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ABSTRACT

We present fabrication and characterization of a membrane based on carbon nanotubes (CNTs) and parylene. Carbon nanotubes have shown orders of magnitude enhancement in gas and water permeability compared to estimates generated by conventional theories [1, 2]. Large area membranes that exhibit flux enhancement characteristics of carbon nanotubes may provide an economical solution to a variety of technologies including water desalination [3] and gas sequestration [4]. We report a novel method of making carbon nanotube-based, robust membranes with large areas. A vertically aligned dense carbon nanotube array is infiltrated with parylene. Parylene polymer creates a pinhole free transparent film by exhibiting high surface conformity and excellent crevice penetration. Using this moisture-, chemical- and solvent-resistant polymer creates carbon nanotube membranes that promise to exhibit high stability and biocompatibility. CNT membranes are formed by releasing a free-standing film that consists of parylene-infiltrated CNTs, followed by CNT uncapping on both sides of the composite material. Thus fabricated membranes show flexibility and ductility due to the parylene matrix material, as well as high permeability attributed to embedded carbon nanotubes. These membranes have a potential for applications that may require high flux, flexibility and durability.

Keywords: membrane, carbon nanotube, parylene, high-flux

1 INTRODUCTION

Carbon nanotubes provide unique structures in studying nanoscale mass transport and flow phenomena that can be employed in a variety of important applications. Having nanometer-scale diameters of innermost walls whose graphitic surface is atomically smooth, they give rise to newly discovered phenomena of ultra-efficient transport of water through these ultra-narrow molecular pipes [5]. According to the experiment, water and gas flows through carbon nanotubes are enhanced by 3-5 and 1-2 orders of magnitudes, respectively, compared to conventional theories [1, 2]. One can employ these unique nanoscale phenomena in energy efficient filtration such as water desalination [3] and gas sequestration [4].

For the use of the CNT-based membranes in those applications, required are scaling up the membrane area and keeping flexibility and durability of those large-area membranes. To achieve this goal, choice of materials considering chemical/biological/mechanical compatibility with CNTs, ease of fabrication, flexibility and durability is important.

As a course of effort toward scaling up the size of the carbon nanotube-based membrane, we explore a parylene-CNT composite in terms of fabrication and mass transport characterization. In section 2, briefly addressed are currently available CNT-based membrane techniques and so far revealed flow behaviors in CNTs. Properties of parylene and its composite with CNTs will follow in section 3. Then, we present a preliminary result of gas and water flows through a membrane of a parylene-CNT composite.

2 FLOW THROUGH CNTS

2.1 Water Transport - Simulation

The task of observing and understanding fluid and gas flows in CNT pores raises a set of unique fundamental questions [6]. First, it is surprising that hydrophilic liquids, especially water, enter and fill very narrow and hydrophobic CNTs. If water does enter CNTs, what influence does extreme confinement have on the water structure and properties? It is important to evaluate how these changes in structure influence the rates, efficiency, and selectivity of the transport of liquids and gases through CNTs. As is often the case, MD (molecular dynamics) simulations have provided some of the first answers to these questions. Hummer et al. [7] have used MD simulations to observe the filling of a (6,6) CNT (0.81 nm in diameter and 1.34 nm in length) with water molecules. Surprisingly, they find that water fills the empty cavity of a CNT within a few tens of picoseconds and the filled state continues over the entire simulation time (66 ns). More importantly, the water molecules confined in such a small space form a single-file configuration that is unseen in the bulk water. Several experimental studies also provide some evidence of water filling of CNTs [8,9]. Further analysis of the simulation results of Hummer et al. shows that water molecules inside and outside a nanotube are in thermodynamic equilibrium. This observation illustrates one of the more important and counterintuitive phenomena associated with nanofluidic systems: nanoscale confinement leads to a narrowing of the interaction energy distribution, which lowers the chemical potential [7]. In other words, confining a liquid inside a nanotube channel actually lowers its free energy. Further simulations by the same group have shown that the filling equilibrium is very sensitive to water-nanotube interaction parameters: a 40% reduction in the carbon-water interaction potential results in the emptying of the CNT cavity, while a 25% reduction results in a fluctuation between filled and empty states (bi-stable states) [7,10]. This sharp transition between the two states has been observed for other hydrophobic nanopores as well [11,12]. MD simulations have also studied the dependence of CNT hydration on other properties of CNTs such as nanotube wall flexibility, charge, chirality, length, and diameter [5].

2.2 Gas Transport - Simulation

MD simulations also provide an indication that the intrinsic smoothness of the graphitic wall of CNTs is a defining feature for the gas phase transport in these channels. Sholl and colleagues [13] have shown that gas flux in CNTs reaches a value almost three orders of magnitude higher than in zeolites with equivalently sized pores. In these simulations, transport diffusivities of light gases such as hydrogen and methane reach almost the same level as that of the bulk gas diffusivity ($O(10^{-1})$ cm2/s). Depending on the nanotube size, the diffusivity is as large as 10 cm^2/s for hydrogen. In a follow-up set of simulations, the same group presents a more detailed picture of gas molecule behavior inside a SWNT pore by displaying a density profile and molecular trajectories [14]. The picture of gas transport through CNTs that has emerged from these simulations centers on the predominantly specular nature of the molecule-wall collisions inside CNTs. As a result, a CNT is remarkably effective in allowing gas transport since most of the gas molecules travel along the tube in an almost billiard-balllike manner [13-15]. Sokhan, Quirke, and others [16-18] have performed a series of MD simulations and reached a similar conclusion to Sholl and coworkers. They simulated both an atomic network of carbons and a smooth imaginary surface with a given slip boundary condition. Maxwell’s coefficient or tangential momentum accommodation coefficient (TMAC) determined by the simulation are of the order of 10^{-3} (these values indicate that statistically only 0.1% of gas molecules in the nanotube are thermalized by the wall and randomize their reflection velocities). At the same time, Sholl’s group [14] indicates that some of the gas molecules adsorb on the nanotube walls. Therefore, such behavior could give rise to the alternative mechanism of transport based on two-dimensional surface diffusion.

2.3 Membrane Fabrication

Testing these seemingly exotic predictions of fast transport through CNTs, which have emerged from MD simulations, has required the fabrication of a robust test platform. Practical considerations dictate that experimental efforts focus on a geometry that would allow observation of transport through multiple nanotube pores, such as a CNT membrane geometry. These membranes typically consist of an aligned array of CNTs encapsulated by a filler (matrix) material, with the nanotube ends open at the top and bottom. While there are many ways to produce such a structure, (a notable early result by Martin and coworkers was based on fabrication of amorphous CNTs within porous alumina membrane template [19]), the most fruitful approach to date involves growing an aligned array of CNTs, followed by infiltration of a matrix material in between the CNTs. The extremely high aspect ratio of the gaps between the nanotubes in the array (length/diameter on the order of 1000 or larger) presents a fabrication challenge. Fortunately, researchers have developed successful strategies to overcome this issue [1,5,20-22].

2.4 Water and Gas Flow Measurement

We have measured the bulk flow rate of air through a SiN_x/DWNT membrane by mounting it in an O-ring sealed flow cell and applying a pressure gradient of ~1 atm [1]. To compare experimental data with simulations, we need to calculate the flow rate per nanotube and, therefore, we have to estimate the density of open pores. This estimate introduces the single largest uncertainty in the measurement of flow per pore. Estimation obtained by plan-view TEM images of the membrane gives an upper limit to the membrane pore density (this number provides an upper limit because not all of the imaged pores span the entire 2–4 μm thickness of the membrane). This pore density estimate from TEM of 2.5×10^{11} cm^{-2} agrees well with the density of nanoparticles that catalyze nanotube synthesis. Using this number as an upper boundary, we can estimate a lower limit to the measured flow per nanotube. Even using this lower limit, it is readily apparent that there is a significant transport enhancement; the measured gas flows are up to 100 times greater than the predictions of the conventional Knudsen model for gas transport in rarefied environments (Fig. 1c). These experiments cannot definitively determine the cause of the observed gas flow enhancement. However, a change in the nature of molecule-wall collisions from diffuse to specular, as indicated by the MD simulations, provides a very likely explanation [13]. This conclusion is supported by the observation that nonhydrocarbon gas species tested in these experiments exhibit Knudsen-like $M^{-1/2}$ scaling of their membrane permeability (Fig. 1a), where M is the molecular weight. Another interesting observation is that the sub-2-nm CNT membranes exhibit some gas selectivity for hydrocarbon transport [1]. Hydrocarbon gases show a deviation from Knudsen scaling and instead exhibit slightly higher permeabilities (Fig. 1a). This deviation in scaling may reflect additional surface adsorption and diffusion of these molecules along the surface, although more detailed measurements are needed to establish this as a viable enhancement mechanism.

We have also observed high rates of water transport through sub-2-nm DWNT membranes using pressure-driven flow [1]. Similarly high rates have also been observed by Majumder et al. [2] using MWNT membranes with larger pore diameters. As previously discussed, the single largest uncertainty in quantifying the flux through individual pores lies in determination of the active pore density. Majumder et al. estimate the active pore densities by quantifying the diffusion of small molecules through CNTs. They report enhancements of 4– 5 orders of magnitude compared with the Hagen– Poiseuille formalism. As described above, we estimate the upper bounds of the pore densities so our measurements represent lower boundary estimates. The transport rates we measure reveal a flow enhancement that is at least 2– 3 orders of magnitude faster than no-slip, hydrodynamic flow calculated using the Hagen– Poiseuille equation (Fig. 1b). The calculated slip length for sub-2-nm CNTs is as large as hundreds of nanometers, which is almost three orders of magnitude larger than the pore size. In contrast, a polycarbonate membrane with a pore size of 15 nm has a slip length of just 5 nm. This suggests that slip flow formalism may not be applicable to water flow through CNTs, possibly because of length scale confinement [2,23] or partial wetting between the water and the CNT surface [24]. Interestingly, the measured water flux does not only compare well with that predicted by MD simulations, but it is also similar to the water flow through aquaporin (3.9 molecules/pore). The comparison to the aquaporins is not straightforward since the diameters of our CNTs are twice that of aquaporins and are considerably longer, to name just a few differences. Therefore, we cannot yet imply that the same mechanism is responsible for transport in our CNTs and aquaporins. Nevertheless, our experiments demonstrate that water transport through CNTs starts to approach the efficiency of biological channels.

3 PARYLENE-CNT COMPOSITE

3.1 Properties of parylene

Parylene is a generic name for a series of polymers. The basic member of the series, called Parylene N, is poly-para-xylylene, a completely linear and highly crystalline material. Parylene C is basically the same form as Parylene N with one chlorine atom replacing an aromatic hydrogen atom. Parylene polymer is deposited as a vapor phase, thus forming a continuous film following the shape of a target substrate is possible. Due to the uniqueness of the vapor phase deposition together with good dielectric material properties and chemical inertness, parylene has been a material of choice for pinhole-free coating of critical electronic assemblies.

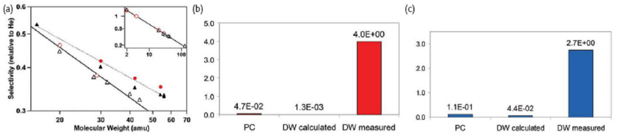

Figure 1: Water and gas transport in sub-2-nm CNT membranes. (a) Gas selectivity (defined as the permeability relative to that of He) data for sub-2-nm CNT (triangle) and MWNT (circles) membranes. Open symbols denote nonhydrocarbon gases, filled symbols hydrocarbon gases. The solid line is a power law fit of the nonhydrocarbon gas selectivity data showing a scaling predicted by the Knudsen diffusion model (exponent of -0.49 ± 0.01). The dashed line is a power law fit of the hydrocarbon gas data showing a deviation from the Knudsen model (exponent of -0.37 ± 0.02). The inset shows the full mass range of nonhydrocarbon gas data, illustrating agreement with the Knudsen model scaling. (b) Comparison of the water flux predicted for a polycarbonate (PC) membrane (left) and a DWNT (center) membrane with the flux measured for the DWNT membrane. (c) Comparison of the air flux predicted for a PC membrane (left) and a DWNT membrane (center) with the flux measured for the DWNT membrane (right).

Recently, researchers have used parylene for coating nanowires and CNTs with big diameters (MWNT). Yang and Majumdar and their colleagues [25] deposited parylene onto their vertically aligned Si nanowire mat as a chemical etch mask. Upon completion of reactions, they could easily remove parylene with embedded silica nanotubes intact. Miserendino et al. [26] used parylene to coat MWNT arrays for a nanoelectrode application. In both nanowire and nanotube cases, the size and gaps between individual pillars were on the order of 100 nm.

3.2 Parylene-CNT composite and membrane fabrication

For producing flexible CNT membrane, we deposited parylene onto our CNT mat. Parylene dimmer (di-para-xylylene) was thermally evaporated at 160^{o}C, dissociated at 670^{o}C, and then deposited onto a CNT mat on top of a Si substrate at room temperature, when it forms parylene polymer (poly-para-xylylene). Although major deposition reaction control factor is temperature, depending on the chamber pressure, the deposition rate may vary. Unlike the previous efforts, the gaps between nanotubes are very small, and the conformal filling may become challenging. If the deposition is too fast, parylene dimers can deposit only on top and hamper an access of fresh dimers further down to the CNT array, thereby coating only a few micrometers from the top of a mat. Parameters influencing conformal coatings of CNTs include (1) vertically aligned but short enough CNTs that do not suffer from fast deposition and (2) deposition speed control. After releasing the composite film from the substrate, the free standing film was dipped in HCl for 24 hrs at room temperature to remove catalyst layers (Fe and Mo). Then, we mounted the freestanding composite on a thin Al plate with a millimeter size hole in the middle. Overly deposited parylene was etched out with gentle O2 plasma. Once CNTs were exposed, we used water plasma to uncap the carbon nanotubes.

With a CNT-uncapped membrane, we pressurized nitrogen and measured flow rate. We obtained O(0.1 cm^3/min) flow rate at 0.7 atm. Water under the same pressure difference showed O(10^{-2} uL/min). The ratio of nitrogen and water flow rates agrees well with previous silicon nitride-encapsulated CNT membranes.

4 CONCLUSION

We fabricated a flexible membrane based on the parylene-CNT composite. Many benign properties of parylene such as environmental friendliness, biocompatibility, chemical inertness, no swelling upon water exposure, and good mechanical and dielectric properties may allow unique properties of this composite material. On the CNT-membrane aspect, this composite has a potential for practical applications.

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