

PRODUCTION OF ORIENTED CARBON NANOTUBE MEMBRANES

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Abstract. With the purpose of obtaining a planar deposition of a dense, thin and oriented carbon nanotubes membrane, the dielectrophoresis technique where applied using four different surfactants (SDS, SDBS, PE6400 and PE6800) in water and a solution only in 1,2-dichlorobenzene. The alignment promoted by dielectrophoresis was analyzed for each nanotube solution, regarding their quality and concentration range of dispersion capability, as a function of the variables which can affect the dielectrophoresis forces: frequency, bias and the AC/DC field ratio. The tests showed that the alignment of carbon nanotubes is characterized by its agglomeration in a "rope" shape in the gap, giving a good aligned structure. The SDBS showed the best solubilization power. However the SDS allows a better surfactant removal after alignment, PE6800 could not hold on through the centrifugation step, PE6400 does not even make a visual good dispersion and 1,2-dichlorobenzene solution showed a weak but stable capability of dispersion but terrible orientation power. Electrical measurements were coherent with the images and demonstrated the efficiency of the surfactant removal process.

1. INTRODUCTION

Since their discovery, [1] carbon nanotubes (CNT) have been intensively studied as a potential building block for nanoelectronics due to their unique electrical properties, like high-conductivity channels in carbon nanotube field-effect transistors (CNFETs) [2,3] and mechanical properties as high frequency resonators in ultrasonic transducers [4]. One of the main problems associated with CNT is the difficulty of a reliable integration. Surface patterning [5-9] and direct growth [10-17] offers nearly the same degree of positioning but require rather specialized materials and patterning techniques. Some large-scale techniques could also be used, such as liquid crystals [18,19], Langmuir films [20,21] and the relatively simple method dielectrophoresis [22-26], which gives several options to reach the same deposition characteristics by the variation of some parameters,

like preferentially aligning metallic CNT from a solution containing others particles as semiconductors CNT and impurities [27,28].

In the present work we describe the dielectrophoresis (DEP) technique adapted to achieve a CNT membrane with the following characteristics (by priority order): i) composed only by CNT ordered in the same direction; ii) the smallest distance between two neighbors CNT, therefore as dense as possible; iii) the thinnest membrane possible and; iv) preferentially formed by metallic CNT.

We studied the solubilization capability of each surfactant and how each experimental parameter (surfactant, concentration, bias, frequency and DC/AC electric field) affects the membrane formation by dielectrophoresis and the mechanism behind it. Our findings present a viable approach for the fabrication of such structure but it still needs more research to be concluded.

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Table 1. Qualitative summary of CNT solutions. “X” specifies the not tested ones.

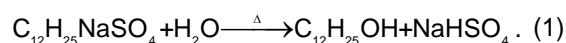
[NT]	SDS		SDBS		PE6400		PE6800		DCB	
Centrifugation	Before	After	Before	After	Before	After	Before	After	Before	After
0,1 mg/ml	Good	Good	Good	Good	Bad	Bad	Good	Medium	Good	Medium
1 mg/ml	Medium	Bad	Good	Good	X	X	X	X	X	X
5 mg/ml	X	X	Medium	Bad	X	X	X	X	X	X

2. MATERIALS AND METHODS

Initially the solutions water/surfactant were prepared with 1% weight of ionic surfactants Sodium Dodecyl Sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS), and 2% weight of anionic surfactants PE6400 (Poli($\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$)) and PE6800 (Poli(Poli($\text{EO}_{74}\text{PO}_{30}\text{EO}_{74}$)) also known as Pluronic®. For each surfactant solution, and another solution containing only 1,2-dichlorobenzene, were added 1 mg/mL of CNT (single-wall, purchased from Kaeria SARL, used as received) and then diluted or added more CNT to prepare other concentrations. After being ultrasonicated for about 24 hours the solutions were centrifuged at 2224g for another 24 hours and the bottom residue was removed. This process was repeated several times until there is no remnant residue at the bottom.

Afterwards each solution droplet was deposited on a silicon wafer containing gold electrodes with 2 μm and 5 μm gaps. The electrodes are wire-bonded to an external circuit from which they are connected to wires that lead to a voltage source (Agilent 33250A) in such a way that each test allows multiple depositions. After 10 minutes the remaining solution was removed by a nitrogen blow concentrated directly over the solution, while the electric field is still applied. To ensure reproducibility, all depositions were made at least at two separate times and in three pairs of gaps (2 and 5 μm) simultaneously.

In order to withdraw the post-deposition surfactant from the membranes it was used specific properties of each class. For SDS, the hydrolysis reaction below (adapted from reference [30]) was used by heating it up under water infusion for several hours (~8 hours) and drying it at 250 °C (~8 hours) until the alcohol evaporates. The chemical composition of SDBS is similar to SDS and, therefore, it is expected to have analogous reaction.



The Pluronic removal was made using the sensitivity of this class of copolymers against tempera-

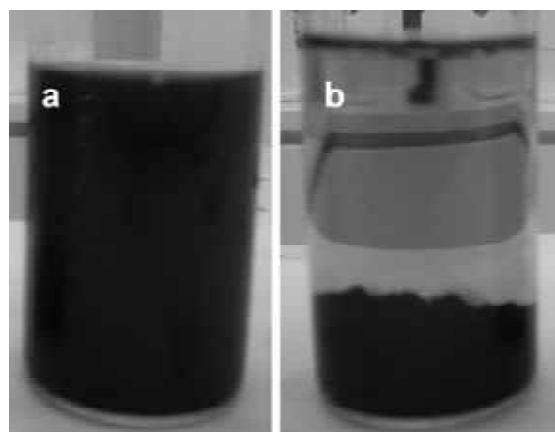


Fig. 1. a) SDS 1 mg/ml before centrifugation: homogeneous; b) PE6400 before centrifugation, after a few hours: two phases.

ture, where decreasing temperature increases its solubility [31]. Thus, after the deposition the samples were previously heated, then cooled (~10 °C) and cleaned with cold water (~0 °C).

The images were taken by the Scanning Electron Microscope CARL ZEISS - TOP 55 and the Atomic Force Microscope Dimension 3100 while the electrical properties were measured by the Prober SUSS MicroTec PA200. Each electrode was previously checked in the optical microscope to ensure that external factors, such as short circuits, compromise the results.

3. RESULTS

3.1. CNT solutions

This section shows the results of different solutions for different CNT concentrations visually analyzed. A summary of the results can be seen in Table 1.

SDS solutions prepared with 1mg/ml and 0.1 mg/ml CNT are stable before centrifugation (Fig. 1a). After centrifugation, particles (or poorly dispersed CNT) deposited in the bottom for both samples but in much larger quantities for the 1 mg/ml solution, showing that at this concentration range, CNT are

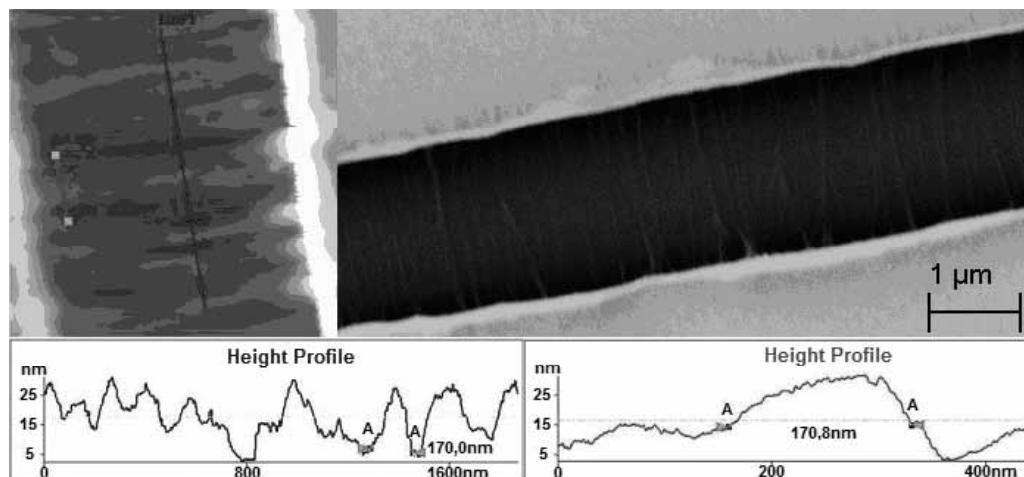


Fig. 2. SEM image (on top) and AFM image (at the bottom) of the deposit on a 2 μm gap of SDS with 0.1 mg/ml of CNT at 10 MHz and 10 Vpp bias.

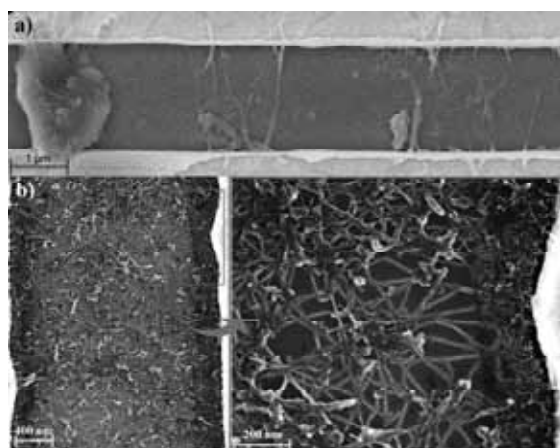


Fig. 3. a) PE6800 with 0.1 mg/ml of CNT at 10 MHz and 10 Vpp bias: region of CNT filled with impurities. b) Dichlorobenzene with 0.1 mg/ml of CNT at 10 MHz and 10 Vpp bias. Distorted structures over CNT.

no longer dispersed. SDBS solutions showed the best results: with 0.1 and 1 mg/ml of CNT, both solutions seem homogeneous with small deposits after centrifugation. The 5 mg/ml solution, however, separated into two phases after the first spin. This improved solubility agrees with the conclusions of reference [29].

PE6800 solution with 0.1 mg/ml of CNT dispersed well before centrifugation, CNT did not decant even after several days. Nonetheless, the solution did not withstand centrifugation, separating into a solid phase (thick deposit) and a slightly darker solution. On the other hand, PE6400 solution gave us the most disappointing results where the 0.1 mg/ml solution had the CNT decanted even before the centrifugation (Fig. 1b). The lower solubility of PE6400

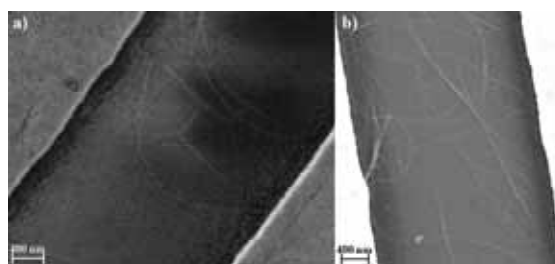


Fig. 4. a) SDS at 16 Vpp bias and b) PE6800 at 20 Vpp bias.

compared to PE6800 agrees with the conclusions of reference [32], it states that as larger the blocks of ethylene oxide (hydrophilic part) in the Pluronic formula are, greater its CNT dispersion ability will be.

The dichlorobenzene (DCB) solution proved to be stable but with low dispersion capacity. Before and after the centrifugation a homogeneous solution is present, however the amount of CNT deposited in the bottom of the glass tube after centrifugation is much larger than with the SDS and SDBS.

3.2. Alignment

The five stable solutions, SDS 0.1 mg/ml, SDBS 0.1 and 1 mg/ml, PE6800 0.1 mg/ml (without centrifugation) and dichlorobenzene 0.1 mg/ml, were analyzed. For each factor taken into account, the other variables were kept constant. The SDS sample with 0.1 mg/ml of CNT under 10 Vpp bias and 10 MHz frequency was established as the standard for which comparisons were related.

The aligned structures are characterized by the formation of CNT “ropes” or “strings”: a bundle of

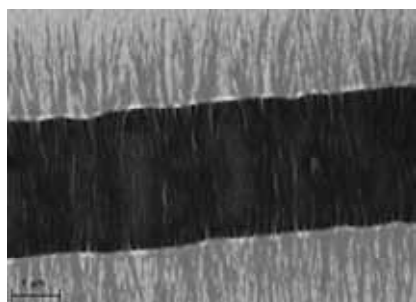


Fig. 5. SDS at 15 MHz (0,1 mg/ml of CNT at 10 Vpp bias). Several “ropes” of well aligned CNT, apparently overlaid at different heights.

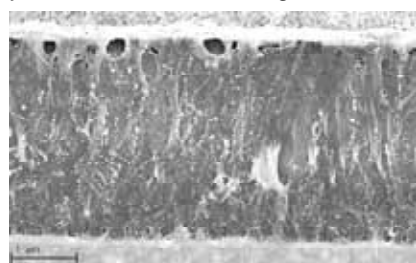


Fig. 6. SDS with 0.1 mg/ml of CNT at 10 Vpp/4 V_{DC} bias and 10 MHz.

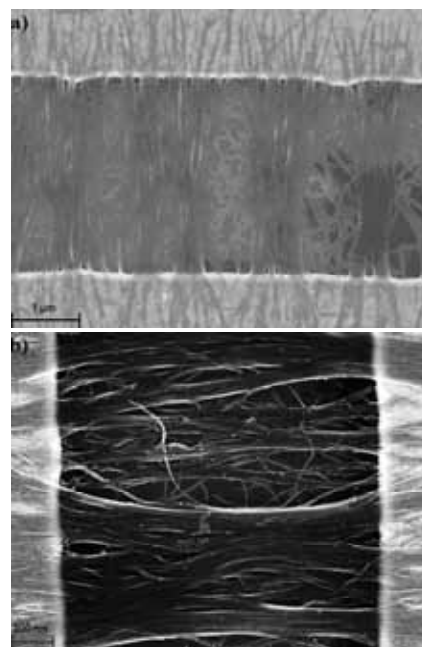


Fig. 7. a) SDS with 0.1 mg/ml de CNT at 10 Vpp/2 V_{DC} and 15 MHz bias in a 2 μm gap; b) Larger but still thin “ropes” (SDS with 0.1 mg/ml of CNT at 20 MHz and 10 Vpp/2 V_{DC} bias).

individual CNT or smaller ropes. The more aligned CNT are, more packed they are in the “rope” shape while the misaligned CNT appear almost individually. At the strongly oriented samples, a lot of “ropes” appear over the gap.

Surfactant: The three solutions containing surfactant had similar results, the same amount of CNT present in the gap (and not outside of it) and a good alignment (Fig. 2), while the dichlorobenzene (Fig. 3b) solution showed a completely random deposit with a distorted unidentified structure above it. The PE6800 (Fig. 3a) on the other hand has a large amount of impurities due to the absence of the centrifugation steps, distorting the membrane conception at these points.

Concentration: the deposit made with the SDBS solution with 1 mg/ml of CNT did not show almost any CNT in the gap and those who appeared have no specific orientation. This is attributed to a poor dispersion in this solution, although the solution is stable after centrifugation, it probably contains mostly small CNT bundles, and since DEP acts preferentially on single CNT, the bundles are not attracted to the gap.

Bias: As the bias was increased to 16 Vpp and 20 Vpp (Fig. 4), the results were similar to the results obtained when increased the concentration: lack of oriented CNT in the gap and misalignment. As increasing the bias, other forces may become

more relevant and affect the system, such as electrothermal forces due to the temperature difference between the gap (Joule heating) and other regions of the drop. These forces are well discussed to microfluidic circuits in reference [23] and are not the objective of this study.

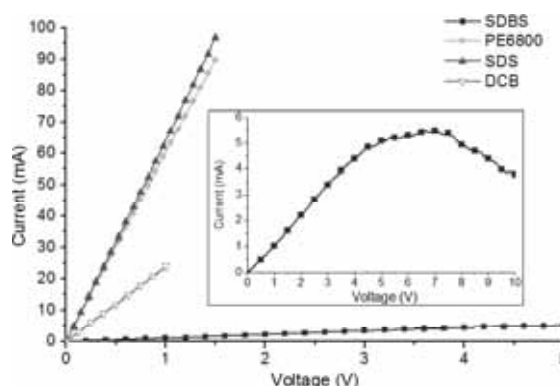


Fig. 8. The graphic shows the curve current/voltage for the membranes with different surfactants (2 mm gap, 0.1 mg/ml of CNT at 10 MHz and 10 Vpp bias). The inset shows the role SDBS curve. The maximum voltage here is not the same once that the other membranes reach the equipment maximum current at much lower voltages.

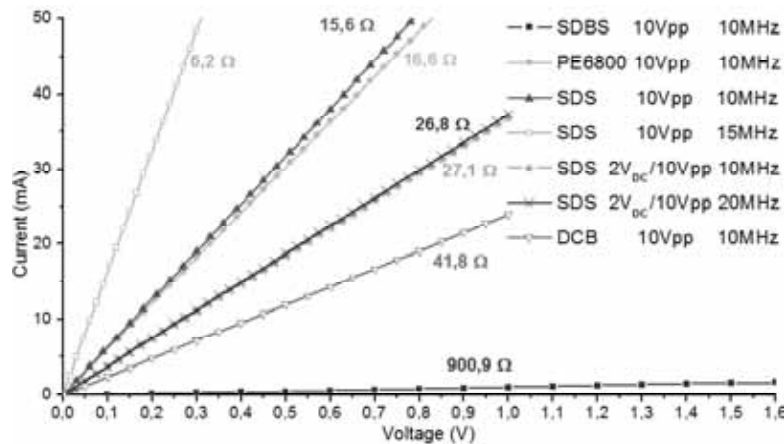


Fig. 9. The graphic shows the curves current/voltage for all membranes and their related resistivity.

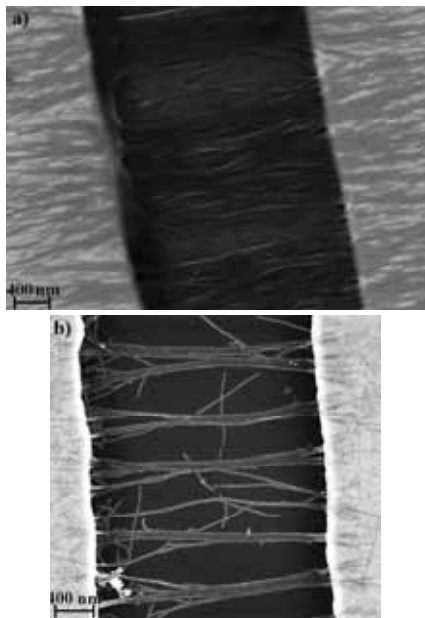


Fig. 10. SDS with 0.1 mg/ml of CNT at 10 Vpp and 15 MHz bias. a) before the overcurrent; b) after the overcurrent.

Frequency: The increased frequency of the AC electric field to 16 MHz (Fig. 5) showed a great improvement in the alignment and amount of CNT in the gap, piling them up in an ordered way but at different depth levels of the gap. These results confirm the theory that a higher frequency of the electric field increases the DEP, and hence the amount of deposited CNT between the electrodes. This also shows that the frequency used is still below the critical transition frequency DEP positive/negative [25].

Electric field DC/AC: Adding the DC component under the DC/AC ratio of 0.40 (10 Vpp with 4 V_{DC}) a sudden but substantial distortion in the orientation

of the membrane and a greater number of impurities (as well as CNT) appeared (Fig. 6). This result proves effectively that the DC field can attract other particles, including impurities, in this case possibly the metal catalyst.

Electric field DC/AC at a higher frequency. Once that raising the frequency showed good results, there is still the question of whether the advantages provided by the DC electric field theory [27] will emerge in this circumstances, like the improvement in the alignment of individual CNT and consecutive reduction in membrane thickness. With a DC/AC ratio of 0.20 and a frequency of 15 MHz, the CNT between the electrodes are still in a huge amount (Fig. 7a) as in the test at 15 MHz but spatially better distributed. The CNT are apparently forming a thin layer with reduced amount of empty spaces between the “ropes”, being very close from the goals outlined at the beginning of this paper.

A further frequency increase to 20 MHz (keeping a 10 Vpp/2 V_{DC} bias and SDS with 0.1 mg/ml of CNT) causes a further increase in the amount of CNT, which implies a greater number of CNT (“ropes” wider and denser) as well as new distribution of CNT in the gap’s depth profile (Fig. 7b). However, it is clearly seen that the CNT ropes are thinner, or flattened. This confirms the theory of CNT repulsion between them due to DC voltage, limiting the overlap of CNT in the same “rope”.

3.3. Electrical measurements

The main information given by these measurements comes from the junction membrane/electrode: the great electrical resistivity present in the SDBS membrane suggests that the decomposition reaction

originally developed for the SDS does not apply to SDBS. The SDBS probably covers the CNT, forming an insulating layer between the tubes and electrodes. SDS and PE6800 clearly show a good agreement between their poor membrane conductivity, indicating that in both cases the surfactant was partially removed (Fig. 8). The dichlorobenzene (DCB) solution shows a slightly lower conductivity, perhaps due to the structures present in the membrane, shown by the SEM image, but also by the lower amount and orientation degree of CNT in the gap.

Fig. 9 shows the total resistivity of each membrane for each tested parameter. Not only a larger amount of CNT decreases the membrane resistivity, but also a more effective alignment improves the conductivity by percolation. It is obvious that the sample with the highest total number of CNT, SDS at 10 Vpp and 15 MHz bias, has a lower resistivity. Under 10 Vpp and 10 MHz, SDS and PE6800 show similar SEM images, therefore show similar results.

At $2 V_{DC}/10$ Vpp, SDS has an even lower resistivity, reinforcing the theory that the DC current induces a repulsive force along each CNT, decreasing their amount in the gap and consequently, increasing the membrane resistivity. The only factor that is contradictory is the fact that the sample at a higher frequency (20 MHz), which contains more CNT (at least visually), presents an almost identical resistivity, slightly lower than at 10 MHz.

Electrical “burning” point: All curves have an initial ohmic behavior up to a point of great fluctuation in relative high voltages, from which the current drops dramatically (see graph inserted in Fig. 10). At this point, the CNT begin to disintegrate (Joule effect), hence the resistivity rises due to the smaller number of CNT between the electrodes.

Fig. 10 shows the same sample in the SEM image before and after the electrical “burning”. The reduction on the CNT number between the electrodes is huge, what remains are “ropes” probably formed mostly by semiconductor CNT.

4. CONCLUSION

It was possible to obtain oriented planar membranes formed by carbon nanotube using four different surfactants (SDS, SDBS, PE6400, and PE6800) in water and a solution only in 1,2-dichlorobenzene. The tests showed that the alignment of carbon nanotubes is characterized by its agglomeration in a “rope” shape in the gap, giving a good aligned structure. The SDBS showed the best solubiliza-

tion power. However the SDS allows a better surfactant removal after alignment, PE6800 could not hold on through the centrifugation step, PE6400 does not even make a visual good dispersion and 1,2-dichlorobenzene solution showed a weak but stable capability of dispersion but terrible orientation power. Electrical measurements were coherent with the images and demonstrated the efficiency of the surfactant removal process. The surfactant has no direct relation with the alignment but affect the way that CNT are dispersed, which affects the alignment, but in its absence (as seen in dichlorobenzene sample) the process parameters need to be readjusted. Once that the dispersion step was performed, applying the electric field it is easily reproducible, the process parameters gave a feedback consistent with the literature [27]:

- A DC electric field really changes the electric field around the CNT, promoting more individual alignment, but on the other hand attracts impurities more easily; and
- The amount of CNT in the gap is directly tied up to the AC field frequency.

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