remain the intermolecular energy ($E_{\text{inter}}$) and vdW pressure, as Table 2 reports the DFT structural parameters for WNT@BNNTs. The same trend observed for WNT@CNT systems, flat bands indicate more localized carriers, which cause strong intermolecular interaction between the water tube and BNNTs. These results are consistent with DFT intermolecular energies presented in Table 2.

Second, the distribution of stop bands (no phonon wave propagation) differs with that of the isolated WNT, in which the stop bands are shifted up and become wider and denser for larger tubes. The phonon group velocity of flat bands related to the slope of the flat dispersion curves becomes smaller or zero when the branches are completely at something missing here, leading to localized intermolecular interactions between the WNT and the BNNT. These flat bands originate from the insulator feature of BNNTs and dipole–dipole interactions between the water tube as a polar system and the BNNT.

Figure 10 is a schematic of the state diagram vs the intermolecular energy of the WNT@BNNTs and interfacial pressure for BNNTs of different diameters. The blue diamonds plot the intermolecular energies of different systems, showing WNT@BNNT(10,0) is unstable, WNT@BNNT(11,0) is metastable, and WNT@CNT(13,0) is the most stable structure. In this regard, black triangles indicate the vdW pressure exerted on the WNT in different BNNTs, showing how the pressure varies with the BNNT diameter. The unstable system, that is, WNT@BNNT(10,0), suffers from high pressure (∼0.5 GPa), while for the most stable system, that is, WNT@BNNT(13,0), the pressure is decreased to (∼0.1 GPa).

4. CONCLUSIONS

In summary, our comprehensive theoretical computations revealed that considerable intermolecular interactions and vdW pressure exist between a water tube and a CNT/BNNT and demonstrated that the phase behavior of the water tube captured within a CNT or BNNT is diameter dependent. The state diagram of this system shows that decreasing the vdW pressure helps stabilize a square water NT, converting it to an ice NT. The vdW pressure is 0.3(0.5) GPa for the most unstable system, that is, CNT/BNNT(10,0), which decreases to 0.09(0.12) GPa for the most stable system, that is, CNT/BNNT(13,0). The interfacial properties of WNT@BNNT are stronger than those of CNTs.

The phonon calculation of different WNT@CNTs/BNNTs compared with an isolated square-tube water confirmed that (10,0) CNT/BNNT is unstable, while (11,0) is metastable.
with negative phonon bands. However, the remaining structures are stable, and CNT/BNNT(13,0) is the most stable system with a diameter of 10.5 Å, in line with experimental observation.11 Our results suggest that the water tube transition to ice NT is strongly diameter dependent. This work suggests that the intermolecular interaction between a WNT and a hydrophobic CNT/BNNT could lead to the design and fabrication of nanometer-scale capillaries.

### ASSOCIATED CONTENT

© Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b00856.

Water nanotube encapsulated in armchair carbon nanotube; structural analysis; optimized WNT between armchair CNTs (PDF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The supercomputer machines utilized in this work were supported in part by the NIH award NCRR S10RR02950 and an IBM Shared Rice University Research (SUR) grant.

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