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feature

The Potential of Carbon Nanotube Membranes for Analytical Separations

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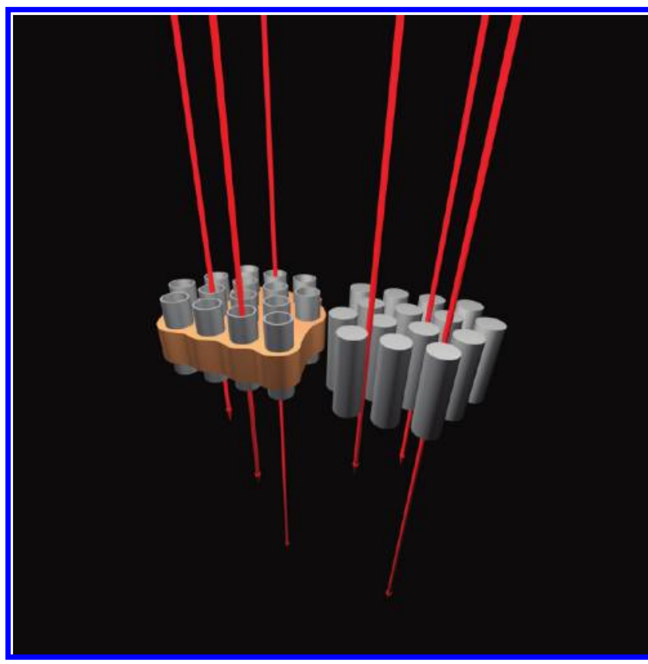
Advances in nanotechnology have enabled the development of nanoporous membranes based on carbon nanotubes, which, by virtue of their exceptional properties, constitute excellent supports for analytical processes, including the selective separation of some molecules.



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Optimizing a membrane separation process requires careful control of pore size and uniformity in the membrane. In this respect, the inner core of carbon nanotubes (CNTs) provides an effective alternative to existing ordered porous structures such as anodized alumina or polycarbonate membranes at pore diameters of 0.3 nm to 0.6 μm. One major advantage of CNTs is that they provide a uniform membrane pore size (typically 6−7 nm with multiwalled nanotubes [MWNTs] and 1.3−2 nm with double-walled nanotubes [DWNTs]) that can be fine-tuned via the catalyst particle size. CNT-based membranes have opened up new prospects for analytical chemistry, such as selective separation of microorganisms,[1] nanoparticles,[2,3] or biomolecules[4] from complex samples by filtration.

Since their discovery in 1991, CNTs have aroused much attention from researchers in a number of fields. Thus, their favorable adsorption properties have fostered use as sorbent materials in many analytical processes, e.g., as sorbents in solid-phase (micro)extraction, stationary phases in GC and LC, or pseudostationary phases in CE. More recently, CNT-based membranes have been found to possess unique fluid properties; thus, some properties of fluids confined at molecular dimensions diverge from those in the bulk fluid.

The starting point for the development of CNT membranes was the study of fluid flow through CNTs by molecular simulation, which revealed that water molecules can be carried through nanotubes in a membrane[5] by effect of the tight hydrogen bonding network present inside each tube. Transport rates are extremely high when the membrane is placed under the influence of an osmotic gradient.[6] These theoretical discoveries have been implemented in real membranes for efficient water desalting/desalination by reverse osmosis.[7]

Additional theoretical studies on the analytical possibilities of these membranes include one on electrophoretic transport of single-stranded RNA molecules through 1.5-nm-wide pores in CNT membranes.[8] Conformational dynamics controlled RNA entry into the nanotube pores, while hydrophobic attachment of RNA bases onto pores controlled its exit. Another study predicted binary permeance of CH_4/H_2 mixtures through defect-free (10,10) single-walled nanotubes (SWNTs) acting as a membrane at room temperature.[9] CNTs seem to be highly selective for CH_4 over H_2 when a mixture of these gases permeates through the membrane. For instance, the binary selectivity for the membrane with a pressure drop of 197.4 kPa and a CH_4 fraction in feed of ~0.3 was 20. Finally, a study using molecular dynamics assessed the possibility of separating different atom species by using twisted CNTs.[10]

Molecular dynamic simulations have predicted excellent fluxes for gases and water through CNT membranes; this useful

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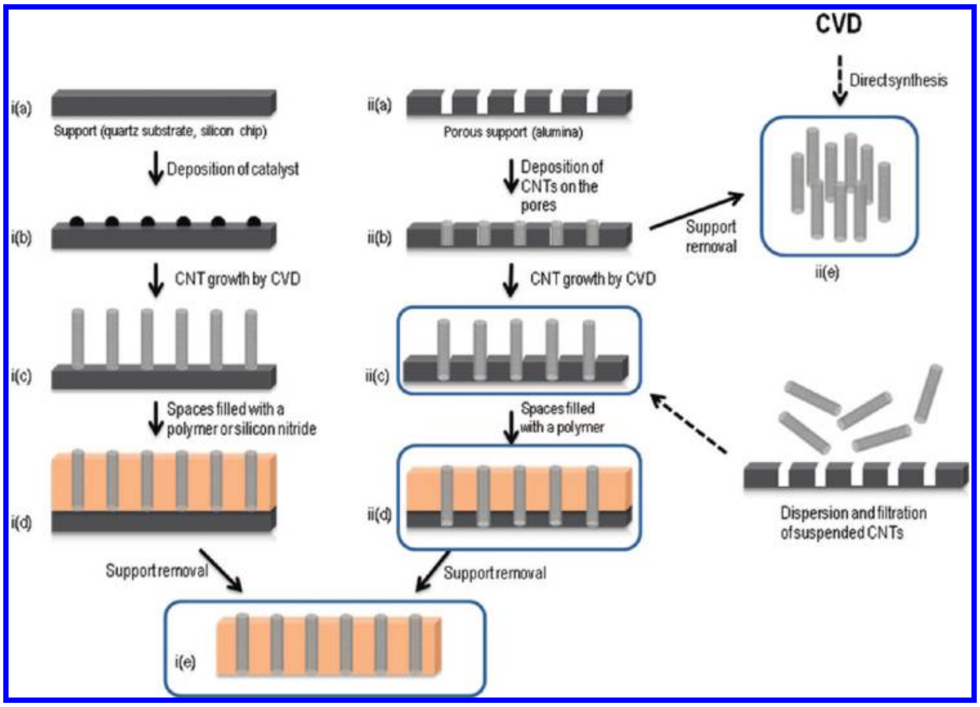

Figure 1. (i) Simplified scheme of the synthetic procedure for free-standing membranes with vertically aligned CNTs embedded in a polymeric (polystyrene)[17] or silicon nitride[13] matrix. The quartz substrates for CVD growth are removed at the end. (ii) Method for fabricating vertically aligned CNT membranes by CVD growth of nanotubes within the pores of an alumina substrate. Membranes can be directly used (iic) or spaces within CNTs filled with a polymer (iid). In addition, the alumina template can be removed (ie). Membranes consisting exclusively of vertically aligned CNTs (iie) can be obtained by removing the alumina template once nanotubes have been deposited into pores. Finally, (iic) membranes can be obtained by CNT dispersion and filtration of the solution through a porous membrane.

property, based on CNTs' hydrophobic nature, has promoted the development of membranes containing embedded nanotubes. Liquid flow is 4−5 orders of magnitude faster than predicted by conventional fluid-flow theory[11] because of the presence of an almost frictionless interface at CNT walls. The presence of MWNTs in membranes increased selectivity in the filtration of H_2/CH_4 mixtures through nanocomposite fabricated membranes.[12] In addition, CNT membranes can be turned into "gatekeepers" by functionalizing CNT tips;[13,14] this, as explained later on, carefully controls fluxes and improves selectivity. More recently, membranes based on DWNTs have been fabricated in reduced diameters comparable to those used in molecular simulation tests, and mass transport of water through them has been confirmed.[15]

Mass transport in nanoporous media can be useful for many technologically important reasons. So far, membranes have been used to deliver therapeutic molecules such as drugs and genes through cellular matrixes,[8] to treat nicotine addiction and opioid withdrawal symptoms transdermally,[16] and to introduce volatile analytes into mass spectrometers by directly fitting the membrane in place of a capillary tube.[17]

This Feature provides an overview of the state of the art and analytical potential of CNT membranes. Though we cannot provide a comprehensive review here, interested readers can find further information about nanofluidic transport through CNTs elsewhere.[18] This article has been structured in accordance with the two main arrangements of CNTs in membranes: vertically aligned or as bundles.

MEMBRANES WITH VERTICALLY ALIGNED CARBON NANOTUBES

The synthesis and characterization of ordered nanoporous materials is an active research area because producing an appropriate membrane structure with a highly ordered vertical orientation of pores is a major challenge. At present, the problem is usually addressed by embedding CNTs in a matrix (e.g., a polymer or silicon nitride) and using them as such to form the membrane.

CNT membranes contain two different types of pores: those between individual nanotubes and those in the nanotube lumina. This allows membranes to be established from open-ended nanotubes or from the interstitial spaces between nanotubes.

Aligned Carbon Nanotubes Embedded in a Matrix. In some CNT membranes, the interstitial spaces are filled with silicon nitride[19] or polymers (polystyrene,[20] polysulfone[21]). The spacing between CNTs is filled with a continuous matrix, and the usually closed ends of the nanotubes are etched open, so filtration occurs through the open nanotubes, the only available pathway for mass transport. Synthesis of this type of membrane involves chemical vapor deposition (CVD) of nanotubes onto a support such as quartz or a silicon chip (Figure 1, ia-ic), followed by filling of the volume between nanotubes with a polymer or silicon nitride (Figure 1, id) and, in free-standing membranes, removal of the film from the substrate (Figure 1, ie). Finally, excess matrix material is removed, and CNT tips are opened by oxidation with H_2O plasma.

The difficulty of using free-standing[20] and silicon chip supported[22] CNT membranes in large-scale industrial applications has spurred the development of alternative, vertically aligned CNT membranes on porous alumina supports, which can be scaled up

Table 1. Comparison of CNT Membranes

Study	Mi et al.[23]	Hinds et al.[20]	Holt et al.[19]	Kim et al.[21]
Membrane structure	Porous alumina support	Free-standing (removed from dense quartz support)	Silicon wafer	PTFE filter
Matrix	Polystyrene	Polystyrene	Silicon nitride	Polysulfone
CNT layer thickness (μm)	~10	5–10	5	6
CNT areal density (#/cm^2)	1.87×10^9	6×10^{10}	2.5×10^{11}	$7.0 \pm 1.75 \times 10^{10}$
CNT structure	Multiwalled	Multiwalled	Double-walled	Single-walled
CNT outer diameter (nm)	20	NA	2	--
Pore diameter (d_p) (nm)	6.3	7.5	1.6	1.2
CNT tortuosity factor (τ)	1.26	1.1	1	--
Areal porosity (ε)	6.2×10^{-4}	2.7×10^{-2}	5.0×10^{-3}	--
Knudsen number (λ/d_p)	1.2–2.2	~1	10–70	--
Enhancement over Knudsen model	~4	~1	16–120	--

as needed.[23] The support may have disk geometry or a tubular or multichannel structure. Nanotubes are grown on its pores (Figure 1, iib-iic), and the inner CNT gaps in the membrane filled with polystyrene (Figure 1, iid). The synthetic procedure differs in how excess polymer is removed from the surface and CNT tips are opened (by mechanical polishing). Some authors have successfully used a combination of self-assembly and filtration to fabricate a SWNT/polymer (polysulfone) nanocomposite membrane.[21]

In general, membranes consisting of MWNTs have pore diameters of 6−7 nm. However, interest is growing in producing membranes with smaller nanopores-those in the same size range as the molecules—to facilitate fast transport and size selectivity for gas mixtures. Pore sizes of 1.3−2 nm can readily be produced by growing DWNTs on a silicon chip.[22]

Table 1 summarizes the characteristics of vertically aligned CNT membranes. Unlike conventional ceramic membranes, which typically have tortuosity factors and porosities of ~3−5 and 0.3−0.6, respectively, CNT membranes have a near-unity tortuosity factor but very low areal porosity, which suggest the presence of straight pores and large gaps between nanotubes, respectively. CNT membranes with porous alumina as support are the least porous because of their low areal density. The enhancement over the Knudsen diffusion model increases with decreasing pore size or increasing Knudsen number (i.e., the ratio of molecular mean free path to pore diameter). Knudsen diffusion occurs when the mean free path of the gas molecules is larger than the pore radius of the membrane and there are more collisions with the pore walls than between gas molecules. The enhancement indicates that the gas transport takes place primarily through the carbon nanotubes, with very little transport through the ultrathin polymer matrix. Membranes on porous alumina supports have low areal tube densities relative to membranes on dense silicon and quartz supports.

Carboxylated CNTs obtained by oxidation can be easily derivatized by carbodiimide chemistry with a molecule that binds to a bulky receptor that can open or close the pore entrance (Figure 2). For example, a desthiobiotin (DSB) derivative[13] attached to the membrane binds reversibly to streptavidin and improves the selectivity of chemical transport across the membrane.[14] Incubating a streptavidin-coordinated membrane with biotin caused streptavidin to be released and the flux of methyl viologen (MV^{2+}) restored, allowing reversible binding to regulate transport through the membrane.

Many applications require increasing the density of tethered molecules with modest separation factors[14] such as MV^{2+} and $Ru(bipy)_3^{2+}$ (1.7−3.6) relative to porous alumina, in which separation coefficients can be as high as 1500.[24] Electrochemical grafting of functional diazonium salts to exposed CNT tips increases functionalization of the latter—and the density of functional molecules as a result. One important constraint is that the molecules binding to CNT pores should be small enough not to block the core themselves. Moreover, membranes consisting of an array of aligned CNTs and functionalized with charged molecular tethers exhibit voltage gated control of ionic transport through the cores of CNTs. The selectivity between $Ru(bipy)_3^{2+}$ and MV^{2+} flux can be as high as 23 with −130 mV bias applied to the membrane as a working electrode.[25]

As noted earlier, despite their hydrophobicity, CNT membranes have the exceptional property of allowing fast flow of a fluid such as water, a result of the formation of water wires and clusters held by tight hydrogen bonds. Also, water wire formation is believed to be important for proton transport, which was 40× higher within 0.8-nm-diameter CNTs than in bulk water.[26] This property expedites filtration of aqueous solutions, which, together with CNTs' extraordinary ability to adsorb nonpolar analytes via $\pi-\pi$ interactions, can facilitate some steps of the analytical process. In fact, Raman spectroscopy measurements[27] have suggested that gas molecules are adsorbed in the inner pores of MWNTs, so sorption must occur on the polymer binding matrix or in membrane defects. An ideal membrane must possess a high selectivity and high permeance; both properties are dictated by the affinity of the molecules to be adsorbed and the relative speed with which they can diffuse through the membrane. CNT membranes, which have proved highly compliant with both requirements, may thus be the ideal platforms for analytical separations.

Polymeric membranes containing CNTs have proved useful for transporting gas molecules such as N_2[13,14] or aqueous ions such as $Ru(NH_3)_6^{3+}$,[20] $Ru(bpy)_3^{2+}$,[13,14,25,28] and MV^{2+}.[13,14,25] For instance, a $Ru(NH_3)_6^{3+}$ flux of 0.07 μmol/cm^{2}h can be raised to 0.9 μmol/cm^{2}h by treating the membrane with acid. This flux level is comparable to that of ordered alumina membranes.[29] Also, the flux of MV^{2+} before binding of streptavidin to a DSB-functionalized CNT membrane,[13] 4.8 nmol/cm^{2}h, was reduced to 0.2 nmol/cm^{2}h upon binding; this result testifies to the ability to control the flux by adjusting the membrane properties. CNT membranes on silicon nitride have been used to remove some small ions such as Cl^-, K^+, $Ru(bipy)_3^{2+}$, Ca^{2+}, and $Fe(CN)_6^{3-}$ from aqueous solutions.[30,31]

In the place of a capillary tube, a membrane with CNTs grown within the pores of anodic aluminum oxide was directly coupled to a mass spectrometer[17] to introduce volatile analytes; the membrane exhibited preferential transmission of methane. Conductance decreased with increasing total pressure, but the effect decreased progressively for the following sequence of gases: $CH_4 > N_2 > O_2 > Ar > CO_2$.

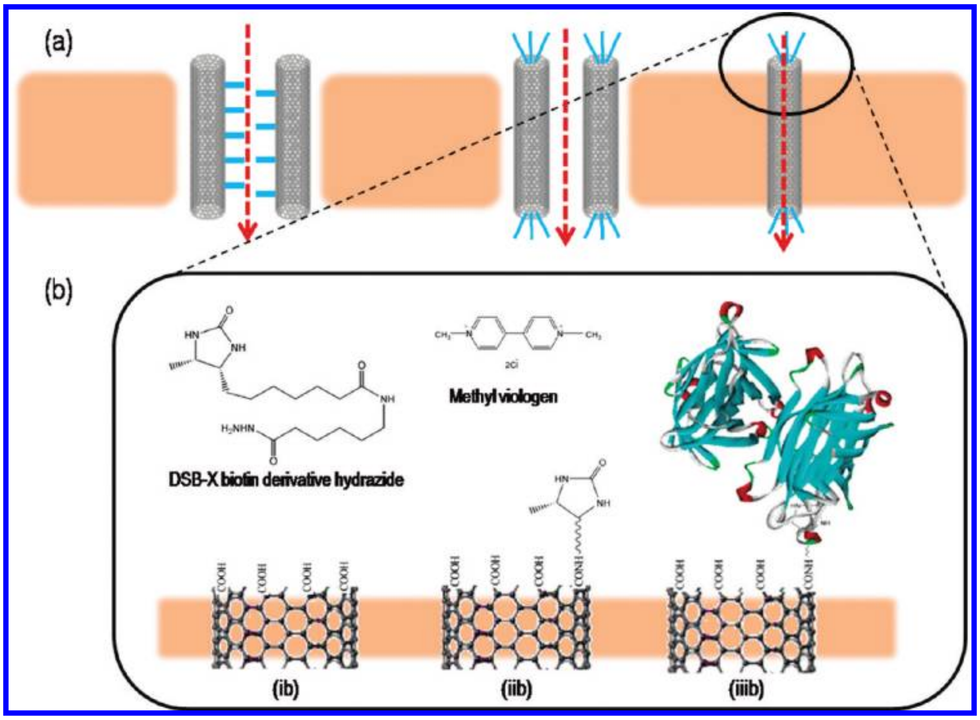

Figure 2. (a) Pore types present in a CNT membrane: within and between nanotubes. (b) More detailed view demonstrating binding of streptavidin to DSB-functionalized tips of CNTs at the surface of a CNT−polystyrene composite membrane. (ib) Open tips of CNTs with carboxylic end groups; (iib) DSB-X biotin hydrazine functionalized tip of a CNT; (iiib) Streptavidin bound to the functionalized membrane. The structures of DSB-X biotin hydrazine and methyl viologen are also shown. Adapted from ref. 13.

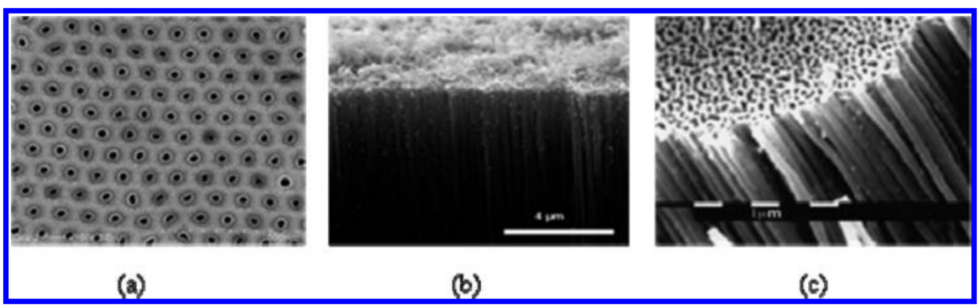

Figure 3. (a) Scanning electron micrograph of a CNT membrane surface after ion milling. The dark areas in the image are open pores, the light rim around the pore is the CNT, and the remainder substrate the aluminum oxide film. (b) Cross-sectional scanning electron image of a CNT-modified anodized alumina membrane with pore size 200 nm. (c) Scanning electron micrograph of a template-synthesized carbon tubular membrane after the alumina template is dissolved. The edge (lower part of the image) with the tubules and the surface (upper part) are shown. Adapted with permission from refs. 17, 33, and 34.

Membranes Consisting Exclusively of Aligned Carbon Nanotubes. The membranes consisting of vertically aligned CNTs described above posses a matrix that fills the spaces between CNTs and/or the support onto which nanotubes are grown and is subsequently removed in some cases. By contrast, the membranes described in this section contain no binder or support. Most are obtained by growing CNTs by CVD on a substrate[2,32] such as the pores of a microporous alumina template[33,34] or glass;[35] the nanotubes are peeled off the membrane at the end of the process (Figure 1, iie). Alumina templates, for instance, can be removed by leaching with a NaOH solution.[34] New synthetic procedures producing aligned CNTs without a support[36] may in the near future enable the direct synthesis of CNT membranes. Figure 3 shows scanning electron micrographs of membranes with alumina template.

This type of membrane can also be obtained with other methods such as continuous spray pyrolysis,[37] which creates hollow carbon cylinders up to a few centimeters in diameter and several centimeters long with walls consisting of micrometer-length aligned MWNTs. Alternatively, membranes can be produced by self-assembly of oxidized SWNTs. The surface of a soaked glass substrate immersed in a SWNT water dispersion forms a thin film through natural vaporization of water. Nanotubes are uniaxially aligned in the direction of the air/water/substrate triple line,[38] and the membrane is peeled off by stirring the glass in water.

One other way of obtaining an array of CNTs is to grow them by CVD into dense membranes via the capillary forces of solvent evaporation and then allow them to collapse.[2] These membranes have an average spacing between CNTs after shrinkage of ∼3 nm-comparable to the pore size of the nanotubes-and a density 8−270× higher than that of previous membranes. Because the interstitial pores are not sealed, gases can permeate through both the nanotubes and their interstitial pores.

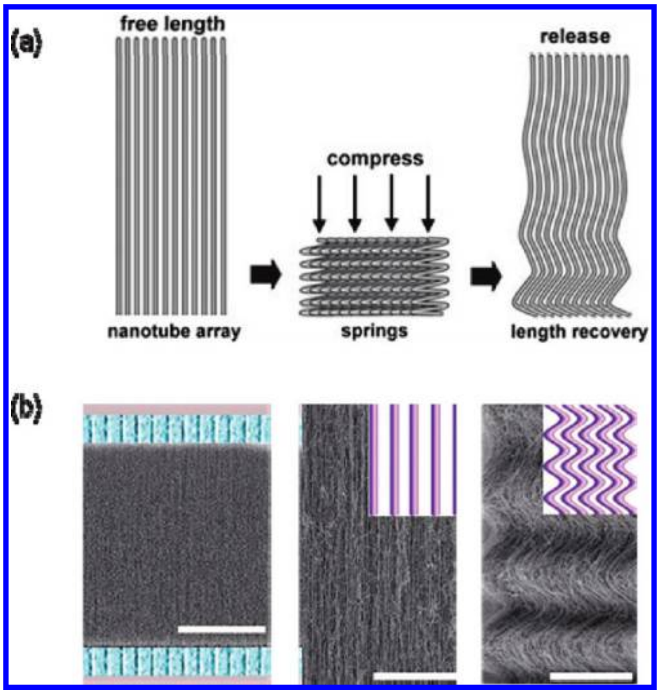

Figure 4. (a) Compression testing of aligned CNT films. A schematic illustration shows a nanotube array compressed to folded springs and then regaining its free length upon release of the compressive load. (b) Scanning electron micrographs of a membrane both compressed and uncompressed. Adapted with permission from refs. 41 and 42.

These free-standing membranes contain a parallel array of CNTs that spans their full thickness. Well-aligned CNTs cannot always be obtained; in some cases, the material deposits mainly as bundles of curved CNTs.[34] Electroosmotic flow (EOF) can be driven across by separating two electrolyte solutions with the membrane and using an electrode in each solution to pass a constant ionic current through the nanotubes.[39,40] Based on the EOF direction, the nanotubes have negative surface charge that can be boosted by electrochemical derivatization with *p*-aminobenzoic acid. On the other hand, membranes with positive surface charge can be prepared by electrochemical derivatization with 2-(4-aminophenyl)ethylamine.

This type of membrane is super-compressible[41] and fully elastic; the pores can be tuned simply by mechanical compression and release (Figure 4).[42] This unique property has enabled the separation of species of different sizes within the tunable pore size range by simply adjusting the membrane thickness by uniaxial compression, eliminating the need to replace the filter.

An advantage of CNT membranes over conventional filters is that they can easily be cleaned by ultrasonication and autoclaving (or purging) to restore their filtering efficiency. Other water-filtration membranes (e.g., cellulose nitrate/acetate membranes) cannot be reused because they adsorb bacteria heavily during filtration. Moreover, CNTs are thermally stable, so their membranes can be used at higher temperatures than conventional polymer membrane filters (~400 °C versus ~50 °C). In summary, the exceptional thermal and mechanical stability of nanotubes and the high surface area and easy and cost-effective fabrication of nanotube membranes make them competitive with commercially available ceramic and polymer-based separation membranes.

The membranes described in this section have been used in a variety of applications including nanofiltration of gold nanoparticles and N_2 adsorption.[2] Because no filler is used, they also allow permeation through the interstitial spaces. Cylindrical membranes of this type are useful for removing multiple components of heavy hydrocarbons from petroleum and for filtering bacterial contaminants such as *E. coli* or the nanometer-sized poliovirus from water.[37] Filtering seems to occur mostly through interstitial spaces; however, there might be some additional transport through the inner hollow channels of the nanotubes. These membranes have also been used to separate a larger molecule (triisopropyl orthoformate) from a smaller molecule (*n*-hexane) during pervaporation.[2] This testifies to their potential for separating not only gases—the permeance of which is roughly 450× higher than predicted from Knudsen theory—but also liquid mixtures.

MEMBRANES WITH BUNDLES OF CARBON NANOTUBES

Unlike those in membranes described in the previous section, CNTs are not aligned vertically in membranes containing bundles of nanotubes. As a result, filtration does not rely on size exclusion or sieving in the inner core of the tubes but rather on the sorption capabilities of the material.

Bundles of Carbon Nanotubes on Inert Membranes. Unlike buckypapers (below), CNT-modified membranes require an inert membrane. There are two different types of filters: those with electrostatic and those with covalent interaction of CNTs with the membrane. Because CNT bundles are not aligned, they can form aggregates and facilitate interaction of the analytes with both their walls and the interstitial spaces. Adsorption of the analytes is favored by $\pi-\pi$ electrostatic interactions and the typically large surface area of CNTs.

CNT-modified filters are usually prepared by passing a dispersed solution of CNTs through a membrane. The nanotubes are dispersed by means of a surfactant such as SDS[43] or Triton X-100[3] or DMSO;[1] alternatively, MWNTs functionalized with poly(diallyldimethylammonium) chloride[44] can be filtered directly. These membranes are available in various formats including cellulose ester membranes,[44] PVDF,[1] nylon-encased filters,[3] or qualitative filter paper.[43] When DMSO or a surfactant is used to disperse the CNTs, the dispersant must be removed by passing an appropriate solvent such as methanol or ethanol through the membrane.

Some crucial properties of CNTs such as their high surface area, tendency to aggregate and form highly porous structures, and antibacterial action (of SWNTs) have been exploited to develop membranes incorporating nanotube bundles. Among other applications, these membranes have enabled 1) selective isolation and preconcentration of acidic proteins such as BSA[44] (increased sample loading and elution flow rates resulted in a 146-fold improvement in the sorption capacity of BSA); 2) preconcentration and determination of carboxylic SWNTs from spiked environmental water samples[3] (separated electrophoretically with recoveries of 70−85% and precision of 6.4−7.3%); 3) retention of bacteria, which were effectively inactivated upon contact with a SWNT filter, and removal of viruses, which were captured by nanotube bundles inside the SWNT layer;[1] and 4) enrichment of phthalate esters, bisphenol A, 4-*n*-nonylphenol, 4-*tert*-octylphenol,

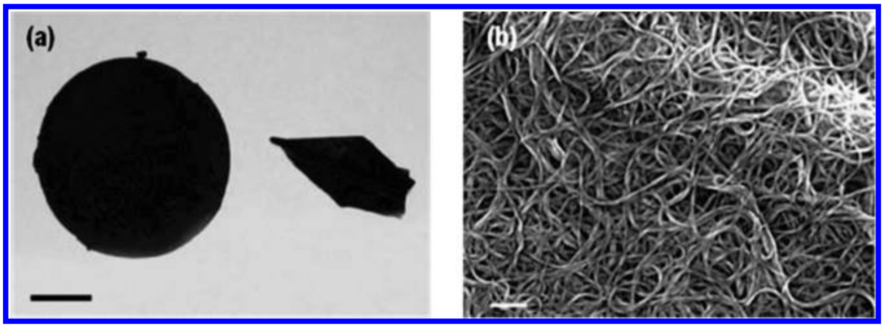

Figure 5. Production of pure, clean DWNTs in a high yield. (a) Photograph of DWNT buckypaper. The paper (left) is tough and flexible enough to fold into an origami airplane (right). Scale bar: 1 cm. (b) Scanning electron micrograph of DWNT paper showing CNT bundles. Scale bar: 300 nm. Adapted with permission from ref. 48.

and chlorophenols from variable volumes of solution.[43] A comparative study showed that a system comprising two stacked SWNT disks containing 60 mg of nanotubes exhibited extraction capabilities on a par with those of a commercial C^{22} disk loaded with 500 mg of sorbent for nonpolar or moderately polar compounds. The former system proved more powerful than the latter in extracting polar analytes and exhibited easier desorption after loading.[43]

A membrane-protected CNT micro-solid phase extraction device[45] was prepared by enclosing MWNTs within a polypropylene sheet membrane envelope that was heat-sealed to secure the contents. The device was used to extract organophosphorus pesticides from a stirred solution. The porous membrane filtered out extraneous materials, so no further cleanup was required. After extraction, the analytes were desorbed in hexane and analyzed by GC/MS. The method exhibited good linearity over the concentration range 0.1−50 μg/L, RSD values of 2−8%, and low limits of detection (1−7 pg/g);[45] it also proved an accurate, rapid, cost-effective alternative to other microextraction techniques.

Though they do not necessarily contain an inert membrane, we have included nanocomposite membranes in this section because the CNTs within are embedded in a polymer matrix that acts as a support for nanotube bundles. The unique electronic, adsorptive, mechanical, and thermal properties of CNTs can make these nanocomposite membranes useful for a number of applications that may benefit from cooperative and synergistic effects between the polymer and carbon phases. The following are a few examples among many illustrating the potential of nanocomposite membranes. Nanocomposites of MWNTs with poly(bisphenol A-co-4-nitrophtalic anhydride-co-1,3-phenylene diamine)[12] and CNTs with poly(vinyl alcohol) (PVA)[46] have been used to successfully separate H_2/CH_4 and benzene/cyclohexane mixtures, respectively. Using a high molecular weight CNT concentration resulted in significantly improved permeability and selectivity for H_2, CO_2, and CH_4.[12] With 10% CNT loading, for example, the H_2/CH_4 selectivity was ∼8 and the CO_2/CH_4 selectivity 3.8. Incorporating CNTs previously dispersed with β-cyclodextrin by grinding into PVA membranes was found to boost permeate flux and increase separation factors; for example, 50/50 (w/w) benzene/cyclohexane mixtures exhibited a permeation flux of 61.0 g/m^{2}h and a separation factor of 41.2 at 333 K.[46]

Membranes Consisting Exclusively of Carbon Nanotube Bundles (Buckypapers). Nanometer-sized CNTs have a tendency to self-aggregate via strong van der Waals forces. This intrinsic property of CNTs can be used to obtain paper-like sheets called "buckypapers" from dispersed nanotubes in solution.

Buckypapers are self-supporting entangled assemblies of CNTs arranged as a planar film held together by van der Waals interactions at tube−tube junctions. The greatest difference between buckypapers and CNT-modified filters is that the inert membrane used to prepare the paper in the former—usually by filtratio—is removed at the end of the process. As a result, buckypapers consist solely of packed bundles of CNTs. Ideally, buckypapers should have all CNTs connected with one another to form a network structure and the nanotubes should be long and straight.[47]

This type of membrane has been prepared using DWNTs[48−50] (Figure 5), SWNTs,[51−53] and MWNTs;[54,55] the most popular method involves dispersion and filtration of a suspension of CNTs. Unfunctionalized nanotubes tend to agglomerate in solvents, which hinders their filtration. The resulting buckypapers are often brittle and tend to crack upon drying. Acid oxidation[51] improves dispersion but introduces extensive surface functionalization. One alternative procedure uses a surfactant such as Triton X-100 or SDS or a solvent such as dimethylformamide[54,56] or acetyl acetone;[56] any residual surfactant or solvent remaining after the buckypaper has been prepared should be carefully removed. PTFE,[49] ceramic,[51] and Whatman nylon filters[54] have been used for filtration. The ensuing filtration procedures have some advantages including homogeneity in the films and the ability to control their thickness with nanometric accuracy via the nanotube concentration used and suspension volume filtered.

The pore structure of MWNT buckypapers is independent of the type of solvent, sonication time, and buckypaper surface density used.[56] However, control over the structure is a prerequisite for engineering buckypaper-based separation technology applications.[54] The pore characteristics of buckypapers can be controlled via the length distribution of their CNTs.

Buckypaper-like membranes have also been fabricated in other ways (Figure 6). Evaporation of a small amount of a SWNT/oleum dispersion[53] from a Petri dish formed a SWNT film, and a large-area double-walled film was obtained by spreading purified DWNTs with ethanol or acetone.[50] Another study accomplished fabrication of buckypaper from unfunctionalized MWNTs without the aid of a surfactant or surface modification technique by using a frit compression method.[55] Also, aligned buckypaper was obtained by operatively rotating CNTs in vertically oriented arrays (forests) to make self-supporting 5-cm-wide, 1-m-long transparent sheets.[57]

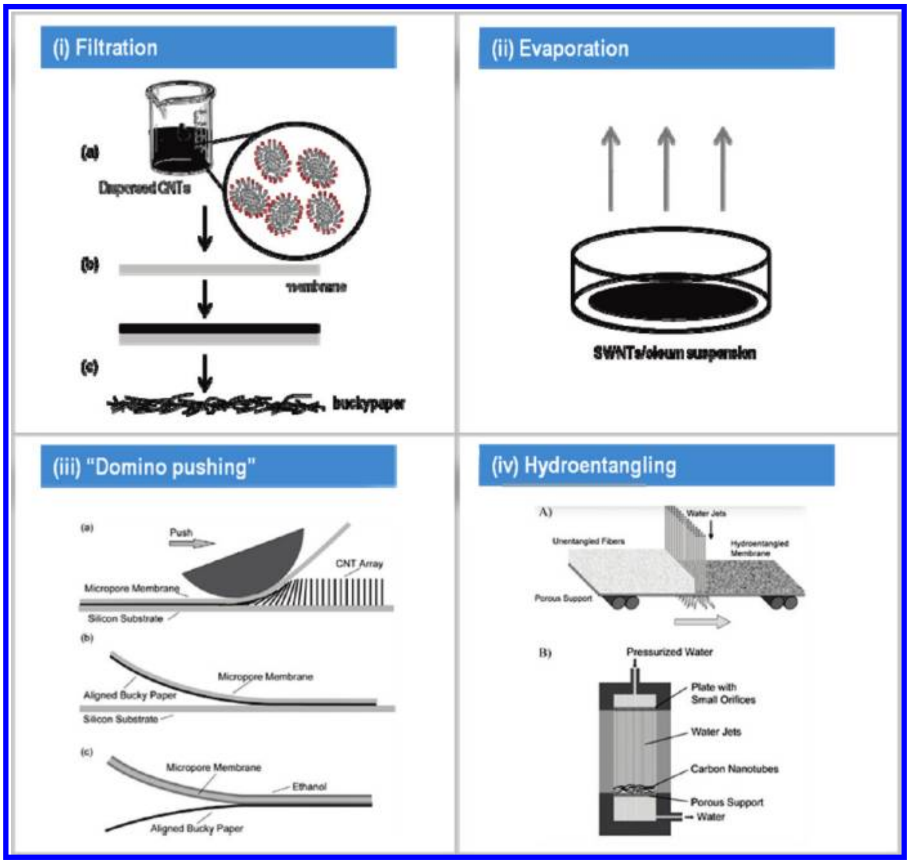

Figure 6. Most common buckypaper synthetic procedures. (i) Filtration involves three steps: (a) dispersion; (b) filtration; and (c) peeling off the membrane. (ii) Evaporation of a small amount of a SWNT/oleum suspension. (iii) Scheme of the domino pushing method: (a) formation of aligned buckypaper; (b) peeling of the buckypaper off the silicon substrate; (c) peeling of the buckypaper off the microporous membrane. (iv) Hydroentangling of CNTs: (A) continuous hydroentangling; (B) bench-top hydroentangling setup used to obtain batches of hydroentangled CNT membranes. Adapted with permission from refs. 47 and 58.

Table 2. Main Analytical Applications of the Different Kind of Membranes

	Type of membrane	Filtration mechanism	Selectivity	Stability	Applications	Ref.
Membranes with vertically aligned CNTs	Aligned CNTs embedded on a matrix	Size exclusion or sieving through open CNTs	Modest separation factors; increased by CNT tip functionalization; membranes with smaller diameters, size exclusion	Good	Transport of N_2	13, 14
					Transport of [$Ru(NH_3)_6^{3+}$, $Ru(bpy)_3^{2+}$ and MV^{2+}]	20, 13, 14
					Removal of ions (Cl^-, $Ru(bpy)_3^{2+}$, Ca^{2+}, $Fe(CN)_6^{3-}$) from aqueous solutions	30, 31
	Aligned CNTs only	Size exclusion or sieving through open CNTs or their interstitial space	Good; achieved by compression (pore-tunable property) or CNT wall functionalization	Moderate	Separation of CH_4 from H_2	9
					N_2 adsorption	2
					Water desalination	7
					Selective filtration of proteins	42
					Elimination of multiple components of heavy hydrocarbons from petroleum	37
					Filtration of bacterial contaminants	37
					Nucleic acid transport	8
					Transport of $Ru(NH_3)_6^{3+}$, $Ru(bpy)_3^{2+}$ and MV^{2+}	6
					Nanofiltration of gold nanoparticles	2
Membranes with bundles of CNTs	Bundles of CNTs on inert membranes	Based on sorption capabilities	Low; separation is based on π–π electrostatic interactions	Good	Separation of CH_4 from H_2	12
					Separation of benzene/cyclohexane	46
					Removal of viral and bacterial pathogens from water	1
					Selective isolation of acidic proteins	44
					Preconcentration of organophosphorus pesticides	45
					Preconcentration of carboxylic SWNTs	3
					Preconcentration of phthalate esters, bisphenol A, 4-*n*-nonylphenol, 4-*tert*-octylphenol, and chlorophenols	43
	Buckypaper	Based on sorption capabilities	Low; separation is based on π–π electrostatic interactions	Poor*	Removal of CO_2 from a flowing stream of CO_2/N_2	59

* Often brittle and cracking upon drying.

A macroscopic manipulation procedure for aligned CNT arrays called "domino pushing" allowed the "dry", in situ preparation of aligned, thick buckypapers with large areas.[47] The procedure involves three steps: 1) covering the CNT array with a piece of microporous membrane and forcing the array down in one direction, which attracts nanotubes together via van der Waals forces to form an aligned buckypaper; 2) peeling off the membrane from the silicon substrate; and 3) spreading ethanol to facilitate peeling of the aligned buckypaper off the membrane.

Finally, in a novel approach called "hydroentangling",[58] dry CNT powder is directly laid onto a porous support, and the drag force of water jets overcomes van der Waals forces to generate entangled CNT structures. The thickness of hydroentangled CNT membranes can be easily controlled by selectively adjusting the amount of powder that is laid on the support. In addition to separation applications, the electrochemical properties of these membranes may also be suitable for developing electroanalytical electrodes.

The effective diffusivity of six common laboratory gases (O_2, N_2, H_2, He, CO_2, CH_4) through buckypapers thicker than 186 μm was in the $3-12 \times 10^{-9}$ m^2/s range and correlated with the kinetic diameter of the gases.[56] Transparent, conductive SWNT films[52] were used to construct an electric field activated optical modulator, which is an optical analog to the nanotube-based field effect transistor. A packed bed of MWNTs completely removed CO_2 from a flowing stream of CO_2/N_2 and exhibited rapid uptake kinetics for CO_2.[59]

CONCLUSIONS

In summary, Table 2 shows a comparison and the main analytical applications of each kind of membrane discussed in this article.

CNT membranes provide an effective alternative to commercially available membrane filters for analytical separations. Their combination of excellent flow and adsorptive properties allows the rapid filtration of polar solutions. Also, membranes consisting of vertically aligned CNTs possess quite good selectivity by virtue of their filtration mechanism of size exclusion or sieving through open-ended CNTs and/or interstitial spaces. Their selectivity can be further improved by functionalization. In some cases, their tunability via pore size allows strict control over pore diameters by pressure.

One disadvantage of membranes consisting exclusively of CNT bundles is their poor selectivity; thus, nonpolar compounds (particularly aromatic compounds) are retained via $\pi-\pi$ interactions. By contrast, this type of membrane is much easier to prepare than those consisting of vertically aligned nanotubes. Finally, buckypapers provide a promising alternative platform for analytical separation but are still brittle and prone to cracking upon drying, so they will require more research before they can be rendered as useful as their CNT-based counterparts. Although buckypapers are still at the development stage, they may find a host of applications in the near future like vertically aligned and CNT-modified membranes have since their inception.

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