Large-scale polymeric carbon nanotube membranes with sub–1.27-nm pores

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We report the first characterization study of commercial prototype carbon nanotube (CNT) membranes consisting of sub–1.27-nm-diameter CNTs traversing a large-area nonporous polysulfone film. The membranes show rejection of NaCl and MgSO₄ at higher ionic strengths than have previously been reported in CNT membranes, and specific size selectivity for analytes with diameters below 1.24 nm. The CNTs used in the membranes were arc discharge nanotubes with inner diameters of 0.67 to 1.27 nm. Water flow through the membranes was 1000 times higher than predicted by Hagen-Poiseuille flow, in agreement with previous CNT membrane studies. Ideal gas selectivity was found to deviate significantly from that predicted by both viscous and Knudsen flow, suggesting that surface diffusion effects may begin to dominate gas selectivity at this size scale.

INTRODUCTION

Membranes for nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) are designed for aqueous separation of small molecules (<1000 Da) and dissolved salts. They suffer from limitations in their selectivity, permeability, and chemical resistance, particularly with respect to oxidants, which hampers the effectiveness of fouling mitigation (1, 2). The development of membranes based on novel nanoscale materials, such as carbon nanotubes (CNTs), graphene, and biological or biomimetic pores, has been proposed to address these limitations (3–12).

Previous studies of CNT membranes have shown that enhanced flow of water and gases through the interior of CNTs can result in very high membrane permeabilities (3–7). Modeling has predicted that subnanometer CNTs will be capable of high salt rejections in highly saline waters, such as seawater desalination (6). Furthermore, the physical and chemical robustness of CNTs may allow aggressive cleaning techniques, such as bleach or other oxidants, which are currently unavailable to conventional membranes for NF, RO, and FO (13).

The availability of techniques for precise sorting of CNTs by diameter may enable the fabrication of membranes with a wide range of selectivity. Tight control of CNT fabrication for making batches of CNTs with narrow diameter distribution or monochiral chemistry offers the potential for angstrom-level selectivity of molecules based on size (14). For instance, in gas separations, membranes with pores in the subnanometer range have demonstrated gas selectivity, and CNT materials are available in subnanometer diameters, indicating that CNT membranes may be practical for these separations, including separating CO₂ from air or flue gases, O₂ and N₂, alkanes and alkenes, and CO₂ and CH₄, based on both size exclusion and condensability phenomena, depending on the sizes of CNTs and the gases involved (15–17). The primary limitations in the fabrication of CNT membranes consisting of small CNTs traversing a nonporous polymer film have been the scalability of the fabrication process used, the expected cost of these membranes at commercial scale, and the difficulty of using subnanometer CNTs for membrane fabrication, particularly because these CNTs have not been shown to readily grow in alignment (18).

RESULTS

We report here the first experimental study of aligned CNT membranes consisting of CNTs with inner diameters (IDs) smaller than 1.27 nm embedded in a large-scale dense polysulfone polymer matrix, as well as the first study of subnanometer CNT membranes that examine both water and gas transport. The type of CNTs incorporated into membranes in this study was arc discharge (AD) nanotubes with IDs between 0.67 and 1.27 nm (7, 19, 20). The sample format was a flexible polymer sheet approximately 8" × 11" (20.3 cm by 27.9 cm), with a gray coloring (shown in Fig. 1A, inset), a larger scale of fabrication for single-walled CNT membranes than has been reported previously. The methods of fabrication for these membranes have been described by the manufacturer previously in the patent literature (21, 22). The membranes were received from the manufacturer and tested without modification.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the CNT membrane, showing the orientation and density of the CNTs, are shown in Fig. 1 (A to C). The images indicate that the average tube density of the CNT membranes is approximately 500 CNTs/μm². This density is the same order of magnitude reported for studies of membranes consisting of chemical vapor deposition aligned-growth multiwalled CNT and filter-aligned AD CNT membranes, but approximately 1/10 the density reported for aligned-growth double-walled CNT membranes (3, 4, 23).

A cross-flow RO system was used to test the membranes in aqueous separations (fig. S1). Tests included pure water permeability and the rejection of a series of analytes, including salts and small–molecular weight dyes spanning a range of diameters from 0.72 to 2.3 nm. The samples were tested with and without the presence of a 2000-ppm (parts per million) NaCl (34 mM) background electrolyte to discriminate between charged-based and size-based steric exclusion effects.

The pure water permeability of the membranes was 5.1 ± 0.4 liter m⁻² h⁻¹ bar⁻¹ (LMH)/bar. This membrane permeability represents an enhancement over Hagen-Poiseuille flow of approximately 1000, in the same range as those in previous findings of enhanced water flow through CNT membranes (3, 4). The rejections of the analytes, along with their dimensions, are shown in Fig. 2. The high rejection of chlorophyll indicates that any defects in the membrane, if present, may be estimated to be below 1.24 nm in size, the narrowest...
diameter of the analyte, which is below the diameter of the largest CNTs. No defects are visible in SEM imaging, which has a resolution of approximately 1 nm, supporting the hypothesis that any defects present are most likely near or below this resolution limit. Similarly, no defects are visible in TEM imaging.

The rejection of dyes with a background ionic strength (IS) of 34 mM NaCl indicate that CNT entrance charge effects are important for both Malachite Green (MG) and FD&C Blue #1. The rejection of salts was substantially higher at the ISs tested than has been reported previously in salt rejection tests of CNT membranes, with rejections of >10% for NaCl (34 mM IS) and MgSO₄ (66 mM IS). In previous studies, no significant rejection of KCl was observed at IS higher than 10 mM through CNTs with IDs of 1.6 nm, although it is important to note that different testing conditions were used in these studies, including dead-end versus cross-flow modes and lower transmembrane pressures, both of which can result in lower observed rejections (24).

To assess CNT membranes’ tolerance to being cleaned with oxidants, the salt rejection and permeability of CNT membranes were tested before and after immersion in 2000-ppm NaClO for 2 hours. The water permeability increased slightly, and salt rejection was not significantly changed after immersion. This result indicates that oxidant cleaning of these membranes is likely to be feasible, which would allow their use in fouling environments that would prove difficult for current polymeric NF, RO, or FO membranes, which are not tolerant toward oxidants, as well as potentially extending the useful life of CNT membranes in these environments (2, 25).

Gas permeance testing was performed with a constant flux gas permeation system (fig. S2). The permeances increased slightly with pressure, as shown in Fig. 3A, which differs from the pressure-independent behavior predicted for Knudsen flow (26). The absence of a relationship between gas viscosity and selectivity is shown in Fig. 3B, indicating that viscous flow through large defects does not appear to explain this pressure dependence. The analyte/He selectivities of several gases, plotted against their molecular weights, are shown in Fig. 3C. The selectivities of the gases, particularly the hydrocarbon gases, deviated substantially from Knudsen selectivity, in which the individual gas selectivities would be correlated with the inverse square root of their molecular weights.

**DISCUSSION**

Knudsen selectivity has been observed in previous CNT membrane studies for CNTs with IDs larger than 1 nm, with the exception of hydrocarbons in sub-2-nm CNTs, which also did not follow this relationship, potentially due to the effects of surface diffusion (4). Previous studies of subnanometer CNTs aligned in zeolite membranes indicated significant deviation from Knudsen flow, including both non-Knudsen selectivity and non-Knudsen pressure-dependent permeance, for a wide range of gases studied, which was attributed to the increased role of surface diffusion transport in these small CNT pores (26).

In modeling studies of gas transport through pores at the nanoscale, the contribution of Knudsen flow to the overall pore flow is found to decrease as the ID of the pore decreases, with surface diffusion along the pore wall becoming the dominant transport mechanism below an ID of approximately 1.2 nm (27, 28). The relative importance of surface diffusion continues to increase until the ID of the CNT approaches the diameter of the gases, at which point molecular sieving occurs, with gases rejected from the CNT entrance based on size (28). This modeling, along with the previous subnanometer CNT gas transport data, may offer an explanation for the deviation from Knudsen selectivity observed.

Fig. 1. Images of the membranes tested in this study. (A) SEM image of the CNT membrane surface, showing CNT tips emerging from the polymer. Inset shows the membrane sample without magnification. (B) SEM image of the surface of the CNT membrane using an imaging technique that uses high voltage without sputter coating to reveal the CNTs below the membrane surface. (C) TEM image of the CNT membrane in planar view, showing CNT pore openings, indicated by red circles, emerging from CNTs below the membrane surface.
in the CNT membranes of this study, as surface diffusion could be a significant contributor to gas transport.

CNT membranes with subnanometer pores for aqueous separations offer promising permeability, solute rejection, and chemical robustness characteristics. Oxidant-tolerant NF membranes that separate small dissolved solutes, but do not substantially desalinate or soften, may be particularly useful for water treatment, because they would not produce brine discharges or induce scale formation and could be routinely cleaned with bleach. The use of these membranes to remove pathogens and natural organic matter before the addition of residual disinfectant for distribution would prevent the formation of disinfectant by-products, which are currently difficult to prevent in drinking water systems (29, 30). Desalination by RO or FO using CNT membranes of this type will require reduction in the size of the CNTs used, going from IDs of a maximum of 1.24 nm in this study to below 0.72 nm, the hydrated diameter of the sodium ion, to be practical. Gas separations using sub-nanometer CNT membranes based on size exclusion, preferential adsorption, and pore condensation effects are promising but will require further analysis using mixed gases across a range of pressures to identify optimal operating conditions for practical applications of these membranes.

MATERIALS AND METHODS

Aqueous separation tests

Determination of water, salt, and dye transport through the CNT membranes was performed using a standard RO test system, as shown in fig. S1. The membrane cells exposed 19.9 cm² of the membrane area to the feed solution, which was circulated through the membrane channels at 1.0 liter/min, resulting in a flow velocity of approximately 21 cm/s and a corresponding Reynolds number of approximately 1200. Temperature in the system was maintained at 20°C.

Water flux was determined gravimetrically, with the flux of any solutes across the membranes having a negligible impact on the final result. The determination of the hydraulic permeability coefficient was conducted at three pressures of 345, 690, and 1380 kPa, and the flux of water was found to be proportional to the feed pressure.

Solute rejection was determined via testing at 1400 kPa, and the concentration of the solutes was measured using an Oakton CON 11 conductivity meter with a “Consen91W” conductivity probe (for salts) and a Thermo Scientific GENESYS 10S UV-Vis spectrophotometer (for dyes). The feed concentration of both salts and dyes was found to be within the linear range of the instruments used; therefore, the rejection can simply be expressed as

\[
\% R = \frac{S_f - S_p}{S_f} \tag{1}
\]

where \(S_f\) is the signal in the feed (for example, optical absorbance and electrical conductivity) and \(S_p\) is the signal in the permeate.

After addition of a probe salt, the RO system was allowed to come to steady state over a period of 30 min before taking any measurements. The probe dyes used in this study, whose chemical structures are provided in fig. S3, were observed to adsorb to the membrane polymer matrix as well as the RO system tubing. To subtract this effect from the measurement of dye rejection, periodic samples of the solute rejection were taken until a stable value was obtained. Malachite green was observed to adsorb strongly over a period of several hours, with apparent rejection dropping from ca. 80 to ca. 20 to 40%. FD&C Blue #1 was observed to
Fig. 3. Gas transport properties of CNT membranes. (A) Graph of the relationship between He permeance and pressure showing pressure dependence. GPU, gas permeation units. (B) Graph of the relationship between analyte/He selectivity and viscosity (viscous flow selectivity shown as a dashed line), indicating that no correlation with viscous flow is present. Viscosities for gases are taken from Yampolskii and Freeman (27). (C) Graph of the relationship between analyte molecular weight and analyte/He selectivity at 138 kPa. Knudsen selectivity is shown on the dashed line. Analyte selectivities deviate substantially from Knudsen, particularly the hydrocarbons and CO₂ (shown in red data points). AMU, atomic mass units.
adsorb to a lesser degree, and no adsorption of chlorophyllin copper was observed.

The effect of charge screening of the dye molecules was investigated by measuring the rejection of the dye in the presence of 2000-ppm sodium chloride. Trials in which both salt and dye were present assumed that the contribution to the conductivity of the permeate sample was entirely due to the presence of the salt and that the optical absorbance of the permeate sample was entirely due to the presence of the dye. Because the addition of salt may change the adsorption of solutes in the membrane polymer matrix, periodic tests of rejection were conducted until the measured dye rejection was stable. Malachite green rejection in the presence of sodium chloride was always observed to be slightly negative, that is, the optical absorbance of the permeate solution was 2 to 6% higher than that of the feed solution, potentially indicating an extremely long (more than several days) desorption cycle. The rejection of sodium chloride in the presence of dyes was unchanged. During the experiments, membrane permeability fell by more than 50%, likely due to the accumulation of particulate material (for example, dust and rust particles) on the membrane surface; this was likely due to the absence of a particulate filter in-line in the RO system (3I). After the initial permeability decline, it remained steady throughout testing, a phenomenon similar to initial permeability declines observed in conventional polymeric membrane testing (1).

**Oxidation resistance and cleaning with sodium hypochlorite**

To evaluate the membrane’s ability to withstand cleaning via sodium hypochlorite (“bleach”), a 2000-ppm solution of sodium hypochlorite (Chlorox, ~8.25%) in deionized (DI) water was circulated through the RO test system in contact with previously tested AD membranes with no transmembrane pressure and at flow conditions identical to those used in RO testing. After 1 hour of exposure, the system was flushed thoroughly with DI water before the membranes were evaluated for sodium chloride rejection at a concentration of 2000 ppm. The bleach cleaning protocol increased membrane permeability slightly while not significantly changing the sodium chloride rejection, indicating that the CNT membrane rejection does not decrease upon exposure to bleach and that the recovered flux does not appear to be a result of degradation of the polymer matrix.

**Gas permeance tests**

The permeation of pure gases was determined using a constant pressure gas permeation system (32), as shown in fig. S2. Membrane samples were mounted with epoxy under brass discs, and the effective membrane area was determined with image analysis using ImageJ software.

Membrane samples were mounted in a permeation cell immersed in an air bath held at 35°C and were flushed on both sides with the feed gas for ~10 min before measuring permeance. The flux of gas was measured via a bubble flow meter at atmospheric pressure. Three pressures 138, 441, and 690 kPa of feed gas were tested across three representative membrane samples. Three series of gases were tested: (i) He, O₂, N₂, CH₄, CO₂; (ii) He, N₂, C₂H₆; (iii) He, N₂, CF₄. Membrane samples were not used for additional testing after being exposed to plasticizing or potentially plasticizing gases (CO₂, C₂H₆, CF₄).

**SEM procedure**

A unique imaging method for CNT in the polymer matrix was used. To visualize the CNT network embedded in the polymer, a high accelerating voltage (20 kV) was used to image an untreated sample (no sputter coating), which was well grounded through the use of silver paint. In the resulting image, the polymer was transparent, whereas the tubes were rendered opaque.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/3/e1700938/DC1

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