CNT-polyamide nanocomposite membranes for gas and water

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ABSTRACT

We have developed asymmetric carbon nanotube /polyamide membranes for gas sorption and desalination applications. The carbon nanotubes are functionalized with zwitterionic groups that control the sorption of gases and the rejection of ionic species while permitting the transport of water. The molecular-level events controlling the adsorption of gases and the transport of fluids through functionalized carbon nanotubes, including entrance effects have been studied using molecular dynamics. The simulations show that water signficantly changes the adsorption dynamics of gases and that ions are rejected through a combination of electrostatic and steric factors.

Keywords: carbon nanotubes, functionalized, sorption, desalination

1 INTRODUCTION

There has been a long-standing technical interest in carbon nanotubes (CNTs) driven by their exceptional electrical, thermal and mechanical properties [1]. More recently, molecular simulations and experimental studies have discovered unique transport properties of fluids within CNTs due to the unprecedented smoothness and regularity of the CNT pores [1,2]. However, gas selectivities of single walled carbon nanotubes (SWNT) membranes generally followed the Knudsen model, being quite low in comparison to selectivities offered by neat polymer membranes [3]. This limitation can be attributed to the large pore size of the carbon nanotubes, typically on the order of 10 - 15 Å for SWNT and 100 Å for multi-walled carbon nanotubes (MWCNT), in comparison to the kinetic diameters of small gases ranging from 2.7 Å to 6 Å, making molecular sieving difficult. One way to get around this problem is to introduce functionalized moieties at the carbon nanotube tips that can have specific molecular interactions with particular gases and/or whose presence partially blocks the access to the CNT pores, thereby decreasing the effective CNT pore size.

In this study we compare the gas sorption and desalination properties of single walled carbon nanotubes functionalized with COOH and with zwitterion groups.

Molecular dynamic simulations were performed to elucidate the atomic-level details of the sorption and desalination processes. Simulations were performed for pristine, COOH functionalized and zwitterion functionanlized SWNTs. The diameter of the SWNTs used in the simulations is about 1.57 nm, corresponding to a (20,0) SWNT. The length of each tube is about 40 Å.

2 EXPERIMENTS AND SIMULATIONS

Carboxylic acid functionalized SWNTs, of outer diameter 1.5 nm and length 1µm were purchased from Nano Lab Inc. (MA, USA). The COOH groups on the SWNTs served as precursors for the addition of zwitterion groups.

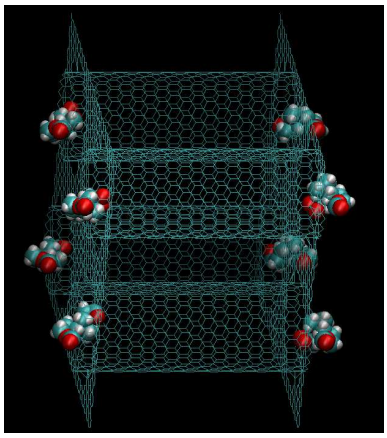

Figure 1: Model SWNT membrane used in the simulations. Each end of each SWNT is functionalized with one zwitterion. The nanotubes were embedded between two graphene sheets to form the membrane.

Detailed atomistic simulations were performed for hypothetical SWNT membranes as shown in Figure 1. The carbon atoms in the CNTs and graphene sheets were modeled using aromatic carbon 'CA' in the CHARMM27 force field [4]. The simulation cell with one zwitterionic group on each end of each nanotube is shown in Figure 1. All of the carbon atoms in CNTs and graphene sheets were held fixed during the simulation. CO_2 molecules were treated as rigid molecdules and the parameters for CO_2 and functional groups were also taken from CHARMM27 force field. Water molecules were simulated using the TIP3P water model [5]. The temperature of the system was

controlled by a Nosé-Hoover thermostat [6]. Periodic boundary conditions were applied in all three dimensions. All of the calculations were performed with the LAMMPS package[7] using a time step of 1 femtosecond.

3 RESULTS AND DISCUSSION

3.1 Gas sorption isotherms

The approximate size of zwitterion and COOH functional group is around 1.1-1.2 nm and 0.4 nm, respectively. Thus, the presence of the groups may affect the effective pore diameter of the SWNTs. Although the small size of the COOH groups is not large enough to completely block the opening of the carbon nanotubes, the presence of the COOH groups still affects the sorption of gases in SWNTs, as has been demonstrated in on our previous studies [8], where the sorption of CO_2 was lowered by half in COOH functionalized SWNTs compared to non-functionalized nanotubes.

Thermal gravimetric analysis of zwitterion functionalized SWNTs has suggested that these SWNTs loose water molecules upon heating to 200°C. Hence, the gas sorption isotherms were measured in both heated and unheated zwitterion functionalized SWNTs. Unheated Zwitterion functionalized SWNTs are sorption selective for CO_2 over CH_4 at 10 bar. However, the absolute value of concentration of gas sorbed in unheated zwitterion functionalized SWNTs is lower than in COOH-functionalized carbon nanotubes. The concentration of N_2 sorbed in COOH functionalized and zwitterion SWNTs is shown in Figure 2. These results suggest that the zwitterionic groups block access to the carbon nanotube pores.

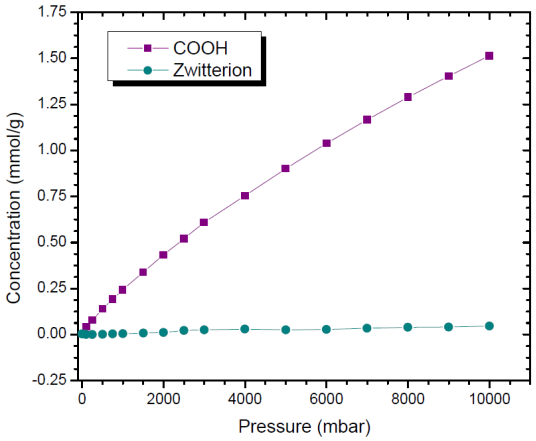

Figure 2. N_2 gas sorption isotherm at 35 °C in COOH and zwitterion functionalized (not heated) SWNTs.

In zwitterion functionalized SWNTs heated to 200 °C, a significant weight loss of the sample was observed and the concentration of gas sorbed in subsequent isotherms increased. At 10 bar, the concentration of gas increased by almost two orders magnitude in non-hydrated zwitterion SWNTs compared with hydrated zwitterion SWNTs. This is a significant increase, reflecting the removal of water molecules blocking the SWNTs pores.

We have also found the same trend for the sorption of CO_2 in our simulations, as shown in Figure 3. The dynamic adsorption of CO_2 in pristine tubes and several functionalized tubes have been computed from molecular dynamics. For an external pressure of about 10 bar and over a time of 6 ns, the number of CO_2 adsorbed into the pristine tube is almost the same as into tubes functionalized with five COOH groups or one zwitterion group without water. When the tube entrances are functionalized with three zwitterion groups we find that the zwitterions significantly block the tube entrances. The adsorption of CO_2 decreased about 80% comparing with the pristine tube membrane. When 200 water molecules were added into the system, we found all of water molecules intially aggregate around the entrances and and then move into the tube. Hence, the simulations indicate two modes for reducing the amount of gas sorbed into the unheated (hydrated) zwitterion functionalized nanotube. Firstly, the water at the entrance of the SWNTs acts as a kinetic barrier, dramatically increasing the time needed to reach equilibrium. Secondly, water is imbibbed into the nanotubes with the help of the zwitterion functional groups, reducing the equilibrium amount of gas that can be sorbed.

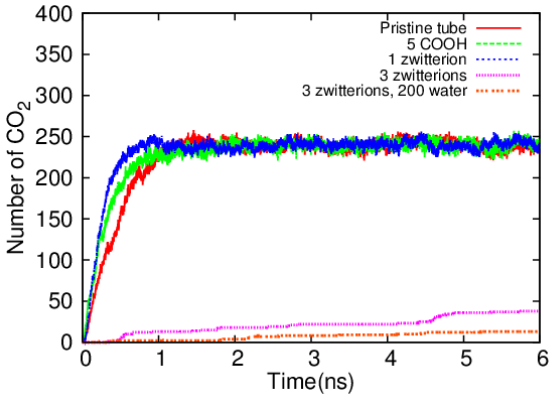

Figure 3: At The number of CO_2 molecules adsorbed into the CNT membrane as a function of time from molecular simulation. The external pressure of CO_2 is roughly 10 bar.

3.2 Desalination

The desalination results were gathered from a reverse osmosis testing of zwitterionic-functionalized CNT nanocomposite membrane.

At 530 psi, the salt rejection is more than 98% and there is no significant drop in the water flux of ~15 gallons per square foot per day (GFD) after three days of teseting. The membrane is durable and stable against surface fouling by salt water.

For comparison, RO membranes consisting of neat polyamide coating of similar thickness (without CNTs) on the same support had much lower water flux (0 – 7 GFD) and lower rejection rates (less than 57%).

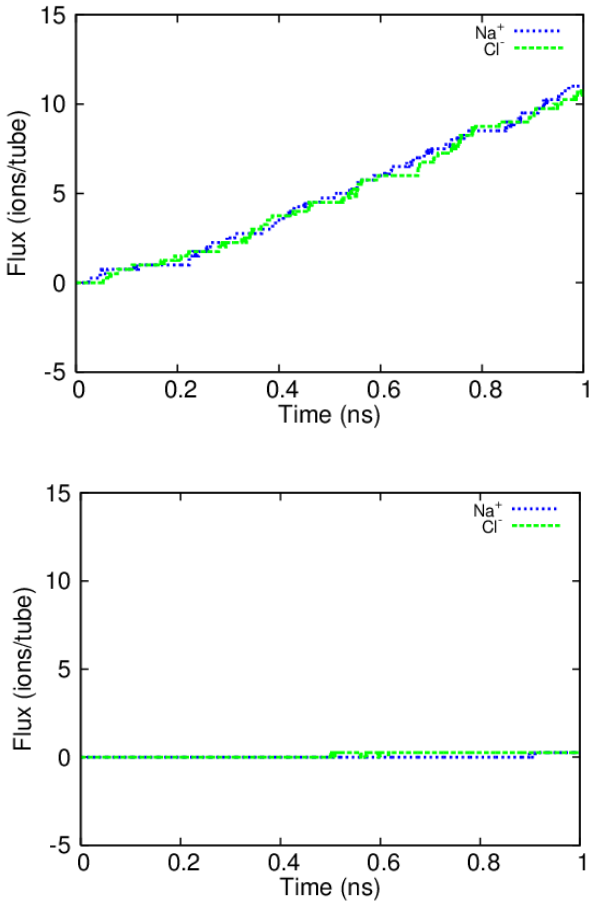

Figure 4. Computer simulations of the flux of salt ions through a pristine SWNT membrane (top) and through a SWNT membrane functionalized with two zwitterions on the end of each nanotube (bottom). The zwitterions effectively block the salt flux under identical conditions of operation.

We have calculated the flux of water and ions through pristine SWNTs and functionalized SWNTs using molecular dynamics simulations. Flow of water and ions was induced in the simulation by imposing a pressure drop across the membrane and carrying out simulations for 1ns. The flux of water, sodium ions (Na^+) and chloride ions (Cl^-) through the model membrane was measured during the course of the simulation. Results for pristine and zwitterion functionalized nanotubes are plotted in Figure 4. The results of the simulations provide a proof-of-concept that zwitterions can function as gatekeeper molecules to effectively inhibit the flow of salt ions (Na^+ and Cl^-) through the nanotube membrane. Simulations under identical conditions for the pristine nanotubes (Figure 4, top) show that the flux of salt ions through the membrane increases linearly with time, and hence the membrane is ineffective at blocking salt transport and would therefore not be effective for use in a desalination membrane. On the other hand, the simulations clearly demonstrate that functionalizing the ends of each of the nanotubes with two zwitterion functional groups makes the ion flux drop to almost immeasurable values over the length of the simulation. Hence, the zwitterions are effective gatekeeper moieties that turn an unselective membrane into a highly selective membrane suitable for desalination. These simulations provided the motivation for carrying out experiments on functionalized nanotubes to verify the predictions.

4 CONCLUSION

Functionalized carbon nanotube membrane is found to serve as sorption sobents and water desalination materials. Unheated zwitterion functionalized SWNTs are sorption selective for CO_2 over CH_4 and N_2. The removal of water molecules in zwitterion functionalized SWNTs obviously increase the sorption of gases. All of the desalination results indicate that zwitterion functionalzied SWNT membranes are proomising materials for water purification.

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