Silicon Carbide Nanotube as a Chloride-Selective Channel

Tamsyn A. Hilder,*^{,†} Rui Yang,^{†,‡} Dan Gordon,[†] Alistair P. Rendell,[‡] and Shin-Ho Chung[†]

[†]Computational Biophysics Group, Research School of Biology, Australian National University, ACT 0200, Australia

[‡]Computer Science, Faculty of Engineering and Information Technology, Australian National University, ACT 0200, Australia

Supporting Information

ABSTRACT: Using several computational techniques, we examine the conduction of water and ions through single-wall nanotubes of various radii, constructed from silicon carbide (SiC). In particular, using classical molecular dynamics, we examine the rate of water and ion conduction through the (5, 5), (6, 6), and (7, 7) SiC nanotubes 36 Å in length. We then determine the current–voltage–concentration profiles using distributional molecular dynamics. The (5, 5) SiC nanotube rejects all ions and conducts water an order of magnitude faster than aquaporin and current reverse osmosis membranes. As expected, the water conduction is shown to increase with increasing diameter, but ions are no longer rejected. In fact, the (6, 6) and (7, 7) SiC nanotubes are shown to be chloride-selective with a conduction of 4.1 and 6.2 pA, respectively, under an applied potential of 200 mV.



INTRODUCTION

Nanotubes, with their nanoscale diameters and simple surface chemistry, present a promising candidate to mimic some of the key functions of biological ion channels. These nanotubes could lead to potential applications in the pharmaceutical and desalination industries. Given the rapid advances in the methods of fabricating nanomaterials, it may only be a matter of time until practical nanodevices, which are less complex than biological systems but possess the functionality of membrane ion channels, are successfully created and widely utilized.

Although carbon nanotubes^{1,2} have received the most attention, nanotubes can also be fabricated from materials such as boron nitride³ and silicon carbide.^{4,5} To date, researchers have successfully designed and fabricated water- and ion-selective nanotubes constructed from carbon^{6–14} and boron nitride^{12,15–17} atoms. Hilder et al.¹³ design a chloride-selective carbon nanotube with carbonyl ends that has a chloride conduction 4 times larger than the ClC-1 biological chloride channel. Recently, Lee et al.¹⁴ were able to fabricate single-wall carbon nanotube ion channels which were selective to protons.

Silicon carbide (SiC) nanotubes are a new class of nanotube, first synthesized⁴ in 2001, and are yet to be investigated as an ion-selective nanopore. Bulk silicon carbide has long been used in mechanical and electronic devices due to its unique physical and electronic properties such as high strength and high thermal conductivity. Therefore, silicon carbide nanotubes hold promise as alternate nanopores to carbon. For example, silicon carbide nanotubes have demonstrated improved hydrogen storage compared to carbon nanotubes.¹⁸ In recent work we investigated, using first principles, the water structure with various sized SiC nanotubes.¹⁹ The structure and properties of water molecules within SiC nanotubes were shown to be similar to the corresponding carbon nanotubes.¹⁹ Moreover, Khademi and Sahimi²⁰ examine water flow through SiC nanotubes using molecular dynamics simulations. They find that water flow is enhanced in SiC nanotubes when compared to carbon nanotubes

and that smaller pressure gradients are required to achieve this enhancement. $^{\rm 20}$

Using a number of computational techniques, we investigate the water and ion conduction behavior of SiC nanotubes with different pore radii. We first construct models of single-walled, armchair-type, tubular-shaped nanotubes of various radii by rolling up a hexagonal array of alternating silicon and carbon atoms. Molecular dynamics simulations are then used to investigate the free energy of ions as they traverse the nanotube and determine the rate of water conduction. In addition, using distributional molecular dynamics (DMD)²¹ which combines classical molecular dynamics with stochastic dynamics, we further investigate the ion permeation through the nanotubes at time scales of 0.8 μ s.

We demonstrate that the (5, 5) SiC nanotube rejects all ions, and the (6, 6) and (7, 7) SiC nanotubes are exclusively selective to chloride ions. These nanotubes present advantages over carbon nanotubes for ion selective membranes since chemical functionalization of their surface is not required to achieve selectivity.

THEORETICAL CALCULATIONS

Nanotube Construction. SiC nanotubes are constructed from a hexagonal array of alternating silicon and carbon atoms. The hexagonal array is then rolled up to form a tubular structure, as illustrated schematically in Figure 1A and with physical properties given by Dresselhaus et al.²² All nanotubes are defined by their chiral vector, $C = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m)$, where \mathbf{a}_1 and \mathbf{a}_2 represent the unit vectors of the hexagonal lattice and n and m are integers. There are three types of nanotubes, namely zigzag (n, 0), armchair (n, n), and chiral (n, m),²² but

Received:November 24, 2011Revised:January 30, 2012Published:February 2, 2012



Figure 1. Schematic illustration of (A) a typical nanotube with a single-file chain of water molecules and (B) the nanotube embedded in a lipid bilayer separating two reservoirs containing water molecules. A constant force f is applied to region labeled A. For clarity, only a small portion of water molecules in the upper and lower reservoirs is shown.

here we consider only armchair type nanotubes. Specifically, we investigate (5, 5), (6, 6), and (7, 7) nanotubes embedded in a lipid bilayer, as shown in Figure 1B, with a total length of ~36 Å.

The silicon and carbon atoms forming each nanotube acquire a partial charge. All SiC nanotube structures show significant charge transfer of 0.6 *e* from silicon to carbon atoms owing to the more electronegative carbon atoms.²³ We thus use the partial charge of $\pm 0.6 e$ for our simulations on these structures.

The SiC nanotube structure has been shown to buckle.^{24,25} It is therefore important to determine their equilibrium structure using *ab initio* simulations. The SiC nanotube is initially constructed using a bond distance of 1.80 Å,²⁶ and the structures are subsequently optimized using *ab initio* molecular dynamics, namely Car–Parrinello molecular dynamics (CPMD).²⁷ This is a plane-wave pseudopotential implementation of density functional theory. The unit cell length in CPMD is set to $15 \times 15 \times 14.76$ Å³ (15 Å was found to be sufficiently large to avoid spurious image effects on the total energy). The CPMD optimization is performed with the BLYP generalized gradient approximation functional, with a fully nonlocal norm-conserving Troullier–Martins pseudopotential in the Kleinman–Bylander separable form.

We also investigate the binding energies of a single water molecule confined in the SiC nanotubes. The binding energy is determined by using the ω B97XD hybrid functional with dispersion correction and basis set superposition error (BSSE) correction as implemented in Gaussian 09.²⁸ The 6-311+g** basis and 6-31g* basis are used for the water and nanotube, respectively.

Molecular Dynamics. Molecular dynamics (MD) simulations are performed using NAMD²⁹ and visualized using VMD.³⁰ The MD domain consists of a nanotube embedded in a POPE (palmitoyloleoylphosphatidylethanolamine) lipid bilayer between two reservoirs containing water and ions (sodium and chloride), as illustrated in Figure 1b. The CHARMM27 force field^{31,32} and the TIP3P water model are used in all simulations. The system is replicated periodically in all three dimensions, and particle mesh Ewald electrostatics³³ is used. The POPE membrane is chosen as the embedding material for the reason that it would not have an influence on the water conduction within the nanotube and to draw a direct comparison to the results of aquaporin. MD simulations are used to (i) determine the potential of mean force (PMF) of both a sodium and a chloride ion moving through each of the nanotubes and (ii) examine water and ion conduction under the influence of a hydrostatic pressure. We refer the reader to the Supporting Information for details of these MD simulations.

Distributional Molecular Dynamics. Distributional molecular dynamics (DMD), which combines molecular and stochastic dynamics,²¹ enables the permeation of ions across these artificial channels to be determined at long time scales which would require considerable computing hours to determine using MD simulations. Using this method, we are able to obtain ion conduction data at time scales much larger than possible with MD. The theoretical basis for this procedure and a detailed test using gramicidin A is given by Gordon et al.²¹ and has been used previously to investigate the ion selectivity of boron nitride nanotubes embedded in a silicon nitride membrane¹⁷ and chloride-selective carbon nanotubes.¹³

The three-dimensional free energy profile (or PMF) determined from MD simulations, and the distribution of frictional and random forces that are measured over discrete segments of the channel, are incorporated into the DMD simulations based on the nonlinear generalized Langevin equation, which is given by

$$\frac{\partial}{\partial t} \mathbf{q}(t) = m^{-1} \mathbf{p}(t)$$
(1a)
$$\frac{\partial}{\partial t} \mathbf{p}(t) = \mathbf{F}_{\mathbf{D}}(\mathbf{q}(t)) - \int_{0}^{t} dt' K(t') \mathbf{p}(t-t') + \mathbf{F}_{\mathbf{R}}(t)$$

(1b)

where *m* is the mass and $\mathbf{q}(t)$ and $\mathbf{p}(t)$ are the coordinate and momentum at time *t*, respectively. Here, \mathbf{F}_{D} represents the deterministic force or free energy, the second term is the frictional force in which K(t) is the friction kernel determined from MD, and \mathbf{F}_{R} is the random force. The PMF is determined using the weighted histogram analysis method, as described previously. The data gathered for the weighted histogram analysis method is also used to determine the friction kernel, K(t). For each ion trajectory we determine the momentum autocorrelation function C(t) and derive K(t) by numerically solving

$$\frac{\partial}{\partial t}C = -\int_0^t K'(t-t')C(t') \, \mathrm{d}t' \tag{2}$$

The inverse velocity decay time due to friction, γ , is then determined as the time integral of K(t) from t = 0 to $t = \infty$.

Note that the diffusion coefficient *D* can be determined using γ and the Einstein relation $D = kT/(m\gamma)$. Thus, using this relation, we can represent the diffusion coefficient within the tube. We then assume the friction kernel can be approximated by an exponential function, thus

$$K(t) = \gamma \kappa \exp(-\kappa t) \tag{3}$$

so as to determine the inverse decay time of the friction memory kernel, κ . The random force F_R is assumed to be Gaussian and is related to the friction kernel using the fluctuation–dissipation theorem, given by

$$\langle F_{\mathbf{R}}(0)F_{\mathbf{R}}(t)\rangle = kTK(t)m \tag{4}$$

The simulation space is divided into two regions, namely a channel region and a bulk region consisting of two reservoirs. The channel region extends 9 Å in the z-direction from each end of the nanotube. In the channel region, the nonlinear generalized Langevin equation eq 2 is solved using the threedimensional PMF and friction kernel determined from MD. In the channel region we use a shorter time step, and in our simulations we use a time step of 1 fs. In the bulk region, normal Brownian dynamics and macroscopic electrostatics is performed with a longer time step, in this case 100 fs. The entire simulation space is approximately 100 Å by 50 Å. A fixed dielectric boundary between the nanotube/lipid system and the bulk/channel region is defined by embedding a cylindrically symmetric idealization of the shape of the channel within a dielectric slab that represents the lipid bilayer. Boundaries are treated as being perfectly elastic at the edges of the reservoirs, with a stochastic boundary being used to maintain the ionic concentration at the top and bottom reservoir. For more detail we refer the reader to ref 21.

Investigations of ion permeation using DMD are generated at a voltage of 200 mV and an ionic concentration of 500 mM. The current at this voltage and concentration is then calculated using the relationship $I = qn/\Delta t$, where *n* is the average number of ions that cross the membrane, *q* is the charge of the ion, and Δt is the simulation time of one run (8 × 10⁶ timesteps or 0.8 μ s).

RESULTS AND DISCUSSION

SiC Nanotube Optimized Structures. The equilibrium configurations of the SiC nanotubes give a silicon-carbon bond length of 1.792 Å, which are in good agreement with other ab initio results.²⁶ As reported in previous work,²⁶ the more electronegative carbon atoms are located further from the tube axis compared to silicon atoms after relaxation. This structure is reminiscent of that seen for group III nitride nanotubes where the more electronegative nitrogen atoms are located further from the tube axis relative to the group III atoms.³⁴ This buckling effect is more pronounced in smaller diameter nanotubes as shown in Table 1, and this compares well with the work of Alam and Ray.^{24,25} Radial buckling is calculated by subtracting the mean silicon radius from the mean carbon radius. The diameter of the nanotube is defined as the average diameter of silicon and carbon atoms in the SiC nanotube, and this is also listed in Table 1. The resulting optimized structures are used in subsequent molecular dynamics simulations.

Energy Landscape Encountered by lons. Figure 2A shows the free energy profiles a sodium ion encounters as it traverses across nanotubes of three different radii constructed from silicon–carbide atoms. The height of the free energy profile decreases rapidly as the diameter of the nanotube

Table 1. Diameter and Extent of Buckling of the SiC Nanotubes

nanotube type	diameter (Å)	buckling (Å)
(5, 5) SiC	8.590	0.090
(6, 6) SiC	10.293	0.070
(7, 7) SiC	11.997	0.057



Figure 2. Free energy profile for (A) sodium and (B) chloride ions inside (n, n) SiC nanotubes.

increases. For example, the barrier height for sodium ions decreases from 90 to 40 kT and then to 10 kT, as the diameter is increased.

A similar set of the free energy profiles for chloride ions traversing the pore are displayed in Figure 2B. Chloride ions exhibit a smaller energy barrier than sodium ions with the barrier height reducing from approximately 15 to 3 kT as the diameter is increased. For the larger nanotubes we considered, the barrier height is sufficiently low that some ions may overcome the barrier and easily move through them.

As shown in Figure 2, the interiors of all the nanotubes examined here are inhospitable to charged particles. As an ion attempts to traverse the pore, it faces a steeply rising energy barrier, with the height of this barrier remaining fairly constant throughout the pore. In bulk water ions are usually bound by

The Journal of Physical Chemistry C

between four and six water molecules. The energy cost of removing these water molecules from this tightly bound hydration shell (cost of dehydration) is higher for a sodium ion. As a result, the magnitude of the energy barrier encountered by a sodium ion is larger than that of a chloride ion.

In all cases the barrier height is systematically reduced as the diameter of the tube is stepwise increased. For the smaller diameter nanotubes, the ion must be stripped of water from its first hydration shell which comes at an energy cost.¹¹ As the nanotube diameter increases, the tightly bound water molecules in the first hydration shell can remain intact, thus reducing the energy barrier encountered by the permeant ions. Thus, the reduction in the height of the barrier with an increasing pore radius reflects the net changes in the water—ion geometry as hydrated ions move inside of the pore.

The variation in energy barrier between sodium and chloride ions reflects the difference between the interaction between the water molecules and atoms forming the nanotubes. As mentioned, the buckled structure of the SiC nanotubes results in the positively charged silicon atoms being located closer to the tube axis. Therefore, the nanotube interior is more favorable to chloride ions.

Ion Conduction Characteristics. Initially, we investigate the conduction of ions traversing these tubes using molecular dynamics. In particular, we investigate the ion conduction through the (6, 6) and (7, 7) SiC nanotubes under the influence of a hydrostatic pressure of 150 MPa (see Methods) and with an ionic concentration of 500 mM. In our 5 ns simulation, no sodium ions were found to conduct across either tube, but both tubes allow some chloride ions to pass. In particular, we find 1.5 and 3 chloride ions traverse the (6, 6) and (7, 7) SiC nanotubes in the 5 ns simulation. Moreover, both the (6, 6) and (7, 7) nanotubes conduct a large number of water molecules, 164 and 524 water molecules in the 5 ns simulation, respectively.

Using DMD, we are able to investigate the conduction of ions across all tubes studied for times of 0.8 μ s, a much larger time scale than possible with MD. Both the (6, 6) and (7, 7)SiC nanotubes allow chloride ions to move across the membrane. Figure 3A illustrates the current-voltage profile of chloride ions at an ionic concentration of 500 mM for the (6, 6) and (7, 7) SiC nanotubes. For both nanotubes the current increases linearly with applied potential, with a current of 1.6 and 2.2 pA at 100 mV, respectively. These currents are a similar magnitude to those obtained from the biological chloride channels, ClC-1 and GABA_A, at the same applied potential, 1.8 and 4.6 pA, respectively.^{35,36} By fitting a linear regression to the data points, we obtain a conductance of 21.0 ± 0.7 and $34.2 \pm$ 1.7 pS for the (6, 6) and (7, 7) SiC nanotubes, respectively. No sodium conductance was observed for all investigated voltages and concentrations for the (6, 6) SiC nanotube. A negligible sodium conductance was observed for the (7, 7) SiC nanotube (0.04 pA at 300 mV and 500 mM NaCl concentration). We also examined the ion conduction through the (5, 5) SiC nanotube using DMD simulations and found that no ions traverse the nanotube for applied potentials as large as 300 mV.

Figure 3B illustrates the current-concentration profile of chloride ions at an applied potential of 200 mV for the (6, 6) and (7, 7) SiC nanotubes. The current is shown to increase with increasing concentration, following a linear relationship rather than Michaelis-Menten form.

As mentioned, due to their buckled structures, SiC nanotubes exhibit a slightly positively lined pore. As a result, their



Figure 3. Ion conduction through the nanotubes. (A) Current– voltage profile for chloride generated at an ionic concentration of 500 mM and (B) current–concentration profile for chloride generated at an applied potential of 200 mV. Each data point represents the average of five sets of simulations each simulation lasting 8×10^6 timesteps (0.8 μ s). Error bars represent one standard error of the mean, and error bars smaller than the data points are not shown.

interior is more favorable for anions. Thus, as the nanotube increases above a critical radius so that hydration energy is reduced chloride ions conduct. Sodium ions continue to be rejected. Unlike the carbon nanotube, this effect is achieved without the need to functionalize the nanotube surface. This simplicity in structure represents a significant advantage for manufacturing an ion-selective nanodevice.

The (7, 7) SiC nanotube has a larger chloride conductance than the (6, 6) SiC nanotube (Figure 3A). This is due to the increased number of water molecules, and therefore water chains, within the nanotube. On average, at any given time there are more chloride ions present in the (7, 7) SiC nanotube than the (6, 6) SiC nanotube. For example, at an applied potential of 300 mV there are on average 0.03 and 0.09 chloride ions present in the (6, 6) and (7, 7) SiC nanotubes, respectively. **Water Conduction.** Table 2 shows the water conduction for all nanotubes at a hydrostatic pressure of 100 MPa. As expected, water conduction increases with increasing diameter. Corry¹¹ observe a similar trend for carbon nanotubes. Furthermore, similar to Corry,¹¹ we also note that conductance increases as the number of water chains in the pore increases. Table 2 also shows the BSSE corrected binding energy of a

Table 2. Water Conduction at 100 MPa and BSSE Corrected Binding Energy for the (n, n) SiC Nanotubes

nanotube type	conduction (no. water molecules/ns)	binding energy (eV)
(5, 5) SiC	17.16	-0.060
(6, 6) SiC	32.33	-0.029
(7, 7) SiC	69.26	-0.011

single water molecule confined in the SiC nanotubes.¹⁹ As the nanotube diameter increases, water conduction increases, and the binding energy decreases. We also ran for a range of pressures (data not shown) and found that, as expected, conduction increased with increasing pressure. To compare more directly with aquaporin and reverse osmosis membranes, we determine an osmotic permeability, p_{θ} for the three nanotubes using

$$\frac{j_n}{\Delta P} = \frac{p_f}{kT} \tag{5}$$

where j_n is the number of water molecules per second, ΔP is the pressure difference (see Theoretical Calculations), k is Boltzmann's constant, and T is the absolute temperature in kelvin. We obtain an osmotic permeability of $(7.34 \pm 0.55) \times 10^{-13}$, $(13.83 \pm 0.56) \times 10^{-13}$, and $(29.63 \pm 0.92) \times 10^{-13}$ cm³/s for the (5, 5), (6, 6), and (7, 7) SiC nanotubes, respectively. All tubes exhibit an osmotic permeability an order of magnitude larger than both aquaporin and currently used reverse osmosis membranes. In particular, aquaporin³⁷ has an osmotic permeability of $(7.1 \pm 0.9) \times 10^{-14}$ cm³/s, and the FILMTEC SW30HR-380 premium grade seawater reverse osmosis element produced by Dow Water Solutions³⁸ achieves an osmotic permeability of 7.66×10^{-14} cm³/s, assuming a pore density equal to the carbon nanotube embedded membrane $(2.5 \times 10^{15} \text{ pores/m}^2).^{39}$

As a result of the near frictionless interior of the nanotube, water conduction is expected to be largely length independent as suggested previously.^{6,11} Water conduction is primarily limited by the energy barriers at the entry and exit of the nanotube pore.⁶

CONCLUSIONS

Using a combination of molecular dynamics and distributional molecular dynamics, we determined the water and ion conduction through SiC nanotubes of various sizes. The use of distributional molecular dynamics enabled us to examine ion conduction at much larger time scales than using molecular dynamics (order of microseconds compared to nanoseconds). SiC nanotubes are a new class of nanotube and are yet to be investigated as a water conducting or ion-selective nanopore.

We find that the (6, 6) and (7, 7) SiC nanotubes are exclusively selective to chloride ions, and the (5, 5) SiC nanotube rejects all ions. The current is shown to increase linearly with both voltage and concentration. By fitting a linear regression to the current–voltage curve, we obtain chloride

conductances of 21.0 ± 0.7 and 34.2 ± 1.7 pS for the (6, 6) and (7, 7) SiC nanotubes, respectively. The current of both these nanotubes is a similar magnitude to the ClC-1 and GABA_A biological chloride channels. These channels could lead to applications in pharmaceuticals, for example as an antibiotic similar to gramicidin.

The water conduction rates of all the nanotubes studied in this paper are predicted to be an order of magnitude greater than those obtained in aquaporin and in current RO membranes. Moreover, as the nanotube diameter increases, water conduction increases and the binding energy of a single water molecule decreases. Because of its ability to reject all ions, the (5, 5) SiC nanotube presents a possibility for use in a desalination device.

ASSOCIATED CONTENT

S Supporting Information

Details of the MD simulations used to (i) determine the potential of mean force (PMF) of both a sodium and a chloride ion moving through each of the nanotubes and (ii) examine water and ion conduction under the influence of a hydrostatic pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tamsyn.hilder@anu.edu.au.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the support from the National Health and Medical Research Council and the Medical Advances without Animals Trust. Rhys Hawkins from the Visualization Laboratory at the Australian National University and Silvie Ngo provided excellent technical assistance, for which we are grateful. The calculations upon which this work is based were carried out using the Sun X6275 blades and SGIAltix clusters of the Australian National University Supercomputer Facility.

REFERENCES

(1) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Lamy de la Chapelle, M.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, 388, 756–758.

(2) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91–97.

- (3) Li, L.; Li, C. P.; Chen, Y. Physica E 2008, 40, 2513-2516.
- (4) Pham-Huu, C.; Keller, N.; Ehret, B.; Ledoux, M. J. J. Catal. 2001, 200, 400–410.
- (5) Sun, X. H.; Li, C. P.; Wong, W. K.; Wong, N. B.; Lee, C. S.; Lee, S. T.; Teo, B. K. J. Am. Chem. Soc. **2002**, 124, 14464–14471.
- (6) Kalra, A.; Garde, S.; Hummer, G. Proc. Natl. Acad. Sci. U. S. A. 2003, 100, 10175–10180.
- (7) Waghe, A.; Rasaiah, J. C.; Hummer, G. J. Chem. Phys. 2002, 117, 10789–10795.
- (8) Lopez, C. F.; Nielsen, S. O.; Moore, P. B.; Klein, M. L. Proc. Natl. Acad. Sci. U. S. A. 2004, 101, 4431–4434.
- (9) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. Nature 2005, 438, 44.

(10) Fornasiero, F.; Park, H. G.; Holt, J. K.; Stadermann, M.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 17250–17255.

The Journal of Physical Chemistry C

- (11) Corry, B. J. Phys. Chem. B 2008, 112, 1427-1434.
- (12) Suk, M. E.; Raghunathan, A. V.; Aluru, N. R. Appl. Phys. Lett. 2008, 92, 133120.
- (13) Hilder, T. A.; Gordon, D.; Chung, S. H. Biophys. J. 2010, 99, 1734–1742.
- (14) Lee, C. Y.; Choi, W.; Han, J. H.; Strano, M. S. Science **2010**, 329, 1320–1324.
- (15) Hilder, T. A.; Gordon, D.; Chung, S. H. Small 2009, 5, 2183-2190.
- (16) Won, C. Y.; Aluru, N. R. J. Phys. Chem. C 2008, 112, 1812–1818.
- (17) Hilder, T. A.; Gordon, D.; Chung, S. H. Small 2009, 5, 2870–2875.
- (18) Mpourmpakis, G.; Froudakis, G. E.; Lithoxoos, G. P.; Samios, J. Nano Lett. 2006, 6, 1581–1583.
- (19) Yang, R.; Hilder, T. A.; Chung, S. H.; Rendell, A. J. Phys. Chem. C 2011, 115, 17255-17264.
- (20) Khademi, M.; Sahimi, M. J. Chem. Phys. 2011, 135, 204509.
- (21) Gordon, D.; Krishnamurthy, V.; Chung, S. H. J. Chem. Phys. 2009, 131, 134102.
- (22) Dresselhaus, M. S.; Dresselhaus, G.; Saito, R. Carbon 1995, 33, 883-891.
- (23) Mavrandonakis, A.; Froudakis, G. E.; Schnell, M.; Mühlhäuser, M. Nano Lett. 2003, 3, 1481–1484.
- (24) Alam, K. M.; Ray, A. K. Nanotechnology 2007, 18, 495706.
- (25) Alam, K. M.; Ray, A. K. Phys. Rev. B 2008, 77, 035436.
- (26) Menon, M.; Richter, E.; Mavrandonakis, A.; Froudakis, G.; Andriotis, A. Phys. Rev. B 2004, 69, 115322.
- (27) CPMD V3.13 Copyright IBM Corp. 1990–2008, Copyright MPI fuer Festkoerperforschung Stuttgart, 1997–2001.
- (28) Frisch, M. J.;et al. Gaussian 09 Revision A.1; Gaussian Inc.: Wallingford, CT, 2009.
- (29) Kale, L.; et al. J. Comput. Phys. 1999, 151, 283-312.
- (30) Humphrey, W.; Dalke, A.; Schulten, K. J. Mol. Graphics 1996, 14, 33-38.
- (31) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. J. Comput. Chem. **1983**, *4*, 187–217.
- (32) MacKerell Jr., A. D.; Brooks, B.; Brooks III, C. L.; Nilsson, L.; Roux, B.; Won, Y.; Karplus, M. CHARMM: The energy function and its parametrization with an overview of the program. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P., Scheafer III, H. F., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 1, pp 271–277.
- (33) Toukmaji, A. Y.; Board, J. A. Jr. Comput. Phys. Commun. 1996, 95, 73-92.
- (34) Park, N.; Cho, J.; Nakamura, H. J. Phys. Soc. Jpn. 2004, 73, 2469–2472.
- (35) Miller, C. Philos. Trans. R. Soc. London, B 1982, 299, 401–411.
 (36) O'Mara, M. L.; Cromer, B.; Parker, M.; Chung, S. H. Biophys. J. 2005, 88, 3286–3299.
- (37) Zhu, F.; Tajkhorshid, E.; Schulten, K. *Biophys. J.* 2004, *86*, 50–57.
 (38) Dow Water Solutions [online], http://www.dow.come/liquidseps/prod/sw30hr 380.htm (accessed Jan 2009).
- (39) Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Science* **2006**, *312*, 1034–1037.