Published in final edited form as:

Nanotechnology. 2012 November 16; 23(45): 455101. doi:10.1088/0957-4484/23/45/455101.

Mass transport through vertically aligned large diameter MWCNT embedded in parylene

P Krishnakumar¹, P B Tiwari⁴, S Staples¹, T Luo¹, Y Darici⁴, J He^{4,+}, and SM Lindsay^{1,2,3,+}

¹Department of Physics, Arizona State University, Tempe, AZ 85287

²Biodesign Institute, Arizona State University, Tempe, AZ 85287

³Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287

⁴Department of Physics, Florida International University, Miami, FL 33199

Abstract

We have fabricated porous membranes using a parylene encapsulated vertically aligned forest of multi-walled carbon nanotube (MWCNT, about 7nm inner diameter). The transport of charged particles in electrolyte through these membranes was studied by applying electric field and pressure. Under an electric field in the range of 4.4×10^4 V/m, electrophoresis instead of electroosmosis is found to be the main mechanism for ion transport. Small molecules and 5 nm gold nanoparticles can be driven through the membranes by an electric field. However, small biomolecules, like DNA oligomers, cannot. Due to the weak electric driving force, the interactions between charged particles and the hydrophobic CNT inner surface play important roles in the transport, leading to enhanced selectivity for small molecules. Simple chemical modification on the CNT ends also induces an obvious effect on the translocation of single strand DNA oligomer and gold nanoparticle under a modest pressure (<294 Pa).

Keywords

nanofluidics; nanopore; nanochannel; vertical aligned carbon nanotube forest; parylene thin film

1. Introduction

In recent years, there has been enormous interest in utilizing carbon nanotubes as nanochannels or nanopores [9, 20, 27, 22, 35, 11, 7, 8]. From a biological point of view, the CNT is an ideal model to help understand the transporter proteins on cell membrane that work in aqueous environments with hydrophobic inner walls and nanometer channel sizes. From the point of view of fundamental research, it is an exciting system in which to test classical theories of fluid mechanics and dynamics at nanoscale, especially below 10 nm. CNTs have several advantages as nanopores or nanochannels. (1) They require no special nanofabrication to achieve a pore size of molecular size (ranging from less than 1 nm to more than 10 nm). They have an atomically smooth surface and perfect uniformity over large distances, resulting frictionless motion of fluid and particles. Recent studies have observed significantly faster transport in CNT comparing with nanochannels made from conventional materials[7, 37, 8, 17]. (2) For high quality CNTs, the chemistry and structures of the interior surface are well-defined, which simplifies theoretical simulations. (3) The excellent electrical properties of CNT provide new routes to electrical detection, trapping and manipulation of charged biomolecules and nanoparticles. (4) Well-defined sites are

⁺jinhe@fiu.edu, Stuart.Lindsay@asu.edu.

available for chemical functionalization at the ends of the tubes. Such modifications will be extremely useful for ion and molecule selection, gating or separation. To develop a fundamental understanding of mass transport inside CNT, transport measurement based on single SWCNT (diameter <2nm) has been developed in recent years [15, 31, 26]. However, the individual CNT based nanofluidic device is difficult to fabricate and the measurement results are still limited. Currently, measurements of mass and charge transport in the CNT are made mainly with membranes containing a large quantity (i.e., 10^9 – 10^{11} tubes/cm²) of CNTs, the orientation of which is either aligned or not aligned [8, 19, 37, 32]. The membranes with aligned CNTs generally show better performance. However, it is difficult to grow high quality aligned CNT with diameters below 2nm [8, 37]. Various polymers have been cast onto the CNT film to fill the gaps between CNTs and form an impenetrable membrane. Subsequently, both ends of the CNT were opened by oxygen plasma. Recent research on CNT based nanofluidic devices has yield exciting applications in efficient gas filtration, chemical and biological separation, water desalination and programmable transdermal drug delivery [4, 2, 38].

We have fabricated vertically aligned MWCNT membranes (about 7nm in tube inner diameter and 42 μ m in tube length) by depositing parylene on a vertically aligned MWCNT forest. The parylene deposition process is simple, reproducible, and is compatible with current microfabrication techniques. Parylene film is chemically inert, electrically resistive, pin-hole free and has low permeability to moisture and gases. Parylene is also known for its capability to conformally cover all surfaces regardless of the configuration of the surface, including configurations with high aspect ratio [3, 21]. MWCNT forests embedded in parylene have been used in several applications, including electrochemical sensors [21, 1, 34], but not as a membrane for mass transport. Although there are several different methods for fabricating CNT membranes, new CNT membrane geometries will always provide new insight to the mass and charge transport in CNT due to the heterogeneous physical properties of CNT and the complexity of CNT based nanofluidics. Here, we report measurements using this new type of CNT membrane to help improve our understandings in several aspects: 1. Understand the transport of particles through CNT under electric field. Pressure and electric field are often used to drive particles through the CNT [19]. Diffusion due to concentration gradient is normally not efficient for these CNT membranes because of the extremely small pore diameter and surface interactions. Pressure driven gas, fluid flow and small particle transport through CNT membranes have been investigated extensively [22, 8, 19, 17, 7]. In contrast, there are only a few studies of electric field driven particle transport [32, 37]. 2. Understand the effect of CNT diameter, length and electrostatic environment to the particle transport under electric field. In electrolyte, the applied electric field will drive the transport of charged particles by both electrophoresis and electroosmosis. Electrophoretic flow is proportional to the external electric field, the particle mobility and the ion concentration. The electrophoretic flow only increases moderately (i.e., several times) with a decrease of CNT diameter [24, 37]. Electroosmotic flow is proportional to the external electric field, the fluid velocity and the net (unbalanced) charge density of the fluid inside the channel. The fluid velocity is sensitive to slip boundary condition at the CNT inner surface. The net charge density is directly affected by charge selection at the entrances and the surface charge density at the CNT inner surface. Electroosmosis is more sensitive to the CNT diameter than electrophoresis. Greatly enhanced electroosmosis (i.e., several orders of magnitude) has been observed in smaller diameter SWCNTs [24] due to increased slip length at smaller diameter and increased net charge density inside smaller diameter CNT. Electroosmosis has been used as an efficient pump to drive ions and small molecules (charged or neutral) through small diameter SWCNTs. However, as suggested by simulations and experiments, electroosmosis is much weaker in bigger diameter CNTs. In addition, the CNT length and electrostatic environment will also affect electroosmosis and electrophoresis differently. So the motion of particles under an electric field is complicated

and depends on the specific conditions. 3. Most of previous works focused on the transport of gas molecules, water, ions and small molecules. The transport of biomolecules has not been well-studied in these CNT membranes. In this report, the translocation of small molecules, DNA and nano particles are studied, especially driven by an electric field. Molecule-carbon surface interactions are found to play important roles in the transport of these particles. Furthermore, the chemical modifications on the MWCNT membrane also strongly affect the transport of big particles across the membrane.

2. Experimental methods

2.1 MWCNT forest growth and characterization

A 30 nm thick aluminum (Al) layer and 1nm thick iron (Fe) layer were deposited sequentially on a silicon chip containing a silicon nitride membrane (see section 2.2) using ion-beam sputtering or electron-beam deposition. The vertically aligned MWCNT forest was grown from this catalyst by chemical vapor deposition (CVD) using Ethylene as the carbon source at 850°C for 70 seconds [8]. A scanning electron microscope (SEM) image of the as-grown vertically aligned MWCNT forest is shown in Figure 1a. The height of the CNT forest is about $42 \pm 5 \mu\text{m}$ under our growth condition. The inset in Figure 1b shows a transmission electron microscope (TEM) image of individual CNTs, confirming that these CNTs are multi-walled (~5–10 layers) and the inner and outer diameters are about 7 nm and 11 nm respectively. Bamboo structure is not observed in these MWCNTs. By analyzing more than 100 CNTs in TEM images, we obtained a histogram (Figure 1b) of the CNT inner diameter distribution, with the peak around 7 nm. These carbon nanotubes were also characterized by Raman spectroscopy, confirming MWCNT structures (Figure S1).

2.2 Parylene coated MWCNT forest membrane fabrication

The fabrication of vertically aligned MWCNT forest membrane is based on the procedure developed by Holt et al. [8]. In brief, a 5mm square silicon chip with a square shaped free standing silicon nitride membrane (35–100 μm in width, 300nm in thickness) in the center is first fabricated by potassium hydroxide (KOH) anisotropic wet etching. After the MWCNT forest is grown uniformly on the whole surface, parylene is vapor deposited onto the MWCNT forest at room temperature using a PDS 2010 LABCOTER (Specialty coating systems, Indianapolis, IN). Immediately after deposition, the parylene film is planarized by thermal annealing at 350°C for two hour in argon atmosphere [28]. SEM images in Figure 1c suggest that the CNT forests are fully embedded in parylene. A two-step reactive ion etching (RIE) process is used to sequentially remove the excess parylene film and the 300nm SiN layer from the backside of the chip. Then the chip is sequentially immersed in 45°C PAN etch solution ($\text{H}_3\text{PO}_4\text{:H}_2\text{O: HNO}_3\text{:CH}_3\text{COOH}$ (16:2:1:1, volume ratio) for 5 minutes and in HCl (50% of concentrated HCl) for 30 minutes, to remove the exposed Al and Fe layers from the backside. Then oxygen plasma (2–4 minutes, 7.2W, 550–600 mTorr) is used to remove the excess parylene, and to expose and open the CNT ends. The surface of the membrane after oxygen plasma is shown in Figure 1d. The as-grown parylene surface is hydrophobic. However, the parylene surface becomes hydrophilic after oxygen plasma treatment. The hydrophilic parylene surface is stable and facilitates the transport of particles. The schematic of the final device is shown in Figure 1e. We have also measured the porosity of a CNT membrane (after 3 minutes oxygen plasma treatment) using a KCl diffusion method [19]. A pore area of $7.2 \times 10^{-11}\text{m}^2$ and porosity of 0.89% is obtained for one of the CNT membranes. Based on the average CNT diameter (7nm), we obtained a CNT area density of $0.23 \times 10^{11}/\text{cm}^2$. This is in line with estimates by other groups[41, 7] but subject to considerable uncertainty – for example, the pore diameter estimated from the membrane conductance is about a factor three too large (an error that may also reflect enhanced ion mobility in the interior of the CNTs).

Some of the MWCNT membranes are chemically modified. The MWCNT membranes are immersed in aqueous solution composed of 20mM EDC and 20mM of sulfo-NHS for 2 hours at room temperature. Then the membranes are rinsed by H₂O and immersed in 20mM Ethanolamine hydrochloride for 20 minutes. The parylene film is also modified by ethanolamine, as demonstrated by contact angle measurements (Figure S4b).

2.3 Materials, Chemical reagents and solution preparation

5nm and 10 nm gold nanoparticles (NPs) were purchased from Ted Pella. These gold nanoparticles are capped with negative ligand citrate and the size is very accurate with only 10% size variation. No aggregation is observed when these particles are dissolved in pure water or aqueous solution with low salt concentration (<15 mM KCl solution) [5]. A single strand DNA oligomer (GTCGTCGTCGTC) is obtained from IDT (Integrated DNA Technologies). Other chemical reagents are purchased from Sigma Aldrich and used without further purification. All solutions are prepared using deionized (DI) water (~18M Ω) from water purification system (Ultra Purelab system, ELGA/Siemens). For some measurements, the water is further purified using a double-distillation system. The prepared salt solution is filtered through a 0.2 μ m filter and degassed by sonication. For comparison, we also use Anodic aluminum oxide (AAO) nanoporous membranes (Anodisc, Whatman Co.) with pores of nominal diameter 20 nm and thickness of 60 μ m. The AAO membrane is placed on the same silicon chip with small opening the center. The porosity of the AAO membrane is 25–50% of the total exposing surface area.

2.4 Measurement

The experiment setup is shown in Figure 2a. The fabricated CNT forest membrane is sandwiched between two flat polydimethylsiloxane (PDMS) slabs with punched holes (~1mm diameter) as fluid pathways. The sandwich structure is further clamped between two Polystyrene optical cuvettes with 1mm diameter fluid holes. The measurement setup is placed in a home-built Faraday cage to reduce noise. Bias is applied through Ag/AgCl electrodes (prepared by dipping clean 0.25mm diameter Ag wire into bleach with a distance of 1–1.5cm for 30 minutes) across the membrane at a fixed distance (~1.2cm). The applied bias is mostly below 2V and never above 3V to avoid water electrolysis, electrode polarization, and electric potential damage to molecules. The measurement is carried out at room temperature (~22C). No temperature change in solution is observed when applying 3V for 2 hours across the CNT membrane. The *cis* side is always grounded and the applied bias is defined as positive when the potential at the *trans* side is more positive. The analytes are always added in the *cis* side. The ionic current data are collected with a Keithley 2636A (Keithley Instruments, Cleveland, Ohio). All the measurements are performed at room temperature. The electrical resistance of the fluidic pathway (without the membrane) is at least one order smaller than the resistance of the CNT membrane (see Figure S3b in supplementary information). A pressure gradient is introduced by adjusting the height difference between the water surface level in *cis* and *trans* reservoirs. No obvious change in the height difference is observed for a 10 hours experiment. The measured ionic current of the same device is normally stable for weeks if the membrane is rinsed properly and stored in water all the time.

The concentration of permeates at the *trans* reservoir is measured by UV-vis spectrometer (Ocean optics, USB2000+ or Shimadzu UV1700 Spectrometer) and square wave voltammetry (CHI instrument, CHI 760D).

3. Results and discussions

We have carried out several control experiments to prove that within our applied bias and pressure range, the transport is through the inside of the CNT and not through the cracks and avoids in the parylene film. We measured the ionic current through the membrane by using the setup as shown in Figure 2a. When the control devices with pure parylene thin film is fabricated and treated by the same process (see experiment methods section), no ionic current is measured. When the CNT membrane is not treated by oxygen plasma, there is no measurable ionic current. With the increase of the oxygen plasma time, the measured ionic current initially increases and then flattens out (see supplementary information). The dependence of ionic current on oxygen plasma time implies the ionic current is proportional to the number of opened CNTs in the membrane. We also studied the translocation of gold nanoparticles with well-defined size under pressure and electric field. The 5nm Au NP is smaller than the average CNT inner diameter and the 10 nm Au NP is bigger than the average CNT inner diameter. We have measured more than 10 membranes and about 80% of the membranes only allow 5nm AuNPs to pass with only electric field applied (see one example in Figure 4b). However, the ratio reduced to about 40% when a pressure (294 Pa, about 3cm height difference) is applied. We discard the 60% membranes that also allow the passage of 10nm NPs. This fact also suggests that these parylene encapsulated CNT membranes are not suitable for high pressure applications. Therefore, we mainly study the transport driven by electrical field. If a pressure gradient is needed, the pressure is always below 294 Pa, a level at which no leaks are detected in the parylene membranes.

To understand the ion transport mechanisms in these large diameter MWCNTs, we measured the ionic conductance in KCl solution as a function of KCl concentration and solution pH. We first measured the ionic current through CNT forest membrane at different bias. The current-voltage (IV) curves are symmetric in the applied bias range ($<2V$) and a typical curve taken in 100mM KCl solution is shown in the inset of Figure 2b. The ionic conductance can be derived from the slope of the IV curve. We then plot the ionic conductance data as a function of KCl concentration in logarithmic scale. As shown in Figure 2b, the ionic conductance is proportional to the KCl concentration when it is above 0.1mM. A deviation is observed when the concentration is below 0.1mM. The deviation at low salt concentration was previously explained by surface charge on the nanochannel/nanopore [30]. However, the conductance departs from linear relationship at much higher salt concentration ($>10mM$) for silica nanochannels with surface charge density $\sim 60mC/m^2$ at pH 7. Even for an octadecyltrichlorosilane (OTS) modified silica channel with significantly reduced surface charge density, the deviation appears at around 1mM KCl concentration [30]. Therefore, we concluded that the surface charge density at the inner surface of MWCNTs is extremely low. The proportionality at KCl concentration 0.1mM–1M suggests the transport mechanism under electric field is electrophoresis. This is very different from the transport mechanism in individual SWCNTs with inner diameter below 2nm [24, 15]. A unique power law relationship with exponent smaller than 1 is always observed in those single SWCNT fluidic devices. The origin of such behavior is attributed to the strong electroosmotic flow inside smaller diameter SWCNT. We further studied the ionic conductance as a function of pH and the result is shown in Figure 2c. We did not observe obvious change in ionic conductance when changing the pH of the KCl solution (both 1M and 10 mM concentrations) from 3 to 9, which is very different from the results of small diameter SWCNT. This result confirms the low surface charge density at the MWCNT inner surface and low net charge density of KCl solution inside the MWCNT. Possible reasons why the surface charge density is low at the inner surface of the MWCNT are: 1. Because of the inert nature of CNT inner surface, there are very few charged groups at the CNT inner surface. Charged groups (i.e., carboxyl group) distribute mostly at the CNT ends. 2. The CNT inner surface may also acquire charges due to polarization when contacting

charged solution or affected by nearby environmental charges. However, the net charge density of the solution inside the large diameter MWCNT is low, as we discussed before. In addition, the conducting outer layers of MWCNT can effectively screen the environmental charges. In summary, the electroosmotic flow is much weaker in these MWCNTs of average 7nm diameter comparing with small diameter SWCNT. Due to the low surface charge, ion enrichment and ion depletion are not expected in our system [42, 25]. Electrophoresis will be the dominant transport mechanism. This conclusion is also consistent with previous experiments and theoretical calculations [33, 19]. It worth noting that increased electroosmotic flow has been observed by grafting small charged molecules at the inner surface of MWCNT[36]. However, such modification will also increase the roughness of the CNT inner surface and a decrease in slip length is expected.

We then studied the transport of small molecules through these membranes. Anions $\text{Fe}(\text{CN})_6^{3-}$ (hydrated diameter ~ 0.95 nm)[4] and cations $\text{Ru}(\text{bipy})_3^{2+}$ (hydrated diameter ~ 1.18 nm)[4] were used in this study. The molecular structures of both ions are shown in Figure 3a. We first measured the IV curves and the results are shown in Figure 3b. The solutions in the *cis/trans* reservoirs are $\text{K}_3\text{Fe}(\text{CN})_6/\text{KCl}$, $\text{Ru}(\text{bipy})_3\text{Cl}_2/\text{KCl}$ and $\text{Ru}(\text{bipy})_3\text{Cl}_2/\text{K}_3\text{Fe}(\text{CN})_6$. The KCl solution concentration is always 75 mM and the $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Ru}(\text{bipy})_3\text{Cl}_2$ solutions are always 12.5 and 25mM, which keep the solution ionic strength at both reservoirs the same ($I_c = 1/2 \sum c_i Z_i^2$). As shown in Figure 3b, at the same bias (*i.e.*, 0.25V), the ionic current magnitude is in the following sequence: $[\text{KCl}/\text{KCl}] > [\text{K}_3\text{Fe}(\text{CN})_6/\text{KCl}] > [\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{KCl}] > [\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{K}_3\text{Fe}(\text{CN})_6]$. The same sequence is observed for all the MWCNT membranes we measured. In order to verify the CNT effect, we also performed IV measurements without the presence MWCNT membrane in the ionic pathway. The measured ionic current magnitude at the same bias (*i.e.*, 0.25V) is in the following sequence: $[\text{KCl}/\text{KCl}] > [\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{KCl}] > [\text{K}_3\text{Fe}(\text{CN})_6/\text{KCl}] > [\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{K}_3\text{Fe}(\text{CN})_6]$ (see Figure S3a in supplementary information). The switch of sequence between $\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{KCl}$ and $\text{K}_3\text{Fe}(\text{CN})_6/\text{KCl}$ with and without the presence of MWCNT membrane suggests that cation $\text{Ru}(\text{bipy})_3^{2+}$ passes the MWCNT membrane less easily, reflecting the extra interactions between cation $\text{Ru}(\text{bipy})_3^{2+}$ and CNT inner surface (see more discussions in the next paragraph).

Here the ionic current is contributed by the transport of all the ion species in the solution. In order to study the transport of individual ion, we also directly measure the concentration of translocated ions at *trans* reservoir after applying a bias between two reservoirs for 90 minutes. In this experiment, the *cis* reservoir is filled with 25mM $\text{K}_3\text{Fe}(\text{CN})_6$ or $\text{Ru}(\text{bipy})_3\text{Cl}_2$ in 100mM KCl (pH 7) solution. The *trans* reservoir is filled with 100mM KCl solution. The concentration of $\text{Fe}(\text{CN})_6^{3-}$ ions is determined by the pronounced redox peak at 0.18 V *versus* Ag/AgCl in square wave voltammetry. The concentration of $\text{Ru}(\text{bipy})_3^{2+}$ ion is determined by the two adsorption peaks at 285nm and 450nm in UV-vis spectra. As shown in Figure 3c, the anion $\text{Fe}(\text{CN})_6^{3-}$ can only be driven across the membrane by positive bias and the cation $\text{Ru}(\text{bipy})_3^{2+}$ can only be driven across the membrane by negative bias. In addition, the concentration of transported ion increases with the applied bias. At zero bias, the concentration of transported ion is not detectable, confirming diffusive transport is inefficient for these membranes. These results are consistent with the electric field induced electrophoretic transport. Between the two ions, the anion $\text{Fe}(\text{CN})_6^{3-}$ is apparently much easier to transport through the MWCNTs and the concentration is about 25 times higher at the *trans* reservoir when the bias magnitude of 1.5V is applied for 90 minutes between the two reservoirs. This observation is consistent with the IV curves in Figure 3b. What is the reason for the big difference in transport between anion $\text{Fe}(\text{CN})_6^{3-}$ and cation $\text{Ru}(\text{bipy})_3^{2+}$? Interestingly, the much higher rejection of cation $\text{Ru}(\text{bipy})_3^{2+}$ than anion $\text{Fe}(\text{CN})_6^{3-}$ is opposite to the observation in small diameter DWCNTs[4], in which the anion is rejected by the negative charged carboxyl groups at the CNT ends. Because of the

much bigger diameter of MWCNT in these membranes, the charges carried by the ions and at the CNT ends are likely fully screened by the electric double layer (EDL) at 100mM KCl concentration. Therefore, the electrostatic interactions between ions and CNT ends are not important. In addition, the hydrated diameter of anion $\text{Fe}(\text{CN})_6^{3-}$ is only slightly smaller than cation $\text{Ru}(\text{bipy})_3^{2+}$. So size induced steric hindrance will not contribute significantly to such obvious ion selectivity. One reason may be due to the different bulk electrophoretic mobility between $\text{Fe}(\text{CN})_6^{3-}$ ($\sim 10.4 \times 10^{-8} \text{ m}^2/\text{sV}$) and $\text{Ru}(\text{bipy})_3^{2+}$ ($\sim 4.0 \times 10^{-8} \text{ m}^2/\text{sV}$). However, the mobility of $\text{Fe}(\text{CN})_6^{3-}$ is only about 2.5 times higher than the mobility of $\text{Ru}(\text{bipy})_3^{2+}$, which cannot account for the 25 times concentration difference at the *trans* reservoir. The main reason may be attributed to the stronger molecular interaction between the cation $\text{Ru}(\text{bipy})_3^{2+}$ and the curved CNT inner surface. The origin of interaction may be from van der Waals force and pi-pi stacking between the rings of $\text{Ru}(\text{bipy})_3^{2+}$ cation and the CNT inner surface. We also compared the transport between anion $\text{Fe}(\text{CN})_6^{3-}$ and cation $\text{Ru}(\text{bipy})_3^{2+}$ through nominal 20 nm pore diameter AAO membrane and the difference is still obvious but much smaller (see Figure S3). This control experiment supports that the ion selectivity in CNT membrane is mainly due to surface interactions.

We also studied the transport of DNA through these membranes. Theoretical simulations have made predictions that single-stranded DNA can pass through a CNT under external electric field [39, 6]. The translocation of short single-stranded DNAs through SWCNT has also been reported.^{10,29} TEM revealed clear images of ssDNAs inside SWCNT, which were injected by electrical field [13]. Interestingly, the ionic current signatures during DNA translocation in individual SWCNT are quite different from those in silicon based nanopore/nanochannel [14, 10, 12]. There are still no studies on the transport of DNA through big diameter MWCNT membranes. Here, we investigated the translocation of a 12mer ssDNA (GTCGTCGTCGTC) through the MWCNT membrane. As shown in Figure 4a, no DNA is detected in UV-vis spectrometer at the *trans* reservoir when a bias of 3V is applied across the membrane for 60 minutes. The same magnitude of bias is also applied for a longer time (> 120 minutes) and still no DNA is detected by UV-vis spectrometer. The DNA may be driven through the MWCNT membrane at a bias higher than 3V. However, electrode polarization and water hydrolysis prevent studies at a higher bias. The difficulty of transporting ssDNA through these MWCNT membranes is probably due to (1) the strong interactions between CNT inner surface and ssDNA, and (2) the lack of electroosmosis in these big diameter MWCNTs. It has been well-studied that ssDNA will adsorb strongly to CNT outer surface due to hydrophobic interaction and pi-pi stacking of DNA bases on the CNT[40]. Molecular dynamics simulations[6], transmission electron microscopy (TEM) studies [23, 29] and dynamics force microscopies[16] also suggest DNAs interact with CNT inner surface through hydrophobic and van der Waals forces. Therefore, without the efficient electroosmotic pumping, the moderate applied electric field is likely not enough to overcome the interaction force between ssDNA and CNT inner surface and cannot drive ssDNA through the large diameter MWCNT. To test this hypothesis, we increase the driving force by adding a small pressure difference (98 Pa) between two reservoirs. As the green curve shown in Figure 4a, ssDNA is detected at the *trans* reservoir. We also studied the electrophoretic transport of negatively charged 5nm gold nanoparticles. As shown in Figure 3b, 5nm gold nanoparticles can be detected at the *trans* reservoir by UV-vis spectrometer after applying a 2V bias across the membrane for 6 hours. Although the 5nm gold nanoparticle has bigger size than 12mer ssDNA, the interaction between gold NPs and CNT surface is presumably weaker than ssDNA due to the citrate coating on the surface of gold NPs. Therefore, 5nm gold NPs are easier to transport through the MWCNT membrane. These results suggest the interactions between particles and the hydrophobic CNT inner surface strongly affect their electrophoretic transport through these large diameter MWCNT membranes.

Finally, we studied how chemical modification of CNT membrane affects particle transport. The chemical modification at the CNT ends may affect the particle transport by steric hindrance, electrostatic interactions and chemical bonding. During the fabrication, the CNT ends acquire carboxylate groups due to the oxygen plasma process. A variety of chemical modifications on the CNT ends can be easily accomplished by using well-established carbodiimide chemistry to couple carboxylic acid group with amine group. Similar to previous reports [18, 15], a very simple molecule, ethanolamine is used to modify the membrane, which will neutralize the negatively charged carboxyl groups (when $\text{pH} > 4$) and may hinder the particle transport at the pore entrance. The schematics of the unmodified and modified CNT ends are shown in the inset of Figure 5a. We first measured ionic current through these MWCNT membranes before and after the chemical modification in KCl solution. No difference in the ionic current was observed (see Figure S4). This suggests that the modification does not affect the transport of small ions, such as K^+ and Cl^- . We then measured the transport of bigger particles, including 12mer ssDNA (GTCGTCGTCGTC) and 5nm gold NPs under a small pressure (~ 147 Pa). The results are shown in Figure 5. The transport of ssDNA and 5nm diameter gold NPs across the membrane is obviously suppressed by the ethanolamine modification (blue curves in Figure 5 a and b). The observed effect is most likely due to steric hindrance because there is no charge on the CNT ends after modification. To further confirm the chemical modification effect, we use oxygen plasma to remove the modified molecules and then redo the modification. As shown in Figure 5a, the transport of ssDNA across the CNT membrane is correspondingly recovered (green curve) and then hindered (blue curve). Here we just use a simple molecule to demonstrate the capability of reversible chemical modification on these parylene embedded MWCNT membranes. By using rational designed molecules, we expect to enhance selectivity and electroosmotic flow in these MWCNT membranes [32]. Here, the ethanolamine molecules mainly modified the CNT ends. The grafting of rationally designed charged molecules inside the CNT will be another way to enhance the selectivity.

4. Conclusions

In summary, we have successfully fabricated parylene encapsulated vertically aligned large diameter MWCNT membranes. In contrast to small diameter DWCNTs and SWCNTs, electroosmosis in these large diameter MWCNTs is weak. Therefore an electric field can only provide a weak force to drive ions and small molecules. The transport is also significantly affected by the interactions with the hydrophobic CNT inner surface, leading to enhanced selectivity for small molecules. Chemical modification on these MWCNT membranes also shows obvious effect on the translocation of particles.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We acknowledge Garrett Nelson for contact angle measurements, the use of nanofab within Center for Solid State electronic research (CSSER) and SEM and TEM within the Center for Solid State Science (CSSS) at Arizona State University, and the nanofab within AMERI at Florida International University (FIU). This work was supported by the DNA Sequencing Technology Program of the National Human Genome Research Institute (1RC2HG005625-01, 1R21HG004770-01) and the start-up funds from FIU. P. Tiwari would also like to thank FIU School of Integrated Science & Humanity, College Arts & Sciences for the research assistantship.

References

1. Cai D, Ren L, Zhao H, Xu C, Zhang L, Yu Y, Wang H, Lan Y, Roberts MF, Chuang JH, Naughton MJ, Ren Z, Chiles TC. A molecular-imprint nanosensor for ultrasensitive detection of proteins. *Nat Nano*. 2010; 5:597–601.
2. Corry B. Designing Carbon Nanotube Membranes for Efficient Water Desalination. *The Journal of Physical Chemistry B*. 2007; 112:1427–34. [PubMed: 18163610]
3. Derylo MA, Morton KC, Baker LA. Parylene Insulated Probes for Scanning Electrochemical-Atomic Force Microscopy. *Langmuir*. 2011; 27:13925–30. [PubMed: 21961960]
4. Fornasiero F, Park HG, Holt JK, Stadermann M, Grigoropoulos CP, Noy A, Bakajin O. Ion exclusion by sub-2-nm carbon nanotube pores. *Proceedings of the National Academy of Sciences*. 2008; 105:17250–5.
5. Gao C, Ding S, Tan Q, Gu L-Q. Method of Creating a Nanopore-Terminated Probe for Single-Molecule Enantiomer Discrimination. *Analytical Chemistry*. 2008; 81:80–6. [PubMed: 19061410]
6. Gao H, Kong Y, Cui D, Ozkan CS. Spontaneous Insertion of DNA Oligonucleotides into Carbon Nanotubes. *Nano Lett*. 2003; 3:471–3.
7. Hinds BJ, Chopra N, Rantell T, Andrews R, Gavalas V, Bachas LG. Aligned Multiwalled Carbon Nanotube Membranes. *Science*. 2004; 303:62–5. [PubMed: 14645855]
8. Holt JK, Park HG, Wang YM, Stadermann M, Artyukhin AB, Grigoropoulos CP, Noy A, Bakajin O. Fast Mass Transport through Sub-2-Nanometer Carbon Nanotubes. *Science*. 2006; 312:1034–7. [PubMed: 16709781]
9. Hummer G, Rasaiah JC, Noworyta JP. Water conduction through the hydrophobic channel of a carbon nanotube. *Nature*. 2001; 414:188–90. [PubMed: 11700553]
10. Karnik R, Fan R, Yue M, Li D, Yang P, Majumdar A. Electrostatic Control of Ions and Molecules in Nanofluidic Transistors. *Nano Lett*. 2005; 5:943–8. [PubMed: 15884899]
11. Lee CY, Choi W, Han J-H, Strano MS. Coherence Resonance in a Single-Walled Carbon Nanotube Ion Channel. *Science*. 2010; 329:1320–4. [PubMed: 20829480]
12. Li J, Stein D, McMullan C, Branton D, Aziz MJ, Golovchenko JA. Ion-beam sculpting at nanometre length scales. *Nature*. 2001; 412:166–9. [PubMed: 11449268]
13. Li Y, Chen S, Kaneko T, Hatakeyama R. Electrically moving single-stranded DNA into and out of double-walled carbon nanotubes. *Chemical Communications*. 2011; 47:2309–11. [PubMed: 21152585]
14. Liang X, Chou SY. Nanogap Detector Inside Nanofluidic Channel for Fast Real-Time Label-Free DNA Analysis. *Nano Lett*. 2008; 8:1472–6. [PubMed: 18416580]
15. Liu H, He J, Tang J, Liu H, Pang P, Cao D, Krstic P, Joseph S, Lindsay S, Nuckolls C. Translocation of Single-Stranded DNA Through Single-Walled Carbon Nanotubes. *Science*. 2010; 327:64–7. [PubMed: 20044570]
16. Lulevich V, Kim S, Grigoropoulos CP, Noy A. Frictionless Sliding of Single-Stranded DNA in a Carbon Nanotube Pore Observed by Single Molecule Force Spectroscopy. *Nano Lett*. 2011 ASAP. 10.1021/nl104116s
17. Majumder M, Chopra N, Andrews R, Hinds BJ. Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes. *Nature*. 2005; 438:44. [PubMed: 16267546]
18. Majumder M, Chopra N, Hinds BJ. Effect of Tip Functionalization on Transport through Vertically Oriented Carbon Nanotube Membranes. *Journal of the American Chemical Society*. 2005; 127:9062–70. [PubMed: 15969584]
19. Majumder M, Chopra N, Hinds BJ. Mass Transport through Carbon Nanotube Membranes in Three Different Regimes: Ionic Diffusion and Gas and Liquid Flow. *ACS Nano*. 2011; 5:3867–77. [PubMed: 21500837]
20. Mattia D, Gogotsi Y. Review: static and dynamic behavior of liquids inside carbon nanotubes. *Microfluidics and Nanofluidics*. 2008; 5:289–305.
21. Miserendino S, Yoo J, Cassell A, Tai Y-C. Electrochemical characterization of parylene-embedded carbon nanotube nanoelectrode arrays. *Nanotechnology*. 2006; 17:S23. [PubMed: 21727350]
22. Noy A, Park HG, Fornasiero F, Holt JK, Grigoropoulos CP, Bakajin O. Nanofluidics in carbon nanotubes. *Nano Today*. 2007; 2:22–9.

23. Okada T, Kaneko T, Hatakeyama R, Tohji K. Electrically triggered insertion of single-stranded DNA into single-walled carbon nanotubes. *Chemical Physics Letters*. 2006; 417:288–92.
24. Pang P, He J, Park JH, Krsti PS, Lindsay S. Origin of Giant Ionic Currents in Carbon Nanotube Channels. *ACS Nano*. 2011; 5:7277–83. [PubMed: 21888368]
25. Pu Q, Yun J, Temkin H, Liu S. Ion-Enrichment and Ion-Depletion Effect of Nanochannel Structures. *Nano Lett*. 2004; 4:1099–103.
26. Qin X, Yuan Q, Zhao Y, Xie S, Liu Z. Measurement of the Rate of Water Translocation through Carbon Nanotubes. *Nano Lett*. 2011; 11:2173–7. [PubMed: 21462938]
27. Schoch RB, Han J, Renaud P. Transport phenomena in nanofluidics. *Rev Mod Phys*. 2008; 80:839.
28. Scott M, et al. Electrochemical characterization of parylene-embedded carbon nanotube nanoelectrode arrays. *Nanotechnology*. 2006; 17:S23. [PubMed: 21727350]
29. Shoda M, Bandow S, Maruyama Y, Iijima S. Probing Interaction between ssDNA and Carbon Nanotubes by Raman Scattering and Electron Microscopy. *The Journal of Physical Chemistry C*. 2009; 113:6033–6.
30. Stein D, Kruithof M, Dekker C. Surface-Charge-Governed Ion Transport in Nanofluidic Channels. *Phys Rev Lett*. 2004; 93:035901. [PubMed: 15323836]
31. Strano MS, Dyke CA, Usrey ML, Barone PW, Allen MJ, Shan H, Kittrell C, Hauge RH, Tour JM, Smalley RE. Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization. *Science*. 2003; 301:1519–22. [PubMed: 12970561]
32. Sun X, Su X, Wu J, Hinds BJ. Electrophoretic Transport of Biomolecules through Carbon Nanotube Membranes. *Langmuir*. 2011; 27:3150–6.
33. Thomas JA, McGaughey AJH. Reassessing Fast Water Transport Through Carbon Nanotubes. *Nano Lett*. 2008; 8:2788–93. [PubMed: 18665654]
34. Wang Z, Ou Y, Lu T-M, Koratkar N. Wetting and Electrowetting Properties of Carbon Nanotube Templated Parylene Films. *The Journal of Physical Chemistry B*. 2007; 111:4296–9. [PubMed: 17408260]
35. Whitby M, Quirke N. Fluid flow in carbon nanotubes and nanopipes. *Nat Nano*. 2007; 2:87–94.
36. Wu J, Gerstandt K, Majumder M, Zhan X, Hinds BJ. Highly Efficient Electroosmotic Flow through Functionalized Carbon Nanotube Membranes. *Nanoscale*. 2011; 3:3321–8. [PubMed: 21727982]
37. Wu J, Gerstandt K, Zhang H, Liu J, Hinds BJ. Electrophoretically induced aqueous flow through single-walled carbon nanotube membranes. *Nat Nano*. 2012; 7:133–9.
38. Wu J, Paudel KS, Strasinger C, Hammell D, Stinchcomb AL, Hinds BJ. Programmable transdermal drug delivery of nicotine using carbon nanotube membranes. *Proceedings of the National Academy of Sciences*. 2010; 107:11698–702.
39. Xie Y, Kong Y, Soh AK, Gao H. Electric field-induced translocation of single-stranded DNA through a polarized carbon nanotube membrane. *The Journal of Chemical Physics*. 2007; 127:225101. [PubMed: 18081421]
40. Zheng M, Jagota A, Strano MS, Santos AP, Barone P, Chou SG, Diner BA, Dresselhaus MS, McLean RS, Onoa GB, Samsonidze GG, Semke ED, Usrey M, Walls DJ. Structure-Based Carbon Nanotube Sorting by Sequence-Dependent DNA Assembly. *Science*. 2003; 302:1545–8. [PubMed: 14645843]
41. Zhong G, Warner JH, Fouquet M, Robertson AW, Chen B, Robertson J. Growth of Ultrahigh Density Single-Walled Carbon Nanotube Forests by Improved Catalyst Design. *ACS Nano*. 2012; 6:2893–903. [PubMed: 22439978]
42. Zhou K, Kovarik ML, Jacobson SC. Surface-Charge Induced Ion Depletion and Sample Stacking near Single Nanopores in Microfluidic Devices. *Journal of the American Chemical Society*. 2008; 130:8614–6. [PubMed: 18549214]

Figure 1.

(a) SEM image of the cross-section of the as-grown vertically aligned MWCNT forest. The average height of the CNT forest is about $42 \mu\text{m}$. (b) Low resolution TEM image of a large number of MWCNTs. The inset at the top left corner is a high resolution TEM image of one MWCNT. The inset at the top right corner shows the histogram of inner diameters of these MWCNTs. (c) A SEM image shows the cross-section of the parylene coated MWCNT membrane. (d) A SEM image shows the membrane surface after oxygen plasma treatment. (e) The schematic of the parylene encapsulated MWCNT forest membrane on a silicon support with a square window with size $35\text{--}100 \mu\text{m}$.

Figure 2.

(a) Diagram of the ionic current measurement setup. The “h” is the solution height difference between two reservoirs. (b) The ionic conductance vs. KCl concentration on a log-log scale. The solid line is a linear fit to the experimental data. The inset shows the I–V curve of the membrane in 100mM KCl solution. (c) The ionic conductance through the membrane as a function of pH in 1M KCl (red circle) and 10mM KCl (blue triangle) solutions. The solid lines are guides for the eye.

Figure 3.

(a) Schemes of the molecular structure of anion $\text{Fe}(\text{CN})_6^{3-}$ and cation $\text{Ru}(\text{bipy})_3^{2+}$ and their hydrated diameters. (b) The measured I–V curves when the *cis* and *trans* reservoirs are filled with KCl/KCl (black curve), $\text{K}_3\text{Fe}(\text{CN})_6/\text{KCl}$ (green curve), $\text{Ru}(\text{bipy})_3\text{Cl}_2/\text{KCl}$ (blue curve) and $\text{Ru}(\text{bipy})_3\text{Cl}_2/\text{K}_3\text{Fe}(\text{CN})_6$ (red curve), respectively. The concentration of KCl solution is 75 mM and the concentration of anion $\text{Fe}(\text{CN})_6^{3-}$ and cation $\text{Ru}(\text{bipy})_3^{2+}$ is 12.5 and 25 mM respectively. (c) The concentration of anion $\text{Fe}(\text{CN})_6^{3-}$ (red square) and cation $\text{Ru}(\text{bipy})_3^{2+}$ (blue triangle) at the *trans* reservoir as a function of the applied bias. The time is always 90 minutes. The solid lines are guides for the eye.

Figure 4.

(a) UV-vis spectra of 12mer ssDNA at the *trans* reservoir after applying 3V bias (red) and after applying 3V bias and 98 Pa pressure simultaneously for 60 minutes (green). The solution in the *cis* reservoir is 5 μ M ssDNA in 100mM KCl solution. (b) UV-vis spectra of 5nm (red) and 10nm (blue) Au nanoparticles at the *trans* reservoir after applying a 2V bias for 6 hours. No pressure is applied. The concentration of Au NPs at the *cis* reservoir is 60 μ M in 1mM KCl solution.

Figure 5.

(a) UV-vis spectra of 12mer ssDNA at the *trans* reservoir after applying 147 Pa (1.5cm water height difference) for 120 minutes for membrane after ethanolamine modification (red), after removing the modification by oxygen plasma (green) and after ethanolamine modification again (blue). The initial concentration of ssDNA at the *cis* reservoir is 5 μ M. (b) UV-vis spectra of 5nm Au NPs in 1mM KCl at the *trans* reservoir before (green) and after (blue) ethanolamine modification. The concentration of Au NPs at the *cis* reservoir is 10 μ M in 1mM KCl solution. A pressure of 147 Pa is applied for 36 minutes.