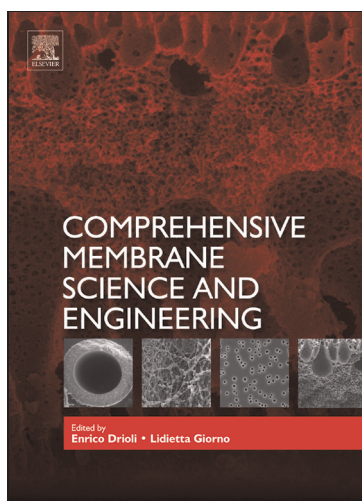


Provided for non-commercial research and educational use only.
Not for reproduction, distribution or commercial use.

This article was originally published in *Comprehensive Membrane Science and Engineering*, published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, distribution to specific colleagues, and providing a copy to your institution's administrator.



All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

M Majumder and P M Ajayan (2010) Carbon Nanotube Membranes: A New Frontier in Membrane Science. In: Enrico Drioli and Lidietta Giorno, *Comprehensive Membrane Science and Engineering*, volume 1, pp. 291–310 Oxford: Academic Press.

© 2010 Elsevier B.V. All rights reserved.

1.14 Carbon Nanotube Membranes: A New Frontier in Membrane Science

M Majumder, Monash University, Clayton, VIC, Australia

P M Ajayan, Rice University, Houston, TX, USA

© 2010 Elsevier B.V. All rights reserved.

1.14.1	Introduction	291
1.14.2	CNT Membranes	292
1.14.2.1	Template-Synthesized CNT Membrane	292
1.14.2.2	Dense-Array Outer-Wall CNT Membrane	294
1.14.2.3	Open-Ended CNT Membrane	295
1.14.2.4	Mixed-Matrix CNT Membranes	296
1.14.3	Properties and Application of CNT Membranes	297
1.14.3.1	Functionalization of CNT Membranes	297
1.14.3.2	CNT Membranes for Gas/Vapor Transport Applications	297
1.14.3.3	CNT Membranes for Stimuli-Responsive Applications	299
1.14.3.4	CNT Membrane in Liquid Transport Applications	300
1.14.4	Directions of Future Research	305
References		307

1.14.1 Introduction

Iijima, in 1991, [1] reported the first detailed transmission electron microscope images of arc-grown multiwalled carbon nanotube (MWCNT). The single-walled carbon nanotubes (SWCNTs) were reported later on [2]. There have been other reports, predating these, for the observation of filamentous forms of carbon, some of them resembling the well-formed tubular structures of nanotubes [3]. However, the proper characterization of the real structure of nanotubes has kindled the imagination of the nanoscience community and impacted the field in many ways. Research efforts over the past 17 years have been focused on the electrical, optical, and mechanical properties of this material [4–6]. Although several early experiments [7–10] had shown the ability to open up carbon nanotubes (CNTs) to serve as nanoscale containers, it is in the past 4–5 years that experimental molecular transport through CNTs, or the interstice between vertically oriented CNTs, has become a subject of intense interest. This interest has been generated by the discovery of the fascinating mass-transport properties of this nanoscale material. For example, the transport rate of water is almost four to five orders of magnitude higher than that of other porous materials of comparable size, and is very close to that of

biological membrane channels, such as aquaporin [11]. An artist's rendition of this novel phenomenon is shown in **Figure 1**, while transport properties of liquids through the inner core of ~ 7 -nm-diameter nanotubes are shown in **Table 1**. Although molecular dynamic (MD) simulation studies indicate extremely fast mass transport of gases and liquids through the inner core of CNTs [12, 13], membranes fabricated from crystalline as-formed CNTs have experimentally verified these enticing mass-transport predictions through the smooth, hydrophobic, and crystalline interior of the nanotubes. Owing to this significant advantage, there has been a major interest in nanotube membranes as a technological alternative even to mature processes such as reverse osmosis for desalination [14]. Therefore, a review showcasing the major milestones in CNT membrane research and their application is pertinent.

While the CNTs are grown by bottom-up approaches, such as chemical vapor deposition (CVD), fabrication of macroscopically useful membranes from these nanoscale materials is often a combination of several top-down components, such as electrochemical anodization of a metal film, polymer processing, chemical etching, and plasma etching. We discuss the state-of-the-art approaches for processing the CNT membranes and critically evaluate the advantages and/or drawbacks of these

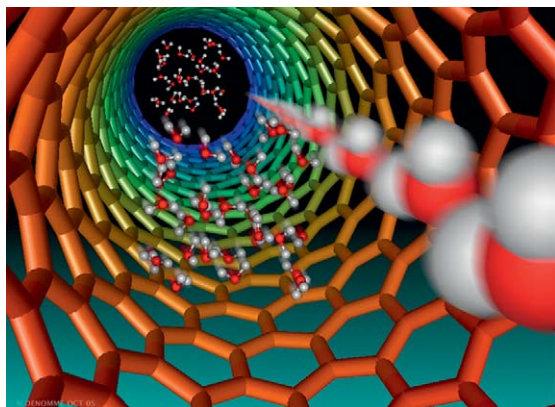


Figure 1 Artist's rendition of water molecules zipping through the inner core of carbon nanotube (CNT). Courtesy of Mark Denomme from the University of Kentucky. This chapter examines the state of the art in membranes based on CNTs.

approaches. The potential of these novel membrane materials for liquid separation, gas/vapor separations, and membrane reactor applications is elaborated. Membranes have traditionally been used for large-scale applications. However, there is considerable interest in integrating nanoporous membranes to microfluidic devices as they can integrate multiple functionalities in a device [15] – how nanotube membranes could be seamlessly integrated with microfluidic devices is also discussed. Apart from the extremely fast mass-transport properties, additional benefits of membranes based on CNTs are their ability to be functionalized – allowing them to be chemically tuned to suit applications. Furthermore, CNTs have inherent properties, such as super-compressibility and electrical conductivity, which can be exploited for designing active membrane structures. Finally, the chapter touches upon

the future directions in CNT membrane research from a technology-enabling point of view.

1.14.2 CNT Membranes

Primarily, there are four approaches to the synthesis of membranes based on CNTs:

1. deposition of carbonaceous materials inside pre-existing ordered porous membranes, such as anodized alumina, also known as the template-synthesized CNT membranes [16];
2. membranes based on the interstice between nanotubes in a vertical array of CNTs, subsequently referred to as the dense-array outer-wall CNT membrane [17];
3. encapsulation of as-grown vertically aligned CNTs by a space-filling inert polymer or ceramic matrix followed by opening up the CNT tips using plasma chemistry, or the open-ended CNT membrane [18, 19]; and
4. membranes composed of nanotubes as fillers in a polymer matrix, also known as mixed-matrix membranes.

1.14.2.1 Template-Synthesized CNT Membrane

In the template synthesis approach, a preexisting ordered porous membrane serves as a template for deposition of carbonaceous materials, usually using CVD [16, 20] at elevated temperatures, resulting in pore structure with reduced dimensions. The template is usually a ceramic membrane formed by the electrochemical anodization of metal films. The anodized membranes have extremely small

Table 1 Summary of pressure driven liquid flow measurements in CNT membranes. The permeable pore density is estimated from salt diffusion experiments

Liquid	Permeable pore density (# per m ²)	Membrane thickness (m)	Flow velocity normalized at 1 bar (ms ⁻¹)	Viscosity (cP)	Enhancement factor
Hexane	3.4 × 10 ¹³	126 × 10 ⁻⁶	5.6 × 10 ⁻²	0.3	1.09 × 10 ⁴
Decane	3.4 × 10 ¹³	126 × 10 ⁻⁶	0.67 × 10 ⁻²	0.9	3.9 × 10 ⁴
Water	1-3.4 × 10 ¹³	34-126 × 10 ⁻⁶	26.1 (±17.2) × 10 ⁻²	1.0	6 (±1.6) × 10 ⁴
EtOH	3.4 × 10 ¹³	126 × 10 ⁻⁶	4.5 × 10 ⁻²	1.1	3.2 × 10 ⁴
IPA	3.4 × 10 ¹³	126 × 10 ⁻⁶	1.12 × 10 ⁻²	2	1.4 × 10 ⁴

Note that the enhancement factor, that is, the ratio of the observed flow velocity to the Hagen–Poiseuille flow velocity for ~7-nm pipes, is ~10000–100000, suggesting strong deviation from no-slip hydrodynamic flow. Adapted with permission from Majumder, M., Chopra, N., Andrews, R., Hinds, B.J. *Nature* **2005**, 438, 44.

(<10%) porosity, are mechanically very brittle, and fabrication of anodized membranes with small pore size (<5 nm) is often irreproducible. However, anodization of metals is an interesting approach to synthesize ordered membrane structures with controlled pore-size distribution and small tortuosity. Although these membranes have found applications in size-based separations [21] and as catalytic membrane reactors [22], further modification by

carbonaceous material deposition provides many possibilities.

The synthesis and characterization of template-synthesized membranes have been pioneered by Charles Martin's group at the University of Florida. A schematic and scanning electron microscopy (SEM) image of the template-synthesized CNT membrane is shown in **Figure 2(a)**. In the schematic, the dark-gray intrusions are the

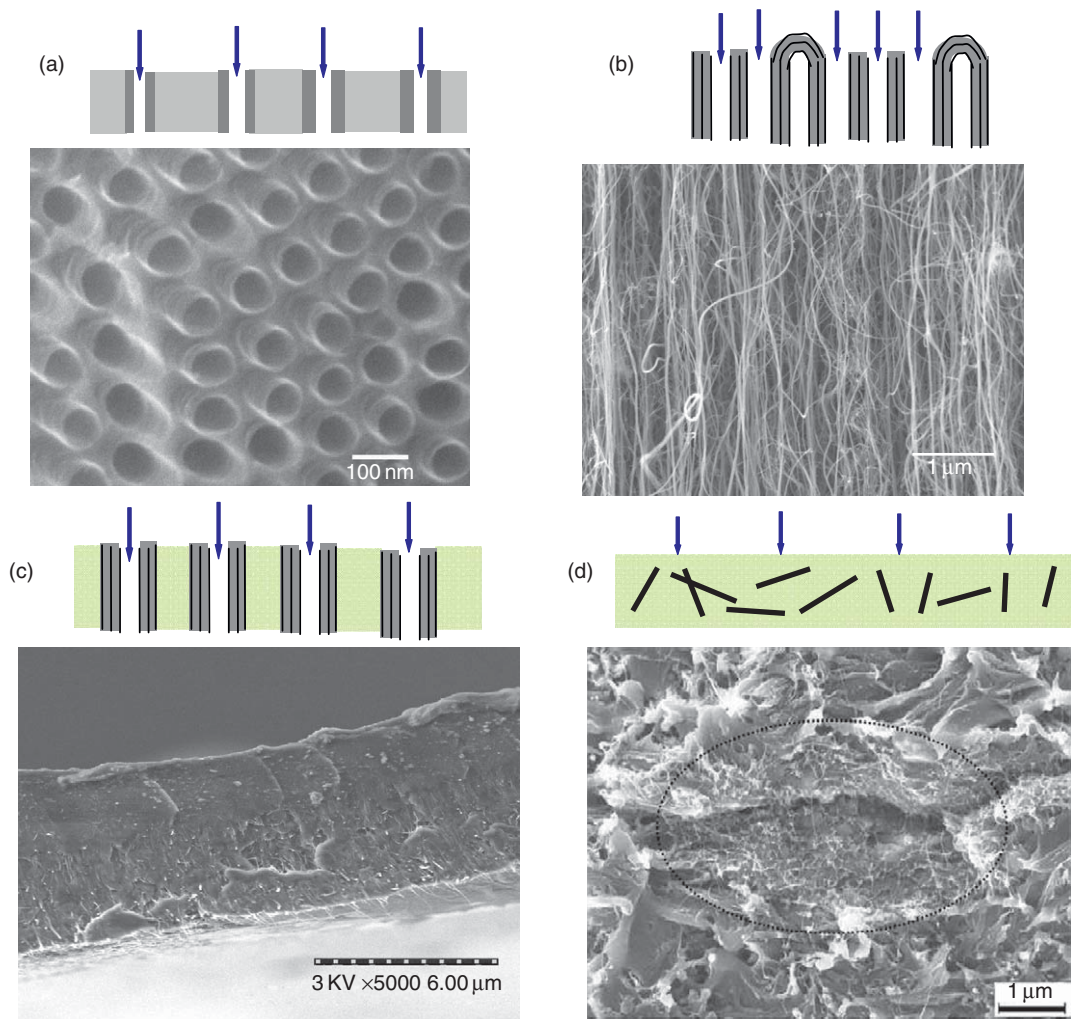


Figure 2 Different approaches to carbon nanotube (CNT) membrane synthesis. (a) Template synthesis approach—carbonaceous material deposited inside anodized alumina template; (below) scanning electron micrograph (SEM) micrograph of the nanotubes after dissolution of the template. (b) Dense-array outer-wall CNT membrane; SEM image demonstrating the dense array of CNTs. The fluid transport is through the interstice between the nanotubes, although some transport can occur through some open-ended tubes [17]. (c) Open-ended CNT membrane; (below) SEM image showing the cross section of the membrane with aligned CNTs in an impervious polymer matrix; transport in this membrane structure occurs through the inner core of the CNT [18]. Image taken with permission from Majumder, M., Zhan, X., Andrews, R., Hinds, B. J. *Langmuir* **2007**, *23*, 8624–8631. (d) Mixed-matrix membrane composed of CNTs in a polymer matrix; (below) SEM image of the composite-membrane structure. Image taken with permission from Geng, H.-Z., Kim, K. So, K., Lee, Y., Chang, Y., Lee, Y. J. *Am. Chem. Soc.* **2007**, *129*, 7758–7759.

carbonaceous material deposited inside the light-gray (anodized alumina) template. The deposition of carbonaceous materials inside template membranes by CVD of ethylene can reduce the pore size from ~ 300 to ~ 200 nm, but further reduction was not observed [23]. It is likely that faster kinetics of this deposition process is less controllable for obtaining smaller dimension of pores, and is the reason for much of Martin's later work devoted to the use of a more-controlled solution-based electroless deposition technique for steric separation of small molecules [24]. This conjecture is further supported by the work of Alsyouri *et al.* [20], in which CVD, using trimethyl ammonium and water, resulted in the reduction of porosity of ~ 20 -nm templates and not their pore size. The CNT membranes synthesized by this method also contain amorphous or partially graphitized CNTs and are chemically different from the membranes based on the highly ordered graphitic CNTs. They can, however, be graphitized by heat treatment at higher temperature. This was shown in template-synthesized partially graphitic nanotubes, which can be annealed at a higher temperature ($>2000^\circ\text{C}$) to form graphitic nanotubes, as evidenced by electrical conductivity, transmission electron microscopy, and contact angle measurements [25]. It should, therefore, be possible to convert template CNT membranes to partially graphitized CNT membranes by heat treatment, although such treatments are likely to increase the cost of the membranes.

In this vein, it is worthwhile to point readers to the fabrication of well-controllable, hierarchically branched, and crystallized CNT architectures by Ajayan and coworkers [26] using this template approach. The well-branched porous architecture has smaller pore dimensions at one end and larger pore structure at the other end – similar to the asymmetric membranes commonly used for filtration purposes [26]. Fluid flow or permeability of these novel nanoscale architectures will verify its applicability in nanofluidic applications. A major advantage of the template synthesis approach is that the modular components of thin-film deposition, electrochemical treatment, and CVD can be integrated to microfluidic device fabrication platforms. However, other approaches using as-formed graphitic CNTs seem to be more realistic for producing CNT membrane for large-scale applications. In the subsequent sections, we discuss membranes based on as-formed CNTs.

1.14.2.2 Dense-Array Outer-Wall CNT Membrane

Aligned arrays of CNTs can be used as membranes, where transport occurs primarily through the interstice between the CNTs, although some of the nanotubes might be open – as shown schematically in **Figure 2(b)**. The CNTs, in this membrane structure, are held together by van der Waals bonding between tubes and carbonaceous materials formed during the CVD process. The pore size of this membrane is usually in the range of 40–100 nm – suitable for ultrafiltration applications.

In some cases of CNT synthesis, such as by high-pressure CO conversion (HiPco) or laser oven processes, the nanotubes are produced as an entangled mesh held together by van der Waals forces [27]. Alignment of CNTs, from such an entangled mesh, can be achieved by the application of some externally applied forces. Partial alignment of CNTs ($\sim 50\%$) inside a polymer matrix can be attained by mechanical stretching during extrusion of a polymer–nanotube composite melt [28, 29] – although the degree of alignment would be limited by the high viscosity of the melt, especially for samples with large volume fraction of CNTs. Researchers at Rice University were able to align purified SWCNT bundles, in plane, using a magnetic field (~ 7 T) during filtration of a nanotube suspension [30, 31], which is contrary to out-of-plane alignment requirements for filtration application. Therefore, a particular emphasis in the fabrication of CNT membranes is formation of macrostructures with CNTs aligned perpendicular to the substrate. CVD from carbon-containing source and a metal catalyst can readily produce aligned CNT arrays over a substrate, such as Si and SiO_2 .

In the early 1990s, primarily after the discovery of fullerene, research efforts were directed to synthesize carbon nanostructures in large-scale capabilities. There was also a concerted effort to produce controlled nanostructures composed of aligned CNTs, with the goal of investigating the anisotropic properties of CNTs applicable in field-emission devices. The earliest report of aligned MWCNT films was by deHeer *et al.* in 1995 [32] using the arc evaporation process. Subsequently, other methods, such as CVD, a scalable and industrially viable process, became popular [33]. Aligned MWCNTs were also grown on nickel-coated glass substrates by plasma-enhanced hot-filament CVD from a mixture of acetylene and ammonia below 666°C [34]; however, the CNTs produced by this method had significant bamboo-type structures

making them unsuitable for flow-through applications. Among others, efforts at the Center for Applied Energy Research (CAER) at the University of Kentucky were focused on perfecting and scaling up production of MWCNT arrays from a continuous source of ferrocene and xylene at $\sim 650^\circ\text{C}$ [35].

The overall geometry of the aligned CNT structure depends on the shape of the substrate on which the CNTs are deposited. Srivastava and coworkers succeeded in materializing this concept and formed hollow cylinders of aligned MWCNT (up to few centimeters long) along the walls of a tubular quartz reactor. The cylinders are composed of radially oriented MWCNTs of about 300–500- μm length and have been utilized for liquid and gas filtration application [17]. More importantly, the mechanical strength of the CNT filter is high enough to allow liquid filtration by tangential cross flow, which is widely used in industrial membrane filtration. Molecular transport in these membranes occurred, primarily, through the interface between nanotubes, although transport through the inner core of the open nanotubes cannot be overruled. Inter-nanotube distance in the MWCNT arrays is in the range of 40–100 nm, which sets the pore size of the membranes. A potential drawback of this membrane structure is the considerable variation in the size distribution of the filtration pores – although these dimensions could be tuned with closer packing of nanotubes or with nanotubes of smaller outer diameter [36].

1.14.2.3 Open-Ended CNT Membrane

A contemporary approach in CNT membrane research is the use of open-ended CNT channels as conduits for molecular transport. A composite film is synthesized from an aligned array of the CNT by a space-filling polymer [18] or ceramic matrix [19]; however, maintaining the alignment of the CNTs during this processing step is critical. Subsequently, the tips of the CNTs are oxidized by plasma chemistry to form open-ended and conducting CNT channels. A schematic and SEM image of a typical nanotube membrane fabricated by such a process is depicted in **Figure 2(c)**.

The open-ended CNT membranes, with space-filling polymers, have been primarily based on poly(styrene) [18]. The choice of poly(styrene) in this work is dictated by its high wettability [37] with CNTs allowing easy penetration into the MWCNT array ($\sim 10^{10}$ tubes cm^{-2}) by a simple film fabrication process. However, other

mechanically robust polymers and conformal deposition techniques can substitute polystyrene. The CNT–polymer film is released from the quartz substrate, on which the CNTs grow, by hydrofluoric acid (HF) etch. The vertically oriented CNTs in the polymer matrix often have a graphitic end cap (which have larger concentration of defects and are easily oxidized compared to the side walls) or a catalyst metal particle sealing the graphitic interiors, which are etched away using mild plasma oxidation without destroying the mechanical structure of the CNTs [38]. High-temperature oxidative [39] or acidic oxidation treatments can compromise the mechanical integrity of the membrane and are not suitable for the membrane fabrication process. The elegance of the plasma-oxidation process stems from its controllable oxidation kinetics, and the ability to fabricate a macroscopic CNT array device. This plasma-oxidation process, inherent to the membrane fabrication process, performs three very important functions:

1. It removes excess polymers by oxidative trimming, since the oxidation kinetics of the polymer (CNT) is faster than that of the CNTs. This results in the exposure of the CNTs out of the polymer matrix, making the membrane electrically conducting.
2. The plasma-oxidation process also removes amorphous carbon and Fe impurities, aided by HCl treatment. Note that the permeable pore densities ($\sim 10^9 \text{ cm}^{-2}$) of membranes in **Table 1**, estimated from salt-diffusion experiments, are almost a magnitude smaller than the density of the CNTs in the arrays ($\sim 10^{10} \text{ cm}^{-2}$) estimated from microscopy experiments. This is attributed to the incomplete removal of the iron nanocrystals from the interiors of the CNTs.
3. The plasma-oxidation process introduces functional groups (mainly $-\text{COOH}$) at the CNT tips, which makes the tips amenable to facile functionalization-chemistry approaches.

The CNT membrane structure after the plasma-oxidation process showed a pore-size distribution of $\sim 6 \pm 2 \text{ nm}$, which is consistent with TEM observations of the inner core of $\sim 7 \text{ nm}$.

In a similar work, aligned CNTs (with sub-2-nm diameter) were grown on a Si chip patterned with metal catalyst using a CVD process. A conformal deposition of a ceramic material, Si_3N_4 , filled up the space between the nanotubes. Standard etching

procedures were adopted to create openings on the Si chip; subsequently, excess Si_3N_4 and catalyst nanoparticles were removed by Ar-ion milling, while the CNTs were uncapped by reactive ion etching [19]. In both these works, the production of the CNT membranes relied on standard lithography tools commonly associated with microelectronic industry.

More traditional inorganic membrane fabrication research groups have focused on making robust and cost-efficient CNT membranes by using macroporous membrane support layer and avoiding the use of lithographic tools. In this effort, aligned CNT arrays were grown over macroporous alumina supports and the interstitial space between the CNTs was filled by poly(styrene); however, the viscosity of the polymer was high enough to preclude its entry into the macroporous alumina support. Mechanical polishing and acid treatment were adopted to remove the polymer overlayer and to open up the CNTs [40].

The methodologies for fabrication of the first-generation CNT membranes were aimed at understanding the fundamental transport behavior. They suffer from several drawbacks, for example, the porosity of these membranes and the overall permeability is uncertain, due to the presence of considerable amount of Fe nanocrystals from the vapor deposition process and the overall yield is painstakingly small. The research approaches discussed earlier [18, 19, 40] have utilized as-formed aligned CNTs for the fabrication of membranes; an alternative route is to adapt colloidal processing approaches. In this regard, Kim *et al.* [41] claim to have developed a scalable process for the fabrication of open-ended nanotube membranes by filtering a CNT suspension through a hydrophobic porous polytetrafluoroethylene (PTFE, 0.2- μm pore diameter). Quite surprisingly, a substantial number ($\sim 10^{10} \text{ cm}^{-2}$) of CNTs were observed to stick out of the filter surface, most likely due to the hydrophobic-hydrophobic interaction between the nanotubes and the filter surface. A thin polymer binder filled up the interstice between the nanotubes, leading to the formation of the membrane. The key advantage of this approach lies in the ability to use purified nanotubes (lower amount of Fe catalyst) with larger through porosity and to use diameter-sorted CNT suspensions. Scalability and the overall simplicity of the colloidal approach have the potential to lower the cost of CNT membrane fabrication.

In sum, the fabrication of the open-ended CNT membranes is complex, but it offers tighter control

over pore size as the transport occurs through the inner core of CNTs.

1.14.2.4 Mixed-Matrix CNT Membranes

Polymeric membrane materials are intrinsically limited by a tradeoff between their permeability and their selectivity, yet they have been the basis for high-performance gas-separation applications. Virtually, all gas separations in polymeric membranes are limited by an upper boundary in a log-log plot of gas selectivity and permeability [42]. One approach to increase the selectivity is to include dispersions of inorganic nanoparticles, such as zeolites, carbon molecular sieves, or CNTs, into the polymeric membranes – these membranes are classified as mixed-matrix membranes. In these membranes, the choice of both these components is a problem of materials selection, and also involves several fundamental issues, such as polymer-chain rigidity, free volume, and the altered interface – all of which influence transport through the membrane [43]. Several research groups are investigating the effects of incorporation of CNTs to develop mixed-matrix membranes. Schematic and SEM image of mixed-matrix CNT membranes are shown in **Figure 2(d)**. In the dense-array or open-ended CNT membranes, transport is through the pores of CNTs and interparticle pores in CNT array – a mechanism quite similar to porous ultrafiltration or nanofiltration membranes, whereas transport through the mixed-matrix membranes is predominantly by a solution-diffusion mechanism. Eva Marand and coworkers have incorporated open-ended and amine-functionalized CNTs (with $\sim 13.6\text{-\AA}$ pore diameter) into poly(sulfone) [44] and poly(imide-siloxane) copolymer [45]. Incorporation of CNTs increases the permeability of most gases by up to 60%, but the selectivity does not improve compared to the polymeric membranes. However, appropriate manipulation of the interface can significantly improve the separation performance. Considering the plethora of polymeric materials at the disposal, the combinatorial selection of components for membrane formulation may pose a problem of plenty. Therefore, modeling and simulations are needed for predicting the transport properties of the mixed-matrix membranes *a priori*. Further, rational design of experiments for optimization of materials processing and property relationships can pave the way for the development of high-performance CNT-based mixed-matrix membranes.

1.14.3 Properties and Application of CNT Membranes

In this section, we discuss the properties of the CNT membrane with particular emphasis on their potential applications.

1.14.3.1 Functionalization of CNT Membranes

Selective chemical transport through porous membranes can be affected by steric, electrostatic, or chemical interactions – often a combination of these mechanisms results in the desired selectivity. For example, membranes can be engineered with polyelectrolytes containing charged amino and carboxyl groups to achieve separation of ions by electrostatic adsorption [46], or proteins by an affinity-based separation [47]. CNTs are composed of rolled-up grapheme sheets consisting of sp^2 -hybridized carbon; however, liquid-phase (acid) and gas-phase (air and plasma) treatments introduce surface functional groups. Experimental results indicate that liquid-phase treatments tend to introduce carboxylic acid groups, whereas gas-phase treatments introduce less-oxidized groups such as hydroxyl and carbonyl [48]. Water plasma treatment for opening the CNTs is most likely to introduce the carboxyl groups on the tips of the CNT membrane, because the high reactivity of the plasma precludes its entrance deep into the pores, limiting the functionalization to the surface [49]. These functional groups, particularly carboxylic acids can then be further modified by covalently attaching molecules of interest to these anchor points, using carbodiimide-mediated coupling of the carboxylic acid groups with amine groups of the desired molecule. Modulation of ionic transport through the CNT membrane, by selective chemical functionalization at the CNT tips, has been demonstrated [50]. Transport through the membrane of two different-sized, but equally charged, molecules (ruthenium–bipyridine $[\text{Ru}-(\text{bipy})_3^{2+}]$ and methyl viologen $[\text{MV}^{2+}]$) was quantified to understand the effect of the functionalization chemistry. The selectivity of the permeating molecules varied from 1.7 to 3.6 and a hindered diffusion model to explain the observed selectivity was consistent with a geometry of functionalization concentrated at the CNT tip and not along the length of the CNT core. Furthermore, it is possible to increase the density of functional molecules by using electrochemical

approaches, such as diazonium grafting chemistry. Such chemistries enhanced the electrostatic interactions between the membrane and the permeating species [51]. Molecular transport through membranes can also be driven by an electric field. This process, known as electro-osmosis, arises from the drag exerted by counterions on solvent molecules and provides a means to manipulate liquids by an electric field, particularly in microfluidic devices. The direction of overall molecular transport is in the direction of counterion migration, and is directly related to the bound surface charge. Researchers have shown that template-synthesized CNT membrane functionalized with charged groups demonstrate controlled electro-osmotic transport [16]. In general, readers should be aware that a wide range of literature for electrochemical (or chemical) functionalization of the CNTs exists [52]; however, selection of appropriate chemistry compatible with the mechanical integrity of the CNT membranes and pertinent application is critical. Nevertheless, these experiments (Figure 3) indicate the feasibility of functionalizing CNT membranes and should offer avenues for imparting antifouling, biocompatible, molecular recognition or selective adsorption properties, whenever desired.

1.14.3.2 CNT Membranes for Gas/Vapor Transport Applications

Gas transport through the hollow interiors of CNTs has been the fancy of many scientists. Preliminary answers to how gaseous molecules are transported through these nanoscale and highly smooth conduits came through MD simulations. Several research groups in the US and UK studied the transport properties of CNTs. Prominent among them are David Sholl and Karl Johnson at the Carnegie Mellon University. They investigated the transport of small gas molecules, such as N_2 , Ar, and CH_4 , through nanoporous materials, including CNTs, with the overarching goal of screening inorganic materials for potential gas-separation applications. In 2003, they reported that the transport diffusivities of Ar through CNTs were almost three to four orders of magnitude larger than through zeolitic pores of comparable dimensions [13]. Arguments based on specular reflection of the gases along the smooth and frictionless graphitic interface were forwarded. Some work on MD simulations on gas transport was also conducted by the Susan Sinnott group at the University of Kentucky and their simulations

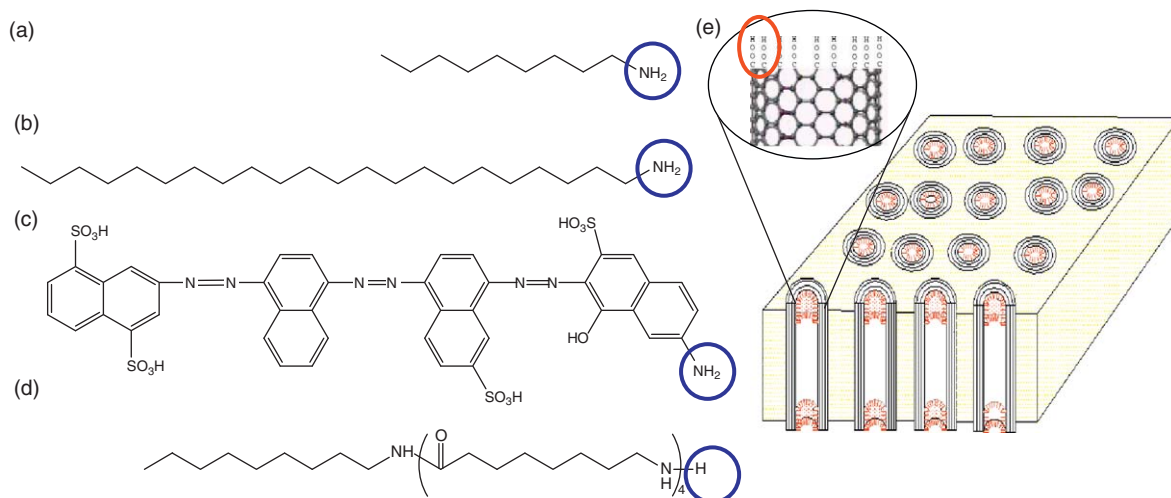


Figure 3 Functionalization of the CNT membrane via coupling chemistry between amine groups (in blue circle) of the functional molecule and the carboxylic acid (in red) with (a) short (C9)-chain amine, (b) long (C22)-chain amine, (c) charged dye molecule with SO_3^{2-} groups, and (d) long-chain polypeptide resulted in change of transport properties through the CNT membrane (e) Figures (a) through (e) adapted with permission from Majumder, M., Chopra, N., Hinds, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 9062–9070. These experiments indicate the feasibility of functionalizing CNT membranes and should offer avenues for imparting antifouling, biocompatible, molecular recognition or selective adsorption properties, whenever desired.

also predicted extremely fast transport of gases through CNTs [53]. Nick Quirke's group at Imperial College investigated hydrodynamics of low-Knudsen-number fluid flow through graphitic pores. Their simulation results indicated the presence of large slip lengths for such flows [54]. In 2002, they proposed for the first time the presence of slip-boundary conditions in Poiseuille flow of fluids, such as CH_4 on smooth CNT surfaces [55]. In summary, several research groups computationally predicted the extremely fast mass-transport characteristics through the inner core of the hydrophobic, and smooth CNTs.

From an experimentalist's viewpoint, gas transport through mesoporous materials is generally a combination of (1) viscous or Poiseuille flow, (2) Knudsen diffusion, and (3) surface diffusion [56, 57]. While the Poiseuille permeation scales inversely with the viscosity, the characteristics of Knudsen-type transport are an inverse scaling with the square root of molecular weight of the gases – paralleling arguments for the kinetic theory of gases. Knudsen diffusion becomes prominent when the mean free path of the diffusing species is larger than the pore diameter. In some cases of porous membranes, a surface-adsorption-based preferential diffusion may lead to highly selective transport, especially in carbon membranes with extremely small pore dimensions (<1 nm) [58, 59].

Careful control experiments, such as retention of Au nanoparticles and size-dependent separation of molecules, have validated the membrane structure consisting of open-ended CNTs inserted inside an impermeable polymer matrix [11, 19]. Pore density (number of pores/ m^2) in these membranes can be estimated with reasonable accuracy by direct visualization using SEM or by diffusive transport measurements. Often, a large number of CNTs, which are visible by electron microscopy, can have their cores blocked by the catalyst particles (especially in the case of membranes composed of large-diameter MWCNTs), so the microscopy experiments can provide a higher estimate to the number of open-ended nanotubes. Nonetheless, this estimation is crucial for understanding the molecular transport properties through the CNT membranes, as it allows the macroscopic transport measurements to be converted to that for single nanotubes. It is also worthwhile to recollect that the mean free path for gases (~ 600 Å for air) is significantly larger than the pore diameter of the CNT membrane (~ 12 – 70 Å) – therefore, Knudsen diffusion is the likely gas-transport mechanism. For gas transport through smooth pores, such as CNTs, it is worth commenting that Knudsen diffusivity can exceed the diffusivities predicted from the kinetic theory of gases because of specular reflection along the CNT walls [60]. Indications that such behavior can be true is provided

by gas-transport measurements in a template-synthesized CNT membrane ($\sim 20\text{--}30$ nm thick and 200-nm pore diameter) – the authors concluded that $\sim 50\%$ of the gas collisions were specular [61]. However, for more comprehensive assessments, gas-transport measurements through the open-ended CNTs are critical. Indeed, the observed permeability of gases in these CNT membranes scales inversely with the molecular weight by an exponent ~ 0.4 (for ideal Knudsen diffusion this is 0.5); however, the diffusivities are around one to two orders of magnitude larger than Knudsen diffusivity predictions [19, 62]. Thus, a Knudsen-type diffusive transport, but with a highly specular reflection along the CNT walls, is the dominant gas-transport mechanism for open-ended CNT membranes. The next obvious question is how can we utilize these amazing mass-transport properties for real-life gas-separation applications. We must recognize that in such applications one is interested not only in the throughput, but also in the selectivity; here is the caveat. The smoothness of the graphitic interiors, which is the reason for fast transport, is actually responsible for the lack of selectivity – the selectivity will be limited by the Knudsen-type selectivity. For all practical applications, it would, therefore, be necessary to impart selectivities based on either functional molecules or surface adsorption–diffusion in CNTs with much smaller diameter (<1 nm) [63].

A school of thought is to include these nanoscale materials in conventional membranes to augment vapor/gas-transport efficiencies. For example, let us consider membrane distillation, a thermal-membrane process for desalination of seawater. In this process, water vapor is preferentially transported through the hydrophobic pores of membranes over saline water to affect the separation. The advantage of the membranes, here, is to lower the thermal requirements due to convective mass-transport effects. Open-ended CNTs, where the kinetics of gas transport is much larger than Knudsen-type diffusion, could be a potentially interesting additive to the conventional microporous and hydrophobic membranes. Indication about the validity of such concepts comes from pervaporative separation of benzene/cyclohexane using membranes based on polyvinyl alcohol–CNT–chitosan mixed-matrix membranes [64]. Pervaporation is a process by which a component in a liquid mixture is preferentially vaporized through the membranes. It was observed that the incorporation of CNTs increased not only the permeability of benzene but also its

selectivity compared to similar membranes without the CNTs.

Let us now address, from the perspective of gas separations, where membranes based on CNTs stand. Zeolites have been the basis of the chemical industry from selective adsorptive separations for several decades. However, synthesis of defect-free zeolite membranes is yet to reach commercial success, mainly because their irregular grain and pore structure is incompatible to large-area synthesis of membranes. If CNTs, with their crystalline pore and small pore dimensions (<1 nm), could achieve the selectivity of zeolites, the recent developments in the synthesis of defect-free CNT membranes would be important in several gas-separation applications. However, the smallest dimensions (1–2 nm) of the CNT membranes made till date are not suitable for such sieving purposes and the gas-separation properties of open-ended CNT membranes are, at best, modest. Mixed-matrix CNT membranes seem to be potentially more attractive toward gas-separation applications [65].

1.14.3.3 CNT Membranes for Stimuli-Responsive Applications

CNTs have several unique properties, including high electrical conductivity and elasticity, which have been exploited in creating stimuli-responsive membranes. An account of such demonstrations and how it might influence some technologies is presented in this section.

Researchers have demonstrated that superhydrophobic CNT arrays can be rendered hydrophilic by application of an electric potential. These membranes are analogous to dense outer-wall membranes, but are superhydrophobic; water transport through the CNT arrays can be controlled by the application of an electrical bias to the membrane (see **Figures 4(a) and 4(b)**) [66]. Although this potential-dependent wicking behavior through the CNT membrane is analogous to the well-known phenomenon of electrowetting, the ability to control water transport through a membrane structure by an external stimulus can be useful in applications where controlled transport of water droplets is necessary, for example, in lab-in-a-chip devices.

Another example of controlled molecular transport through CNT membranes is an effort to mimic the complex functionality of biological voltage-gated membrane channels in artificial systems. In simplified terms, biologists have shown that charged

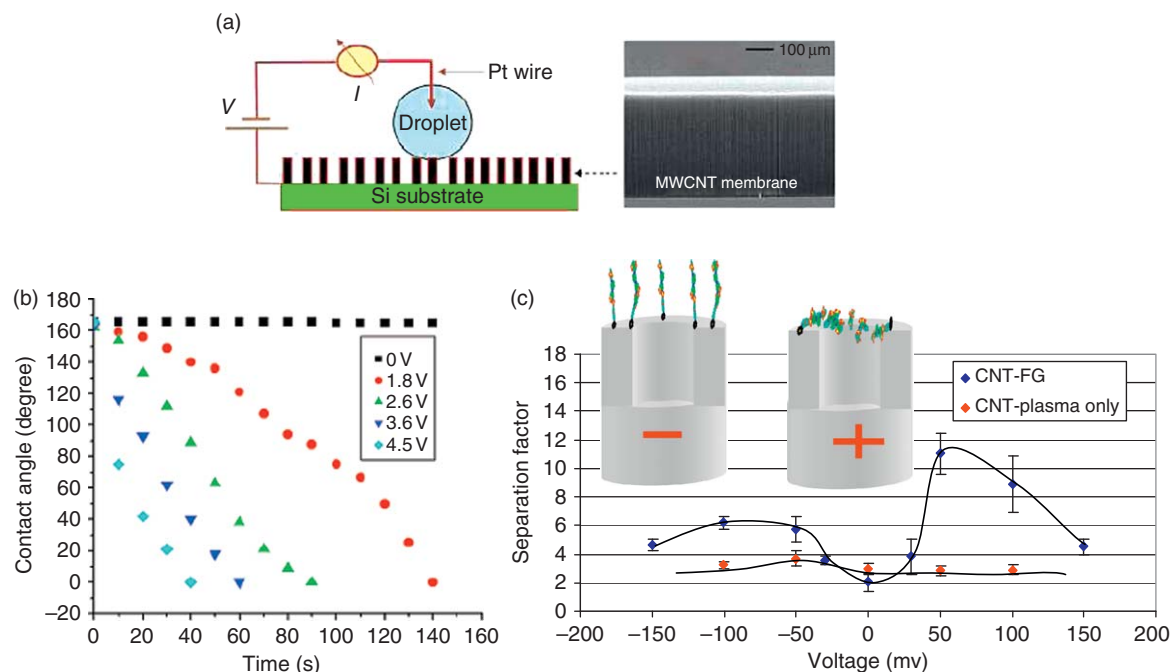


Figure 4 Voltage-controlled transport through carbon nanotube (CNT) membranes. (a) Contact angle measurements on dense-array outer-wall CNT membrane as a function of applied electrical potential. (b) Variation of contact angle with applied potential. Change of contact angle allows control of transport of water droplets for drop-in-demand-type applications. Figures (a) and (b) used with permission Wang, Z. K., Ci, L. J., Chen, L., Nayak, S., Ajayan, P. M., Koratkar, N. *Nano Lett.* **2007**, *7*, 697–702. (c) Voltage-gated membrane channels, in which large macromolecules tethered to the conducting pores of CNTs can be actuated to selectively occlude the pores. Figure used with permission from Majumder, M., Zhan, X., Andrews, R., Hinds, B. J. *Langmuir* **2007**, *23*, 8624–8631. This results in a voltage-controlled transport, mimicking biological membranes, for transdermal drug delivery-type applications.

protein segments in the membrane channels induce paddle-like conformational changes, in response to an external stimuli, such as voltage, thereby changing the transport through the channel [67]. Molecules attached to the walls and entrances of CNT membranes can be actuated electrostatically, thereby selectively occluding the pores and altering transport of molecules through the pores [68]. In these experiments, the electrically conducting CNT membrane is the electrode in a three-electrode electrochemical cell, and demonstrates the ability of these membranes to mimic voltage-gated channels found in nature (see Figure 4(c)). Such electrostatically actuated molecular transport is being considered as the enabling principle in transdermal drug delivery devices.

From voltage-controlled transport properties to mechanically regulated transport, CNT membranes can exhibit them all. Membranes that change pore size in response to compressive forces are found in the kidney. Li *et al.* [69] have utilized the super-compressible property of CNTs to mimic such behavior. Super-compressibility is a spring-like property

of vertically oriented CNTs in which the arrays can be compressed to a zigzag configuration, but retain their original texture when the force is released [70]. Application of compressive force to the vertically oriented dense outer-wall membrane flattens the nanotubes and decreases the pore size between them, resulting in the concomitant increase in steric selectivity and decrease in water permeability (see Figure 5).

The concept of stimuli-responsive membranes is pertinent to biological membrane channels and mimicking them in artificial systems to create functional membranes can be fundamentally elegant, as well as useful in practical applications, such as in microfluidics and lab-on-a-chip devices.

1.14.3.4 CNT Membrane in Liquid Transport Applications

There had been several early experiments demonstrating the ability of the tubular interior of the CNTs to be used as nanoscale containers or conduits

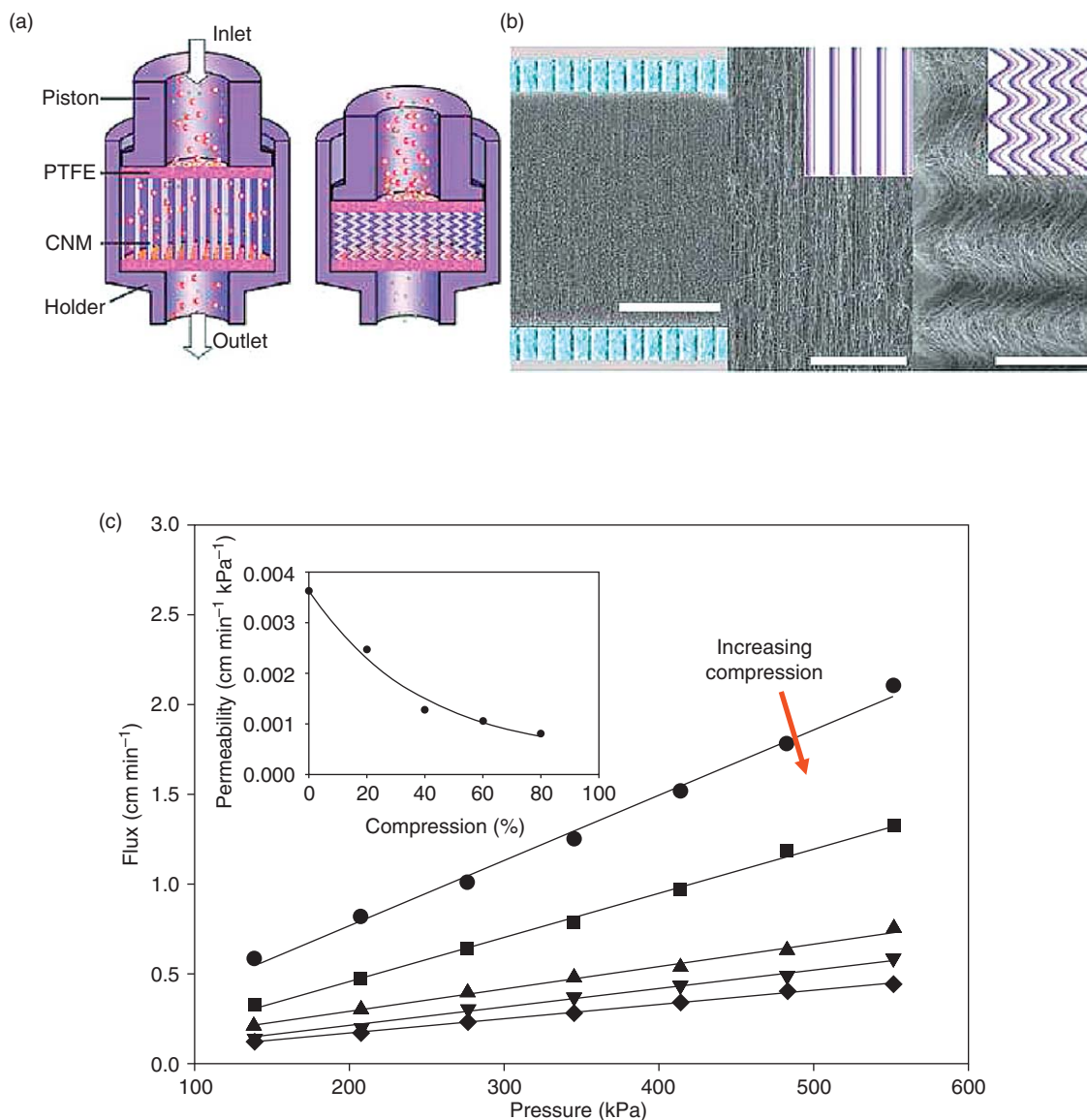


Figure 5 Compression-modulated transport through carbon nanotube (CNT) membrane. (a) The experimental apparatus for water transport studies in the dense-array outer-wall CNT membrane, simultaneously with applied compressive force (b). SEM images showing that the compressive force causes the membranes to shrink the inter-nanotube distance with a concomitant decrease in liquid permeability (c). This is yet another demonstration that transport through membranes composed of CNTs can be tuned by an external stimuli such as pressure. All pictures obtained with permission from Li, X., Zhu, G., Dordick, J. S., Ajayan, P. M. *Small* **2007**, *3*, 595–599.

for mass transport. The earliest experiments demonstrating the feasibility of infiltration of liquid molten metal, such as lead, inside the inner cores of CNTs were conducted by Ajayan and Ijima in 1993 [7]. In a subsequent publication in the same year, the group reported that inorganic materials, such as lead oxide, were more difficult to incorporate inside open-ended CNTs than molten metals [8]. Dujardin *et al.* [9, 10]

also studied the wetting behavior of CNTs by infiltration of molten metals in bulk MWCNT samples with diameters of 2–20 nm. It was concluded that liquids with surface tension less than $\sim 80 \text{ mN m}^{-1}$ will wet the MWCNTs. Hence, liquids such as water ($\sim 80 \text{ mN m}^{-1}$ at 20°C) and organics (e.g., ethanol has a surface tension of $\sim 20 \text{ mN m}^{-1}$ at 20°C), which have significantly less surface tension, could

easily wet MWCNTs. Nevertheless, the important conclusion from these early reports was the feasibility of opening the CNTs using gas-phase oxidation such that the CNTs would act as nanoscale containers for host materials [71].

However, the initial foray into the transport behavior of liquids, such as water, through the CNTs, as in the case of gases, was through computer simulations. At the National Institutes of Health in Maryland, Gerard Hummer's interest in water transport through CNTs was primarily derived from their hydrophobic nature and similarity to protein channels. CNTs perhaps provided the possibility of a much simpler model for MD simulations compared to complex protein channels. Their seminal publication in 2001 suggested that hydrophobic CNT channels, aided by the frictionless and smooth graphitic walls along with a cooperative behavior of a single-file hydrogen-bonded network, allow water to be transported at extraordinary speed [12]. Kalra *et al.* [72] studied the osmotically driven transport of water through CNTs, and the simulated water-flow velocities were very close to those found in natural water channels such as aquaporin. More esoterically, Klaus Schulten's group at the University of Illinois Urbana-Champaign studied water and proton transport behavior through CNTs. In their simulations, the water dipoles were found to be aligned unidirectionally in pristine nanotubes, but somewhat disturbed in CNTs containing charged groups, indicating a structural change in the water structure inside defective CNTs [73]. Nick Quirke's group at Imperial College reported extremely rapid wicking kinetics of oil in CNTs and that the kinetics were not explainable by the conventional Washburn equation [74]. Overall, the simulation studies by all these scientists indicated that the physics of the interaction of liquids, particularly water, with CNTs is something special and needs efforts from their experimental counterparts.

Yuri Gogotsi and coworkers of Drexel University have experimentally studied the behavior of water inside hydrothermally synthesized CNTs by *in situ* microscopy techniques. In 2002 [75], the group reported that the flow velocities of water is $\sim 0.5 \times 10^{-6} \text{ m s}^{-1}$ in 50-nm inner-diameter nanotubes. Although this study conclusively proved the presence of water in equilibrium with a gas inside the CNTs, uncertainty remained as to the driving force of this transport measurement. In a subsequent work, MWCNTs were hydrothermally filled with water,

frozen at -80°C , and examined by high-resolution transmission electron microscopy and electron emission loss spectrometry [76]. Two key observations emerged from this study. The first one indicated that the CNTs with larger pore diameter (20–100 nm) had water segments interspersed with intermittent air pockets, while a rather continuous cylinder of water existed in CNTs with smaller pore diameter in the range of 5–10 nm. In the other case, an air gap of $\sim 4 \text{ \AA}$ between the graphitic walls and frozen water was also observed, especially in the case of smoother graphitic nanotubes [77]. This observation of an air gap between the graphitic surface and the proximal layer of water is remarkable and can be explained by drying transitions of water in nanoscale hydrophobic objects [78].

The earliest experimental mass-transport measurements through CNTs were undertaken on single-pore CNT membranes of $\sim 120\text{-nm}$ pore diameter by the Crooks group, formerly at Texas A&M University [79]. The large-diameter single-pore nanotubes did not exhibit any unusual transport properties and were suited as Coulter counting devices. A Coulter counter is a device that can count biological cells or colloidal particles based on the measurement of ion current through the pores [80]. Based on this approach, there is potential for the development of single-pore membranes of (1–2-nm diameter) for stochastic ion-channel sensing of DNA/RNA translocation [81].

For more macroscopic measurements, flow velocity of liquids (\mathcal{J}) through porous membranes can be predicted using the Hagen–Poiseuille equation and is given by

$$\mathcal{J} = \frac{\varepsilon_p \cdot \mu \cdot r^2 \cdot \Delta P}{8 \cdot \mu \cdot \tau \cdot L}$$

where ε_p is the relative porosity, r_0 the pore radius, P the applied pressure, μ the dynamic viscosity, τ the tortuosity, and L the pore length. The basic assumptions behind this equation are laminar flow and no slip at the boundary layer (i.e., the velocity of the fluid at the CNT wall is zero) and is available in any standard fluid mechanics text.

Pressure-induced transport of a variety of liquids, including water, ethanol, isopropyl alcohol, hexane, and decane, was studied through the inner core of open-ended CNT membrane structure. Enhancement factors for different liquids, shown in **Table 1**, are calculated from the equation

Enhancement factor

$$= \frac{\text{Experimentally observed flow velocity}}{\text{Hagen–Poiseuille flow velocity}}$$

The flow velocities were found to exceed predictions of liquid flow with no-slip boundary condition by 10 000–100 000-fold, suggesting frictionless flow through the CNT cores [11]. The observed flow velocities were consistent with MD simulation predictions by Hummer *et al.*, and have also been confirmed in sub-2-nm CNTs by another independent research group [19]. Interestingly, progressive functionalization of the CNT tips and cores by bulk macromolecules slowed down the flow of liquids through the membrane, confirming the hypothesis that the enhanced flow velocities are due to the noninteracting nature of the graphitic cores [62]. However, the mechanism of fast water transport through CNTs is still unclear. Hummer's MD simulations [12] were obtained for very small nanotubes (~0.8 nm) and suggested a hydrogen-bonded single-file transport of water molecules. It is possible that these simulation results are not applicable to larger nanotubes, such as those in the recent experimental observations in nanotubes with ~1.6- or ~7-nm diameters. More applicable for these dimensions of nanotubes is the concept of slip boundary conditions. Theoretically, the existence of micron-scale slip lengths has been explained by the presence of a gas–liquid or a depletion interface, which provides a nonzero velocity at the walls [82, 83]. Recent MD simulations have attempted to understand the water structure at the depletion region of a smooth nanotube interface and relate it to the water-transport properties [84]. Although water transport in tubular nanoscale channels made from, for example, boron nitride, Si, or CNTs with rough surfaces behaved in a usual manner, the enhancement factors on 1.6-nm-diameter CNT showed excellent agreement with prior experimental data. These simulations underline the direct relationship between the noninteracting graphitic interface and their unique mass-transport properties. Despite these developments, there remain several unresolved questions regarding the structure and properties of liquids in the hydrophobic cores of CNTs. It is likely that the experimental scaffolds made from CNTs, using methods as discussed earlier, can shed light on some of these nanoscale transport phenomena.

Transiting to the more worldly applications of these membranes—liquid filtration studies on dense outer-wall membranes made from CNTs can

separate bacteria such as *Escherichia coli* and *Staphylococcus aureus* and even polio virus in the size range of ~25–30 nm. A competitive advantage of these membranes over polymeric counterparts is the ability to use autoclave processes at ~121 °C for steam cleaning [17]. These membranes could be an alternative to commercial ultrafiltration membranes for separation of bacteria, virus, and proteins. One must also recognize another unique advantage of these membranes – the high electrical conductivity can enable several flux regeneration strategies using principles of electrochemistry.

The concept of membrane reactors, which combine reaction and separation to increase efficiency based on laws of mass action, is well established [85]. The development of electrochemical membrane reactors has been stymied by the lack of electrical conductivity of the membrane materials used to date. As discussed earlier, the high electrical conductivity, chemical inertness of the dense-array outer-wall CNT membranes make them a candidate for simultaneous electrochemical reaction and separation, particularly for destruction of hazardous organic compounds [86]. The concept of such a membrane reactor is shown in **Figure 6**, which could possibly oxidize phenol to benign compounds such as carbon dioxide, water, and aliphatic compounds such as oxalic acid, along with CO₂ and H₂O [87].

The fast water transport through the inner core of CNTs along with the steric and electrostatic selectivity offered by the pores of the nanotubes will have competitive advantage over traditional liquid filtration membranes. In this vein, researchers are considering the use of CNT membranes for developing compact and energy-efficient desalination systems – all stemming from the exceptional mass-transport properties of the CNTs. The inspiration for CNT-membrane-based desalination comes from biological protein channels known as aquaporin, which can transport water at extraordinary speed and selectivity [88] (see **Figure 7**).

Although the ability of CNTs to transport water at speeds close to that of aquaporin has been shown by several research groups, rejection of monovalent ions (in the range of 80–90%) by nanotubes has not been demonstrated. The book-chapter was written in late 2008. However, recently, Donnan-type exclusion has been realized in CNT membranes. Please see the article by Fornasiero *et al.* for more details. Therefore, it remains one of the grand challenges in CNT membrane research – the possibilities being

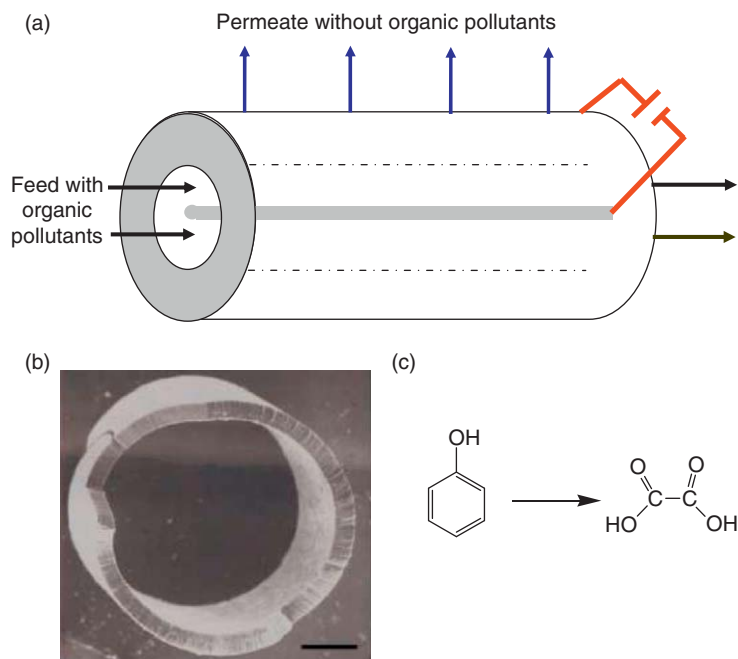


Figure 6 (a) Illustration of a cross-flow electrochemical membrane reactor based on carbon nanotube (CNT) membranes. (b) Scanning electron microscopy (SEM) of a cylindrical-shaped dense-array CNT membrane. Adapted with permission from Srivastava, A., Srivastava, O. N., Talapatra, S., Vajtai, R., Ajayan, P. M. *Nat. Mater.* **2004**, 3, 610–614. (c) Example of electrochemical oxidation of an organic compound, phenol, at the CNT membrane electrode. The removal of the products can aid in increased conversion efficiency based on Le Chatelier's principle and could be accomplished either by the CNT electrode alone or with functional nanoscale catalysts. Although the reaction shown here is representative of the concept of conversion of a hazardous material such as phenol to a benign compound such as oxalic acid, this general concept could be extended to other hazardous organic compounds.

rejection of ions by nanotubes through electrostatic rejection by charged groups on the CNTs via a Donnan exclusion mechanism or by an energy-barrier-based exclusion mechanism [89] in smaller-diameter (~ 1 nm or smaller) CNTs. There have been reports for synthesis of CNTs with ~ 0.8 nm [90], and even smaller diameter of ~ 0.3 nm [91], providing credence to the concept of nanotube membranes for desalination. While the Donnan-type separation is likely to produce ~ 50 – 60% salt rejections [92] – similar to nanofiltration membranes – the presence of functional groups will decrease the permeability. A mechanism based on smaller-diameter CNTs, although a significant technical challenge, can obtain both selectivity and permeability not observed in conventional membrane materials. It is estimated that CNT membranes with ion-rejection capabilities, similar to those in reverse-osmosis membranes, can reduce the cost of desalination by as much as 75% [93]. Owing to this significant advantage, Shanon *et al.* [14] have identified desalination by

nanotube membranes as the technology for the coming decade.

Another potential application of these membranes is as solvent-resistant nanofiltration membranes for recovery and reuse of transition-metal catalysts in the size range of 1 – 3 nm [94]. The current state-of-the-art membranes based on polymers, such as poly-dimethyl siloxane or poly-imides, are lacking in chemical stability, selectivity, and flux [95]; CNT membranes, with their chemical stability, high solvent transport characteristics, and steric selectivity based on the inner core of the CNTs, can be a dramatic improvement over the conventional membrane materials.

Finally, we move from the larger to smaller scale applications, that is, interfacing nanofluidic materials, particularly CNTs, with microfluidic devices [15]. Although assembly and hierarchical synthesis strategies for seamlessly integrating the nanofluid channels with microfluidic devices constitute a significant challenge for the scientific community (Figure 8),

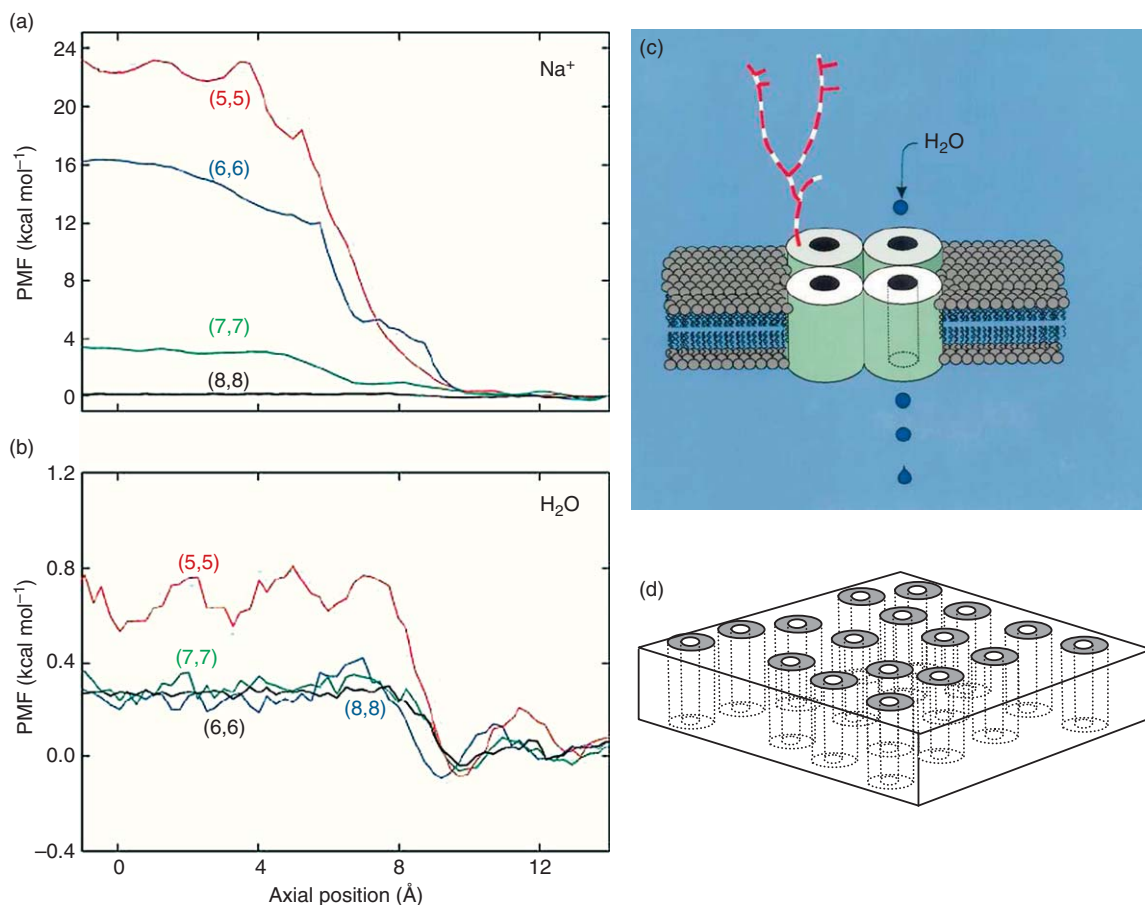


Figure 7 Molecular dynamic studies of ion (a) and water (b) permeation through an open-ended carbon nanotube (CNT) membrane composed of (5,5), (6,6), (7,7), and (8,8) CNTs. Potential of mean force (PMF) is the force for pulling an ion (a) or water molecule (b) from the bulk solution ($z = 14$) to the center of the pore ($z = 0$). Note the considerably large energy barrier for penetration of Na^+ for small-diameter nanotubes. Figures (a) and (b) used with permission from Corry, B. *J. Phys. Chem. B* **2007**, *112*, 1427–1434. The recent enthusiasm of CNTs for salt removal is inspired by protein channels such as aquaporin (c), which can transport water very selectively and with extraordinary speed. Figure used with permission Nielsen, S., Frokiar, J., Marples, D., Kwon, T.-H., Agre, P., Knepper, M. A. *Physiol. Rev.* **2002**, *82*, 205–244. This forms the inspiration for developing CNT membranes (d) for desalination. Figure (d) used with permission from Majumder, M., Zhan, X., Andrews, R., Hinds, B. J. *Langmuir* **2007**, *23*, 8624–8631.

CNTs can provide multifunctional properties, such as frictionless flow, voltage-controlled transport, and electrokinetic mixing at the nanoscale. Therefore, such themes are emerging areas of research in CNT membranes.

1.14.4 Directions of Future Research

CNT membranes represent an emerging branch of membrane science with myriad opportunities in materials science and engineering, which can spawn applications in diverse areas concerning our environment and energy. Researchers may be inspired by the

fact that a concerted effort in the United States, presently, is considering CNT membranes as alternatives to mature materials, such as thin-film composite membranes, for desalination of seawater. At this point, it may be worthwhile to reiterate that this novel class of membranes can provide several competitive advantages, such as:

1. very fast liquid- and gas-transport properties;
2. tighter control over the pore-size distribution;
3. chemically tuned mass-transport properties;
4. stimuli-responsive behavior; and
5. well-defined nanofluidic scaffolds for understanding molecular transport at the nanoscale.

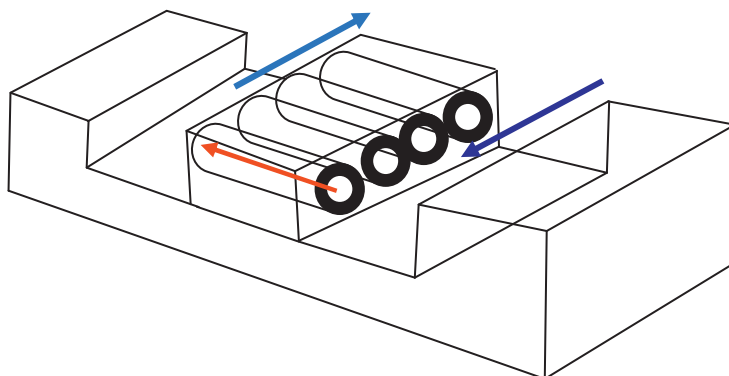


Figure 8 Illustration of carbon nanotubes (CNTs) as an interface between two microfluidic channels. The CNTs could act as filtration channels, control transport of molecules through external stimuli, such as voltage, or aid in mixing via electrokinetic phenomena at the nanoscale. While some of these application potentials have been demonstrated in voltage-controlled transport experiments in macroscopic membranes [66, 68], the template synthesis allows seamless integration of these nanoscale transport channels into microfluidic platforms.

It is not surprising that a wide range of applications in controlled-release devices, sensors, membrane reactors, and nanoscale fluidic interconnects in microfluidic devices along with traditional membrane separations (which we will discuss later) can be easily conjured. Such a wide range of properties, not obvious with traditional membrane material, is why CNT-based membranes are a new frontier in membrane science. In this chapter, we have discussed different approaches for the fabrication of these membranes and showcased their novel transport properties. To further aid our readers, a summary of the demonstrated and future applications (as thought

by the authors) of membranes based on CNTs is presented in **Table 2**. For example, the dense-array outer-wall CNT membranes are potentially attractive for ultrafiltration applications such as protein separations. Their electrical conductivity could be useful for flux regeneration and environmental remediation applications as electrochemical membrane reactors. Open-ended CNT membranes are being considered for desalination applications, while mixed-matrix membranes could provide materials with novel transport properties for conventional membrane processes, such as membrane distillation, pervaporation, or gas separation.

Table 2 Current status and future applications of CNT membrane

Type of CNT membrane	Pore size	Applications demonstrated	Future applications
Template-synthesized CNT membrane	20 nm [20] 200 nm [23]	Water-vapor/oxygen separation [20] Electro-osmotic transport [23]	Nanofluidic interconnects in microfluidic platforms
Dense-array outer-wall CNT membrane	20–100 nm [17]	Heavy hydrocarbon (liquid) separation [17] Bacteria separation [17] Voltage-controlled transport [66] Protein separation [69] Compression-modulated transport [69]	Ultra filtration membranes Electrochemical membrane reactors
Open-ended CNT membrane	1–2 nm [19] ~7 nm [18]	Nanoparticle separation [50] Small-molecule separation [50] Voltage-gated transport for transdermal drug delivery [68]	Desalination [14] Recovery of homogenous catalysts Dialysis Stochastic sensing [81]
Mixed-matrix CNT membranes	Nonporous	Gas separation [44] Pervaporation [64]	Gas separation Pervaporation

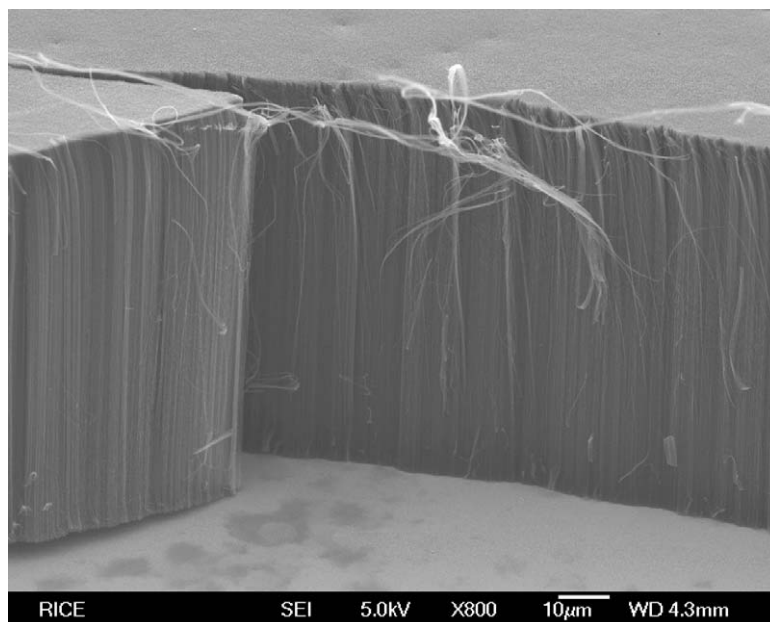


Figure 9 Future research has to be focused on tuning the growth of CNTs with closer packing, finer (1–2 nm) pores, and less spread in pore sizes. Several critical applications, such as desalination and separation of homogenous catalysts, require uniformity of the dimensions of the nanotube in large areas. Shown here is a scanning electron microscopy (SEM) image of an array of SWCNT, in which the theoretical inner diameter can be as small as 0.4 nm. Courtesy of Dr. Robert Hauge, Chemistry, Rice University.

Despite this euphoria, challenges remain to synthesize these membranes reproducibly, cost effectively, and with minimum spread of diameters over large areas. For example, desalination membranes for >95% salt rejection (a very modest number for desalination purposes) would require less than 1 in 100 tubes above 1-nm diameter [89]. These approaches could be controlled at the formation stage, that is, understanding and fine-tuning the growth of nanotubes. An array of SWCNT (with inner diameter ~3 nm) grown by hot-filament CVD technique at Rice University is shown in **Figure 9**.

The alternative approach would require utilization of diameter-controlled sorting of CNTs from SWCNT suspensions [96], followed by alignment of CNTs based on self/electric-field-based assembly. To sum, research on CNT membranes is at its nascent stage of evolution – several real-life applications can emerge in the near future – however, several fundamental and engineering questions still remain unaddressed. Therefore, this highly rewarding and crosscutting multidisciplinary research area needs synergistic contributions from nanoscale materials science, composite materials engineering, and transport phenomena to bring paradigms to several conventional technologies.

References

- [1] Iijima, S. *Nature* **1991**, *354*, 56–58.
- [2] Iijima, S., Ichihashi, T. *Nature* **1993**, *363*, 603–605.
- [3] Monthieux, M., Kuznetsov, V. L. *Carbon* **2006**, *44*, 1621–1623.
- [4] Fischer, J. E., Dai, H., Thess, A., *et al. Phys. Rev. B* **1997**, *55*, R4921.
- [5] Frank, S., Poncharal, P., Wang, Z. L., Heer, W. A. *Science* **1998**, *280*, 1744–1746.
- [6] Dai, H., Wong, E. W., Lieber, C. M. *Science* **1996**, *272*, 523–526.
- [7] Ajayan, P. M., Iijima, S. *Nature* **1993**, *361*, 333–334.
- [8] Ajayan, P. M., Ebbesen, T. W., Ichihashi, T., Iijima, S., Tanigaki, K., Hiura, H. *Nature* **1993**, *362*, 522–525.
- [9] Dujardin, E., Ebbesen, T. W., Hiura, H., Tanigaki, K. *Science* **1994**, *265*, 1850–1852.
- [10] Dujardin, E., Ebbesen, T. W., Krishnan, A., Treacy, M. M. J. *Adv. Mater.* **1998**, *10*, 1472–1475.
- [11] Majumder, M., Chopra, N., Andrews, R., Hinds, B. J. *Nature* **2005**, *438*, 44.
- [12] Hummer, G., Rasaiah, J. C., Noworyta, J. P. *Nature* **2001**, *414*, 188–190.
- [13] Ackerman, D. M., Skoulidas, A. I., Sholl, D. S., Johnson, J. K. *Mol. Simul.* **2003**, *29*, 677–684.
- [14] Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Marinas, B. J., Mayes, A. M. *Nature* **2008**, *452*, 301–310.
- [15] Whitby, M., Quirke, N. *Nat. Nanotechnol.* **2007**, *2*, 87–94.
- [16] Miller, S. A., Young, V. Y., Martin, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 12335–12342.
- [17] Srivastava, A., Srivastava, O. N., Talapatra, S., Vajtai, R., Ajayan, P. M. *Nat. Mater.* **2004**, *3*, 610–614.

- [18] Hinds, B. J., Chopra, N., Rantell, T., Andrews, R., Gavalas, V., Bachas, L. G. *Science* **2004**, *303*, 62–65.
- [19] Holt, J. K., Park, H. G., Wang, Y., et al. *Science* **2006**, *312*, 1034–1037.
- [20] Alsyouri, H. M., Langheinrich, C., Lin, Y. S., Ye, Z., Zhu, S. *Langmuir* **2003**, *19*, 7307–7314.
- [21] Sano, T., Iguchi, N., Iida, K., Sakamoto, T., Baba, M., Kawaura, H. *Appl. Phys. Lett.* **2003**, *83*, 4438–4440.
- [22] Cho, S.-H., Walther, N. D., Nguyen, S. T., Hupp, J. T. *Chem. Commun.* **2005** 5331–5333.
- [23] Miller, S. A., Young, V. Y., Martin, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 12335–12342.
- [24] Jirage, K. B., Hulteen, J. C., Martin, C. R. *Science* **1997**, *278*, 655–658.
- [25] Mattia, D., Rossi, M. P., Kim, B. M., Korneva, G., Bau, H. H., Gogotsi, Y. *J. Phys. Chem. B* **2006**, *110*, 9850–9855.
- [26] Meng, G., Jung, Y. J., Cao, A., Vajtai, R., Ajayan, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 7074–7078.
- [27] Bronikowski, M. J., Willis, P. A., Colbert, D. T., Smith, K. A., Smalley, R. E. Vacuum, Thin Films, Surfaces/Interfaces, and Processing NAN06. In *The 47th International Symposium*, Boston, MA, 2001; pp 1800–1805.
- [28] Jin, L., Bower, C., Zhou, O. *Appl. Phys. Lett.* **1998**, *73*, 1197–1199.
- [29] Thostenson, E. T., Chou, T.-W. *J. Phys. D: Appl. Phys.* **2002**, *35*, L77–L80.
- [30] Smith, B. W., Benes, Z., Luzzi, D. E., et al. *Appl. Phys. Lett.* **2000**, *77*, 663–665.
- [31] Casavant, M. J., Walters, D. A., Schmidt, J. J., Smalley, R. E. *J. Appl. Phys.* **2003**, *93*, 2153–2156.
- [32] deHeer, W. A., Bacsza, W. S., Chatelain, A., et al. *Science* **1995**, *268*, 845–847.
- [33] Li, W. Z., Xie, S. S., Qian, L. X., et al. *Science* **1996**, *274*, 1701–1703.
- [34] Ren, Z. F., Huang, Z. P., Xu, J. W., et al. *Science* **1998**, *282*, 1105–1107.
- [35] Andrews, R., Jacques, D., Rao, A. M., et al. *Chem. Phys. Lett.* **1999**, *303*, 467–474.
- [36] Ravavikar, N. R., Schadler, L. S., Vijayaraghavan, A., Zhao, Y., Wei, B., Ajayan, P. M. *Chem. Mater.* **2005**, *17*, 974–983.
- [37] Safadi, B., Andrews, R., Grulke, E. A. *J. Appl. Polym. Sci.* **2002**, *84*, 2660–2669.
- [38] Huang, S., Dai, L. *J. Phys. Chem. B* **2002**, *106*, 3543–3545.
- [39] Chiang, I. W., Brinson, B. E., Smalley, R. E., Margrave, J. L., Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 1157–1161.
- [40] Mi, W. L., Lin, Y. S., Li, Y. D. *J. Membr. Sci.* **2007**, *304*, 1–7.
- [41] Kim, S., Jinschek, J. R., Chen, H., Sholl, D. S., Marand, E. *Nano Lett.* **2007**, *7*, 2806–2811.
- [42] Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165–185.
- [43] Mahajan, R., Koros, W. J. *Ind. Eng. Chem. Res.* **2000**, *39*, 2692–2696.
- [44] Geng, H.-Z., Kim, K. So, K., Lee, Y., Chang, Y., Lee, Y. J. *Am. Chem. Soc.* **2007**, *129*, 7758–7759.
- [45] Kim, S., Pechar, T. W., Marand, E. *Desalination* **2006**, *192*, 330–339.
- [46] Hollman, A. M., Bhattacharyya, D. *Langmuir* **2004**, *20*, 5418–5424.
- [47] Hollman, A. M., Christian, D. A., Ray, P. D., et al. *Biotechnol. Prog.* **2005**, *21*, 451–459.
- [48] Ago, H., Kugler, T., Cacialli, F., et al. *J. Phys. Chem. B* **1999**, *103*, 8116–8121.
- [49] Domingo-Garcia, M., Lopez-Garzon, F. J., Perez-Mendoza, M. J. *Colloid Interface Sci.* **2000**, *222*, 233–240.
- [50] Majumder, M., Chopra, N., Hinds, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 9062–9070.
- [51] Majumder, M., Keis, K., Zhan, X., Meadows, C., Cole, J., Hinds, B. J. *J. Membr. Sci.* **2008**, *316*, 89–96.
- [52] Alison, J. D. *Electroanalysis* **2000**, *12*, 1085–1096.
- [53] Mao, Z., Sinnott, S. B. *J. Phys. Chem. B* **2000**, *104*, 4618–4624.
- [54] Sokhan, V. P., Nicholson, D., Quirke, N. *J. Chem. Phys.* **2001**, *115*, 3878–3887.
- [55] Sokhan, V. P., Nicholson, D., Quirke, N. *J. Chem. Phys.* **2002**, *117*, 8531–8539.
- [56] de Lange, R. S. A., Keizer, K., Burggraaf, A. J. *J. Membr. Sci.* **1995**, *104*, 81–100.
- [57] Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*, 2nd edn.; Cambridge University Press: London, 2003.
- [58] Rao, M. B., Sircar, S. *J. Membr. Sci.* **1993**, *85*, 253–264.
- [59] Fuertes, A. B. *J. Membr. Sci.* **2000**, *177*, 9–16.
- [60] Arya, G., Chang, H.-C., Maginn, E. *J. Phys. Rev. Lett.* **2003**, *91*, 026102.
- [61] Cooper, S. M., Cruden, B. A., Meyyappan, M., Raju, R., Roy, S. *Nano Lett.* **2004**, *4*, 377–381.
- [62] Majumder, M. PhD Dissertation, University of Kentucky, 2007, 43–66.
- [63] Wei, B.-Y., Hsu, M.-C., Yang, Y.-S., Chien, S.-H., Lin, H.-M. *Mater. Chem. Phys.* **2003**, *81*, 126–133.
- [64] Peng, F., Pan, F., Sun, H., Lu, L., Jiang, Z. *J. Membr. Sci.* **2007**, *300*, 13–19.
- [65] Cong, H., Zhang, J., Radosz, M., Shen, Y. *J. Membr. Sci.* **2007**, *294*, 178–185.
- [66] Wang, Z. K., Ci, L. J., Chen, L., Nayak, S., Ajayan, P. M., Koratkar, N. *Nano Lett.* **2007**, *7*, 697–702.
- [67] Jiang, Y., Lee, A., Chen, J., et al. *Nature* **2003**, *423*, 33–41.
- [68] Majumder, M., Zhan, X., Andrews, R., Hinds, B. J. *Langmuir* **2007**, *23*, 8624–8631.
- [69] Li, X., Zhu, G., Dordick, J. S., Ajayan, P. M. *Small* **2007**, *3*, 595–599.
- [70] Cao, A., Dickrell, P. L., Sawyer, W. G., Ghasemi-Nejhad, M. N., Ajayan, P. M. *Science* **2005**, *310*, 1307–1310.
- [71] Ajayan, P. M., Stephan, O., Redlich, P., Colliex, C. *Nature* **1995**, *375*, 564–567.
- [72] Kalra, A., Garde, S., Hummer, G., *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10175–1080.
- [73] Zhu, F., Schulten, K. *Biophys. J.* **2003**, *85*, 236–244.
- [74] Supple, S., Quirke, N. *Phys. Rev. Lett.* **2003**, *90*, 214501.
- [75] Megaridis, C. M., Yazicioglu, A. G., Libera, J. A., Gogotsi, Y. *Phys. Fluids* **2002**, *14*, L5–L8.
- [76] Rossi, M. P., Ye, H. H., Gogotsi, Y., Babu, S., Ndungu, P., Bradley, J. C. *Nano Lett.* **2004**, *4*, 989–993.
- [77] Naguib, N., Ye, H. H., Gogotsi, Y., Yazicioglu, A. G., Megaridis, C. M., Yoshimura, M. *Nano Lett.* **2004**, *4*, 2237–2243.
- [78] Lum, K., Chandler, D., Weeks, J. D. *J. Phys. Chem. B* **1999**, *103*, 4570–4577.
- [79] Sun, L., Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 12340–12345.
- [80] Ito, T., Sun, L., Crooks, R. M. *Anal. Chem.* **2003**, *75*, 2399–2406.
- [81] Bayley, H., Cremer, P. S. *Nature* **2001**, *413*, 226–230.
- [82] Lauga, E., Brenner, M. P. *Phys. Rev. E (Stat., Nonlinear, Soft Mat. Phys.)* **2004**, *70*, 026311-1–026311-7.
- [83] de Gennes, P. G. *Langmuir* **2002**, *18*, 3413–3414.
- [84] Joseph, S., Aluru, N. R. *Nano Lett.* **2008**, *8*, 452–458.
- [85] Denbigh, K. G., Turner, J. C. R. *Chemical Reactor Theory: An Introduction*, 3rd edn.; Cambridge University Press: London, 1984.
- [86] Martinez-Huitle, C. A., Ferro, S. *Chem. Soc. Rev.* **2006**, *35*, 1324–1340.
- [87] Maluleke, M. A., Linkov, V. M. *Sep. Purif. Technol.* **2003**, *32*, 377–385.

- [88] Nielsen, S., Frokiar, J., Marples, D., Kwon, T.-H., Agre, P., Knepper, M. A. *Physiol. Rev.* **2002**, *82*, 205–244.
- [89] Corry, B. J. *Phys. Chem. B* **2007**, *112*, 1427–1434.
- [90] Marn, C., Serrano, M. D., Yao, N., Ostrogorsky, A. G. *Nanotechnology* **2002**, *13*, 218–220.
- [91] Zhao, X., Liu, Y., Inoue, S., Suzuki, T., Jones, R. O., Ando, Y. *Phys. Rev. Lett.* **2004**, *92*, 125502.
- [92] Fornasiero, F., Park, H. G., Holt, J. K., *et al.* *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 17250–17255.
- [93] Lamont, A. Some Results Bearing on the Value of Improvements of Membranes for Reverse Osmosis; UCRL-TR-219746, Lawrence Livermore National Laboratory, 2006.
- [94] Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702–1706.
- [95] Wong, H.-T., See-Toh, Y. H., Ferreira, F. C., Crook, R., Livingston, A. G. *Chem. Commun.* **2006**, 2063–2065.
- [96] Arnold, M. S., Green, A. A., Hulvat, J. F., Stupp, S. I., Hersam, M. C. *Nat. Nano.* **2006**, *1*, 60–65.

Biographical Sketches



Dr. Mainak Majumder received his undergraduate degree from the Calcutta University in 1999 and a master's degree from the Banaras Hindu University in 2001. He then served as a staff scientist for 2 years at the Central Glass and Ceramic Research Institute (CGCRI), a national laboratory in India, with a focus on membrane technologies for water purification. He received his PhD from the University of Kentucky in 2007, where he studied the molecular transport properties through carbon nanotube membranes. At present, he is pursuing research at Rice University on colloidal processing of carbon nanotubes. His research focus is the interface of materials science and chemical engineering, particularly how nanoscale materials can be applied to develop novel materials for energy and environmental applications. Presently he is an academic staff member at the Department of Mechanical and Aerospace Engineering, Monash University, Australia.



Professor Pulickel M. Ajayan received his undergraduate degree from the Banaras Hindu University in 1985, and doctoral degree from Northwestern University in 1989. A pioneer in the area of carbon nanotubes, Prof. Ajayan has been one of the key figures in the development of carbon nanotube technologies. After 10 years at the Rensselaer Polytechnic Institute (RPI), including as director of the RPI Interconnect Focus Center, New York, he joined Rice University as the Benjamin M. and Mary Greenwood Anderson Professor of Engineering in Mechanical Engineering and Materials Science Department. His research goals are oriented toward developing multifunctional nanostructures and hybrid platforms that would have applications in diverse fields, such as alternative energy storage, structural composites, sensors, electronic devices, and biomedical applications. Prof. Ajayan has authored or coauthored about 320 publications, two books, and his work has received more than 25 000 citations and h-index of 72. He has won several awards such as the MRS medal and the Burton medal from the Microscopy Society of America. He was selected as one of 2006 Scientific American 50 by the Scientific American Magazine and has also been selected as Nano50TM Innovator by Nanotech Briefs (2007).