Enhanced durability and hydrophobicity of carbon nanotube bucky paper membranes

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Abstract
Recent work showed that carbon nanotubes could be fabricated into bucky-paper structures as self-supporting membranes and their hydrophobic property used for water desalination by membrane distillation. Carbon nanotube bucky-papers possess very interesting properties such as natural hydrophobicity, high porosity and very high specific surface area, making of them promising candidates for separation applications. However, to inhibit crack formation associated with poor mechanical stability, improved durability structures that retain a high degree of hydrophobicity need to be developed. In this work we chemically modified high purity carbon nanotubes by (i) UV/ozone treatment to create hydroxyl groups and (ii) reacting those groups by substitution with alkoxy silane based groups. The resulting
nanotubes presented a silicon content up to 2.5% and the bucky-papers produced had larger contact angle (140° compared to 125°) and liquid entry pressures. We report here on their fabrication and use as membranes in direct contact membrane distillation.

**Keywords:**
alkoxysilane; carbon nanotube; membrane distillation; hydrophobicity; bucky-papers

**Introduction**

To overcome numerous engineering issues, such as fouling, or wetting, surface energy control is a key topic in current materials research. Furthermore, in separation sciences, super-hydrophobic nano-material based surfaces made of nano-spheres [1], ultra thin layers [2] or nanotubes [3] are being built up to address the increasing demand for non-wettable materials that are both highly thermal and chemical resistant. Carbon Nanotubes (CNTs) especially are very stable structures that can be functionalised [4] in a variety of ways. Their chemistry is still little known and work is required to better estimate their potential and design routes for efficient functionalisation. Previous work reported their successful use in a range of separation applications [5-8] as well as inclusion into nano-composites for improved separation performance [9-12].

In the special case of health and water purification, new treatment techniques that can respond to the exponentially growing demand for fresh water are required. In fact, an alternative and complementary technology to reverse osmosis and conventional thermal desalination based techniques is membrane distillation [13-16]. Direct Contact Membrane Distillation (DCMD) is a process for water desalination where a porous membrane is used as a separation barrier between two liquid streams at different temperatures [15-18]. Highly hydrophobic materials are required to prevent the processed liquids from wetting and wicking into the membrane pores and forming direct bridges between the two streams of water [16, 19, 20]. This wetting criterion is typically evaluated by measuring the
membrane Limit Entry Pressure (LEP), that directly relates to the membrane surface energy through the contact angle of water on the membrane surface [13, 21] (Equation (1)).

\[
LEP \geq -\frac{2\gamma_L \cos \theta}{r_{\text{max}}} 
\]  

(1)

Where \( \gamma_L \) is the liquid surface energy, \( \theta \) the contact angle, \( r_{\text{max}} \) the largest pore in the membrane and \( B \) an experimental constant.

In previous studies we demonstrated that Carbon Nanotube (CNT) Bucky-Paper (BP) membranes could successfully operate in Direct Contact Membrane Distillation (DCMD) for synthetic seawater desalination [12, 22]. However, during DCMD, BPs fabricated from as grown CNTs, endured crack formation across the membrane thickness caused by mechanical ageing. Water infiltrated the cracks thus emphasizing their formation leading to premature failure [22]. The origin of the cracks is still not entirely understood but defects on some CNTs may initiate water drawn in via capillary forces accelerating this phenomenon. Therefore, an increase in hydrophobicity would improve the membrane performance [17, 23], slow the rate of crack formation and the capillary attraction of the water into the pores. It might also reduce surface pore wetting and wicking which potentially limit water permeability [24] by creating a stagnant boundary layer on the surface pores. This phenomenon referred as temperature polarisation [25-28] has been shown to reduce the flux across membranes.

We address these issues by functionalising the outer walls of the CNTs with 3-glycidoxypropyltrimethoxysilane (GPTMS) chains. The CNTs were first UV/ozone treated to create active hydroxyl groups and eventually silanised to enhance their hydrophobicity. Thorough characterisation at different steps of the treatment i.e. (i) after growth, (ii) after ozone treatment and (iii) after silanisation was carried out and the impact of the treatments on the modified membranes analysed. DCMD results for composite structures made of alkoxy silane-functionalised CNTs bucky-papers membranes are presented.

Experimental section
Carbon nanotube growth

The CNTs were grown by chemical vapor deposition using an established method reported elsewhere [29]. The carbon feedstock used was acetylene (mixed with 95% of helium) which was thermally decomposed on iron nano-particles, at temperatures between 650°C and 750°C. The naturally aligned CNTs typically exhibited outer diameters and lengths of respectively 10-15 nm and 150-300 µm (Figure 1) and were scraped from their silicon wafer growth support prior to further treatment.

UV/ozone treatment and alkoxysilanation

Three batches of CNTs were exposed to ozone, generated by a Novascan PDS-UVT, UV/ozone cleaner, in a confined chamber for respectively 10, 30 and 60 min. The samples were positioned at a 30mm distance from the UV lamp which had an intensity greater than 36 mW/cm² and ozone output greater than 50 ppm. This oxidation treatment was necessary to form hydroxyl and carboxylic active sites on the surface of the nanotubes.

The hydroxyl functionalised CNTs were then exposed to lithium aluminium hydride (LiAlH₄) to reduce the carboxylic groups present on their surface. Typically, CNTs were suspended in toluene and horn-sonicated for 30 min in a cooled water bath. LiAlH₄ was added and the solution stirred at 30°C for 60 min. Then 2.0 ml of a 2M HCl solution was added to remove the reducing agent. The CNTs were washed sequentially with toluene, ethanol and acetone prior to being eventually vacuum dried overnight at 100 °C [30].

The second step of the process involved the chemical reaction of the hydroxyl groups with the alkoxysilane moieties. Typically, CNTs were suspended in toluene and sonicated for 15 min. Then a 1.0 wt% GPTMS/toluene solution was added (30 mL for 100 mg of CNTs) and stirred at 65°C for 6 h to achieve silanization. Eventually unreacted GPTMS was washed out with methanol until a clear permeate was obtained and the CNTs backwashed with sequentially deionised water and acetone. The silanised CNTs were dried overnight at 100°C [30, 31].
**CNT characterisation**

Transmission Electron Microscopy (TEM - FEI Tecnai F30) images of the nanotubes and Electron Dispersive Spectroscopy (EDS) fitted in the TEM chamber were respectively used to reveal the CNT morphology after treatment and assess the presence of oxygen and silane groups on the surface of the CNTs. Raman spectroscopy was carried out on a Renishaw Raman spectroscope with a 514 nm laser. The tests were performed with a power of 10% (1.43 mW) of the nominal laser intensity to avoid damaging the CNTs surface.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 150 W, a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (0.3 mm × 0.7 mm slot). The total pressure in the main vacuum chamber during analysis was typically less than 5.10⁻⁸ mbar. Each specimen was analysed at an emission angle normal to the surface. All elements present were identified from survey spectra (acquired at a pass energy of 160 eV). The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer.

Attenuated Total Reflectance Fourier Transform Infra Red (ATR-FTIR) spectroscopy was undertaken with a Nicolet Nexus from Thermo Electron Corporation. The resolution was 1 cm⁻¹ and 32 scans were performed and the results averaged for each sample. The detector was a DTGS KBr with a working range between 400 and 4000 cm⁻¹.

**Bucky-paper fabrication and characterisation**

CNTs were suspended in propan-2-ol and sonicated 5 times at 150 W for 10 min. The solutions were frozen at -17 °C between each sonication interval to improve the dispersion stability. CNT Bucky-paper (BP) flat sheet membranes were then processed by vacuum filtration of CNTs suspension [32-34], dried in a vacuum oven at 65 °C and eventually pealed off to form a self-supporting membrane [32, 35, 36]. The self-supporting BPs were hot pressed at 60°C for 15 min under mild pressure with a porous (55% porous) polyethylene grid [12].
Contact angle with 4 μL drops of deionised water were measured with a Pocket Goniometer PG7 from Fibro system. Liquid Entry Pressure (LEP) was estimated with a 25.4 mm Amicon cell with deionised water and propan-2-ol. The samples were left after each 5 kPa pressure increase to rest for 10 min.

Limit Entry Pressure (LEP) of the membranes was tested with 25.4 mm wide membranes supported on 0.2 μm pore size PES membrane placed in a stainless steel grid in an Amicon test cell. High purity nitrogen was used and pressure steps of 13.8 kPa were used to identify the pressure at which break through occurred. The samples were allowed to equilibrate for 10 min between each pressure increase [21, 23].

**Direct contact membrane distillation setup**

In DCMD, a water vapour pressure difference across a hydrophobic, porous membrane drives water evaporation from the hot stream, diffusion across the membrane air-gap and condensation in the cold permeate.

A peristaltic pump (Cole Palmer Masterflex, model 7521-25) fitted with two coupled heads (Easyload II, Model 77200-60) was used to circulate the hot and cold sides. The membrane was placed into a poly (tetrafluoroethylene) disk-shaped module, with respective diameter and height of 25.4 mm and 2 mm and tests were performed in counter-flow current. The flow rate was kept constant at 300 mL.min⁻¹ on each side, while the temperatures of the water streams were monitored and varied respectively between 55 and 75 °C on the hot side (CS Lauda C6 heater) and was kept constant at 5°C on the cold side (Thermo Scientific Neslab RTE-7 cooler). Electrical conductivity and temperature of the hot and cold electrolytes, as well as the water level transferred to the cold side, were monitored and data logged over time. Deionised water and 35 g.L⁻¹ NaCl solution were respectively used as cold permeate and hot feed. The DCMD setup formed a convenient technique to validate film integrity and hydrophobicity. The membrane exposed surface area was 5 cm². The volume of permeate was measured with a graduated column over time and membrane permeability k calculated from Equation 2:
Equation 2 Membrane permeability

\[ k = \frac{J \times L}{A \times \Delta P} \]

Where \( k \) is the permeability, \( J \) the flux (kg/m\(^2\)*s), \( L \) the thickness (m), \( A \) the test surface area (m\(^2\)) and \( \Delta P \) (kPa) the water vapour pressure difference across the membrane for the given hot and cold bulk temperatures.

**Results and discussion**

**CNT characterisation**

TEM images in Figure 1 show that the as grown CNTs were of high purity and presented homogenous and regular crystalline walls (Figure 1-a). After 10 and 30 min of ozone treatment (respectively 1-b and 1-c) the outer walls were degraded and defects, in the form of hydroxyl and carboxylic groups as well as vacancies, were formed in the structure. Aggregates were visible after silanisation which was attributed to the alkyl chains of the alkoxy silane molecules (Figure 1-d). Amorphous carbon was visible on the outer shells of the CNTs after ozone treatment and seemed to be reduced after silanisation. Presence of silicon was assessed by EDS on the surface of a CNT using the TEM setup (insert 2 Figure 1). The amount of silicon was small but superior to that of the raw nanotubes (insert 1 Figure 1).
Figure 1 Transmission micrographs taken at 100 keV. The scale bar represents 5 nm. a: non treated CNTs; b: 10 min ozone treated CNT; c: 30 min ozone treated CNT and d: 30 min ozone treated CNT after silanisation. Insert 1: EDS of as grown CNTs; Insert 2: EDS of silanised CNTs.

Raman spectroscopy showed a decrease of the G band with increasing treatment. This was shown in previous work to correlate directly to the amount of defects being created on the CNTs [17-20] (Figure 2).
Figure 2 Raman spectra of CNTs before and after silanisation; O = ozone treated only, O+R = ozone treated + reduced, O+R+S = ozone treated + reduced + silanised; The D and G band lie respectively at 1350 and 2750 cm$^{-1}$.

Furthermore, the presence of silane groups after treatment was confirmed by FTIR (Figure 3). Bands at 2848 and 2921 cm$^{-1}$ appeared after silanisation and were attributed to the stretching of Si-O groups present on the GPTMS [30]. Even though the signal was weak due to high signal noise, those groups were still present on the samples even after rinsing away excess GPTMS and washing the bucky-papers, thus indicating the GPTMS was grafted to the CNTs.
XPS was performed on the surface of the CNTs at different stages of their treatment. As shown in Figure 4, before silanisation the content of oxygen increased as a function of UV/ozone exposure time. The amount of oxygen present, attributed to both hydroxyl and carboxylic acid group formation on the CNTs, went up to ≈4.2% after 30 min of UV/ozone exposure while the silicon content remained low and constant. Oxygen atoms were attributed to both hydroxyl and carboxylic groups thus justifying the reduction step before silanisation to reduce the acid groups. The oxygen/carbon ratio decreased after silanisation which can be attributed to the alkyl chains presence from the GPTMS (Figure 4). Furthermore, the Si/C ratio of the silanised CNTs was a factor of 3 greater than the raw nanotubes. This directly correlates with hydroxyl groups being attacked to form the alkoxy silane groups on the surface of the CNTs [30, 31].
Figure 4 XPS analysis showing the oxygen/carbon and silicon/carbon ratios on the hydroxyl-functionalised CNTs before and after silanisation.

Furthermore, TGA performed on both hydroxyl and silanised functionalised CNTs, between 20°C and 900°C showed (i) presence of residuals (2-3%) after carbonization above 600°C, which was attributed to the presence of silicon and (ii) increased oxidation resistance as the CNT decomposition temperature shifted from 515°C to 555°C. The improved thermal behaviour was related to the lower number of reactive sites (hydroxyl groups and amorphous carbon) after silanisation as well as the higher thermal stability of silicon compared to carbon.

Bucky-paper characterisation

Contact angle and LEP

Contact angle measurements were obtained for bucky-papers fabricated at various stages of the CNTs life: after growth, after ozone treatment and after silanisation. The as-grown CNTs offered an average contact angle of 120° clearly indicating their natural hydrophobicity. After UV/ozone exposure the contact angle dropped gradually as a function of ozone exposure time down to 30° after 60 min of ozone treatment. This trend was expected due to the hydroxyl and carboxylic groups presence. After silanisation the CNTs hydrophobicity was found to be enhanced
relative to the as-grown CNTs, and contact angles between 135° and 140° were measured (Figure 5). The practical impact of these surface energy changes were evidenced by conducting direct contact membrane distillation experiments.

Furthermore the LEP drastically increased after silanisation. As grown CNT BPs exhibited LEP of ≈193 kPa while silanised CNT BPs LEP went up to 441 kPa (Table 1). The silanisation, therefore, helped improve the stability of the membrane over pressures larger than that applied during DCMD. The higher LEP is correlated to the improvement of the hydrophobicity as more pressure requires to be applied to permeate water through the membrane.

![Figure 5 Contact angle with deionised water. Samples (i) after hydroxyl grafting and (ii) after silanisation.](image)

**Direct Contact membrane distillation**

A series of silane-functionalised CNT BP membranes were tested and showed improved lifespan, salt rejection and mechanical resistance compared to their non-treated counterparts. As shown in Figure 6, the flux across similar thickness membranes nearly doubled in the case of the silanised nanotubes. The salt rejection of the silanised CNTs membranes was always higher than 97% while the pure CNT BP offered a salt rejection between 95 and 97% (Table 1). Furthermore, lifespan of the membranes also increased by more than 50% (Table 1), which was attributed to the increased hydrophobicity. As the water had more difficulty entering in the
membrane, its ability to propagate cracks was inhibited. The presence of the short aliphatic chains helped repel liquid water and thus limited the wetting of the surface pores offering less surface area for water condensation and wicking.

Figure 6 Water vapour flux across the membranes in DCMD. The feed and permeate stream flowrates were 300 mL/min. Vapour pressure drops were estimated from temperature measurements at the inlets and outlets of the membrane module. The hot solution was a synthetic seawater solution (3.5 wt% NaCl) while the cold stream was deionised water.

Table 1 Properties of the membrane in DCMD. The standard deviation is given when data available.

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<thead>
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<th>Ozone treatment time</th>
<th>min</th>
<th>0</th>
<th>30</th>
<th>60</th>
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<tr>
<td>Thickness of active layer (BP)</td>
<td>μm</td>
<td>75 +/- 5</td>
<td>62 +/- 5</td>
<td>60 +/- 5</td>
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<tr>
<td>Average salt rejection (SR)</td>
<td>%</td>
<td>96.5 +/- 8</td>
<td>98.3 +/- 2</td>
<td>97.9 +/- 2</td>
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<td>Permeability (10^-12)</td>
<td>kg/(m.s.Pa)</td>
<td>3.19 +/- 0.1</td>
<td>4.39 +/- 0.1</td>
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It is noteworthy that the flux across the membranes is likely to be limited by the membrane support that partially screens the BP surface and considerably increases the membrane thickness. This configuration is, however, a good compromise to test all the CNT BP under the same conditions and to prevent the BP from degrading too quickly as previously shown [12]. The increase in flux is attributed to the higher hydrophobicity of the material [37, 38] since the water meniscus surface will be increased thus offering more exchange surface available for
water evaporation. This also seems to reduce the membrane sensitivity to temperature polarisation as the boundary layer gets expelled from within the pores and more exposed to delaminating from the bulk water flow on the membrane surface. Furthermore, the flow curves for both 30 and 60 min silanised membranes were very similar. This could be attributed to either the short lifespan of UV/ozone treatments over time, or to the saturation of the surface with hydroxyl groups before 30 min of ozone treatment. The fact that the contact angle tests were similar also confirms this hypothesis.

**Conclusion**

Comprehensive characterisation of the alkoxy silane functionalised CNTs and of BP membranes at different stage of their treatments was performed. A simple two step alkoxy silane treatment permitted recovery of the hydrophobicity of the UV/ozone modified CNTs. Furthermore, the alkoxy silane modified carbon nanotube membranes presented increased hydrophobicity compared to their untreated counter parts which is likely to be responsible for the increase in lifespan and permeability. Up to 4% of alkoxy silane chains were grafted on the CNT surface but a higher surface coverage might be beneficial to further increase the hydrophobicity and performance.

In fact deeper penetrating pre-treatments on the CNTs such as high energy X-Rays, plasma or gamma irradiation could lead to a treatment over the whole thickness of the BP. This could possibly lead to a higher number of hydroxyl groups formation. Also coating with more hydrophobic additive materials such as fluoro- silane might be a way to engineer super-hydrophobic surfaces.

**Acknowledgements**

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References

in: ICOM08, Honolulu - Hawaii, USA, 2008.
Figure 1
Figure 2
Figure 3
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