

# 6 Nanofluidic Carbon Nanotube Membranes: Applications for Water Purification and Desalination

*Olgica Bakajin,<sup>1</sup> Aleksandr Noy,<sup>1</sup> Francesco Fornasiero,<sup>1</sup>  
Costas P. Grigoropoulos,<sup>2</sup> Jason K. Holt,<sup>1</sup> Jung Bin In,<sup>1,2</sup>  
Sangil Kim,<sup>1</sup> and Hyung Gyu Park<sup>1</sup>*

*<sup>1</sup>Molecular Biophysics and Functional Nanostructures Group,  
Chemistry, Materials, Earth, and Life Sciences Directorate,  
Lawrence Livermore National Laboratory, Livermore, CA, USA*

*<sup>2</sup>Department of Mechanical Engineering,  
University of California at Berkeley, Berkeley, CA, USA*

---

|       |                                                                                                                |    |
|-------|----------------------------------------------------------------------------------------------------------------|----|
| 6.1   | Introduction—Carbon Nanotube Membrane Technology for Water Purification                                        | 78 |
| 6.2   | Basic Structure and Properties of Carbon Nanotubes                                                             | 79 |
| 6.3   | Water Transport in Carbon Nanotube Pores—An MD Simulation View                                                 | 80 |
| 6.3.1 | Water Inside Carbon Nanotubes                                                                                  | 80 |
| 6.3.2 | Carbon Nanotubes as Biological Channel Analogs                                                                 | 82 |
| 6.4   | Fabrication of Carbon Nanotube Membranes                                                                       | 82 |
| 6.4.1 | Polymeric/CNT Membranes                                                                                        | 83 |
| 6.4.2 | Silicon Nitride CNT Membranes                                                                                  | 84 |
| 6.4.3 | CNT Polymer Network Fabrication                                                                                | 85 |
| 6.5   | Experimental Observations of Water Transport in Double-Wall and Multi-Wall Carbon Nanotube Membranes           | 85 |
| 6.6   | Nanofiltration Properties of Carbon Nanotube Membranes                                                         | 86 |
| 6.6.1 | Size Exclusion Experiments in the 1–10 nm Size Range                                                           | 86 |
| 6.6.2 | Ion Exclusion in Carbon Nanotube Membranes                                                                     | 87 |
| 6.7   | Altering Transport Selectivity by Membrane Functionalization                                                   | 88 |
| 6.8   | Is Energy-Efficient Desalination and Water Purification with Carbon Nanotube Membranes Possible and Practical? | 89 |

## Abstract

The unique geometry and internal structure of carbon nanotubes (CNTs) give rise to a newly discovered phenomena of the ultraefficient transport of water through these ultra-narrow molecular pipes. Water transport in nanometer-size nanotube pores is orders of magnitude faster than transport in other pores of comparable size. We discuss the basic physical principles of the ultraefficient transport in CNTs, the fabrication of CNT membranes, and their nanofiltration and ion exclusion properties. A rare combination of transport efficiency and selectivity makes CNT membranes a highly promising technological platform for the next-generation desalination and water purification technologies. We discuss the potential of these applications for improving water quality.

## 6.1 Introduction—Carbon Nanotube Membrane Technology for Water Purification

The availability of safe, clean, and inexpensive water has emerged as an issue that defines global problems in the twenty-first century. Water shortages are some of the root causes of societal disruptions such as epidemics, environmental disasters, tribal and ethnic conflicts, growth shortfalls, and even countrywide political destabilization. Membrane-based filtration is the current leading energy-efficient technology for cleanup and desalination of brackish water, recycled water, and seawater. Membrane-based filtration offers other advantages as filtration through the tight membrane pores can also remove dangerous impurities, such as As, as well as toxic large organic compounds. Factors that limit the efficiency of the membrane purification technologies include the membrane resistance to the flow, membrane fouling, and membrane imperfections that lead to incomplete rejection or to a drop in the membrane rejection properties over time. The latest technological developments and high-efficiency energy recovery systems in particular have pushed the current efficiency of reverse osmosis (RO) membranes to a very impressive  $4 \text{ kWh/m}^3$  [1]; however, this number is still well above the theoretical minimum energy cost of  $0.97 \text{ kWh/m}^3$  for 50 percent recovery [2,3]. To move further, we need to develop transformative membrane technologies that utilize fundamentally new transport and filtration mechanisms for drastic gains in transport efficiency.

Carbon nanotube (CNT) membranes are promising candidates for one such solution primarily because of their transport characteristics. The inner cavity of a CNT forms a natural pore with very small diameter that can in some instances be smaller than 1 nm. Moreover, smooth hydrophobic surfaces of the nanotubes lead to nearly frictionless flow of water through

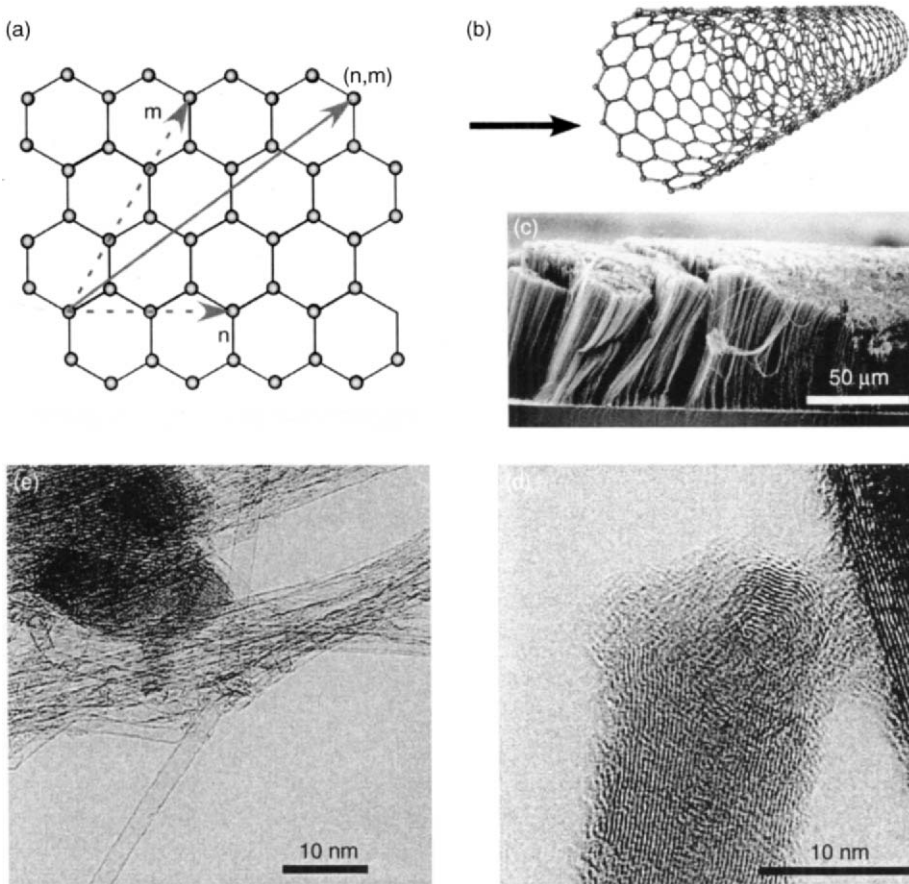
them, enabling transport rates that are orders of magnitude higher than transport in conventional pores. Finally, the structure of CNTs permit targeted specific modifications of the pore entrance without destroying the unique properties of the inner nanotube surface. The combination of these three factors could enable a new generation of membranes whose transport efficiency, rejection properties, and lifetimes drastically exceed those of the current membranes.

This chapter presents a brief overview of the basic physical processes that govern the structure and transport of water inside CNT pores, basic properties that make nanotube pore technologies attractive for water purification and desalination, the fabrication approaches for producing CNT membranes, and the experimental observations of water transport and ion exclusion properties in CNT membranes.

## 6.2 Basic Structure and Properties of Carbon Nanotubes

By now the CNT has firmly established itself as the iconic molecule of nanoscience [4]. A CNT is simply a nanometer-sized rolled-up atomically smooth graphene sheet that forms a perfect seamless cylinder (Fig. 6.1) capped at the ends by fullerene caps. It is common to characterize the structure of the nanotube by its rolled-up vector  $(n,m)$ , called chirality or helicity, which defines the position of the matched carbon rings during the roll-up of the graphene sheet [5]. A CNT can have one (as in case of a single-walled CNT), or several concentric graphitic shells (as in case of multi-walled nanotubes) and it can reach up to several millimeters in length, yet retain a diameter of only a few nanometers.

Several methods of CNT production currently exist. In the laboratory environment, catalytic chemical vapor deposition (CVD) is preferred over other methods such as arc discharge and laser ablation because it produces higher quality CNTs. CVD reactors can produce individual isolated nanotubes, as well as densely packed vertically aligned arrays (Fig. 6.1(c)). Unfortunately, the ultimate goal of the CNT synthesis—producing a uniform population of nanotubes with a given chirality—still remains elusive. Several studies indicated that the size of the catalyst particle during the growth stage determines the size of the CNT to less than 10 percent [6]; yet efforts to control the size of the CNTs with greater precision have been largely unsuccessful. Thus, synthesizing a vertically aligned CNT array with a narrow distribution of sizes still remains a difficult endeavor requiring considerable process development and optimization efforts [6–8]. The task of describing the details of CNT synthesis goes well beyond the scope of this chapter; therefore we refer the readers to a number of reviews on this subject [9–11].



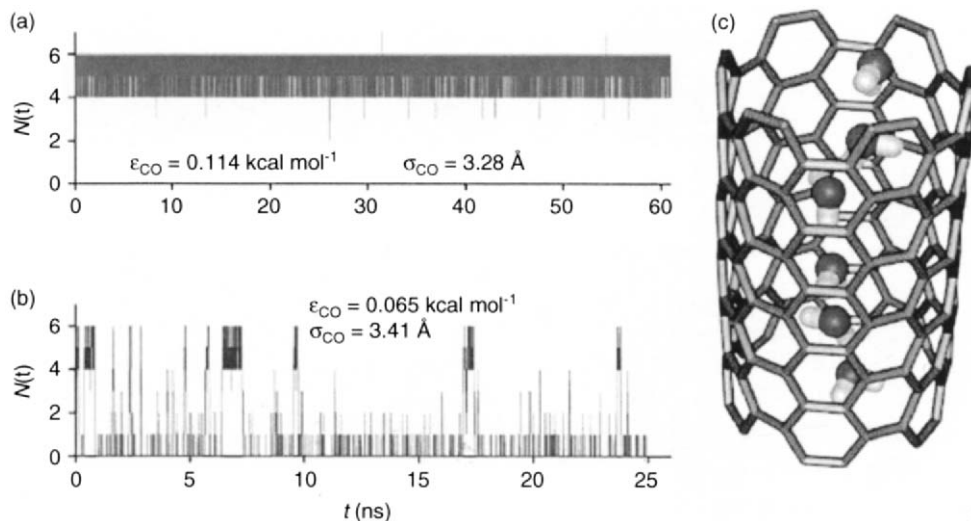
**Figure 6.1** Structure and morphology of carbon nanotubes (CNTs). (a) Schematic representation of a graphene sheet and a CNT roll-up vector. The roll-up vector is perpendicular to the axis of the CNT. (b) A 3-D model of a single-wall CNT. (c) A scanning electron microscope (SEM) image of a vertically aligned array of multi-wall CNT grown on a silicon substrate. (SEM images: M. Stadermann, O. Bakajin, A. Noy, LLNL.) (d,e) Transmission electron microscope (TEM) images of single-wall (e) and multi-wall (d) CNTs. (TEM images: J. Plitzko, A. Noy, LLNL.)

## 6.3 Water Transport in Carbon Nanotube Pores—An MD Simulation View

### 6.3.1 Water Inside Carbon Nanotubes

The task of observing and understanding fluid and gas flows in CNT pores raises a set of unique fundamental questions [12]. First, it is surprising that hydrophilic liquids, especially water, enter and fill very narrow and hydrophobic CNTs. If the water does enter the CNTs, what influence does extreme confinement have on the water structure and properties? It is important to

evaluate how these changes in structure influence the rate, efficiency, and selectivity of the transport of liquids and gases through the CNTs. As it is often the case, molecular dynamics (MD) simulations have provided some of the first answers to these questions. G. Hummer and colleagues used MD simulations to observe (Fig. 6.2(a) and (b)) filling of the (6,6) nanotube (0.81 nm in diameter and 1.34 nm in length) with water molecules [13]. Surprisingly, they found that water filled the empty cavity of the CNT within a few tens of picoseconds and the filled state continued over the entire simulation time (66 ns). More importantly, the water molecules confined in such a small space formed a single-file configuration that is unseen in the bulk water. Several experimental studies also provide some evidence of water filling of CNTs [14–17]. Further analysis of the simulation results of Hummer and colleague showed that water molecules inside and outside the nanotube were in thermodynamic equilibrium. This observation illustrates one of the more important and counterintuitive phenomena associated with nanofluidic systems: nanoscale confinement leads to the narrowing of the interaction energy distribution, which then causes the lowering of the chemical potential [13]. In other words, confining the liquid inside a nanotube channel actually lowers its free energy! Further simulations by the same group showed that the filling equilibrium was very sensitive to the water–nanotube interactions parameters: a 40 percent reduction in the depth of the carbon–water interaction potential resulted in the emptying of the CNT cavity, or a 25 percent reduction resulted in the fluctuation between filled and empty states (bi-stable states) [13,18]. This sharp transition between the two



**Figure 6.2** MD simulations of water transport in carbon nanotubes (CNTs). (a,b). Number  $N$  of water molecules inside an 8.1 Å diameter nanotube as a function of time for  $sp^2$  carbon parameters (a) and reduced carbon–water attractions (b). (c) Structure of the hydrogen-bonded water chain inside the CNT. Reproduced from [13] with permission © 2001 Nature Publishing Group.

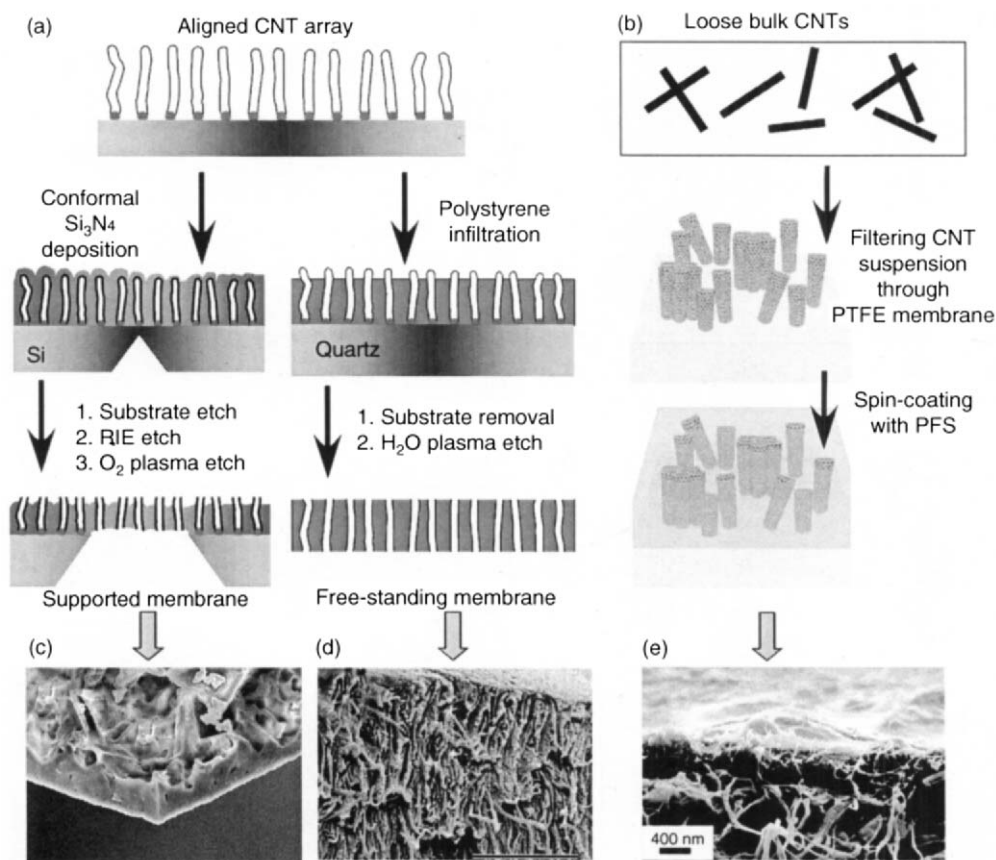
states has been observed for other hydrophobic nanopores as well [19–22]. MD simulations have also studied the dependence of the CNT hydration on other properties of CNTs such as the nanotube wall flexibility [23], charge [24,25], chirality [25,26], length [18], and diameter [24,27,28].

### 6.3.2 Carbon Nanotubes as Biological Channel Analogs

MD simulations show that a defining feature of the water structure in CNTs is the formation of the hydrogen-bonded “water wires” (Fig. 6.2(c)) oriented along the nanotube axis [12,13,29]. Such one-dimensional hydrogen bonded structures are highly reminiscent of the water wires observed in the biological channels specializing in water transport, such as aquaporins [30]. In fact, the similarity between aquaporin channels and CNT channels goes further. Similar to the hydrophobic interior of CNTs, the inner cavity of the aquaporins is lined with hydrophobic residues that facilitate the formation of the one-dimensional hydrogen-bonded water chains [30,31]. Weak interactions of water molecules with the hydrophobic walls combine with the smooth nature of the nanotube walls to enable nearly frictionless transport of water in nanotubes channels. Kalra and Hummer et al. showed that water moves very rapidly through a nanotube channel under osmotic pressure [29]. They observed that friction at the channel walls in that system was so low that water transport was no longer governed by the Hagen–Poisselle flow, but instead depended mainly on the events at the nanotube entrance and exit [29]. As a result, calculated rates of water transport approached 5.8 water molecules/ns/nanotube. Interestingly, these rates are comparable to the water transport rates achieved in aquaporins [32]. Other MD simulations also observed fast water transport through CNTs [33–35].

## 6.4 Fabrication of Carbon Nanotube Membranes

Verification of these seemingly exotic predictions of fast transport through CNTs that emerged from the MD simulations required fabrication of a robust test platform: a CNT membrane. Such membranes typically consist of an aligned array of CNTs encapsulated by a filler (matrix) material, with the nanotube ends opened at the top and bottom. Although there are likely many ways to produce a structure of this type (a notable early result by Martin and coworkers was based on fabrication of amorphous CNTs within porous alumina membrane template [36]), the approach that has proven most fruitful to date involves growing an aligned array of CNTs, followed by infiltration of a matrix material in the gaps between the CNTs (Fig. 6.3(a)). Extremely high aspect ratio of the gaps between the nanotubes in the array (of order 1,000 length/diameter or larger) presents a great fabrication



**Figure 6.3** Fabrication of carbon nanotube (CNT) membranes. (a,b) Process flow diagrams for fabrication of CNT membranes using nanotube array encapsulation with  $\text{Si}_3\text{N}_4$  or polymers (a), and filtration-assisted alignment (b). (c-e) Scanning electron microscope images of (c)  $\text{Si}_3\text{N}_4$ -encapsulated membrane, from [39]; (d) polystyrene encapsulated membrane, from [37]; and (e) filtration-assisted assembly membrane, from [40]. © 2006, 2004 American Association for the Advancement of Science and 2001 American Chemical Society, respectively.

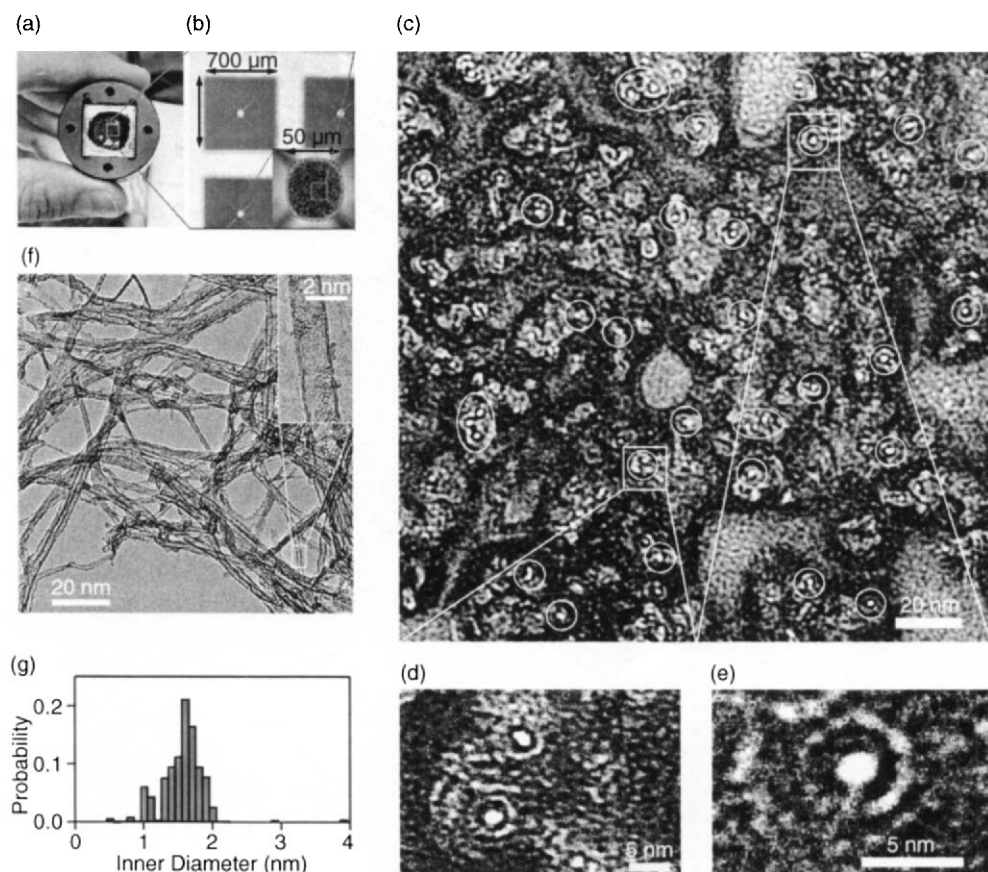
challenge for this approach. Fortunately, researchers have developed successful strategies to overcome this challenge.

#### 6.4.1 Polymeric/CNT Membranes

Hinds' group at the University of Kentucky has pioneered a membrane fabrication strategy based on polymer encapsulation of CNT arrays [37]. They infiltrated multi-wall CNT arrays with polystyrene solution that after evaporation produced a high-density multi-wall CNT membrane of ca. 7 nm pore size (Fig. 6.3(d)). As the process occurs in the liquid phase, care was necessary to ensure that the CNTs do not bundle together upon solvent evaporation.

### 6.4.2 Silicon Nitride CNT Membranes

Our group at the Lawrence Livermore National Laboratory (LLNL) developed a process for encapsulation of a vertically aligned array of CNTs with low-stress silicon nitride by a low-pressure chemical vapor deposition process [38,39]. This is a method widely used for a host of microfabrication processes and it produces an extremely conformal coating around CNTs (Fig. 6.3(c)). The membrane produced is robust and is capable of withstanding pressure gradients in excess of 1 atmosphere. Subsequent to encapsulation, the membrane undergoes a series of etching steps to selectively remove excess silicon nitride from the tips of the CNTs, followed by oxygen plasma to uncap



**Figure 6.4** Sub-2-nm carbon nanotube (CNT) membranes. (a) A photograph of a CNT membrane chip in the sample holder. (b) Optical micrographs of the regions of the chip that contain CNT membrane windows. (c-e) High-resolution transmission electron microscope (TEM) images of the thinned cross-sections of the membrane showing sub-2-nm pores. (f,g) HR-TEM characterization of the CNT size: (f) A TEM image of the dispersed carbon nanotubes from the vertically aligned array used for membrane fabrication. (g) A histogram of measured inner diameters of carbon nanotubes. From [39], © 2006 American Association for the Advancement of Science.



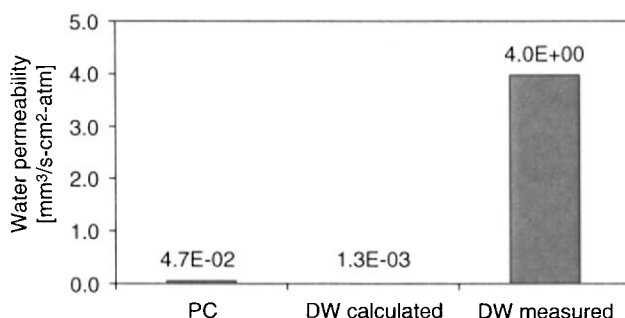
the CNTs. Transmission electron micrographs of thinned-down sections of our double-wall CNT (DWCNT) membranes (Fig. 6.4) suggest that they consist of pores less than 2 nm diameter, consistent with diameters of as-grown nanotubes, and no nano- or microvoids apparent in the structure. We have demonstrated fabrication of membranes with two different CNT pore diameters: double-wall at  $1.1 \text{ nm} < D < 2 \text{ nm}$  and multi-wall at approximately 6.5 nm.

### 6.4.3 CNT Polymer Network Fabrication

A considerably different approach to producing an aligned CNT–polymer composite membrane was recently described by E. Marand and coworkers (Fig. 6.4(b)) [40]. Amine-functionalized CNTs were dispersed in tetrahydrofuran and subsequently filtered through a hydrophobic (0.2  $\mu\text{m}$ ) PTFE poly(tetrafluoroethylene) filter, leading to alignment within the membrane pores (Fig. 6.3(e)). Spin coating with a dilute polymer solution (polysulfone) produced a mechanically stable thin film structure with the CNT tips protruding from the top of the membrane. Membranes produced with this method exhibited enhancements in gas transport rates and non-Knudsen selectivities for binary gas mixtures. This approach has the advantage of being potentially more scalable and economical than direct growth CVD of CNTs on a substrate, although at the current stage of development the nanotube densities (and thus the available pore density) are much smaller than for the membranes produced by CNT array encapsulation.

## 6.5 Experimental Observations of Water Transport in Double-Wall and Multi-Wall Carbon Nanotube Membranes

We also observed high rates of water transport through the double-wall sub-2-nm CNT membranes using pressure-driven flow [39]. Similarly high rates were also observed by Majumder et al. for multi-walled nanotube membranes with larger pore diameters [41]. As previously discussed, the single largest uncertainty in quantifying the flux through individual pores lies in the determination of the active pore density (i.e., those nanotubes that are open and span the membrane). Majumder et al. estimated the active pore densities by quantifying diffusion of small molecules through the CNTs. They measured enhancements of four to five orders of magnitude compared to Hagen–Poiseuille formalism. As described in the previous section, we estimated the upper bounds to the pore densities so that our measurements represent lower boundary estimates. The transport rates that we measured reveal a flow enhancement that is at least two to three orders of magnitude faster than no-slip, hydrodynamic flow calculated using Hagen–Poiseuille equation (Fig. 6.5). The calculated slip length for sub-2-nm CNTs is as large as hundreds of nanometers, which is



**Figure 6.5** Water transport in sub-2-nm carbon nanotube (CNT) membranes. Comparison of the water flux predicted for a polycarbonate membrane (left), and a double-wall CNT membrane (center) with the flux measured for the double-wall CNT membrane (right).

almost three orders of magnitude larger than the pore size and is almost on the order of the overall nanotube length. In contrast, the polycarbonate membrane with a pore size of 15 nm reveals a much smaller slip length of just 5 nm! This comparison suggests that slip flow formalism may not be applicable to water flow through CNTs, possibly due to length scale confinement [41,42] or to partial wetting between water and the CNT surface [43]. Interestingly, the measured water flux compares well with that predicted by the MD simulations [29]. The simulations predict a flux of 12 water molecules/nm<sup>2</sup> (of nanotube cross-sectional area)/ns; our measured flux, extrapolated to the simulation pressure drop, corresponds to 10–40 water molecules/nm<sup>2</sup>/ns [39]. Moreover, the measured absolute flow rates of at least 0.9 water molecule/nanotube is similar to the rate of 3.9 molecule/pore measured for aquaporins. The comparison to the aquaporins is not straightforward since the diameters of our CNTs are twice that of aquaporins and the CNTs are considerably longer, to name just a few differences. Therefore, we cannot yet imply that the same mechanism is responsible for transport in our CNTs and aquaporins. Nevertheless, our experiments demonstrate that the water transport through CNTs starts to approach the efficiency of biological channels.

## 6.6 Nanofiltration Properties of Carbon Nanotube Membranes

### 6.6.1 Size Exclusion Experiments in the 1–10 nm Size Range

Nearly frictionless graphitic walls of CNT composite membranes offer the unique combination of extremely fast flow and very small pore size, which potentially give them a tremendous advantages over traditional membrane materials for energy-efficient, low-cost ultrafiltration and nanofiltration applications. Several experimental studies have used concentration gradient or

pressure driven flow to determine the size exclusion properties of CNT composite membranes. Diffusion studies by Hinds' group showed that 10 nm gold nanoparticles were completely excluded by a multi-wall CNT (MWCNT)-membrane with pore inner diameter of ca. 7 nm, whereas small dyes (0.5–2 nm) diffuse with low hindrance [37,41]. Our aligned DWCNT array membranes completely excluded 2 nm and 5 nm gold nanoparticles in pressure-driven filtration experiments as expected from the transmission electron microscope (TEM) measurements of the pore diameter (Fig. 6.4(f) and (g)). Note that these membrane still exhibited extremely fast water permeation [39].

### 6.6.2 Ion Exclusion in Carbon Nanotube Membranes

With the diameters in the nanometer regime and high water permeabilities, CNTs are a promising platform for ion removal from water, as required for desalination and demineralization. MD simulations [44,45] predict that if the nanotube is uncharged, size-based exclusion of small ionic species such as  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Cl}^-$  requires CNT diameters of about 0.4 nm. These diameters are comparable to the hydrated ion size. At this scale, the ion is forced to lose part of its hydration shell to enter the CNT, implying a very high energy barrier to cross the membrane (approximately 120 kJ/mole). For slightly larger pore sizes ( $>1$  nm), this free energy penalty decays almost to zero (approximately 5 kJ/mole), allowing small ion free access. Molecular simulations [45] have also predicted that CNTs with a diameter of 0.34 nm, decorated with negative charges along the walls, will conduct  $\text{K}^+$  ions while excluding  $\text{Cl}^-$ , whereas positively charged CNTs with a diameter of 0.47 nm diameter will exclude  $\text{K}^+$  ions while conducting  $\text{Cl}^-$ . Experimental verification of MD simulation prediction has not been achieved yet as CNT membranes with such small pore openings have not been successfully fabricated to date. Joseph et al. showed by simulations that the presence of charged groups on the open CNT tips [46] induces preferential ion transport for CNT with a diameter of 2.2 nm. These results in particular suggest that dedicated functionalization of small-diameter CNT membranes (such as the membranes demonstrated by Holt et al. [39]) may enable the control of ionic flow or even the exclusion of very small ions, a particularly exciting prospect for water purification and desalination.

Recently our team has performed the first evaluation of ion exclusion in CNT membranes [47]. That study found that CNT membranes excluded a significant fraction of the ions in the feed solution (in some cases more than 90 percent). The exclusion characteristics of the membrane were also a strong function of the solution ionic strength with lower ionic strength exhibiting higher exclusion ratios. The last property provides a strong clue that electrostatic interactions on the CNT mouth play an important role. Further investigation showed that the rejection properties of the membrane obey the predictions of the Donnan equilibrium model. The exclusion properties observed for the CNT membrane are similar to the exclusion properties of the nanofiltration

membranes with pores in the same size range. Notably CNT membranes are much thicker than the active layers of current nanofiltration membranes, yet they exhibit much higher water flux!

## 6.7 Altering Transport Selectivity by Membrane Functionalization

An important avenue for controlling transport through nanotube channels involves using chemical modifications of the nanotube to alter the channel permeability or exclusion characteristics. To maintain efficient flow through the nanotube these treatments need to preserve the fundamental smoothness and hydrophobicity of the nanotube walls; therefore, we will concentrate on the modification strategies that target only the entrance and the exit of the nanotube. In fact, most membrane fabrication strategies facilitate this approach by using an oxidation step to remove the fullerene cap from the nanotube. These procedures typically produce carboxylic groups at the mouth of the nanotube [48], which not only render the pore mouth negatively charged, but also serve as the target for a variety of chemical modification approaches [49,50].

Most of the recent progress in this area has been associated with the work of Hinds and coworkers who used carbodiimide chemistry to attach a variety of organic and biological molecules to the mouth of CNTs. Interestingly, they observed that, for the polymer matrix based aligned nanotube membranes, the idealized picture of the oxidation step producing only a ring of carboxylic acid groups on the nanotube end and leaving the rest of the nanotube intact misrepresents the reality. Experiments on decorating the nanotube surface with gold nanoparticles showed that the oxidation step produced reactive groups in the nanotube regions that were up to 700 nm away from the tip of the nanotube [50,51], although after only 50 nm of separation from the tip the functional group density was already significantly reduced. Researchers argue [50] that these apparent large penetration depths are consistent with the observation that the manufacturing process produces exposed CNT tips above the polystyrene matrix.

Majumder et al. used carbodiimide chemistry to attach aliphatic chains, charged dye molecules, and polypeptides to the polystyrene-based CNTs membranes [50]. These modifications have a measurable effect on the flux of the two large organic cations [methyl viologen ( $Mv^{2+}$ ), and  $Ru(bpy)_3^{2+}$ ] used for these experiments; for example, attaching a  $C_{40}$  alkane chain reduced the flux of  $Mv^{2+}$  by six times. Interestingly, the researchers did not observe a clear trend for the effect of the modification on the flux of the test species: for example, attaching a bulky charged organic dye to the mouth of the CNT membrane actually increased the ion flux, presumably due to the interactions of the dye molecules with the oppositely charged ions [50]. Also the relationship between the size of the modifier group and the effect on the charged species

flux was complex; the authors of the report speculated that longer hydrophobic aliphatic chains prefer to orient along CNT walls and thus have a reduced effect on the overall flux.

## **6.8 Is Energy-Efficient Desalination and Water Purification with Carbon Nanotube Membranes Possible and Practical?**

The definitive answer to this question will emerge only from continued research and development on the CNT membrane prototype. Yet, several conclusions can be reached even today. The most promising property of CNT membranes for water purification applications is their extremely high permeability. This property should translate into more water per unit of applied pressure, more efficient, smaller purification units and ultimately into lower purification or desalinations costs. Rich possibilities for chemical functionalization, coupled with the rather unique ability to manipulate only the chemistry at the nanotube mouth open up the possibility of producing membranes tailored for specific applications (e.g., RO desalination or impurity purification) while maintaining the basic membrane structure and high permeability.

However, a true assessment of the potential impact of CNT membranes on water purification (and specifically on water desalination) applications requires a more comprehensive comparison of the membrane characteristics with the general requirements of the membrane purification process. At least in the case of RO desalination, the process efficiency comes from three main sources: capital costs, energy costs, and operation costs (which include costs for pretreatment, posttreatment, and membrane cleaning and regeneration). It is instructive to evaluate the potential of the CNT membrane technology against these three areas. We must first note that the CNT technology is still in its infancy; therefore, most attempts at quantitative evaluation will face large uncertainties associated with predicting the future technological milestones, or the fact that some of the major membrane characteristics (e.g., fouling properties) have not been sufficiently evaluated. Another large source of uncertainty is the lack of availability and cost estimates for a manufacturing process that allows scale-up of membrane fabrication. However, we still can reach some qualitative conclusions based even on the limited set of data that is available now. The high flux of CNT membranes provides a clear advantage for both the energy costs and the capital costs, as the same amount of product water could be obtained with smaller driving pressures and less membrane area. However some of the other important advantages of CNT membrane technology could come from the factors contributing to the third cost factor: the operation costs. The uniform pore size of CNT membranes could simplify or even eliminate the requirements for complicated multistage pretreatment efforts. The membrane pore surface is also rather chemically inert, which could

increase the membrane lifetime against the harsh agents used for pretreating water before RO or other purification steps. Unlike most polymeric membrane surfaces, the CNT membrane surface is hydrophilic; therefore, it could offer an increased resistance to fouling, as well as easier cleanup by rinsing or backwashing. These factors could all contribute to an increased membrane lifespan and ultimately to operation cost savings.

If we consider these factors, it becomes clear that the real impact of CNT membrane technology may lie in its potential to improve all of the major areas that contribute to the costs of water purification processes. Clearly, much work needs to be done before these promises translate into field applications. Researchers need to develop approaches for fabricating CNTs with an even narrower distribution of the pore sizes, ideally with pores that are less than 1 nm. Targeted chemical modification of the pore entrances should improve dramatically the rejection characteristics of the membrane. Further studies are necessary to quantify the membrane fouling resistance and useful lifespan. Finally, development of large-scale, low-cost manufacturing processes is imperative to ensure that CNT membrane technology can achieve significant penetration into the water purification market. These are all challenging tasks, yet the potential of CNT membrane technology is high enough for us to have no doubts that it will find its place in the arsenal of the water purification techniques available for mankind.

## Acknowledgments

This chapter has been partially adapted from an invited review written by this team for the *Nano Today* magazine in 2007. C.G. and O.B. acknowledge support from NSF NER 0608964; A.N., C.G., and O.B. acknowledge support from NSF NIRT CBET-0709090. All authors (except C.G.) acknowledge internal developmental funding support from LLNL. Parts of this work were performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

## References

1. S.A. Avlonitis, K. Kouroumbas, and N. Vlachakis, "Energy consumption and membrane replacement cost for seawater RO desalination plants," *Desalination*, Vol. 157(1-3), pp. 151-158, 2003.
2. K.S. Spiegler and Y.M. El-Sayed, *A Desalination Primer: Introductory Book for Students and Newcomers to Desalination*, Balaban Desalination Publications, 1994.
3. M. Shannon, P. Bohn, M. Elimelech, J. Georgiadis, B. Marinas, and A. Mayes, "Science and technology for water purification in the coming decades," *Nature*, 2008, Vol. 452, pp. 301-310.
4. M. Terrones, "Science and technology of the twenty-first century: synthesis, properties and applications of carbon nanotubes [Review]," *Annual Review of Materials Research*, Vol. 33, pp. 419-501, 2003.

5. M.S. Dresselhaus and R. Saito, *Physical Properties of Carbon Nanotubes*, Imperial College Press, 1998.
6. T. Yamada, T. Namai, K. Hata, D.N. Futaba, K. Mizuno, J. Fan, et al., "Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts," *Nature Nanotechnology*, Vol. 1(2), p. 131, 2006.
7. D.N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, et al., "Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes," *Nature Materials*, Vol. 5(12), pp. 987–994, 2006.
8. C.L. Cheung, A. Kurtz, H. Park, and C.M. Lieber, "Diameter-controlled synthesis of carbon nanotubes," *Journal of Physical Chemistry B*, Vol. 106(10), pp. 2429–2433, March 14, 2002.
9. A. Loiseau, X. Blase, J-C. Charlier, P. Gabelle, C. Journet, C. Laurent, et al., "Synthesis methods and growth mechanics," *Lecture Notes in Physics*, Vol. 677, pp. 49–130, 2006.
10. N.R. Franklin, Q. Wang, T.W. Tomblar, A. Javey, M. Shim, H.D., "Integration of suspended carbon nanotube arrays into electronic devices and electromechanical systems," *Applied Physics Letters*, Vol. 81(5), pp. 913–915, 2002.
11. A.A. Puzretsky, D.B. Geohegan, S. Jesse, I.N. Ivanov, and G. Eres, "In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition," *Applied Physics A-Materials Science & Processing*, Vol. 81(2), pp. 223–240, July 2005.
12. G. Hummer, "Water, proton, and ion transport: from nanotubes to proteins," *Molecular Physics*, Vol. 105(2), pp. 201–207, 2007.
13. G. Hummer, J.C. Rasaiah, and J.P. Noworyta, "Water conduction through the hydrophobic channel of a carbon nanotube," *Nature*, Vol. 414(6860), pp. 188–190, 2001.
14. A.I. Kolesnikov, J.M. Zannotti, C.K. Loong, P. Thiyagarajan, A.P. Moravsky, R.O. Loutfy, et al., "Anomalously soft dynamics of water in a nanotube: a revelation of nanoscale confinement," *Physical Review Letters*, Vol. 93(3), 35503, 2004.
15. N. Naguib, H. Ye, Y. Gogotsi, A.G. Yazicioglu, C.M. Megaridis, and M. Yoshimura, "Observation of water confined in nanometer channels of closed carbon nanotubes," *Nano Letters*, Vol. 4(11), pp. 2237–2243, 2004.
16. Y. Maniwa, K. Matsuda, H. Kyakuno, S. Ogasawara, T. Hibi, H. Kadowaki, et al., "Water-filled single-wall carbon nanotubes as molecular nanovalves," *Nature Materials*, Vol. 6(2), pp. 135–141, 2007.
17. E. Mamontov, C.J. Burnham, S.H. Chen, A.P. Moravsky, C.K. Loong, N.R. de Souza, et al., "Dynamics of water confined in single-and double-wall carbon nanotubes," *The Journal of Chemical Physics*, Vol. 124, 194703, 2006.
18. A. Waghe, J.C. Rasaiah, and G. Hummer, "Filling and emptying kinetics of carbon nanotubes in water," *The Journal of Chemical Physics*, Vol. 117(23), p. 10789, 2002.
19. O. Beckstein, P.C. Biggin, and M.S.P. Sansom, "A hydrophobic gating mechanism for nanopores," *Journal of Physical Chemistry B*, Vol. 105(51), pp. 12902–12905, 2001.
20. O. Beckstein, and M.S.P. Sansom, "Liquid–vapor oscillations of water in hydrophobic nanopores," *PNAS*, Vol. 100(12), pp. 7063–7068, June 10, 2003.
21. R. Allen, S. Melchionna, and J.P. Hansen, "Intermittent permeation of cylindrical nanopores by water," *Physical Review Letters*, Vol. 89(17), p. 175502, 2002.
22. R. Allen, J-P. Hansen, and S. Melchionna, "Molecular dynamics investigation of water permeation through nanopores," *The Journal of Chemical Physics*, Vol. 119(7), p. 3905, 2003.
23. S. Andreev, D. Reichman, and G. Hummer, "Effect of flexibility on hydrophobic behavior of nanotube water channels," *The Journal of Chemical Physics*, Vol. 123(19), p. 194502, 2005.
24. J. Wang, Y. Zhu, J. Zhou, and X.-H. Lu, "Diameter and helicity effects on static properties of water molecules confined in carbon nanotubes," *PhysChemChemPhys*, Vol. 6(4), pp. 829–835, 2004.
25. C.Y. Won, S. Joseph, and N.R. Aluru, "Effect of quantum partial charges on the structure and dynamics of water in single-walled carbon nanotubes," *The Journal of Chemical Physics*, Vol. 125(11), pp. 114701–114709, 2006.

26. L-L. Huang, Q. Shao, L-H. Lu, X-H. Lu, L-Z. Zhang, J. Wang, et al., "Helicity and temperature effects on static properties of water molecules confined in modified carbon nanotubes," *PhysChemChemPhys*, Vol. 8(33), pp. 3836-3844, 2006.
27. R.J. Mashl, S. Joseph, N.R. Aluru, and E. Jakobsson, "Anomalous immobilized water: a new water phase induced by confinement in nanotubes," *Nano Letters*, Vol. 3(5), pp. 589-592, 2003.
28. C.Y. Won and N.R. Aluru, "Water permeation through a subnanometer boron nitride nanotube," *Journal of the American Chemical Society*, Vol. 129(10), pp. 2748-2749, 2007.
29. A. Kalra, S. Garde, and G. Hummer, "Osmotic water transport through carbon nanotube membranes," *Proceedings of the National Academy of Sciences* Vol. 100(18), pp. 10175-10180, 2003.
30. H. Sui, B-G. Han, J.K. Lee, P. Walian, and B.K. Jap, "Structural basis of water-specific transport through the AQP1 water channel," *Nature*, Vol. 414(6866), pp. 872-878, 2001.
31. K. Murata, K. Mitsuoka, T. Hirai, T. Walz, P. Agre, J.B. Heymann, et al., "Structural determinants of water permeation through aquaporin-1," *Nature*, Vol. 407(6804), pp. 599-605, 2000.
32. P. Agre, M.J. Borgnia, M. Yasui, J.D. Neely, J. Carbrey, D. Kozono, et al., "Discovery of the aquaporins and their impact on basic and clinical physiology," *Aquaporins*, pp. 1-38, 2001.
33. E.M. Kotsalis, J.H. Walther, and P. Koumoutsakos, "Multiphase water flow inside carbon nanotubes," *International Journal of Multiphase Flow*, Vol. 39, pp. 995-1010, 2004.
34. I. Hanasaki and A. Nakatani, "Flow structure of water in carbon nanotubes: Poiseuille type or plug-like?" *The Journal of Chemical Physics*, Vol. 124(14), p. 144708, 2006.
35. A. Striolo, "The mechanism of water diffusion in narrow carbon nanotubes. nanoletters," Vol. 6(4), pp. 633-639, 2006.
36. G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher, and R.S. Ruoff, "Chemical vapor deposition based synthesis of carbon nanotubes and nanofibers using a template method," *Chemistry of Materials*, Vol. 10(1), pp. 260-267, 1998.
37. B.J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, and L.G. Bachas, "Aligned multiwalled carbon nanotube membranes," *Science*, Vol. 303(5654), pp. 62-65, 2004.
38. J. Holt, A. Noy, T. Huser, D. Eaglesham, and O. Bakajin, "Fabrication of a carbon nanotube-embedded silicon nitride membrane for studies of nanometer-scale mass transport," *Nano Letters*, Vol. 4(11), pp. 2245-2250, 2004.
39. J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, et al., "Fast mass transport through sub-2-nanometer carbon nanotubes," *Science*, Vol. 312(5776), pp. 1034-1037, May 19, 2006.
40. S. Kim, J.R. Jinschek, H. Chen, D.S. Sholl, and E. Marand, "Scalable fabrication of carbon nanotube/polymer nanocomposite membranes for high flux gas transport," *Nano Letters*, Vol. 7(9), pp. 2806-2811, 2007.
41. M. Majumder, N. Chopra, R. Andrews, and B.J. Hinds, "Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes," *Nature*, Vol. 438(7064), p. 44, 2005.
42. C. Cottin-Bizonne, S. Jurine, J. Baudry, J. Crassous, F. Restagno, and E. Charlaix, "Nanorheology: an investigation of the boundary condition at hydrophobic and hydrophilic interfaces," *The European Physical Journal E-Soft Matter*, Vol. 9(1), pp. 47-53, 2002.
43. V.S.J. Craig, C. Neto, and D.R.M. Williams, "Shear-dependent boundary slip in an aqueous Newtonian liquid," *Physical Review Letters*, Vol. 87(5), p. 54504, 2001.
44. C. Peter and G. Hummer, "Ion transport through membrane-spanning nanopores studied by molecular dynamics simulations and continuum electrostatics calculations," *Biophysical Journal*, Vol. 89(4), pp. 2222-2234, October 2005.
45. J.H. Park, S.B. Sinnott, and N.R. Aluru, "Ion separation using a Y-junction carbon nanotube," *Nanotechnology*, Vol. 17(3), pp. 895-900, February 2006.
46. S. Joseph, R.J. Mashl, E. Jakobsson, and N.R. Aluru, "Electrolytic transport in modified carbon nanotubes," *Nano Letters*, Vol. 3(10), pp. 1399-1403, October 2003.



47. F. Fornasiero, H-G. Park, J.K. Holt, M. Stadermann, C. Grigoropoulos, A. Noy, et al., "Ion exclusion by sub 2-nm carbon nanotube pores," *PNAS*, 2008, Published online before print June 6, 2008, doi: 10.1073/pnas.0710437105.
48. H. Hiura, T.W. Ebbesen, and K. Tanigaki, "Opening and purification of carbon nanotubes in high yields," *Advanced Materials*, Vol. 7(3), pp. 275–276, 1995.
49. S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, and C.M. Lieber, "Covalently functionalized nanotubes as nanometre-sized probes in chemistry and biology," *Nature*, Vol. 394(6688), pp. 52–55, 1998.
50. M. Majumder, N. Chopra, and B.J. Hinds, "Effect of tip functionalization on transport through vertically oriented carbon nanotube membranes," *Journal of the American Chemical Society*, Vol. 127(25), pp. 9062–9070, 2005.
51. N. Chopra, M. Majumder, and B. Hinds, "Bifunctional carbon nanotubes by sidewall protection," *Advanced Functional Materials*, Vol. 15(5), pp. 858–864, 2005.