Robust Carbon Nanotube Membranes Directly Grown on Hastelloy Substrates and Their Potential Application for Membrane Distillation

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ABSTRACT: A new class of robust carbon nanotube (CNT) membranes is developed using a scalable chemical vapor deposition method by direct growth of the CNT on a nickel alloy (Hastelloy) mesh with micrometer-sized openings. The developed membranes have a dense, entangled network of CNT with 50-500 nm pore openings and are superhydrophobic. These CNT membranes are resistant to air oxidation up to ~500 °C and chemical corrosion in concentrated HCl or NaCl solutions. Adhesion and ultrasonication tests suggest that the developed CNT membranes are resistant to delamination and demonstrate a high interfacial bonding of the grown CNT with the alloy substrate. Potential application of the developed CNT-Hastelloy membranes for separation is explored by conducting membrane distillation tests using a 10,000 mg/L NaCl solution. The developed membranes show similar salt rejection performance compared with a carbon bucky paper membrane. These robust carbon nanotube membranes are reusable and expected to be less susceptible to fouling because of their superhydrophobic properties. Furthermore, if fouled, they can be regenerated by heating in air or using an acid wash.

1. Introduction

The growth of carbon nanotubes (CNT) on metal substrates (CNTM) has been a subject of interest for the last two decades because of the immense potential of CNTM as functional materials for filtration, sensing, energy storage, and heat transfer [1–7]. Carbon nanotube on metal substrate materials have been developed on sheet or powder substrates or mesh screens with large openings [2,8,9]. A substantial number of studies have been conducted to understand the CNT growth mechanism, characterize the quality of CNT, and evaluate potential applications of CNTM by considering their mechanical and electrical properties [7,9–14]. However, to the best of our knowledge, the development of CNTM on suitable porous or mesh screen substrates, as a method for membrane fabrication, has not been investigated.

Carbon nanotubes grown on CNTM can have superior hydrophobicity, which is a critical property for many applications, such as membrane distillation and condensation heat transfer [15,16]. It is also critical for the grown CNT in the CNTM material to maintain its interfacial bonding and resist delamination when the materials are exposed to high humidity, corrosive gases, or corrosive conditions in aqueous solutions. A limited number of reports have been published on the surface wettability of CNTM materials [3,8,17–19], but no work has been identified that evaluates the performance and stability of CNTM in humid conditions or corrosive environments. For example, De Nicola and co-workers reported that multiwalled CNT grown on stainless steel (SS) have a superhydrophobic property (water contact angle of 154°) [19], and Zhang and Resasco showed that aligned single-walled CNT are superhydrophobic [18]. The deposition of hydrophobic coatings, such as Teflon [20] gold thiol [21] and silicone [22] on top of the CNT forest has also been reported to make the forest superhydrophobic. However, the

thermal or chemical stability of these or other superhydrophobic CNTM materials for practical applications has not been investigated.

CNT is a material of interest for separation because of the unique nanoscale interactions with liquid and gas molecules occurring along the smooth curved graphitic walls [23] leading to enhancement of flux higher than values predicted by continuum hydrodynamics theory [24–29]. Membrane distillation, a desalination technology that purifies water by allowing only water vapor to pass through hydrophobic pores, can benefit greatly from the availability of suitable CNT membranes with high hydrophobicity, high porosity, high specific surface area, enhanced flux due to interaction of water vapor with outer surface of smooth curved graphitic CNT wall, and resistivity to microbial fouling [30,31]. Even though the potential of CNT membranes has been shown, commercially viable, robust CNT membranes is still under development. The higher manufacturing cost involved with CNT membrane preparation steps, the health hazards caused by the presence of CNT in a permeate after dislodging (because of weak interfacial bonding) from the membrane [30], and the stability of the CNT under realistic application conditions (e.g., high temperature, an oxidative atmosphere, or a corrosive environment) are some of the major challenges involved with producing a viable CNT membrane for different applications. Recent reports suggest that CNT membranes, such as bucky paper (BP), are promising materials for membrane distillation because of their superior hydrophobicity, antifouling property, and mechanical strength [32,33]. However, they can suffer from delamination if they are not immobilized by polymers or other chemical treatments [34–37]. Strategies proposed by other researchers to improve the interfacial bonding of CNT-based membranes for membrane distillation include using polymer (e.g. polyvinylidene fluoride (PVDF)) as a glue to immobilize the CNT into another porous support matrix [36], coating the

bucky paper membrane with poly tetrafluoroethylene [37], and functionalization of CNTs (e.g. by silanization of hydroxyl groups formed on CNT) [38].

This work was aimed at the development of robust, functional CNTM membranes that can be utilized for separation or other applications. The CNT can be grown on metallic catalysts by a variety of methods. Table 1 provides a brief review of the CNTM preparation methods. Preparing CNTM involves three main stages: (1) pretreatment, to develop initial catalytic sites; (2) CNT growth, to grow CNT on the catalytic sites by decomposition of the carbon source using a chemical vapor deposition (CVD) process; and (3) posttreatment, for purification or alignment of the grown CNT. Different pretreatments (oxidation, acid pickling, etc.) can be used to form nanometer-sized catalyst sites on metal substrates. Different metals with or without a passivation layer and additional catalysts can be used to grow CNT, with a variety of gases as the carbon source. The gas composition in the CVD chamber and other process conditions (i.e., temperature, pressure, gas residence time, gas velocity, and flow patterns around the CNT deposition substrates) can influence length, diameter, surface coverage, uniformity, purity, and other properties of CNT.

Through a systematic study, we have identified available methodologies for the preparation of CNTM and modified them to develop an appropriate method for fabricating superhydrophobic and corrosion-resistant CNTM membranes. Suitable substrates with micrometer-sized pore openings, including SS, Hastelloy C22 (HAST), silver, and quartz fiber filter, were selected as templates for CNT growth. The substrates were also chosen because of their high temperature and corrosion resistance, mechanical strength, and flexibility. Dense CNT growth on SS and HAST (pretreated by air oxidation) and on nickel-sputtered silver (subjected to dewetting at higher temperature) was achieved by pyrolysis of acetylene and benzene at 750 °C.

After initial characterizations, CNT on HAST (CNTH), because of its superior corrosion resistance, high flexibility, high CNT purity, and superhydrophobicity, was chosen as the best performing material for further analysis and testing using a membrane distillation setup. The robustness of the developed CNTH membrane was demonstrated by the American Society for Testing and Materials (ASTM) adhesion test, ultrasonication in a solvent, and exposure to concentrated HCl and high-salinity water (a 70,000 ppm NaCl solution). We characterized the developed CNTH membranes by the ASTM standard bubble point test and direct contact membrane distillation (DCMD) and compared them with selected commercial membranes. The developed CNTH membranes were superhydrophobic and resistant to delamination and bending. The CNTH membranes showed promising performance in the membrane distillation tests for water desalination, suggesting these new CNT membranes have potential for use in separation applications, particularly in corrosive environments or at high temperatures.

Table 1. Brief summary of methods proposed in the literature for substrate pretreatment, CNT growth on metallic or ceramic substrates, and posttreatment of grown CNT.

Method	Summary
Pretreatment	
Oxidation-reduction	Oxidation of substrate in air [13,39–41]/O ₂ [14]/humid air [9] in the temperature range of 500–1000 °C, followed by heat treatment in H ₂ or in an inert atmosphere.
Acid treatment	Pickling in concentrated HCl for 5–20 min [39,40,42,43].
Abrasion	Abrasion of ceramic substrate with steel. Abrasion pressure influences CNT growth density [44].
Metal catalyst loading by physical vapor deposition	Metal catalyst deposition after depositing a buffer layer of SiO ₂ /Al ₂ O ₃ /Al by E-beam evaporation/sputtering [10,12,45–47].
Metal catalyst loading by electrochemical deposition	Electrophoretic deposition of cobalt [48].
Metal catalyst loading by dip coating	Applying an FeCl ₃ solution on the target substrate by dipping [12,49].
CNT growth on substrates	
Stainless steel (SS)	Growth on SS (after pretreatment) when using C ₂ H ₂ (12 μm SS fiber [2], 2 μm SS fiber [13], 50 μm SS grid and powder [42]), C ₂ H ₂ with C ₆ H ₆ (23 μm SS wire[9]), CO (SS wire[41]), C ₂ H ₆ (63 μm SS wire[40]), or C ₂ H ₄ (SS sheet[39]).
Nickel (Ni)	Growth on Ni foil when using CH ₄ [43], or on a Ni TEM grid when using C ₂ H ₄ [50].
Inorganics on metal mesh	Growth on Al ₂ O ₃ /SiO ₂ , after 1–2 nm Fe deposition, when using C ₂ H ₄ (SS foil [47]) or C ₂ H ₄ with H ₂ O (Si [7,12,46], metal foils [10]).
Alloys	Growth on Permalloy, Invar plate (after pretreatment) when using C ₂ H ₄ [14] or Inconel substrate with Al and Fe layer when using C ₂ H ₄ .
Postprocessing of CNT	
Steam treatment	Five-minute treatment at 800 °C after the growth stage to remove amorphous carbon layer [45].
Oxidation	Oxidation at 400 °C to remove amorphous carbon layer [48].
Capillary densification	Densification of CNT when using condensation of acetone vapor on them [51].

2. Experimental Section

2.1 Materials. The SS mesh (325 × 2300 Micronic 316 L) was obtained from TWP Inc. (Berkeley, CA) as 1 in. discs with a 2 μm pore size. The HAST mesh was purchased from Unique Wire Weaving Inc. (Hillside, NJ) as 1 in. discs with a 10 μm opening. Pure silver membranes (99.97%) with a 0.2 μm particle retention rating were obtained from Sterlitech Corporation (Kent, WA). Poly(tetrafluoroethylene) (PTFE) membranes with a 0.2 μm pore size were obtained from Pall Corporation (New York City, NY). The BP and CNT were purchased from NanoTech Labs, Inc. (Yadkinville, NC). The tissue quartz filters with a 432 nm pore size and 1 in. diameter were obtained from SKC Inc. (Eighty Four, PA). The electroless ammonia-type nickel solution was purchased from Transcene (Danvers, MA). The CVD gases (argon, hydrogen, methane, and acetylene) were acquired from S.J. Smith Co. (Urbana, IL). Other materials used, including benzene, ferric chloride, nickel nitrate, concentrated HCl, isopropyl alcohol, and NaCl were ACS grade and obtained from Fisher Scientific (Waltham, MA).

Preparation of Carbon Nanotube Membranes. Different pretreatment, growth, and posttreatment methods from the literature were evaluated and optimized by performing experiments in our laboratory (Figures S1–S11). A modified method was developed based on these experimental observations that could allow CNT growth at a higher density and with fewer amorphous carbon impurities. The method had slight variations, depending on the pretreatment conditions (oxidation at 750 °C followed by reduction under a mixture of argon and hydrogen/acid pickling in concentrated HCl/metal catalyst loading by sputtering or dip coating, followed by dewetting). After the initial pretreatments, the samples were placed in a quartz tube (a 26 mm diameter quartz tube having a quartz frit fused in the middle) inside a tube furnace

(Lindberg/MPH, Riverside, MI) for CNT growth on the substrate by CVD. During the growth stage, a mixture of acetylene (12.5 standard cubic centimeters per minute (SCCM)), hydrogen (50 SCCM), and argon (125 SCCM) was bubbled in water (at 20 °C) to add water vapor. The flow was bubbled through benzene (at 20 °C) and then sent to the growth chamber. The CVD was performed for 15 to 30 min at 600 to 800 °C. Samples were cooled either under argon or under a combination of argon and water vapor. The CNTM membranes prepared included CNTSS (CNT on SS), CNTH, CNTS (CNT on silver), and CNTQ (CNT on quartz fiber).

2.2 Characterization. The prepared membranes were characterized to obtain several key parameters. The SEM images were obtained using Philips XL30 ESEM-FEG (FEI, Hillsboro, Oregon) and Hitachi S4800 (Troy, MI) instruments. The E-SEM images were obtained at a 4° C sample temperature and 100% relative humidity using an FEI Quanta 450 instrument (FEI, Hillsboro, Oregon). The WCA was measured from the E-SEM images by using ImageJ software [52] with a drop-analysis plugin based on fitting the Young–Laplace equation to the image data. Five different uniform droplets were analyzed in two different 200 x 200 μm^2 sampling areas. Raman microscopy was performed with a Renishaw microPL/Raman microscope (Renishaw Inc., Gloucestershire, UK). The macroscopic WCA of samples were measured with a KSV CAM200 goniometer (KSV Instruments Ltd., Helsinki, Finland). An XPS analysis of the samples was performed with a Kratos Axis ULTRA instrument (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic magnesium or aluminum $K\alpha$ X-ray source and a $0.7 \times 0.3 \text{ mm}^2$ slit for the collection of emitted photoelectrons. Calibration was performed according to the carbon peak at 284.5 eV binding energy, and carbon and oxygen compositions were calculated from their high-resolution spectra (analyzed with CasaXPS software, Casa Software Ltd., Teignmouth, UK) with relative sensitivity factors for carbon and oxygen of 0.278

and 0.711, respectively. Binding energies for the functional groups used in high-resolution XPS spectra curve fitting were selected by using the methodology mentioned in our earlier work [53]. Surface areas of selected samples were determined from adsorption isotherms of nitrogen from a relative pressure (P/P_0) of 10^{-3} to 1 at 77 K by using a Micromeritics Gemini VII instrument. Samples were degassed in a vacuum for 1 h at 180 °C before nitrogen adsorption. Surface area was estimated from the linear range of the Brauner–Emmett–Teller equation from the relative pressure of 0.05 to 0.2. The thermal and oxidation stability values of samples were characterized by using a thermogravimetric analyzer (model VersaTherm HS, Thermo Fisher, Waltham, MA) by measuring the weight of samples while heated with a heating rate of 5 °C/min to 750 °C in air. An ASTM bubble point test was performed by using a membrane holder, one end of which was connected to the nitrogen tank with a digital pressure gauge to monitor the increase in pressure, and with the other end connected to a clear glass tube having isopropyl alcohol in contact with the membrane to observe the emergence of nitrogen bubbles from the membrane under pressure [54]. An ASTM adhesion test was performed by firmly attaching (air bubbles were removed by pressing) adhesive Scotch tape to the sample surface and checking the same surface after peeling the tape off [55]. Ultrasonication tests were conducted for 40 s at a frequency of 20 KHz and an input energy of 240 W/L by using F550 sonic dismembrator equipment from Fisher Scientific (Hampton, NH).

2.3 Membrane Distillation Experiments. The selected developed membranes, BP, and TF-200 were tested by using a direct contact membrane distillation system. A 10,000 mg/L NaCl solution at 80 °C and deionized water at 5 °C were used as feed and permeate streams. The desalination performance of the tested membranes was evaluated by measuring salt rejection and

water flux values. Further description of the DCMD system, experimental method, and related calculations are provided in the Supporting Information.

3. Results and Discussion

A systematic approach has been undertaken to develop new types of CNT membranes grown on various substrates for potential use in membrane distillation or other separation applications. It is desirable that the developed membranes have submicrometer openings and are flexible, nonfragile, superhydrophobic, resistant to delamination, resistant to corrosive conditions, and stable at high temperatures (e.g., up to 500 °C) under oxidative conditions. The experimental results presented here describe the preparation and characterization of different CNTM materials leading to the development of a CNT membrane (i.e., CNTH membrane) with the desired characteristics.

To develop CNTM membranes, it is imperative to obtain uniform and dense coverage of CNT on the substrate. We began with various methods proposed for CNT growth on metallic substrates (Table 1) and modified them to prepare membranes with the desired properties. Summaries of different synthesis methods, including different pretreatments and CNT growth scenarios, along with optical and scanning electron microscope (SEM) images of selected prepared samples under each experimental condition, are shown in Figures S1 and S2. Methods for CNT growth, optical images, and schematic diagrams of the experimental setup are shown in Figures S3 and S4.

For metal and alloy substrates, air oxidation followed by hydrogen reduction (ox-red) or catalyst deposition by physical vapor deposition (sputtering) were the only pretreatments that resulted in dense growth of CNT. Dip coating was also identified as an effective pretreatment method for the quartz fiber substrate. Contrary to the SS substrate, the HAST substrate showed minimal coverage of CNT without any pretreatment (Figure S5). Dense growth of CNT on the HAST substrate has previously been shown with hot filament plasma-enhanced CVD [56], in which plasma helps to break up the substrate surface to smaller catalyst sites. Here, we used a hot-wall atmospheric pressure CVD with ox-red or sputtering pretreatment conditions to generate catalyst sites similar to those generated in the plasma-enhanced CVD system to grow dense CNT networks on the HAST substrate. **Figure 1A** shows SEM images of the CNTH-750 membrane (CNTH prepared at a growth temperature of 750 °C) with the ox-red pretreatment. The ox-red pretreatment helped break up the smooth surface layer to generate a rough surface with nanometer-sized catalyst sites [13]. Dense growth of CNT was observed at those catalyst sites around individual HAST wires (Figure 1A). The CNT were not aligned along any particular direction as they grew around wires with circular cross-sections. It was expected that during CNT growth on the alloy mesh substrate, amorphous carbon would also form simultaneously because of the availability of carbon atoms, which might form graphitic or nongraphitic carbon structures [57]. To reduce the formation of amorphous carbon and prevent coverage of the catalytic sites with these impurities, water vapor was used during the growth stage at 750 °C to etch away the amorphous carbon through a gasification reaction [12]. Compared with amorphous carbon, different forms of graphitic carbon, including CNT, are significantly more resistant to reaction with water at elevated temperatures [12]. As shown in Figure 1A, the presence of amorphous carbon was minimal; amorphous carbon appears brighter in the SEM images because

it is less electrically conductive than CNT or graphitic carbon. When CVD was performed at a lower temperature (600 °C), the CNTM had a substantial amount of amorphous carbon impurities (Figure S2). The balance between catalytic CNT formation and amorphous carbon deposition shifted toward more amorphous carbon deposition when the growth temperature was 800 °C (Figure S2). This result is consistent with the results of Romero and co-workers [57] and is mainly due to rapid decomposition of the hydrocarbon source (acetylene and benzene) at 800 °C. Therefore, a CNT growth temperature of 750 °C was identified as the optimal temperature for CNTH preparation.

Similar results of dense CNT growth at 750 °C were obtained when the HAST mesh was coated with an additional nickel layer (around 600 nm) by sputtering as a pretreatment step (Figure 1B). At this temperature, the thin sputtered nickel layer dewets and forms nanometer-sized nickel catalysts, facilitating the initial formation of CNT bases and the subsequent growth of CNT [58]. Other pretreatments, including acid pickling or electroless nickel deposition (Figures S5 and S6) and Argon plasma bombardment (Figure S7) resulted in poor growth of CNT because of the inability of the pretreatment to produce suitable catalytic sites. Among the other substrates, a dense CNT network was grown on nickel-sputtered silver when nickel sputtering was used as a pretreatment step (Figure S8). However, for tissue quartz filter (a nonmetallic substrate) dipped in the metal catalyst solution or sputtered with nickel, the best temperature for CNT growth was 600 °C instead of 750 °C (Figure S9). We also prepared CNTH samples following the methods of Pattinson and co-workers [13] and Vander Wal and Hall [9] and compared them with a CNTH sample prepared based on our method. Samples prepared based on our method have a similar or better CNT network and appear to be free of amorphous carbon impurities (Figure S10).

Figure 1. CNTH membrane with (A) an air oxidation pretreatment and (B) a 50 nm nickel-sputtering pretreatment. Both membranes were prepared by CNT growth at 750 °C.

All four prepared CNTM membranes, namely, CNTSS, CNTH, CNTS, and CNTQ, were hydrophobic (Figure S1) but had varying degrees of flexibility and corrosion resistance. The CNTSS corroded with prolonged (2-day) exposure to deionized water (Figures S11A,B). The corrosion in SS occurred because of depletion of the protective chromium layer during the CVD stage [59]. The CNTQ and CNTS membranes became brittle in the CVD stage and broke during testing with the membrane distillation setup (Figure S11C). The CNTH-750 membrane showed superior corrosion resistance, hydrophobicity, and mechanical strength and flexibility, as discussed in detail later. Therefore, only CNTH-750 was considered for further material characterization and membrane testing.

Wettability of the CNTH-750 membrane at the macro- and microscale was studied by using a goniometer and environmental SEM (E-SEM; Figure 2). For macroscopic measurements, the goniometer measurement inside a class 100 cleanroom could not produce water contact angle values for CNTH-750. The 4 μL water droplet did not adhere to the sample (Figure 2A). The hydrophobicity of the developed CNTH-750 membrane was compared with that of a conventional CNT BP, and both materials showed similar hydrophobic properties as the water droplet was pinned and stretched during retraction of the pipette (Figure 2A). When water was ejected toward the CNTH-750 from a syringe, droplets bounced and rolled off the surface (Video S1), again confirming the superhydrophobic property of the CNTH-750 membrane. At a microscopic scale, however, it was possible to form water droplets by condensation. Environmental SEM images show the formation of spherical droplets on the CNTH-750 membrane, demonstrating the superhydrophobic property of this membrane (Figure 2 and Video S2). Using Image J software [52], we measured the water contact angle of the droplets in the E-SEM image as 163° .

Figure 2. (A) Goniometer results showing the nonsticking behavior of CNTH-750 and BP. Because the water droplet did not stick to the substrate, no water contact angle could be measured. (B) Water droplet condensation on CNTH observed by using E-SEM. Droplets coalesce and become bigger with time but do not spread on the surface. The time labels in the upper left corner of the images represent elapsed time after reaching 100% saturation pressure. Average water contact angle was 163° with a standard deviation of 6° .

The graphitic nature, defects, and CNT structure of CNTH membranes were investigated by using Raman spectroscopy and transmission electron microscopy (TEM). Figure 3A illustrates the Raman spectra obtained from CNTH membranes prepared at 600°C (CNTH-600) and 750°C (CNTH-750). The distinct peak at $\sim 1600\text{ cm}^{-1}$ (G band) indicates that the form of carbon deposited on the membranes is predominantly graphitic carbon [60]. The distinct shape of this peak also indicates minimal oxidation of the CNT [61]. Figure 3A reveals another peak around 1300 cm^{-1} (D band). This band originates from a hybridized vibrational mode that is usually associated with graphene edges, and it reveals the presence of defects on the graphene structure. This defect can lead to the incorporation of functional groups at those sites. Functional group analysis on the surface of CNTH-750 materials was performed by X-ray photoelectron spectroscopy (XPS) and is discussed later in this section. A significant 2D or G' peak (band at 2700 cm^{-1}) was observed only when the growth took place at 750°C . The intensity ratio between D and G (I_D/I_G) and 2D and G (I_{2D}/I_G) can indicate the density of functional groups on the surface [62]. The intensity ratios for our samples indicate the samples are not oxidized significantly (as in the case of HNO_3 oxidation of CNT), but they are also not free of surface functional groups (as with samples annealed to 2500°C) [62].

Figure 3B shows the TEM image of CNT from CNTH-750, in which a multiwalled CNT can be observed that has a structure similar to a commercial CNT, with a hollow inner core and

multiwalled outer shell (Figure S12). The diameter of the CNT from CNTH-750 is between 25 and 50 nm, based on the analysis of several data points (Figure S12), and the outside wall of the CNT in the CNTH-750 sample appears to be smooth and free of amorphous carbon deposition (Figures 3B and S12).

Figure 3. (A) Raman spectra of CNTH membranes prepared at different temperatures. (B) TEM image of CNT from CNTH prepared at 750 °C.

To further characterize the developed CNTH-750 membrane, BP was also characterized as a baseline carbon nanotube membrane material for comparison. Thermogravimetric analysis and surface area measurements were used to compare the properties of our developed CNTH-750 membrane with the commercial CNT sample used to produce the BP material. The thermogravimetric analysis data of CNTH-750 were similar to those for the commercial CNT and showed that the sample was stable in air up to 500° C (Figure 4A). Brauner–Emmett–Teller surface area results, estimated from nitrogen isotherms at 77 K, for the tested CNT and CNTH-750 materials were similar (98.9 m²/g for the CNT vs. 101.6 m²/g for CNTH-750; Figure 4B).

Thus, the surface area analysis also showed similarity between the commercial CNT and the CNT grown on the CNTH-750.

The as-received HAST mesh was also tested by thermogravimetric analysis to examine possible changes during oxidation pretreatment of the substrate in the membrane synthesis process. Results indicate a slight weight increase of the HAST substrate resulting from minor surface oxidation. Oxidized metals during the oxidation pretreatment stage were reduced in the next reduction pretreatment stage to provide active sites for growth of CNT on the CNTH membrane.

Figure 4. (A) Thermogravimetric analysis of commercial CNT (weight change shown on the left axis), and CNTH-750 and as-received HAST substrate (weight change shown on the right axis). (B) Nitrogen isotherms at 77 K used for the Brauner–Emmett–Teller surface area analysis. STP stands for standard temperature and pressure (CNTH-750 adsorption data are based on the weight of grown CNT on the CNTH-750 membrane).

Surface functionalities associated with the CNTH-750 surface were further investigated by XPS to shed more light on their contribution to surface wettability (Figure 5). According to the XPS scan of the CNTH-750, the amount of surface oxygen is only 1.28%, and the other element detected by XPS is carbon. This result appears quite similar to the XPS spectra of pristine

multiwall CNT reported in the literature [63]. The surface concentration of oxidized hydrophilic CNT can be as high as 15% to 20% [64]. Therefore, the detected oxygen content of the CNTH-750 sample (i.e., 1.28%) was low and was not expected to contribute substantially to surface hydrophilicity. Curve fitting of the C 1s high-resolution spectrum (Figure 5) revealed the presence of hydrophobic CH groups that might contribute to the overall hydrophobicity of the material. Therefore, in addition to the unique topographic structure, and the presence of CH-containing groups may contribute to its superhydrophobic behavior of the CNTH-750 membrane [53].

Figure 5. XPS spectra of the CNTH-750 membrane: (A) survey scan, and (B) high-resolution spectrum with curve fitting.

Interfacial bonding and resistance to harsh environments for the CNTH-750 membrane were investigated to show its robustness for practical applications (Figure 6). The ASTM adhesion test [55] was used to test both the CNTH-750 membrane and, as a reference, BP (Figure 6A). When adhesive tape was peeled from the CNTH-750 membrane surface, a uniform layer was removed. However, after this layer was peeled away, the CNTH-750 membrane was still covered with a

black film (i.e., CNT) and no bare metal substrate was observed. In contrast, for BP, the sample was torn apart because of delamination of the CNT network. The CNTH-750 membrane also showed resistance to ultrasonication for 40 s at a frequency of 20 KHz and an input energy of 240 W/L in isopropyl alcohol (Figure 6A). The BP sample disintegrated when sonicated under the same conditions, whereas the CNTH-750 sample remained intact, with a small amount of CNT released in the isopropyl alcohol solvent (Figure 6A). For the developed CNTH-750 membrane, both the adhesive and sonication tests demonstrated the superior interfacial bonding of CNT with the substrate, stronger entanglement of the grown CNT network, or both. Furthermore, after the membrane distillation tests and upon opening the membrane holder, the BP membrane was torn apart, whereas the CNTH-750 membrane remained intact (Figure S13).

Figure 6B shows the corrosion resistance of CNTH-750 samples after exposure to concentrated (37%) HCl for 30 min and high-salinity water (a 70,000 mg/L NaCl solution) for 24 h. After 1 day, CNTH-750 did not show any signs of corrosion, whereas CNTSS-750 corroded even with exposure to deionized water. Therefore, CNTH-750 showed excellent resistance to harsh media, which is important for challenging applications in water desalination, heat transfer, water harvesting [65], and other separation applications [66].

Finally, we demonstrated one of the potential applications of the developed CNTH-750 membrane by performing water desalination experiments by DCMD. Selected polymeric (TF-200, a Teflon material) and carbon (BP) membranes that have been used by other researchers for the DCMD [15,35] were also tested for comparison. More information about DCMD is provided in the Supporting Information. A schematic diagram of the DCMD setup is shown in Figure S14. Membranes were characterized by the ASTM standard bubble point test [54] to qualitatively evaluate and compare their pore openings. The CNTH-750 membrane had the smallest bubble

point pressure (12.5 ± 0.15 psi), followed by BP (14.23 ± 0.15 psi) and TF-200 (16.43 ± 0.15 psi), indicating an order of CNTH-750 > BP > TF-200 in the largest pore size openings.

Figure 6. (A) Comparison between CNTH-750 and BP of interfacial bonding by the adhesion and ultrasonication tests. CNTH-750 shows superior interfacial bonding compared with BP. (B) Comparison of corrosion resistance between CNTH-750 after exposure to concentrated HCl (37%) for 30 min and concentrated NaCl solution (70,000 mg/L) for 24 h, and CNTSS-750 after exposure to deionized water for 2 days. CNTH-750 is resistant to the concentrated acid and salt solution, whereas CNTSS-750 corrodes when exposed to deionized water.

The performance of the developed CNTH-750 membrane for desalination of a 10,000 mg/L NaCl solution by DCMD was evaluated and compared with the performance of TF-200 and BP membranes under the same conditions (Figure 7). All tested membranes exhibited more than 95% salt rejection during testing for a short duration (Figure 7A). Salt rejection of BP and CNTH-750 declined to ~89% and ~82%, respectively, after 2 h operation. However, salt

rejection performance of both CNT-based membranes (BP and CNTH-750) declined significantly (~65% for BP and ~75% for CNTH-750) during 5 h test (Figure 7A). The decline in salt rejection might be from **changes in the membrane wetting due to longer term operation**.

The TF-200 membrane showed consistently higher performance compared with the CNTH-750 and BP membranes during the first test (Figure 7B). Nevertheless, additional tests of the used TF-200 membrane resulted in a reduction of the water vapor flux, whereas performance of the CNTH-750 and BP membranes remained the same. These tests highlight the sensitivity of the TF-200 polymeric membrane to the elevated temperature and temperature variation (cooling and heating cycles during multiple runs), compared with the more stable performance of both tested carbon nanotube membranes. The flux performances of all three membranes during 5 h test were compared in Figure 7C. BP and TF-200 show consistent flux between 20-30 Kg/m².h. On the contrary, CNTH-750 flux declines with time reaching a consistent value of ~10 Kg/m².h after 2 h. Although CNTH-750 performs well during short term multicycle test, flux becomes less than 10 Kg/m².h when the test duration is longer than an hour (Figures 7B and 7C). More investigation is required to find the change in CNTH-750 pore structure or wettability during long term tests, which may be responsible for this decline.

The three tested membranes had different thicknesses. A cross-sectional SEM image of fabricated CNTH-750 and estimation of CNT-bundle thickness from SEM image are presented in Figure S15 and Figure S16 respectively. From commercial membrane specifications and measurements of CNTH-750, BP and CNTH-750 membranes were 0.6 and 1.5 times thicker than TF-200 (i.e., ratio of the thickness of BP (70 μm) or CNTH-750 (163 μm) to the thickness of TF-200 (110 μm), respectively). Therefore, mass transfer resistance of CNTH-750 is ~1.5 times higher than TF-200. However, the heat transfer resistance of MWCNT BP is three times smaller

than Teflon [67,68]. Water flux is mainly a function of combined heat and mass transfer phenomena across the membrane that may depend on material characteristics and operation specifications and conditions. More investigation is needed to further understand and explain the DCMD results.

Unlike polymeric membranes, BP and the developed CNTH-750 membrane showed consistent performance during two testing cycles (Figure 7B) and could tolerate higher temperature conditions. The CNT membranes appear to be promising materials for application in high-temperature membrane distillation, leading to a significant enhancement of water flux. Singh and Sirkar [69] have shown that the permeate flux of a DCMD system can be tripled if the feed temperature is increased from the conventional membrane distillation temperature of 70 °C to 130 °C. High-temperature DCMD might be also considered to recover and purify high-boiling point solvents.

The developed CNTH-750 membrane is expected to have the antifouling and antibacterial [30,32,70] characteristics of CNT materials while having the unique properties of mechanical robustness and flexibility. An important property of the CNTH-750 membranes is their high interfacial bonding to the solid network of support material and their resistance to delamination, as discussed and demonstrated here (Figure 6A).

As previously discussed, CNTH-750 membranes are resistant to air oxidation up to 500 °C and can tolerate a harsh concentrated acid treatment. These unique properties can be used to regenerate membranes that are fouled with organic or inorganic contaminants after extensive use. Organic foulants (e.g., natural organic matter or oil and grease) can easily be burned off by heating the membranes in air, whereas inorganic foulants (e.g., precipitated calcium and magnesium scales) can be washed away by immersing the membranes in an acid bath. This

research may lead to the development of a new generation of regenerable and reusable robust membranes.

Figure 7. Performance of the developed CNTH-750 membrane for water desalination by direct-contact membrane distillation (10,000 mg/L NaCl solution with a feed and permeate temperatures of 80 and 5 °C) in comparison with conventional polymeric (TF-200) and carbon (BP) membranes: (A) salt rejection during separate short term (45 min) and long term (300 min) experiments, (B) water flux during multicycle tests (each 45 min), and (C) water flux during long (300 min) tests.

4. Conclusions

New types of CNT membranes, grown on various substrates, have been prepared by using a systematic approach. Robust CNT membranes have been developed with a CVD method by direct growth of CNT on a Hastelloy-C alloy with micrometer-sized openings. The CNT membranes grown on HAST at 750 °C (CNTH-750) by CVD using a gas mixture of C_2H_2 , C_6H_6 , H_2 , H_2O , and Ar, after an initial oxidation-reduction pretreatment, have the most desirable properties among all the prepared membranes. The developed CNTH-750 membranes have pore openings of 50 to 500 nm and are superhydrophobic, flexible, resistant to air oxidation up to 500 °C, and resistant to concentrated acid and salt solutions. The developed CNTH-750 membranes show a good resistance to delamination and have demonstrated a high interfacial bonding of the

grown CNT with the alloy substrate, as confirmed by adhesion and ultrasonication tests. Tests of water desalination by membrane distillation reveal that CNTH-750 has a high (>95%) salt rejection performance during short term testing and ~75% salt rejection after 5 h test. CNTH-750 shows consistent flux during multicycle tests and 10 Kg/m².h flux during 5 h test. These robust carbon nanotube membranes are reusable and are expected to be less susceptible to fouling because of their superhydrophobic properties. Furthermore, if fouled by organic or inorganic species, they can potentially be regenerated by heating in air or washing in acid. The developed CNT membranes may have other uses in various separation, heat transfer, energy harvesting, and sensing applications. They demonstrate great promise for separation applications, particularly under high-temperature conditions and in corrosive environments.

Supporting Information and Supporting Videos

More detailed information about the preparation and characterization of materials is provided in the Supporting Information and Supporting Videos (AVI).

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Graphical Abstract