Enhanced selectivity in oil-water emulsion filtration membranes with aligned and compact SWCNT films

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Abstract

Separating oil and water is a major problem across many industries, and the challenge is only exacerbated with stabilized emulsions whose drop sizes scale down to the micro and nanometer range. Advances in membrane technology, such as the introduction of superwetting and nanomaterial-based membranes continue to make these technologies among the most viable treatment options available. Given their scale and desirable wetting characteristics, carbon nanotube (CNT) based membranes have attracted considerable attention for oil-water separation with studies reporting fluxes orders of magnitude higher than what is commercially available [9-12]. In spite of these films' great potential, most studies in the literature have solely focused on films with random morphologies of SWCNT stacking with little attention given to the order of stacking as a tunable parameter to influence filtration performance. Moreover, the transfer of such films has not been widely explored onto not only more porous, but also cheaper substrates, such as filter paper, in order to demonstrate the capability of the method. In this work, we show that in-plane horizontal alignment of SWCNT films can be incorporated as an additional degree of freedom to achieve enhanced selectivity. Our results have significant implications on the potential of using SWCNT films in fabricating ultrathin and tunable membranes for oil-water separation.

Introduction

Filtration of oil water emulsions is important as they are produced in many industries, notably the petroleum, steel and metal working industries, as well as in incidents such as large scale oil spills. Such emulsions often come in solutions with other chemicals that are toxic, posing a danger to residents of surrounding areas and to wildlife [1]. Typical mixtures of oil and water mixtures result in the separation of the mixture into a separate water and oil phase where the oil readily separates from the water via surface energy minimization. However, oil-water emulsions contain oil droplets of sizes ranging from tens of micrometers down to the nanometer scale, where they become stable in uniform solution [1]. As the size of the droplet decreases, it becomes increasingly difficult to separate oil from water or vice versa, making filtration a challenge. Many methods have been attempted to mitigate this challenge in a scalable, cost effective and time efficient manner, including chemical, biological and mechanical methods [1]. With more stringent laws on the rise and industrial discharge limited to 35 mg/L [2], separation of oil-water emulsions becomes an increasingly important challenge to address.

The advent of membrane-based technologies, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have revolutionized separation technology. In the case of solid particles, the filtration is primarily a result of size-sieving effects, where the pore need only be smaller than the smallest particle in solution in order to achieve filtration. However, in the case of separating two phase liquid mixtures—such as oil and water—via applied pressure, the emulsified droplet, even if bigger than the pore size, can be forced through the membrane once the pressure exceeds the breakthrough pressure [3]. For this reason, membranes with superwetting surfaces have attracted considerable attention in the field

given their potential to achieve greater degrees of separation under lower operating pressures as demonstrated by the works of Kota et al. [4] and Zhang et al. [5] among others.

An ideal filtration membrane should be ultrathin, while not jeopardizing pore size and selectivity. Owing to their very small dimensions and ability to introduce superwetting characteristics, nanomaterials, and in particular carbon nanotubes, have emerged as a viable avenue for fabricating membranes with a tunable pore size and an ultrathin active layer [6]. In search of such nanomaterial-based membranes, Lee and Baik [7], and later Lee et al. [8], looked into growing vertically aligned multiwalled carbon nanotubes (VACNT's) on steel meshes through thermal chemical vapor deposition (CVD) for oil-water separation. Shi et al. [9] followed with their study on fabricating ultrathin freestanding single-wall carbon nanotube (SWCNT) films for ultrafast separation of oil-water. This study later set the stage for photoinduced [10], photothermal responsive [11] SWCNT films for oil-water separation, bilayer membranes with asymmetric wettability for both, oil-in-water and water-in-oil separation [12], and PFDTS/CNT membranes [13].

While considerable progress has been made, current CNT-based membranes remain far from commercialization, and a complete understanding of the factors affecting membrane selectivity is lacking. The CNT steel meshes introduced by Lee and coworkers [7, 8], while they possessed a remarkable boost in hydrophobicity and oleophilicity, are non-tunable and their selectivity would be limited by the porosity of the steel mesh. The work presented by Shi et al. [9] featured CNT film transfer onto expensive ceramic membranes, while none of the subsequent studies presented thus far have addressed film transfer onto much cheaper substrates, such as filter paper. In addition, no formal attempt has been made with the goal of minimizing CNT consumption as to achieve the thinnest possible films without sacrificing selectivity.

In the case of making CNT filter membranes via vacuum filtration, it has been reported that slower vacuum filtration rates induce alignment in SWCNT films [14]. More recently, He et al. [15] have been the first to report on the successful fabrication of wafer-scale monodomain in-plane aligned SWCNT films. Unlike the non-aligned CNT film membranes for oil-water separation studied thus far, aligned film membranes are more densely packed and thus have potentially smaller pore sizes, important for oil-water filtration. Compacting SWCNT films by alignment may have the potential to achieve even thinner membrane active layers. However, the performance of these films in oil-water emulsion separation has not been investigated, and our understanding of the effect of the packing structure—which includes the effect of alignment—remains largely unknown.

In this work, we investigate the effect of SWCNT packing structure, specifically the structural alignment, on oil-water separation, and the potential of employing alignment as an additional degree-of-freedom to fabricate membranes with an even more tunable thickness and selectivity. In particular, the effect of film thickness and structural alignment is studied, and successful transfer onto more porous substrates, which give rise to higher in fluxes, is reported. Our results demonstrate that, unlike non-aligned SWCNT films, structurally aligned SWCNT films feature enhanced filtration selectivity with thinner films.

Materials and Methods

Preparation of membranes coated with SWCNT film: 75% SWCNTs were purchased from TUBALL at the OCSiAl online store. Sodium Deoxycholate (DOC), 97% Alfa Aesar was purchased from VWR. A solution of deionized water (DI) was made starting with 1, 2.5, and 5wt.% of DOC in solution with 0.4mg/mL of SWCNTs. A bath sonicator was used for 15 minutes to induce mixing in the solutions. Next, a ~6.4mm diameter tip micro-sonicator was

used to sonicate the SWCNT suspensions for 55 minutes at ~30Watts. Once the solutions were well dispersed, the resultant solution was centrifuged for 4 hours at 4400 rpm to induce the settling of SWCNT agglomerates and to maintain higher purities of the SWCNT solution. After centrifugation, the top supernatant (~top 30%) was collected separately and diluted to either 0.004, 0.009 or 0.015 mg/mL. SWCNT thin films were fabricated by placing a known volume of SWCNT solution onto a 25mm vacuum filtration setup (Figure 1a). 25mm diameter Polyvinylpyrrolidone (PVP)-coated Nucleopore polycarbonate hydrophilic membranes with pore size were purchased from GE Healthcare and Life Sciences and used as a support substrate for deposition of SWCNT film by vacuum filtration.

It is known that controlling the rate of filtration induces order in the manner in which SWCNTs are deposited on the substrate [9,15]. For this purpose, slow and fast filtration rates were used to control the structure of the films by counting the amount of drops being passed through the 100nm Nucleopore polycarbonate membrane on the steel mesh from the SWCNT solution. Fast filtration rates lead to random order of SWCNT films, while very slow filtration rates induce order. The flow rate was measured by the time it took for droplets to be filtered. Films with random order had flow rates faster than around 40 seconds per drop (Figure 1d shows the filtered drop). Aligned films had flow rates in the range of 60 to 80 seconds or less per drop of solution filtered.

Characterization: In order to qualitatively assert induced alignment in the films, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used. Given the flexible nature of the SWCNT thin film membrane, SEM and AFM were performed by transferring the SWCNT film to a flat substrate for mechanical stability. Figure 3a shows a transferred SWCNT film onto a glass slide for characterization. Notably, the thin nature of the film allows it to be

translucent. As expected, slow filtration rates lead to randomly deposited SWCNTs on the Nucleopore membrane surface (one can expect that by fast deposition the SWCNTs do not have enough time to travel to areas of the membrane surface that have less SWCNTs and thereby higher flow rates). Similarly, slow flow rates produce alignment in the SWCNT films, as shown in Figure 3b and Figure 3f. It is worth mentioning that the film surface does not look completely flat. This is due to the pore size of the stainless steel mesh. When the vacuum pressure acts at the interface between the polycarbonate membrane and steel mesh, the GE membrane is strained at the pore openings of the mesh and thus the polycarbonate membrane is deformed at the pores.

Transfer process for imaging SWCNT films: SWCNT films were transferred to Si substrate and glass in order to provide flat and rigid support for characterization under SEM and AFM. SWCNT films prepared on PVP coated polycarbonate membranes were stamped to the surface of the desired substrate. A drop of DI water was applied to induce capillary forces to spread the polycarbonate membrane on the flat substrate surface. Next, the sample was dipped in a bath of chloroform to etch the polycarbonate membrane and leave a thin freestanding SWCNT film on the substrate surface. Multiple rinsing steps were carried out with acetone, ethanol and 2-propanol followed by a final rinse with DI water. The films were then dried using a nitrogen gun.

Transfer of aligned SWCNT films to thin, flexible substrates with higher porosity: SWCNT films were also transferred to more porous filter membranes in order to increase the flux while maintaining selectivity. As purchased nylon membranes with a pore size of 450nm were cut into circular discs with diameters about 10mm larger than those of the 25mm Nucleopore polycarbonate membranes. The GE membrane containing the SWCNT film was placed on top of the nylon membrane and the assembly was placed in an empty glass petri dish. Chloroform was added drop by drop to the petri dish. Care was taken to avoid sudden etching of GE membrane

with chloroform as it led to wrinkles on the SWCNT film due to high stresses induced by the dissolving membrane. After the Nucleopore polycarbonate membrane was etched away completely, the nylon membrane coated with the SWCNT film was air dried for 30 minutes. SWCNT membranes transferred onto nylon (Figure 3c) were then ready for filtration of emulsions.

Preparation of oil water emulsions: Mineral oil, procured from Sigma Aldrich and DI water were mixed in a 90:1 ratio. Span80 was used as an emulsifier and had a concentration of 1% by volume in the final mixture. In order to enable better detection of water droplets in oil, blue food dye was added to the DI water before mixing. The solution was placed on a vortex mixer for 1 hour to ensure complete suspension of water droplets in oil and formation of a stable emulsion.

Filtration of oil-water emulsion through CNT film: The emulsion was filtered through the SWCNT film membrane with the help of a vacuum filtration setup used for coating membranes with CNT (shown in Figure 1a). Vacuum suction at 0.8 bar was used to draw the emulsion through the film. The filtrate was a collected in the conical flask for analysis.

Analysis of filtrate obtained from oil-water experiments: As the water in the emulsion was blue due to the addition of dye, the absence of any water droplets yielded a transparent filtrate consisting of pure mineral oil. This provided a qualitative method to gauge the extent of separation. The filtrate was analyzed with bright field microscopy to check for the presence of water droplets in oil.

Results and Discussion

Experiments were conducted to compare the performance of unaligned versus aligned SWCNT films in terms of flux and separation efficiency. SWCNT films of various thicknesses

were prepared by adding a measured amount of SWCNT solution at various concentrations to the vacuum filtration setup. The vacuum filtration setup utilized to conduct oil-water emulsion separation experiments is shown in Figure 1a. Three different volumes (10, 15, and 20mL) of SWCNT suspension were used to prepare both aligned and unaligned films for performance comparison during filtration. For the experiments, a concentration of 0.004mg/mL of SWCNTs in solution was used to produce both aligned and unaligned films for oil filtration from emulsion. Our initial speculation was that the order of SWCNTs would create an aligned network whereby the flow of fluid would be uninterrupted due to lesser friction. However, we find that the alignment of SWCNTs in a membrane actually enhances its selectivity. We speculate this is due to the close packing that is possible in the aligned SWCNT structure, as shown in Figure 2b.

Figure 4a shows the filtrate on a glass slide imaged using optical microscopy. 10mL unaligned SWCNT films were not able to selectively filter the oil from the emulsion (which contained blue color dye (see Figure 4a,i). The filtrate from this run still contained a substantial amount of water droplets and blue dye. On the other hand, aligned SWCNT films were able to fully separate the oil from the emulsion (Figure 4a, iv-vi). Further, the blue dye was filtered, which gives evidence that the close packed structure from the aligned order of the SWCNTs is able to enhance the selectivity of the membrane, even for very thin membranes (range of 10s of nanometers). Increasing the thickness of SWCNT films (15mL filtration, 50% increase in thickness) allowed unaligned SWCNTs to increase their selectivity to separate oil from the emulsion. However, even at this increased thickness, the unaligned SWCNT films still allow the passage of food color dye and some water droplets (Figure 4a, ii). At a large enough thickness, unaligned SWCNT films reach a point where they are able to filter oil just as the aligned membrane (Figure 4a,iii). However, for this, our experiments show that approximately twice the

amount of SWCNTs are needed (10mL vs 20mL). This translates to higher selectivity with about half as much material, which is attractive.

Although the selectivity that can be achieved with aligned SWCNT film membranes for the amount of material beats that of unaligned films, the close packed structure of the SWCNTs might create a smaller effective pore size which may decrease the flux. Figure 4b confirms this, as the flux for unaligned SWCNTs is approximately ~5x larger than that of the aligned SWCNT films. This comparison is not valid, however, since the unaligned SWCNT membranes did not filter oil from the emulsion with high selectivity for the thinnest membrane (10mL). The aligned SWCNT membranes selectively filtered oil from the emulsion even for the thinnest membranes, while the unaligned membranes achieved highest selectivity only for 20mL SWCNT film membranes.

It is important to disclose that the first filtration experiments (Figure 4b) were all carried out using 100nm Nucleopore polycarbonate membranes, which themselves limit the flux that can be attained due to their small pore size. In order to increase the flux through the membranes while maintaining selectivity at very small thicknesses, as prepared SWCNT membranes were transferred to more porous substrates. 15mL SWCNT membranes were transferred to Nylon membranes with 450nm pore size, ~4x the pore size used for initial emulsion filtrations (Fig 3c). However, increasing the pore size could cause SWCNT aligned membranes to deform or buckle on the bigger pores of the host membrane (which also acts as mechanical support), compromising selectivity by possibly stretching the SWCNT films on the bigger pores, creating cracks or openings and thus a bigger pore size. Surprisingly, emulsion filtration experiments using a 15mL SWCNT film transferred onto 450nm Nylon membranes resulted in ~20x increase in flux without compromise to selectivity (filtrate did not contain blue color dye nor large visible

droplets under optical microscope, and visually appeared as only oil.) Thus aligned SWCNT filter membranes can be transferred to other more porous substrates to potentially increase the flux while maintaining selectivity, as long as the host membrane can provide a flat surface and mechanical support to the thin SWCNT film membrane.

The flow rate and thus suction pressure at which the unaligned films are fabricated is much higher than that for aligned films. It can therefore be expected that at higher flow rates, the SWCNTs would randomly orient themselves on the surface of the support membrane as the deposition rate on the surface is too high and the SWCNTs may not have time to follow electrostatic interactions at the surface to either align or fill in areas of low SWCNT coverage, leading to a non-uniform film surface coverage and thickness. Areas where less SWCNTs are deposited would not be as impermeable to water as the densely packed regions. While non-conformity and non-homogeneity of the surface would be of lesser concern at higher film thicknesses, the effect is more critical at lower film thicknesses where separation efficiency is drastically compromised by unaligned films. However, if the flow rates are slow enough, then there is sufficient time for SWCNTs to orient themselves on the film. Thus, the slower filtration rates produce more robust SWCNT films, and the selectivity can be tuned by degree of alignment. In the best case, SWCNT films would align along the entire support membrane's surface and form a compact structure, such as shown in Figure 2b and Figure 2c.

Typically, the pore size of membranes is a major factor that determines how effective they are in filtration. In our case, the films have properties that can either wet or repel liquids in addition to an effective pore size. For the case of aligned SWCNT films, an effective, or 'slot' pore size (given the aspect ratio of SWCNTs length to diameter) may be able to be estimated based on the stacking of the SWCNTs themselves. From the geometry of a SWCNT, we can

expect that if the stacking can be controlled such as in Figure 2b-c, then the pore size can be distanced by the interstitial spacing between SWCNTs. Given the theoretical inter-plane distance between graphite layers, this size can be estimated as ~3.5Å. Thus, highly compact SWCNT filter membranes not only provide excellent surface tuning properties for filtration, but an effective pore 'length' may be estimated on the order of angstroms.

Conclusion

In conclusion, we report that surface morphology of SWCNTs alters the filtration properties. We tested aligned and unaligned films and found that aligned films show better selectivity due to the close packing of SWCNTs. This spacing is approximated as the interplanar spacing of graphene layers in graphite which is as small as 3.5 angstroms.

Also, we are able to achieve the same selectivity for filtration by using half the amount of SWCNTs in aligned films, as compared to non-aligned films. By tailoring the etching process, we can produce free standing SWCNTs which can be transferred onto other substrates having larger pore sizes to achieve a higher flux. This ultrathin, highly selective membrane is tunable. Selectivity here is a function of pore size and thickness of the film, which can be controlled by varying the concentration of the SWCNT solution and flow rate during the preparation of the film.

Meanwhile, due to the high degree of alignment, our membrane also demonstrates 100% oil-water separation. Our work demonstrates that designing tunable aligned SWCNTs achieves better separation in comparison to non-aligned films.

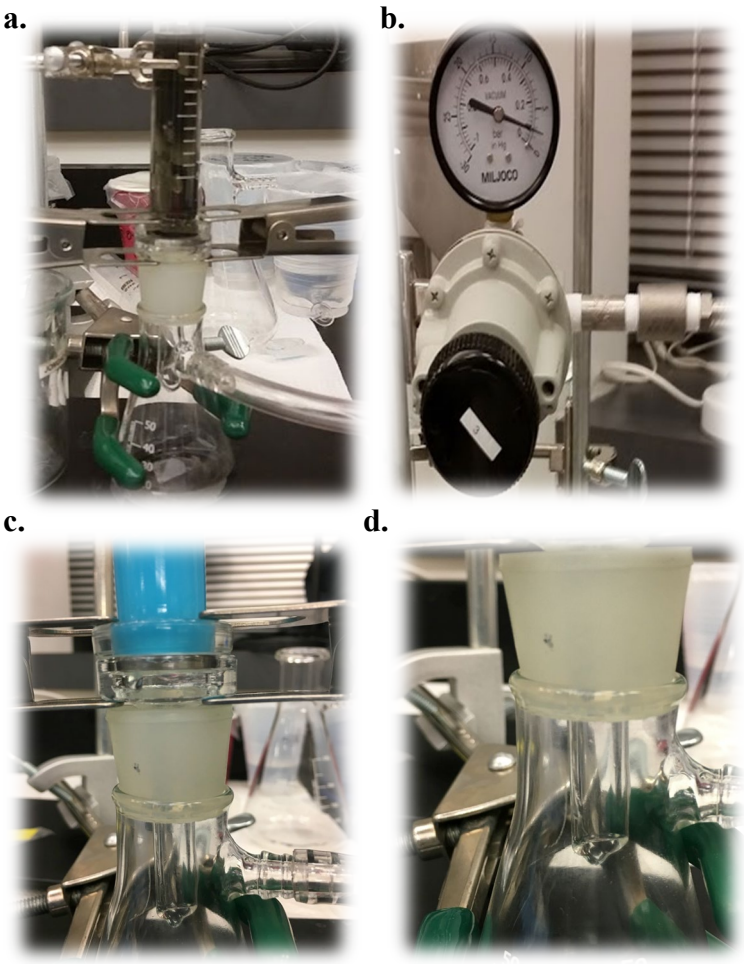


Figure 1. Vacuum filtration setup (a) with SWCNT solution in the filtering process (b) pressure regulator to measure the filtration vacuum (c) filtration of oil-water and blue dye emulsion on the setup, and (d) oil droplet being filtered from the emulsion in image c.

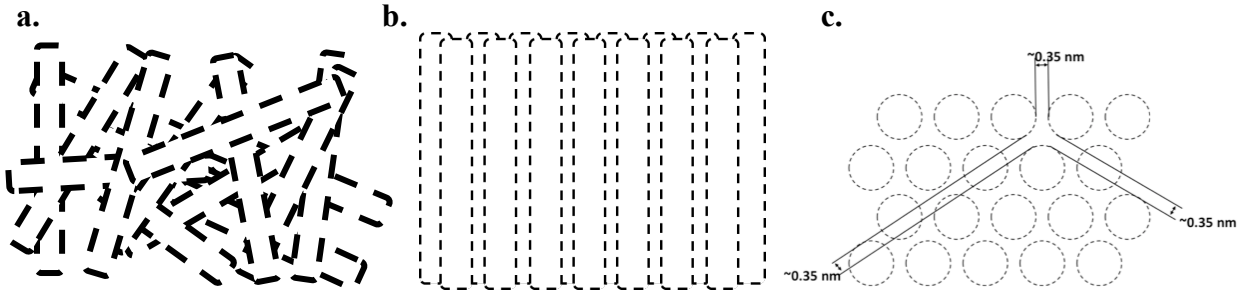


Figure 2. Schematic of ultrafiltration membrane structure of (a) unaligned SWCNT films, (b) aligned SWCNT films, and (c) cross section of aligned SWCNT film showing that SWCNTs can have compact structure with interspace between nanotubes theoretically as low at ~3.5Å.

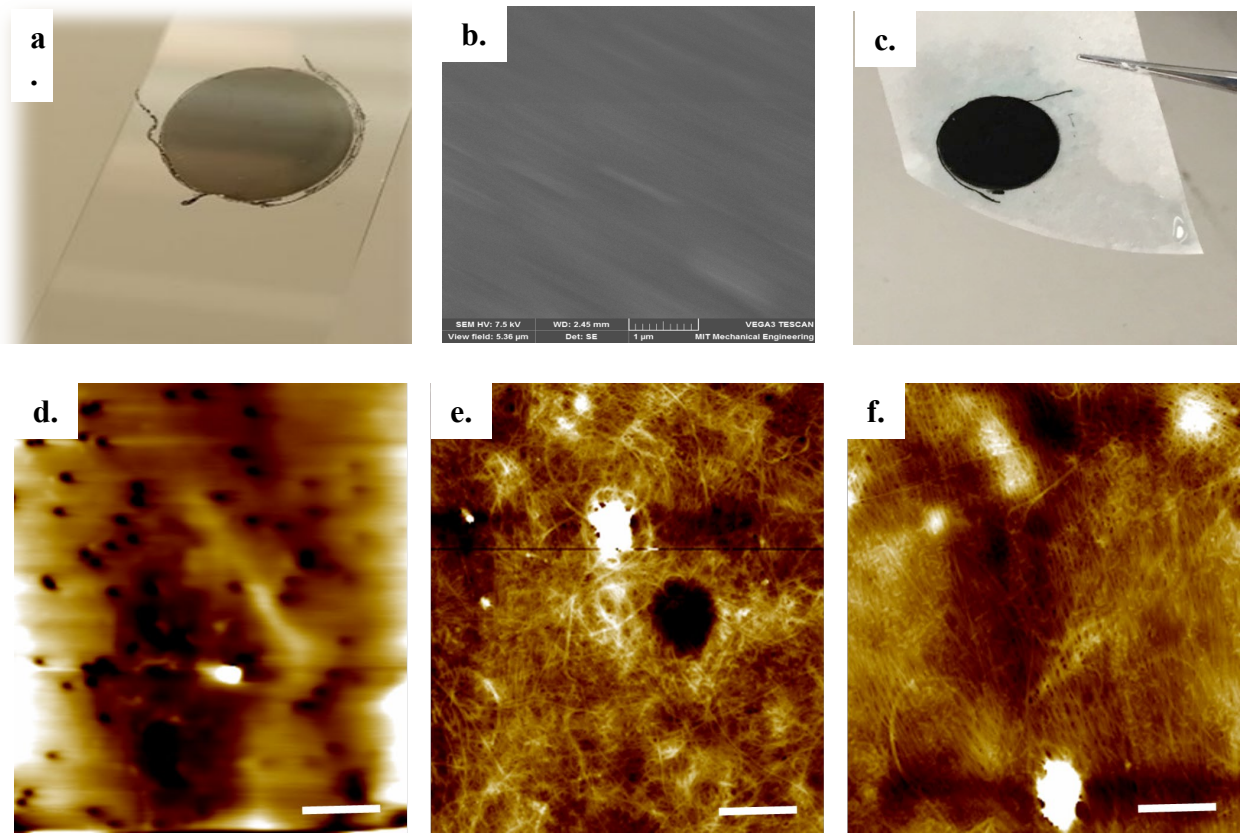
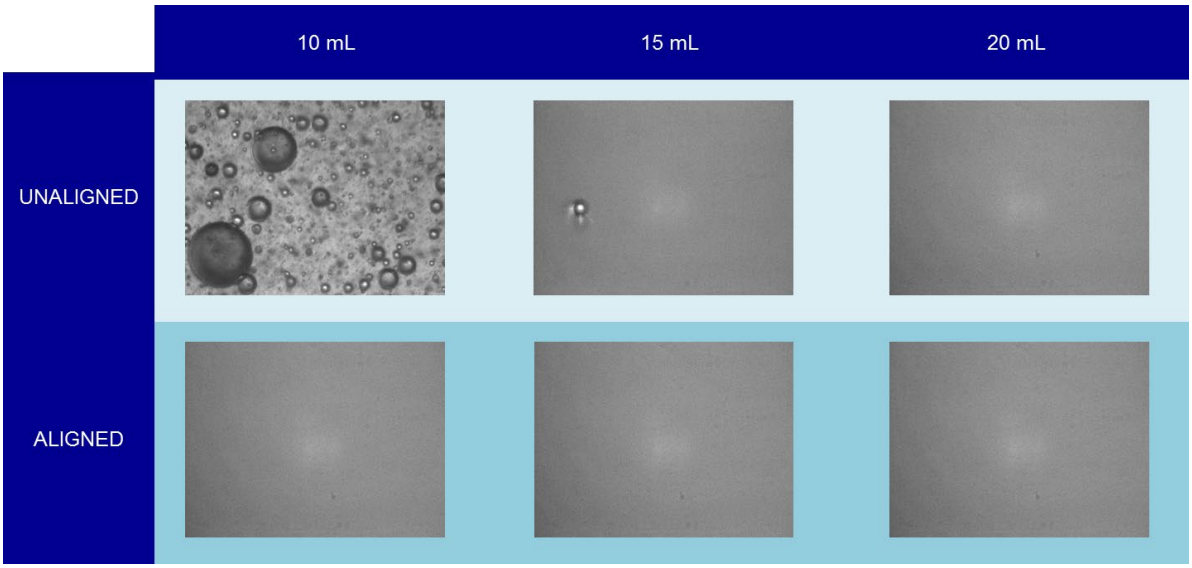


Figure 3. Characterization of as-fabricated SWCNT membranes (a) Transferred SWCNT film from Polycarbonate membranes onto a glass slide (b) SEM image of SWCNT film where the features are indicative of alignment (c) Free standing CNT film transferred onto nylon membrane having a pore size of 450 nm (d) As purchased Polycarbonate Nuclepore membranes showing well defined pores (e) fast filtration unaligned SWCNT film (f) slow vacuum filtration rate yielded aligned SWCNT film. All AFM images are 5µm x 5µm. Scale bars of AFM and SEM scans are 1µm.

a



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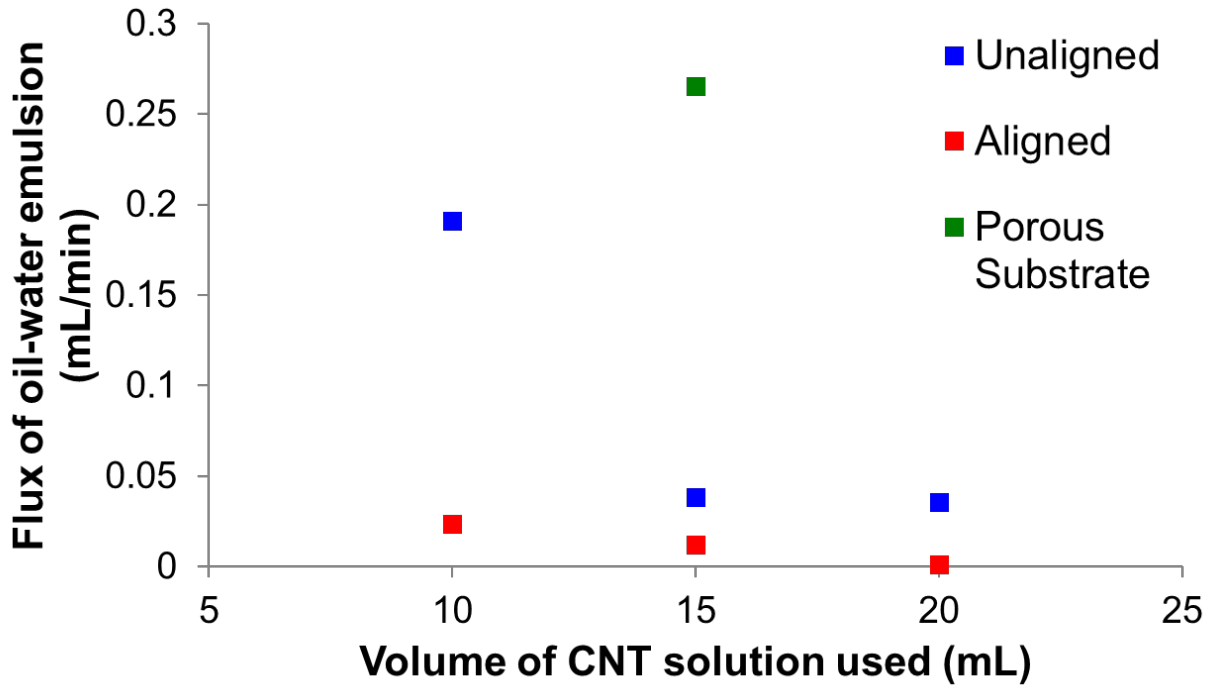

Figure 4. Experimental results from oil-water emulsion filtration experiments (a) optical microscope images of the oil-water emulsion filtrate through membranes made with 10, 15, and 20 mL of SWCNT solution for the aligned and unaligned case. (b) Flux as a function of film thickness

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