1.12 Carbon Nanotube Membranes: A New Frontier in Membrane Science

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Lijima, 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 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.

1.12.2 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.

1.12.2.1 Template-Synthesized CNT Membrane

In the template synthesis approach, a preexisting 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 (<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 CNT membranes. For example, Figure 1 shows the artist’s rendition of water molecules zipping through the inner core of carbon nanotube (CNT) (credit: Mark Denomme from the University of Kentucky.) This chapter examines the state of the art in membranes based on CNTs.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Permeable pore density (# per m²)</th>
<th>Membrane thickness (m)</th>
<th>Flow velocity normalized at 1 bar (m/s)</th>
<th>Viscosity (cP)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>3.4 x 10¹³</td>
<td>126 x 10⁻⁶</td>
<td>5.6 x 10⁻²</td>
<td>0.3</td>
<td>1.09 x 10⁴</td>
</tr>
<tr>
<td>Decane</td>
<td>3.4 x 10¹³</td>
<td>126 x 10⁻⁶</td>
<td>0.67 x 10⁻⁴</td>
<td>0.9</td>
<td>3.9 x 10⁴</td>
</tr>
<tr>
<td>Water</td>
<td>1-3.4 x 10¹³</td>
<td>34-126 x 10⁻⁶</td>
<td>26.1 (±17.2) x 10⁻²</td>
<td>1.0</td>
<td>6 (±1.6) x 10⁴</td>
</tr>
<tr>
<td>EtOH</td>
<td>3.4 x 10¹³</td>
<td>126 x 10⁻⁶</td>
<td>4.5 x 10⁻²</td>
<td>1.1</td>
<td>3.2 x 10⁴</td>
</tr>
<tr>
<td>IPA</td>
<td>3.4 x 10¹³</td>
<td>126 x 10⁻⁶</td>
<td>1.12 x 10⁻²</td>
<td>2</td>
<td>1.4 x 10⁴</td>
</tr>
</tbody>
</table>

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 ~10,000–100,000, suggesting strong deviation from no-slip hydrodynamic flow.
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 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 pores.

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 [26]. (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]. (d) Mixed-matrix membrane composed of CNTs in a polymer matrix; (below) SEM image of the composite-membrane structure [44].
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 (>2000 °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 co-workers [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.

1.12.2.2 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 (∼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 SWNT 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 SiO2.

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 MWNT 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 MWNTs 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 MWNT arrays from a continuous source of ferrocene and xylene at ∼650 °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 co-workers 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 MWNT 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].

**1.12.2.3 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 (~10<sup>10</sup> tubes cm<sup>-2</sup>) 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 (~10<sup>9</sup> cm<sup>-2</sup>) of membranes in Table 1, estimated from salt–diffusion experiments, are almost a magnitude smaller than the density of the CNTs in the arrays (~10<sup>10</sup> cm<sup>-2</sup>) 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 –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 BET pore-size distribution of ~6 ± 2 nm, which is consistent with TEM observations of the inner core of ~7 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<sub>3</sub>N<sub>4</sub>, filled up the space between the nanotubes. Standard etching procedures were adopted to create openings on the Si chip; subsequently, excess Si<sub>3</sub>N<sub>4</sub> 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 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 the 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 (~10^10 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.

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 co-workers have incorporated open-ended and amine-functionalized CNTs (with ~13.6-Å pore diameter) into poly(sulfone) [44] and poly(amide-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.

1.12.3 Properties and Application of CNT Membranes

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