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Gas sorption properties of zwitterion-functionalized carbon nanotubes

Anil Surapathi [a], Hang-yan Chen [b], Eva Marand [a,*], J. Karl Johnson [b,c], Zdenka Sedlakova [d]

[a] Department of Chemical Engineering, Virginia Polytechnic Institute and State University, 138 Randolph Hall, Blacksburg, VA 24061, USA
[b] Department of Chemical & Petroleum Engineering, University of Pittsburgh, 1250 Benedum Hall, Pittsburgh, PA 15213, USA
[c] National Energy Technology Laboratory, Pittsburgh, PA 15236, USA
[d] Ustav Makromolekularni Chemie, Heyrovského Nam., 2, 162 06 Praha 6, Czech Republic

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ABSTRACT

We have functionalized carbon nanotubes with carboxylic acid and zwitterion groups. We have evaluated the effect of functionalization by measuring the sorption of CO_2, CH_4, and N_2 at 35 °C for pressures up to 10 bar. Zwitterion functionalized nanotubes were found to be highly hygroscopic. Thermal gravimetric analysis indicates that water can be desorbed at about 200 °C. The adsorption of gases in zwitterion functionalized nanotubes is dramatically reduced when compared with nanotubes functionalized with carboxylic acid groups. The presence of water on the zwitterion functionalized nanotube reduces the sorption even further. Molecular simulations show that three or more zwitterion groups per tube entrance are required to significantly reduce the flux of CO_2 into the tubes. Simulations also show that gas phase water is rapidly sorbed into the zwitterion functionalized nanotubes, both increasing the free energy barrier to CO_2 entering the tube and also lowering the equilibrium adsorption through competitive adsorption.

1. Introduction

There has been a long-standing technical interest in carbon nanotubes (CNTs) driven by their exceptional electrical, thermal and mechanical properties [1]. Molecular simulations and experimental studies have uncovered unique transport properties of fluids within CNTs due to the unprecedented smoothness and regularity of the CNT pores [2,3]. For example, the transport of simple gases in both multi-walled and single-walled carbon nanotube membranes has been shown to be orders of magnitude larger than that predicted by Knudsen diffusion [4]. However, gas selectivities of single walled carbon nanotube (SWNT) membranes were found to generally follow the Knudsen model, being quite low in comparison to selectivities offered by neat polymer membranes [5–7]. This limitation can be attributed to the large pore size of the carbon nanotubes, typically on the order of 10–15 Å for SWNTs and 100 Å for multi-walled carbon nanotubes, in comparison to the kinetic diameters of small gas molecules, which range from 2.7 Å to 6 Å, making molecular sieving difficult. We propose that one way to improve selectivity is to introduce functionalized moieties at the carbon nanotube entrance points (typically the tips, where the caps have been etched away). The functional groups could act in two ways: they reduce the effective diameter of the pore entrance through steric effects, thereby increasing size selective molecular sieving, and they could also be tailored to have specific molecular interactions with particular gases to facilitate molecular sieving through a chemical recognition or electrostatic repulsion mechanism [8].

Previous modeling work indicates that CNTs may be tailored or functionalized with different functional groups to serve as separation membranes for gases. Liu and Chen designed a hypothetical Y-Junction CNT and used molecular dynamics (MD) simulations to show that this junction acts as a molecular sieve for the separation of gases based on molecular size [9]. Arora and Sandler [10] demonstrated that carbon nanotubes with a constriction can give a high transport resistance for N_2 while allowing O_2 to pass through the constriction. Similarly, Zhang [11] showed that a kinked SWNT has the potential to separate N_2 and O_2 through transfer resistance to N_2 provided by the kink. Corry predicted that charged functional groups bound to the entrance of SWNTs could provide resistance to ion flow in an aqueous salt solution that is otherwise missing in unfunctionalized nanotubes [12]. These simulations provide evidence that steric or electrostatic modification of nanotubes is required in order to impart a high degree of selectivity to CNTs. However, the configurations studied are all hypothetical, especially for constricted and kinked CNTs, since there is no known way to easily produce CNTs with such specific geometries. However, nanotubes can indeed be functionalized, as demonstrated in our previous work where SWNTs were functionalized with long chain alkyl groups and incorporated into nanocomposite mixed matrix membranes [7]. Other simulation studies have examined how the functionalization of

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* Corresponding author. Tel.: +1 540 231 8231; fax: +1 540 231 5022.
E-mail address: emarand@vt.edu (E. Marand).

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nanotubes influences equilibrium adsorption of fluids. Huang et al. [13] studied the influence of $-CH_3$ and $-COOH$ functional groups at the entrance of very narrow nanotubes on the uptake of water. They found that $-CH_3$ groups have little effect on water uptake, but $-COOH$ groups could either increase or decrease the amount of water in the nanotubes, depending on the nanotube studied. Joseph et al. [14] examined the effect of putting functional groups of opposite charge on each end of a short nanotube on the transport of salt ions through the nanotube in an aqueous solution of KCl. They functionalized one end of the tube with $-COO^-$ groups and the other with $-NH_3^+$ groups. They used a static electric field to drive ions through the nanotube in a model membrane. They found that the Cl^- transport rate was much higher than the K^+ rate and attributed this asymmetry to the K^+ ions being "bound" to the $-COO^-$ groups at one end of the nanotube.

In addition to simulations, experimental work has demonstrated that the transport of fluids through CNTs can be altered through functionalizing the nanotube ends. Holt et al. [4,15,16] have constructed nanotube-Si_3N_4 composite membranes using chemical vapor deposition. Using an etching process, they exposed and selectively uncapped the CNTs to introduce hydroxyl, carbonyl, and carboxylic functional groups at the nanotube entrance. Ionization of the carboxylic groups for example, created charged nanochannels that used both steric hindrance and electrostatic repulsion to achieve ion rejection [12]. Hinds and coworkers constructed CNT membranes by microtoming multiwalled CNT (7 nm inner diameter) and SWNT (1.5 nm inner diameter) epoxy composites [17–22]. They studied electro-osmotic flow by measuring the fluxes of both charged and neutral probe molecules through the membranes under external electric fields. An electrochemical diazonium grafting method was employed to enhance the surface anionic charge density of CNTs. The diazonium grafting increased carboxylate density on carbon nanotubes by about 5–6 times as compared to that of the as-produced (plasma-oxidized) CNT membranes. This led to an increase in ionic transport of a positively charged permeate along the CNT core. The surface anionic charge was also further enhanced via a carbodiimide coupling reaction with the dye molecule containing four negatively charged SO_3 groups. This particular functionalization facilitated efficient pumping via electro osmosis of neutral caffeine molecules. Falconer et al. have recently shown that ion diffusion through dense CNT membranes can be gaited due to changes in water wettability [23].

In this study we demonstrate that SWNTs can be functionalized with both COOH and zwitterionic groups. We compare the gas sorption properties of SWNTs functionalized with these groups and present computer simulations to explain the differences observed experimentally in the sorption isotherms.

2. Methods

2.1. Materials

Carboxylic acid functionalized SWNTs, of outer diameter 1.5 nm and length 1 μm were purchased from Nano Lab Inc. (MA, USA). The SWNTs were produced by a CVD method, purified and functionalized with COOH groups by refluxing in sulfuric acid/nitric acid. Purity of the SWNTs was greater than 95% (by TGA). Concentration of COOH groups in the SWNTs was approximately 2–7 wt% (by titration). Reagents, thionyl chloride (99.5%) and 3-dimethylamino-1-propanol (99%), were purchased from Sigma Aldrich, USA and used as received. β-propiolactone (oxetan-2-one) was purchased from Biophoretics Inc., USA.

2.2. Synthesis of zwitterionic functionalized SWNTs

The COOH groups on the SWNTs served as precursors for the addition of zwitterion groups. The three-step chemical reactions required beginning from COOH functional groups to perform this addition are shown in Fig. 1.

In the first step, COOH functionalized SWNTs (A) were reacted with thionyl chloride to form SWNTs with COCl groups (B) as

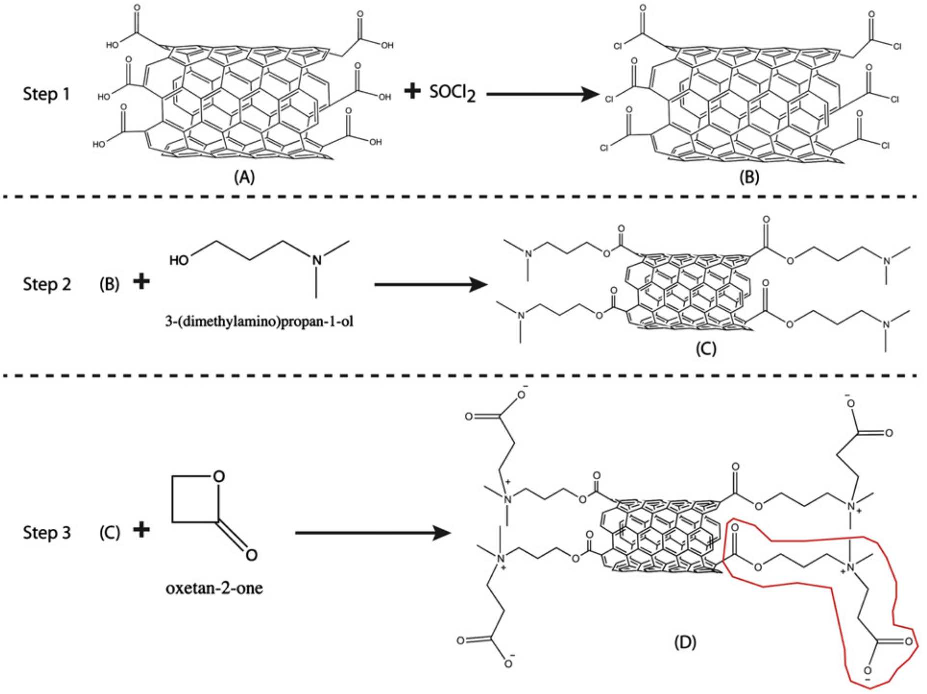

Fig. 1. Schematic of the chemical reactions leading to the formation of zwitterion groups on the carbon nanotube tips. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)