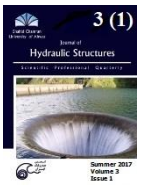
Journal of Hydraulic Structures
***J. Hydraul. Struct.*, 2017; 3(1):1-13**
DOI: 10.22055/jhs.2017.13280



An Overview of Fabrication Methods and Applications of Carbon Nanotube Membrane in Environmental Engineering as Hydraulic Microstructures

Amir Abedin Maghanaki[1]

Abstract

The main purpose of this article is to study fabrication methods and applications of aligned carbon nanotube (CNT) membranes as a hydraulic microstructure in treatment processes. This paper emphasizes the use of CNTs as membrane in separation processes like water and wastewater treatment because of their exclusive advantages. Their most important characteristics are high mechanical strength against pressure, thermal stability and fast fluid transport with a very low pressure gradient inside CNTs. It is predictable to expand using CNT membranes in separation processes and environmental engineering because of their suitable mechanical properties.

Keywords: Membrane, Carbon Nanotubes, Treatment Processes, Environmental Engineering, Hydraulic Microstructures

Received: 03 March 2017; Accept: 14 June 2017

1. Introduction

Membrane technology is used for the separation of various compounds by thin film layer with controlled pore size. The discovery of membranes properties goes back many years. The Osmosis phenomenon was recognized for the first time, by Nollet in 1748 and first synthetic membrane -apparently from Nitrocellulose- Constructed and completed by Fick in 1855 [1-3]. Simultaneously with the discovery of cellulosic membranes, the natural membranes were used in the filtration experiments. In the last decades of the 19th century researchers who studied on the diffusion phenomenon, using from the membranes of animals (bladder of pig and fish, skin of frog and bovine's heart) and plant origin (onion) for dialysis experiments and studies of ultrafiltration [4-8].

Inorganic membranes were developed before 1945. The earlier application of porous inorganic membranes was used for the separation of uranium isotopes; therefore, they were

[1] Department of Civil Engineering, Faculty of Engineering, Islamic Azad University, Roudehen Branch, Tehran, Iran, Phone: +98.912.305.8178, amir.abedin@gmail.com (**Corresponding author**)

mainly used for military purposes or nuclear applications [9, 10]. Non-nuclear applications of inorganic membranes started at the beginning of 1980 [10, 11]. The potential of inorganic membranes was not widely recognized until high quality porous ceramic membranes were produced for industrial usage on a large scale [10, 12]. Nowadays these membranes are widely used in water treatment, dairy industries and gas separation [13-15].

After the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [16], great attraction and scientific interest subsequently followed due to their special physical properties [17-20]. There are different methods for the synthesis of CNTs, such as: laser-ablation, arc discharge and chemical vapor deposition (CVD) [10, 21-23]. CVD is preferred over other methods, because it produces higher quality CNTs [24, 25]. Currently the most useful method is CVD and its changed techniques (such as floating catalyst CVD (FCCVD), plasma enhanced CVD (PECVD), water-assisted CVD) [26-30]. This method is based on the thermal decomposition of carbon sources (carbon feedstock) in the presence of catalyst on a suitable substrate. The ultimate goal of CNT research is driven by the ability to design functional macroscopic structures that can fully integrate the single nanotube properties [31].

2. Membrane Fabrication from CNTs

There are two methods for the preparation membrane from CNTs.

In the first method; CNTs are deposited regularly together -without adhesive materials- on ceramic or metal or any suitable substrate and called self-assembly membranes. In another method, the space between the nanotubes is filled by regularly arranged polymeric materials, as a cohesive.

For the first time, Ajayan et al. (1994) were used the "Aligned Carbon Nanotube" phrase in their article [32]. They formed the aligned carbon nanotube array by cutting a polymer resin-nanotube composite. This composite had been built as strong material and had not applied as membrane. This work represents an important step, but the rather low tube density, incomplete alignment, and the presence of the resin matrix importantly affect the properties as compared with a pure, aligned material [33].

After them, de Heer et al. (1995) reported the production of macroscopic aligned multiwalled carbon nanotube (MWCNT) films, using the arc evaporation process [33]. They studied its optical and electronic properties and diagnosed them unsuitable for flow-through applications.

Until 1999 there was no imagination for growth mechanism of carbon nanotubes; Sinnott et al. (1999) presented several theories for growth mechanism of carbon nanotubes [35]. One theory was based on the assumption that the metal catalyst particles are floating or fixed on the graphite or other substrate. It is likely that the form of catalyst particles will appear spherical or pear-shaped and deposition will only occur on half of the surface (due to the fact that the pear-shaped particles are done in lower curvature).

One theory postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped, in which case the deposition will take place on only one half of the surface (this is the lower curvature side for the pear shaped particles). The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by "extrusion" or "root-growth" in which the nanotube grows upwards from the metal particles that remain attached to the substrate, or the particles detach and move at the head of the growing nanotube, labeled "tip-growth". These mechanisms are illustrated graphically in Fig. 1 [35-37].

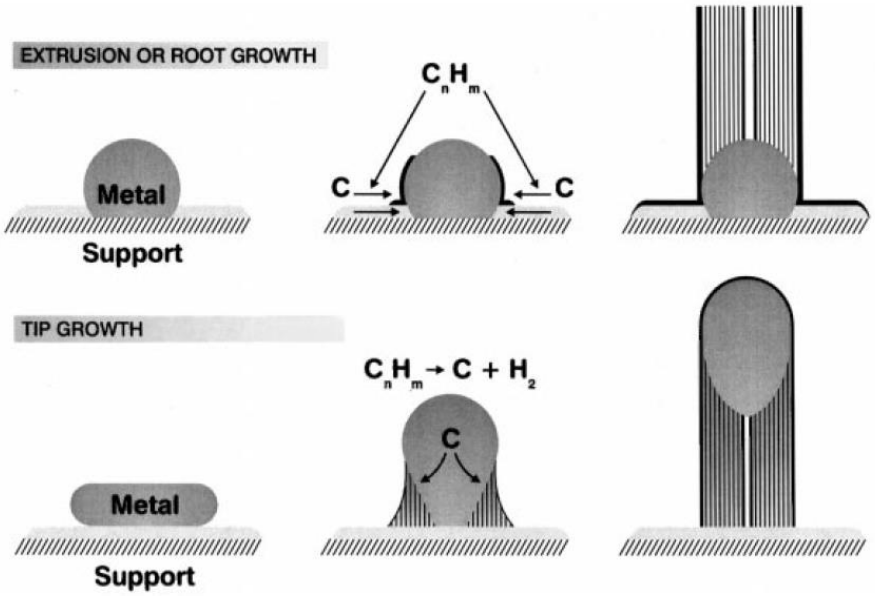


Figure 1. Schematics of root-growth and tip-growth mechanisms for carbon filament growth (Sinnott et al., 1999).

Chengwei et al. (2000) at Lanzhou University of China prepared a well-aligned CNT array membrane on a porous alumina template by CVD [34]. They fed acetylene (as a carbon source) in the presence of an iron catalyst with hydrogen used at temperature 700°C. They stated that the growth property of CNTs was closely related to the structure of the template, particle size of catalyst, process temperature, flow ratio and deposition time.

Then, Casavant and colleagues reported that they have produced the first macroscopic membranes of magnetically aligned single-wall carbon nanotubes (SWNT) in a magnetic field in 2001 and 2003 [38-39]. These membranes were prepared by producing a suspension of SWNT segments, introducing the suspension membrane of SWNT. They exhibited natural cleavage planes parallel to the magnetic field. However, the microstructure specification of the membrane was not presented to determine that the passing flow takes place within the CNTs or from the space between them.

Shimoda et al. (2000) reported that they have produced the self-assembly carbon nanotube membrane in macroscopic scale [40]. They synthesized SWNTs by laser ablation method. The SWNT bundle and individual nanotube diameters were reported in the range of 10–50 and 1.3–1.5 nm, respectively. SWNTs purified by reflux and filtration were chemically etched to short bundles by ultrasonic-assisted oxidation. After removing the acid by filtration, the processed SWNTs were dispersed in de-ionized water. Thin film appeared on the surface of a soaked glass substrate in the SWNTs/water dispersion with natural vaporization of water. The fabricated membrane had a smooth surface and Transmission electron microscopy (TEM) measurements showed that the SWNT bundles were uniaxially aligned. Since the physical properties of the membrane (such as mechanical specification, thermal stability and flow rate) were not offered, we cannot comment on it properly.

Then, Hinds et al. (2003) succeeded in producing a multi-wall carbon nanotubes (MWNT) membrane [41]. An array of aligned carbon nanotubes was incorporated across a polymer film to

form a well-ordered nanoporous membrane structure (Figure 2). Although the outer diameter of MWNTs had significant variation (20-40 nm), the hollow inner core diameter was well controlled at 2-6.6 nm. This inner core diameter is in the size range of many proteins and other important biological macromolecules. They announced that the idealized membrane structure would occur if the space between the CNTs was filled with a continuous polymer film, and the normally closed ends of CNTs were etched open. To accomplish this, the as-deposited CNTs were grown for 30 min (aligned CNT film thickness of 5–10 μm) on quartz substrate in a chemical vapor deposition process using a ferrocene/xylene/Ar/H_2 feed at 700°C. At a high temperature, ferrocene decomposes to iron particles which then act as a catalyst for the nanotube growth while the xylene acts as carbon feedstock [42]. Moreover, they used a 50wt% solution of polystyrene (PS) and toluene to spin coating over the surface. Then, the film was dried in vacuum at 70°C for four days. Hydrofluoric acid was then used to remove the CNT/PS composite from the quartz substrate to produce a free-standing composite film of 5–10 μm thickness. H_2O plasma-enhanced oxidation process was used to remove a thin layer of excess polymer from the top surface and open the CNT tips to form a membrane structure. Scanning electron microscopy (SEM) analysis of this surface has given an estimated areal density of 6 (±3) × 10^{10} CNT-tips/cm^2. TEM of dissolved membranes demonstrated that about 70% of the CNT tips had been opened by the plasma oxidation process under our conditions. The mean pore diameter of 7.5 (±2.5) nm has been calculated using the observed estimate of CNT areal density.

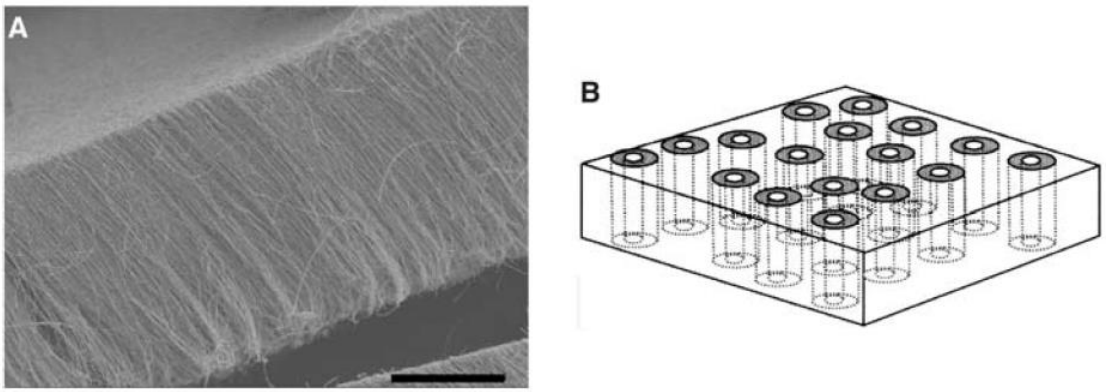


Figure 2. (A) As grown dense multiwalled CNT array from Fe-catalyzed chemical vapor deposition process (Scale bar 50 μm). (B) Schematic of target membrane structure, with a polymer impregnation between CNTs (Hinds et al., 2003).

Srivastava et al. (2004) developed the production of filters using carbon nanotubes [43]. They used continues spray pyrolysis method for growing aligned MWNTs on a quartz tube using ferrocene/benzene solution at 900°C (Figure 3).

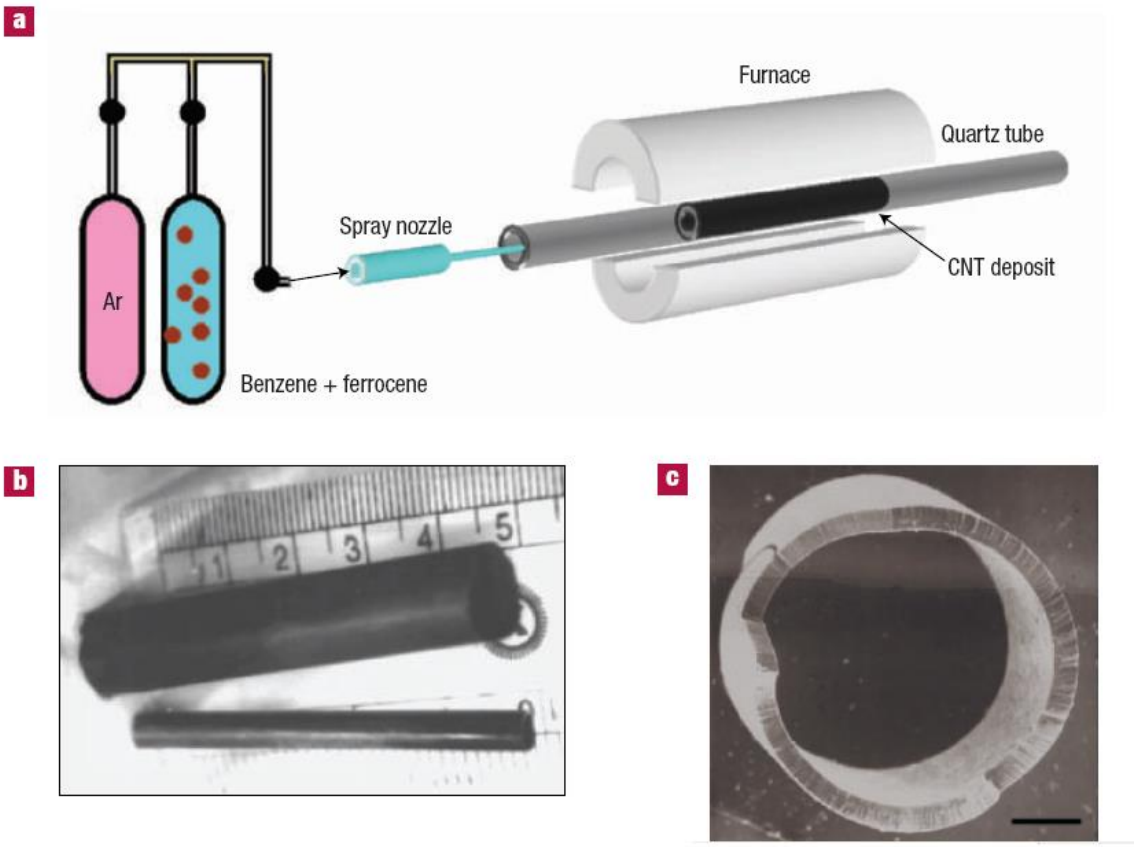


Figure 3 – Production of the macro architecture of aligned nanotubes for use in filtration applications. (a) Schematic of the spray pyrolysis set for growing aligned MWNTs. (b) Photograph of the bulk tube. (c) SEM image of the aligned tubes with radial symmetry resulting in hollow cylindrical structure (scale bar 1 mm) (Srivastava et al., 2004).

This method can be used for fabricating such nanofilters comprising an array of carbon nanotubes (CNTs) containing nanopores between the nanotubes on the surface. This method includes: (a) providing a carbon source gas and a catalyst gas through a nozzle onto a heated surface; (b) forming a carbon nanotube filter; and (c) removing the carbon nanotube filter from the surface. A strong advantage of this method is that CNT bundles are produced in one step, without any prior substrate preparation [43-44].

The range of inner and outer diameters of these nanotubes has been estimated to be ~10–12 nm and ~20–40 nm, respectively from TEM analysis. The value for the tensile strength of filter measured ~2.2 MPa and the Young's modulus obtained from the true stress versus the true strain curves was ~50 MPa. They expressed that this filter is able to eliminate nanoscale pollutants from water and multiple components of heavy hydrocarbons from crude oil, effectively. These filters have very suitable accuracy in different applications, for example they could remove bacterial contaminants such as nanoscale poliovirus and larger pathogens such as Escherichia coli (E. coli) and Staphylococcus bacteria from water. The filtration process itself was driven by gravity as no additional pressure was applied. As many of the nanotube's internal spaces possibly have plugs of metal particles, they believe that most of the filtering occurs in the

interstitial spaces. Holt et al. (2004, 2006) reported synthesis of free-standing and silicon-chip supported vertically aligned CNT membranes by CVD method [45-46]. They entered ethylene/argon/hydrogen feed solution in reaction zone while the temperature is ramped up to the growth temperature of 850°C. Nanotube growth occurs typically for 20 minutes and results in a dense array of multiwalled nanotubes of ~5 μm length and 20-50 nm diameter.

Gu et al. (2006) performed direct tensile tests of double walled carbon nanotube (DWCNT) membranes with thickness of 40–80 nm using a micro-stress-strain puller [47]. The tensile strength and Young's modulus were measured 480–840 MPa and 4.4–8.8 GPa, respectively. It should be mentioned that they used an aluminum foil substrate to prepare the samples used for the tensile test. 12 samples broke between the platforms, and there was no slippage or extension between the membrane and the foil which was selected from more than 30 measured samples. Since the membrane was so thin, they could estimate the free volume only by its plane density which is assumed to be 75% by SEM images. So the percentage of effective cross-sectional area was determined 25%. Therefore, the real tensile strength and Young's modulus was increased four times.

Mi et al. (2007) prepared the CNT layer consisting of fairly straight carbon nanotubes of 6.3 nm in pore diameter running parallel to each other [48]. They used the α-Al_2O_3 disks substrate on one surface, which was polished with sandpaper and cleaned in an ultrasonic acetone bath for 30 min, in CVD method. About 0.1 g of ferrocene vapor was decomposed (at 800°C) and iron nanoparticles were formed and deposited on the surface of the alumina substrate. Mixture of acetylene and nitrogen in 1:10 ratio was later introduced to the CVD reactor at a flow rate of 10 cm^3/min for about 10 min. Then the inter-tube gaps of the CNT array on the alumina support were filled with a 30 wt% solution of polystyrene (PS) in toluene by spin-coating. After coating, the CNT membrane was dried at 60°C for 3 days. The surface of the coated CNT appeared white, indicating that the black CNT was completely covered by the white PS over-layer.

Unlike Hinds et al., these researchers used a simple mechanical polishing method (with soft sand) to remove PS over-layer and to open the closed tips of CNTs. The sanding process continued until black CNTs appeared on the surface. The composite membrane complete removal of encapsulated catalyst particles on the bottom of CNT tips. From SEM micrograph, CNT membranes areal density on the porous alumina was estimated about 1.87×10^9 CNT/cm^2, lower than the CNT membranes on dense silicon and quartz support which is reported in the literature. They show that the gas permeance through the porous alumina-supported CNT membranes is inversely proportional to the squared root of the gas molecules suggesting a Knudsen diffusion mechanism because of minimum mass transfer resistance of CNTs.

Mostafavi et al. (2008) to complete the researches of Hinds and Srivastava, used hexane feed instead of toxic gases -hexane is more environmentally benign than benzene and xylene- and prepared a nanostructure filter to remove viruses from water [44]. Their work's results showed that at pressures of 8-11 bar, the MS2 viruses were removed with a high efficiency by using the fabricated nanofilter. Janowska et al. (2008) was synthesized an aligned carbon nanotube carpet by catalytic chemical vapor deposition (CCVD) process at 800°C with a mixture of ferrocene and toluene, using a removable quartz substrate as macroscopic pre-form and self-supported aligned nanotubes could be obtained (Figure 4) [31]. The aligned nanotube array was efficiently used as removable precursor template in the design of ceramic nanoporous membranes with a mean diameter in the 40–60 nm range. The ferrocene concentration in the toluene solution was 20 g/l which was carried out into the reaction zone by a 1.5 l/min argon flow. The thickness of the carbon nanotube pattern could be accurately controlled by adjusting the synthesis duration, i.e. 1200 μm thickness for 2 h of synthesis and 250 μm for 0.5 h of synthesis.

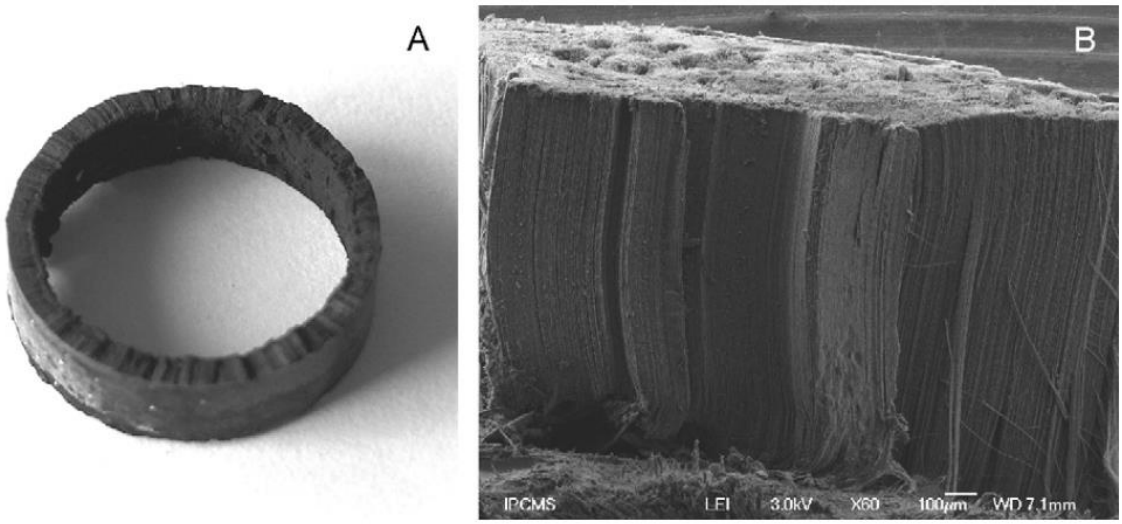


Figure 4. Macrostructures of self-supported aligned carbon nanotubes obtained after dissolving the quartz growth substrate in a HF solution: (A) ring and (B) plate (Janowska et al., 2008)

The CNT array was relatively dense with a spacing of about 100 nm between neighboring CNTs. Since careful SEM observation of the top of the CNT forest didn't show any iron particles attached at the tube tip, it seems the growth mechanism of CNTs has been root-growth in which the iron catalyst remained attached to the substrate surface and the nanotubes were slowly lift-off with aligned morphology.

They treated the aligned CNT carpet in an acidic solution, HNO_3 30 vol.%, at 80°C for overnight in order to remove from the sample the remaining iron-based catalyst. The sample was washed several times with distilled water until the pH reached a neutral value. Scholars believe that wetting and drying processes would induce the tube gathering by the van der Waals forces and would lead to high mechanical strength of structure. According to their statements this membrane can be used for filtration of fine particulate matter such as viruses from water or in airborne conditions.

Prehn et al. (2008) developed catalytically active CNT-polymer-membrane assemblies [42]. The process included the nanotube synthesis, sputter deposition of platinum as a catalyst and the membrane casting. They inserted ferrocene as a catalyst and toluene as carbon source in the process to form iron containing CNTs on a silicon substrate. In the CVD process toluene was used as the solvent and carbon source to which 2 or 8 wt% ferrocene was added. These ferrocene–toluene solutions were inserted into the preheated zone (200°C) of a two-stage oven via a syringe pump. Both materials typically vaporise under these conditions (given vaporization temperatures of 175°C for ferrocene and 110°C for toluene). A mixture of argon and 10 vol.% hydrogen was used as carrier gas with a total flow rate of 750 ml/min while the injection rate of ferrocene–toluene was set to 5 ml/h. Final temperature of the reaction zone reached 760°C. In the first step a polystyrene (PS) foil was hot pressed on the CNT tips that previously were covered with platinum. Specification of CNTs was different based on toluene wt% and synthesis time (Table 1). After producing the CNTs, they were strengthened with polystyrene and platinum. It was the first report of producing a catalytically active CNT membrane.

Table 1. Comparison of CNTs Specification based on toluene wt% and synthesis time

toluene wt%	synthesis time (min)	Mean Length of CNTs (nm)	Mean Diameter of CNTs (nm)
8	60	300	65
2	60	150	45
2	45	65	30

Yu et al. (2008) prepared high-density, vertically aligned carbon nanotube (VA-CNT) membranes [49]. Vertically aligned CNT forests were grown by water-assisted CVD synthesis at 750°C and reached approximately 2 mm in length in 120 min. Then, the free-standing arrays were soaked in n-hexane solvent, and the layers were dried at room temperature. After shrinkage by n-hexane evaporation, the interstitial pores reduced to an average size from 28 nm to 6 nm. As indicated in Figure 5, the as-grown VA-CNT forest shrank to approximately 5% of its original area after n-hexane evaporation and became dense. Also the CNTs were still aligned and no cracks were seen. Their dense membranes had two advantages: their CNT density was 8 to 270 times more than previous CNT membranes, and they did not need any polymeric binder.

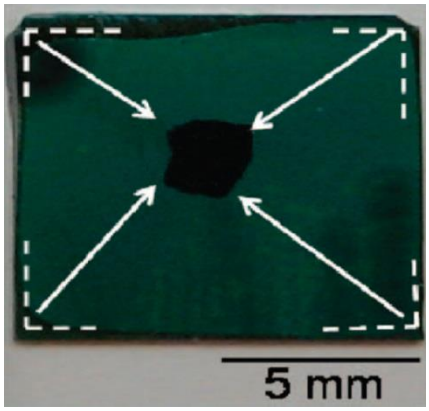


Figure 5. Photograph of a dense CNT membrane after n-hexane evaporation, white dotted lines indicate the original size of as-grown CNT forest (Yu et al., 2009)

Mirbagheri et al. (2012) report an efficient process to grow well-aligned carbon nanotube (CNT) arrays with a good area distribution density [30]. Vertically aligned carbon nanotubes (VA-CNTs) have been produced by controlling flow rate, temperature and catalyst nanoparticles using a floating catalyst CVD technique. They were synthesized on quartz substrates at 800°C from toluene as a carbon source. The Samples were characterized by SEM and TEM, and their surface area and pore size were determined by nitrogen adsorption analysis. The synthesized CNTs have a length of 500 μm and diameters ranging 120±40 nm. As the CNT filaments form a strength structure and exhibit a good vertical alignment, they propose CNT Membranes for separation applications, especially for water and wastewater treatment as hydraulic microstructures.

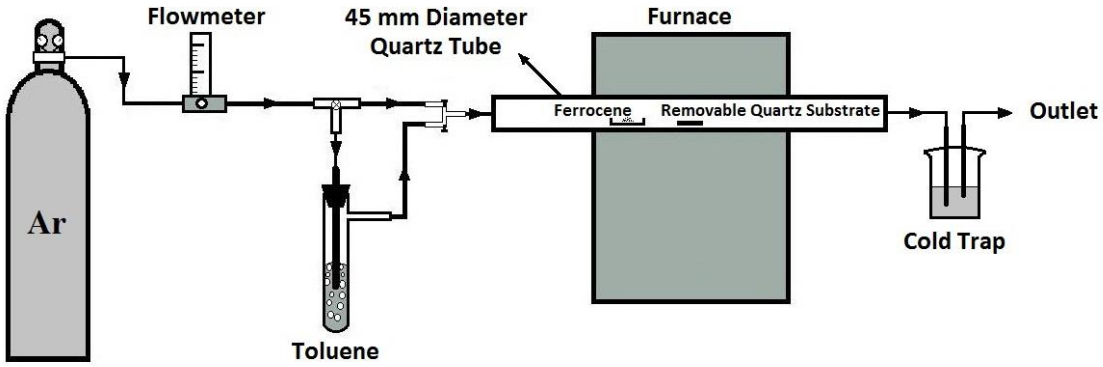
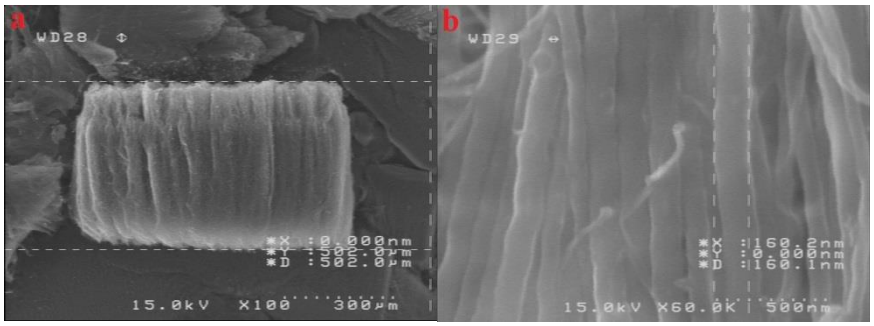


Figure 6. Schematic diagram of FC-CVD method for growing VA-CNTs (Mirbagheri et al., 2012)



mi

Figure 7. SEM image shows align microstructure of samples and (a) length and (b) formation of VA-CNTs (Mirbagheri et al., 2012)

3. Advantages and disadvantages of CNT membranes

CNT is one of the strongest and stiffest materials discovered yet, because of its tensile strength and elastic modulus (Young's modulus). This strength results from the covalent sp^2 bonds formed between the individual carbon atoms [50]. This bonding structure, which is stronger than the sp^3 bonds found in diamonds, provides the molecules with their unique strength. Young's modulus along the CNT's axial direction is enormous [51]. CNTs have remarkable flexibility due to their high length [52]. As a result, they are very suitable for use in compounds that need heterogeneous properties.

In 2000, the tensile strength of a MWNT was measured about 63 GPa [53]. In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. Also, an individual tube has an elastic modulus of about 1 TPa [54]. Since CNTs have a low density for a solid of 1.3-1.4 g/cm^3, its specific strength of up to 48000 kN·m/kg is the best of known materials, compared to steel's 254 kN·m/kg [27, 55-566].

CNT chemical reactivity is directly related to the pi-orbital mismatch caused by an increased curvature [36]. This is why these materials are more resistant to chemical reactions than polymeric materials in hydraulic microstructures (membranes) [3657].

Using CNTs in the membranes caused high speed fluid transport [31, 41, 46], easy cleaning [42, 44], increased mechanical strength, reusability and thermal resistance (about 400°C) [43, 57]. Although the mineral membranes are expensive in comparison to organic membranes, some benefits such as mechanical and thermal strength, align and strong structure of pores and the

chemical resistance still keep them competitive with each other. Since the researchers in recent years are brought to build laboratory membranes, certainly solving the problems and completing their researches will appropriate the industrialization method of fabricating these membranes as hydraulic microstructures.

4. Summary and conclusion

Although membrane technology is used in different industrial parts, due to the prosperous future ahead, extensive research is still being carried out. Regarding CNT membranes, most researchers' attention will be focused on the composition and regularly structure of nanotubes and various compounds will be tested to achieve the best separation properties with long-term and improved resistance in future. Table 2 shows the summary of the information on CNT membranes taken from the literature.

Table 2. Summary of CNT membranes information fabricated by pervious researchers

Group, Year	Carbon Source	Catalytic Source	Substrate	Carrier Gases			Reaction Temperature (°C)	Reaction Time (min)	Mean Diameter of CNTs (nm)	Mentioned Application
				Hydrogen	Argon	Nitrogen				
Chengwei, 2000 [34]	Acetylene	Iron	Alumina	Yes	No	No	700	120-360	60-72	Gas Separation
Hinds, 2003 [41]	Xylene	Ferrocene	Quartz	Yes	Yes	No	700	30	2-6.6	Separation Processes
Srivastava, 2004 [43]	Benzene	Ferrocene	Quartz	No	Yes	No	900	-	10-12	Heavy Hydrocarbons Separation from Crude Oil/ Virus Removal from Water
Holt, 2006 [46]	Ethylene	Iron	Silicone	Yes	Yes	No	850	20	20-50	Separation Processes
Mi, 2007 [48]	Acetylene	Ferrocene	Alumina	No	No	Yes	800	10	6.5	Gas Separation
Mostafavi, 2008 [44]	Hexane	Ferrocene	Quartz	Yes	No	No	900	95	30	Virus Removal from Water
Janowska, 2008 [31]	Toluene	Ferrocene	Quartz	No	Yes	No	800	30-120	40-60	Virus Removal from Water
Prehn, 2008 [42]	Toluene	Ferrocene	Silicone	Yes	Yes	No	760	45-60	30-65	Separation Processes
Mirbagheri, 2012 [30]	Toluene	Ferrocene	Quartz	No	Yes	No	800	60	80-160	Water and Wastewater Treatment

Considering the unique properties of carbon nanotubes, such as high flow rate, easy cleaning, excellent strength, chemical and thermal stability, they could be used as membranes in

separation processes of chemical industries and treatment of nano-scale suspended pollutants of water in environmental engineering.

5. References

1. Van Rijn, C.J.M., "Nano & Micro Engineered Membrane Technology: Vol. 10 (Membrane Science and Technology)", 2004, Elsevier, Netherlands
2. Hubbard, T., "Encyclopedia of Surface & Colloid Science", Vol. 3, 2002
3. Mulder, M., "Basic principles of membrane technology", 1996, kluwer academic publisher, Netherlands
4. Wenten, I.G., "Recent Development in Membrane Science & its Industrial Applications", Songklanakarin Journal Science & Technology, Vol. 24, 2002, Malaysia
5. Baker, R.W., "Membrane Technology & Applications", 2nd Ed., 2004, John Wiley & Sons
6. Strathmann, H., Giorno, L., Drioli, E., "An Introduction to Membrane Science & Technology", Institute on Membrane Technology, 2006, CNR-ITM, Italy
7. Nunes, S.P., and Peinemann, K., "Membrane Technology in the Chemical Industries", 2001, Wiley-VCH
8. Mason, E.A., "from pig bladders and cracked jars to polysulfones: an historical perspective on membrane transport", Journal of Membrane Science, 60, 1991
9. Keizer, K., and Verweij, H., "Progress in inorganic membranes", Chemical Technology, 1996
10. Ismail, A.F., David, L.I.B., "A review on the latest development of carbon membranes for gas separation", Journal of Membrane Science, 193, 2001
11. Soria, R., "Overview on industrial membranes", Catalyst Today, 1995
12. Hsieh, H.P., "Inorganic membranes", Membrane Material Process, 1990
13. Mirbagheri, S.A., Mousavi Rad, S.A., Mohammadi, T., "Treatment of Electroplating Wastewater by Reverse Osmosis Membrane", Proceedings of First International Conference on Advances in Wastewater Treatment and Reuse, 2009, Iran
14. Mousavi Rad, S.A., Mirbagheri, S.A., Mohammadi, T., "Using Reverse Osmosis Membrane for Chromium Removal from Aqueous Solution", Proceedings of World Academy of Science, Engineering and Technology, 57, 2009, Netherlands
15. Kim, S., Jinschek, J.R., Chen, H., Sholl, D.S., Marand, E., "Scalable Fabrication of Carbon Nanotube/Polymer Nanocomposite Membranes for High Flux Gas Transport", Nano Letters, 9, 2007
16. Iijima, S., "Helical microtubules of graphitic carbon", Nature, 354, 1991
17. Ajayan, P.M., "Nanotubes from Carbon", Chemical Reviews, 1999
18. Qian, D., Wagner, G.J., Liu, W.K., Yu, M.F., Ruoff, R.S., "Mechanics of carbon nanotubes", Applied Mechanics Reviews, 55(6), 2002
19. Koohsorkhi, J., Abdi, Y., Mohajerzadeh, S., Hosseinzadegan, H., Komijani, Y., Soleimani, E.A., "Fabrication of self-defined gated field emission devices on silicon substrates using PECVD-grown carbon nano-tubes", Carbon (44), 2006
20. Hosseini, A.A., Taleshi, F., Tajbakhsh, M., Farhang, M., "Synthesis and characterization of sol-gel derived MgO/CNTs nanocomposite", Journal of Chemistry and Chemical Engineering, USA, in press
21. Upadhyayula, V.K.K., Deng, S., Mitchell, M.C., Smith, G.B., "Application of carbon nanotube technology for removal of contaminants in drinking water: A review", Science of the Total Environment, 408, 2009

22. Zhang, W.D., Wen, Y., Liu, S.M., Tjiu, W.C., Xu, G.Q., Gan, L.M., “Synthesis of vertically aligned carbon nanotubes on metal deposited quartz plates”, Carbon, 40, 2002
23. Li, X., Zhu, G., Dordick, J.S., Ajayan, P.M., “Compression-Modulated Tunable-Pore Carbon Nanotube Membrane Filters”, Small, 3, 2007
24. Noy, A., Park, H.G., Fornasiero, F., Holt, J.K., Grigoropoulos, C.P., Bakajin, O., “Nanofluidics in carbon nanotubes”, Nanotoday, 6, 2007
25. Liu, H., Zhang, Y., Arato, D., Li, R., Mérel, P., Sun, X., “Aligned multi-walled carbon nanotubes on different substrates by floating catalyst chemical vapor deposition: Critical effects of buffer layer”, Surface & Coatings Technology, 202, 2008
26. Dai, H., “Nanotube Growth and Characterization”, Topics in Applied Physics, 2001, Springer
27. Miri, S.A.M., "Carbon Nanotubes and Their Fabrication Method", Imam Hossein University Publication, (in Persian), 2006
28. Manafi, S.A., Amin, M.H., Rahimipour, M.R., Salahi, E., Kazemzadeh, A., "Carbon nanotubes synthesized by mechanothermal Method", New Carbon Materials, 24(1), 2009
29. Manafi, S.A., Amin, M.H., Rahimipour, M.R., Salahi, E., Kazemzadeh, A., "High-yield Synthesis of Multiwalled Carbon Nanotube by Mechanothermal Method", Nanoscale Research Letters, 4, 2009
30. Mirbagheri, S.A., Kazemzadeh, A., Maghanaki, A. A., "Macroscopic Synthesis of Vertically Aligned Carbon Nanotubes Using Floating Catalyst Chemical Vapor Deposition Method", Japanese Journal of Applied Physics, 2012
31. Janowska, I., Hajiesmaili, S., Begin, D., Keller, V., Keller, N., Ledoux, M.J., Pham-Huu, C., “Macronized aligned carbon nanotubes for use as catalyst support and ceramic nanoporous membrane template”, Catalysis Today, 2008
32. Ajayan, P.M., Stephan, O., Colliex, C., Trauth, D., “Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin-Nanotube Composite”, Science, 1994
33. de Heer, W.A., Bacsa, W.S., ChAtelain, A., Gerfin, T., Humphrey-Baker, R., Forro, L., Ugarte, D., "Aligned Carbon Nanotube Films: Production and Optical and Electronic Properties", Science, 1995
34. Chengwei, W., Menke, L., Shanlin P., Hulin, L., “Well-aligned carbon nanotube array membrane synthesized in porous alumina template by chemical vapor deposition”, Chinese Science Bulletin, 2000
35. Sinnott, S.B., Andrews, R., Qian, D., Rao, A.M., Mao, Z., Dickey, E.C., Derbyshire, F., "Model of Carbon Nanotube Growth Through Chemical Vapor Deposition", Chemical Physics Letters, 315, 1999
36. Daenen, M., De Fouw, R.D., Hamers, B., Janssen, P.G.A., Schouteden, K., Veld, M.A.J., "The Wondrous World of Carbon Nanotubes", internal report, Eindhoven University of Technology, 2003
37. Hosseini, A.A.,Taleshi, F., “Large diameter MWNTs growth on iron-sprayed catalyst by CCVD method under atmospheric pressure”, Indian Journal of Physics, Springer, 2010
38. Casavant, M. J., Walters, D. A., Schmidt, J. J., Smalley, R. E., “Neat macroscopic membranes of aligned carbon nanotubes”, Journal of Applied Physics, 2003
39. Walters, D.A., Casavant, M.J., Qin, X.C., Huffman, C. B., Smalley, R.E., “In-plane-aligned membranes of carbon nanotubes”, Chemical Physics Letters, 2001
40. Shimoda, H., Fleming, L., Horton, K., Zhou, O., “Formation of macroscopically ordered carbon nanotube membranes by self-assembly”, Physica B, 2002

41. Hinds, B. J., Chopra, N., Rantell, T., Andrews, R., Gavalas, V., Bacha, L. G., "Aligned Multiwalled Carbon Nanotube Membranes", sciencexpress, 2003
42. Prehn, K., Adelung, R., Heinen, M., Nunes, S.P., Schulte, K., "Catalytically active CNT-polymer-membrane assemblies: From synthesis to application", Journal of Membrane Science, 2008
43. Srivastava, A., Srivastava, O. N., Talapatra, S., Vajtai, R., Ajayan, P. M., "Carbon Nanotube Filters", Science: Nature Materials, 2004
44. Mostafavi, S.T., Mehrnia, M.R., Rashidi, A.M., "Preparation of nanofilter from carbon nanotubes for application in virus removal from water", Desalination, 2009
45. Holt, J.K., Park, H.G., Noy, A., Huser, T., Eaglesham, D., Bakajin, O., "Carbon nanotube-based membranes: a platform for studying nanofluidics", 4th IEEE conference on nanotechnology, 2004, Munich, Germany
46. Holt, J.K., Park, H.G., Wang, Y., Stadermann, M., Artyukhin, A.B., Grigoropoulos, C.P., Noy, A., Bakajin, O., "Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes", Science, 2006
47. Gu, Z., Wang, K., Wei, J., Li, C., Jia, Y., Wang, Z., "Tensile properties of ultrathin double-walled carbon nanotube membranes", Carbon, 2006
48. Mi, W., Lin, Y.S., Li, Y., "Vertically aligned carbon nanotube membranes on macroporous alumina supports", Journal of Membrane Science, 2007
49. Yu, M., Funke, H.H., Falconer, J.L., and Noble, R.D., "High Density, Vertically-Aligned Carbon Nanotube Membranes", Nano Letters., 2009
50. Pierson, H.O., "Handbook of carbon, graphite, diamond, and fullerenes: properties, processing and applications", Noyes Publications, 1993
51. Garcia, E.J., John Hart, A., Wardle, B.L., Slocum, A.H., "Fabrication and Nanocompression Testing of Aligned Carbon-Nanotube–Polymer Nanocomposites", Advanced Materials, 2007
52. Iijima, S., Brabec, C., Maiti, A., Bernholc, J., "Structural flexibility of carbon nanotubes", Chemical Physics, 1996
53. Yu, M.F., Lourie, O., Dyer, M.J., Moloni, K., Kelly, T.F., "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load", Science, 2000
54. Forro, L., Salvetat, J.P., Bonard, J. M., Basca, R., Thomson, N. H., Garaj, S., Thien-Nga, L., Gaal, R., Kulik, A., Ruzicka, B., Degiorgi, L., Bachtold, A., Schonenberger, C., Pekker, S., Hernadi, K., "Electronic and Mechanical Properties of Carbon Nanotubes", Technical Report
55. Mori, K., Akita, K., Abe, Y., "Springback behaviour in bending of ultra-high-strength steel sheets using CNC servo press", Machine Tools & Manufacture, 2007
56. Li, Y., Wang, K., Wei, J., Gu, Z., Wang, Z., Luo, J., Wu, D., "Tensile properties of long aligned double-walled carbon nanotube strands", Carbon, 2005
57. Majumder, M. and Ajayan, P.M., "Carbon Nanotube Membranes: A New Frontier in Membrane Science", in: Drioli E., and Giorno, L., "Comprehensive Membrane Science and Engineering", Oxford Academic Press, 2010