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Electrokinetics desalination of water using fluorinated carbon nanotubes embedded in silicon membrane: Insights from molecular dynamics simulation

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HIGHLIGHTS

- Interestingly, this research introduces fluorinated carbon nanotubes for transporting higher flux of water compared to pristine carbon nanotubes.
- Applying electrical field resulted in a dramatic increase in water transport through fluorinated carbon nanotubes.
- Water self-diffusion coefficient through fluorinated carbon nanotubes were more than pristine carbon nanotubes.
- This work with precise analysis of water transport through pristine and fluorinated carbon nanotubes introduce fluorinated CNTs as a promising candidate in water desalination membrane technology.

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ABSTRACT

A molecular dynamics simulation was performed to investigate the transport properties of water, sodium and chlorine ions through double-end fluorinated carbon nanotubes (FCNT) under the horizontal electrical field. The present system consists of a carbon nanotube embedded in silicon membrane and two, water box placed at both sides of the membrane. The flow and structure analysis shows that FCNTs in a specific range of electrical field enhance the water flux. Furthermore, the flow significantly depends on carbon nanotubes radii. In FCNT (8,8) the water flux is increased to ~215 H2O/ns which is 25% more than water flux in pristine carbon nanotubes. In FCNT (10,10) water flux increased to ~600 H2O/ns which interestingly explain the improvement of water flux through fluorinated carbon nanotubes. The transport of water in FCNT and PCNT were scrutinized by other parameters such as hydrogen bonds, radial distribution function (RDF) and ionic current analysis. Results revealed the influence of fluorine functionalization on carbon nanotubes, headed for the increment of water transport through carbon nanotube based nanopore. Our results also put forward that fluorinated SWCNTs may be used as a design model in CNT-based water storage devices and water purification membranes.

1. Introduction

Since the discovery of single-walled carbon nanotubes, a massive research, both theoretically and experimentally, commenced toward using their exclusive characteristics, ranging from structural and mechanical to electromechanical, in various applications such as electronic capacitors (Yin et al., 2007), novel power converters (Collins et al., 2005), chemical desalination of water (Iwamatsu et al., 2004), nanoscale fluidic instrument for biomedical applications (Ramachandran and Sathyamurthy, 2005; Vaitheeswaran et al., 2004), nano-sized water pumps (Giovambattista et al., 2006), nanoscale flow controlling (Leung et al., 2003), drug delivery (Lum et al., 1999) and etc. In particular, because of different water properties in nano-sized confined spaces alike inside carbon nanotubes, it is well established that carbon nanotubes showed different mechanical and thermodynamics properties, which were recognized in different research works for a variety of topics. Inside carbon nanotubes, showed hydrophobic features, which treated as a prototype model for fundamental research, aimed at discovering the physics and structures of water molecules within nanochannels. This issue

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was considered as a vital model for both the theory and the practice with various applications, such as gas storage, (Cao et al., 2003; Liu et al., 1999) Nano electronics (Sazonova et al., 2004), molecular sensors (Snow et al., 1942; Kong et al., 2000), drug delivery (Portney and Ozkan, 2006; Singh et al., 2006), and membrane separation (Hinds et al., 2004; Corry, 2008; Bahr and Tour, 1952).

Chemical functionalization of carbon nanotubes intended to designing new materials with novel properties has been under vast research during the last decades (Tasis et al., 2003). One of the drawbacks in the development of advanced carbon nanotubes in the functionalization process was the great spectrum of size and chirality of CNTs, which resulted in complications associated with the experiment of functionalization. Rapid progress in synthesis and purification methodologies enabled the development of CNTs chemistry (Van Lier et al., 2005). Generally, functionalization will result in our desired properties for application of carbon nanotubes in different areas. Functionalization process will enhance the solubility properties of CNTs and improve the purification methods. Furthermore, nanotubes composites in order to reveal the desired mechanical properties should have strong bonding networks with bulk material which functionalization meet this expectation (Scrivens and Tour, 1993; Corry, 2011).

Toward solving the problem associated with insolubility of carbon nanotubes, which hindered the prospective application of CNTs for above-mentioned applications, it is highly regarded to chemically functionalize CNTs towards improving their chemical properties and making additional processes possible for desired applications (Ruoff et al., 1993; Niyogi et al., 2002; Yao et al., 2003; Abdelkader-Fernándeza et al., 2015). It is believed that functionalization of CNTs leading to a noteworthy improvement in their properties to practical applications. Functionalization of carbon allotropes (physically) consists of non-covalent π-π interaction and covalent bonding. A non-covalent interaction does not change the structure of compound while covalent bonding modifies the hybridization of carbon atoms. Therefore, modify the physical and chemical nature of material (Bekyarova et al., 2009; Some et al., 2012; Hwang et al., 2012, 2006; Holzinger et al., 2003). As a result, the study of CNT functionalization is growing rapidly and has been the subject of recent research efforts. CNTs could be functionalized on their ends, interior and exterior surfaces (Joseph et al., 2003; Zheng et al., 2005). Considering the hydrophobic characteristics of CNTs inside and other incredible physiochemical, properties, water transport through carbon nanotubes, grabbed the attention of many researchers worldwide. In desalination technology, ion rejection besides fast transport of water is of high importance. CNTs revealed considerable strength in this regard and their capability were examined in many simulations and experiments. Functionalization of carbon nanotubes at inner mouth and exterior surface were performed to improve the capabilities of these nanopore for faster transport of water and more ion rejection. This utopia is not as reachable as theory because simulation results and experimental investigations showed lesser water transport, but acceptable ion rejection in CNT-based nanofiltration was reported. Molecular dynamics simulation as a powerful technique was utilized in this era for scrutinizing the physics behind the water flow inside pristine and functionalized carbon nanotubes.

Using molecular dynamics simulation, Halicioglu and Jaffe (2002) studied ionic flow in the carboxylic acid (—COOH) functionalized carbon nanotubes at both terminals of CNTs. They found the possibility of obtaining the selectivity for positive and negative ions by a symmetrical arrangement of functional groups at both terminals. Placing —COOH groups on the inner surface of carbon nanotubes could alter the hydrophobic nature of surface into hydrophilic. Zheng et al., (Huang et al., 2002), conducted molecular dynamics simulation for studying a system consists of carbon nanotubes carrying —COOH groups on the internal surface for water and methanol mixture transport. Results showed the fast transport of water through hydrophilic carbon nanotubes and gentle water motion inside hydrophobic CNTs. Headed for investigating the structure of functional groups at both ends, Halicioglu and Jaffe, (Huang et al., 2002), reported the influence of polar or non-polar groups on stability, demonstrating non-polar groups as folded and polar groups as energetically more stable structure. Different functionalization of CNTs, both hydrophobic (.e.g. —CH3) and hydrophilic (.e.g.—COOH), were investigated in a molecular dynamics simulation and a perfect structural analysis of water surrounding nanotubes was directed by Wongchoosuk et al. (2009). They investigated the effects of helicity, numbers of functional groups and diameters. Furthermore, the helicity of CNTs determines the fluctuations of the —COOH groups, which in turn bring forth the non-uniform distribution of the CNT's electric field and alters the water conduction. For —CH3 groups, the structure of water remained identical to the water molecules inside the pristine CNTs. Gong et al. (2010) studied the hydroxyl (—OH), carboxyl (—COOH) and amide (—CONH2) functional groups on CNTs and concluded that tip functionalization varies the edge orbitals of the pristine tube, but these consequences appear to quickly reduce as the tubule becomes stretched. It was concluded and highlighted that the "completely occupied" functionalization at the open ends of finite-length SWNTs do not considerably alter the geometrical and electronic properties of the original pristine nanotube. Bettinger (2003), to mimic K+ channel in proteins membranes, used molecular dynamics simulation to investigate water transport in a (9, 9) carbonyl functionalized SWCNT to presented a theoretically designed channel model (Bettinger, 2003).

Fluorinated carbon nanotubes, has been comprehensively studied both experimentally and theoretically (Mickelson et al., 1999). It causes an improvement in solubilization of nanotubes in several solvents (Peng et al., 2001). As far as the application is concerned, the mechanical and electrochemical properties of fluorinated carbon nanotubes (FCNTs) have been researched in numerous articles. Furthermore, FCNTs was introduced as electrodes in lithium electrochemical cells (Seifert et al., 2000). An interesting reports about FCNTs was that they do not alter the metallic character of some types of CNTs (Kudin et al., 2001). Moreover, for controlling the length of CNTs and to having shorter nanotubes, FCNTs could be used while they are growing (Gu et al., 2002).

Interesting electrochemical properties of chemical bonds between carbon and fluorine atoms attracted attentions for application of fluorine-functionalized carbon nanoallotropes in desalination and chemical sensors. Between the possible fluorinations, carbon nanotubes could be functionalized on both ends with fluorine atoms to form fluoro tubes (F-SWCNTs) which could be utilized in various application such as electronics and hydrophilic exemplary of membranes (Giraudet et al., 2007). In metal/semiconductor, the electrochemical properties of fluorinated carbon atoms at terminals could be utilized to alter electronic properties of SWCNT-based electronic devices. There are several experimental methods for functionalization of carbon nanotubes by fluorine groups (Zhang et al., 2008; Tressaud et al., 2004; Watanabe et al., 1988; Mickelson et al., 1998; Pehrsson et al., 2003; Kelly et al., 1999; Wang and Sherwood, 2004). Gregory Van Lier et al. using Ab initio method, studied fluorinated carbon nanotubes and introduced FCNT as a novel carbon-fluorine composite for further applications (Khabashesku et al., 2003).

In this research double-end fluorinated, single-walled carbon nanotubes were embedded in silicon membranes, (Fig. 1), for studying water and ions transport through hydrophilic-entrance-functionalized hydrophobic nanopore. It was expected that fluorinated carbon nanotubes could enhance water flow and molecular dynamics evidenced this expectation. It was revealed that fluorine