EVALUATION OF DIFFERENT SURFACTANTS TO 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. 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.

Tópico 4: Materiales Cerâmicos

Keywords: Carbon nanotubes, membrane, surfactant, dielectrophoresis.

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) affects the membrane formation by dielectrophoresis and the mechanism behind it.

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($EO_{13}PO_{30}EO_{13}$)) and PE6800 (Poli(Poli($EO_{74}PO_{30}EO_{74}$) also known as Pluronic®. For each surfactant solution, and another solution containing only 1,2-dichlorobenzene, were added 1mg/mL of CNT (single-wall, purchased from Kaeria SARL, used as received) and than 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 2μm and 5μm 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 5µm) 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[29]) was used by heating it up under water infusion for several hours (~8 hours) and drying it at 250ºC (~ 8 hours) until the alcohol evaporates. The chemical composition of SDBS is similar to SDS and, therefore, it is expected to have analogous reaction.

$$C_{12}H_{25}NaSO_4 + H_2O \xrightarrow{\Delta} C_{12}H_{25}OH + NaHSO_4 \quad (1)$$

The Pluronic removal was made using the sensitivity of this class of copolymers against temperature, where decreasing temperature increases its solubility [30]. Thus, after the deposition the samples were previously heated, than cooled (-10ºC) and cleaned with cold water (~0ºC). The images were taken by the Scanning Electron Microscope CARL ZEISS - TOP 55 and the Atomic Force Microscope Dimension 3100.

3. RESULTS

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 (figure 1a). After centrifugation, particles (or poorly dispersed CNT) deposited in the bottom for both samples but in much larger quantities for the 1mg/ml solution, showing that at this concentration range, CNT are no longer dispersed. SDBS solutions showed the best results: with 0.1 and 1mg/ml of CNT, both solutions seem homogeneous with small deposits after centrifugation. The 5mg/ml solution, however, separated into two phases after the first spin. This improved solubility agrees with the conclusions of reference[31]. 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 (figure 1b). The lower solubility of PE6400 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.

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

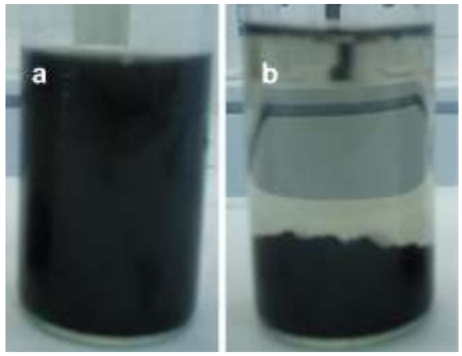

Figure 1 - a) SDS 1mg/ml before centrifugation: homogeneous; **b)** PE6400 before centrifugation, after a few hours: two phases.

Alignment. The five stable solutions, SDS 0,1mg/ml, SDBS 0,1 and 1mg/ml, PE6800 0,1mg/ml (without centrifugation) and dichlorobenzene 0,1mg/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 10Vpp bias and 10MHz 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 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 (figure 2), while the dichlorobenzene (figure 3b) solution showed a completely random deposit with a distorted unidentified structure above it. The PE6800 (figure 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.

CNT concentration: the deposit made with the SDBS solution with 1mg/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.

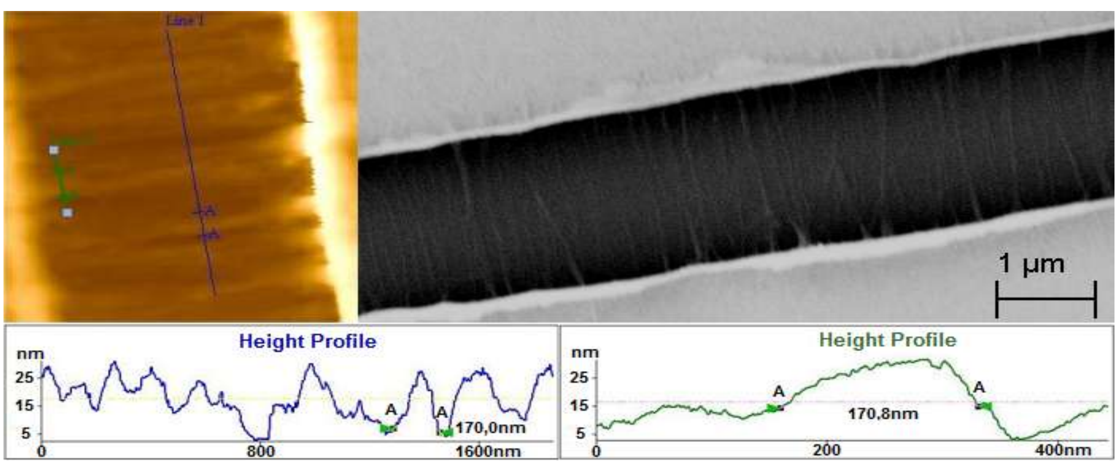

Figure 2 – SEM image (on top) and AFM image (at the bottom) of the deposit on a 2µm *gap* of SDS with 0,1mg/ml of CNT at 10MHz and 10Vpp bias.

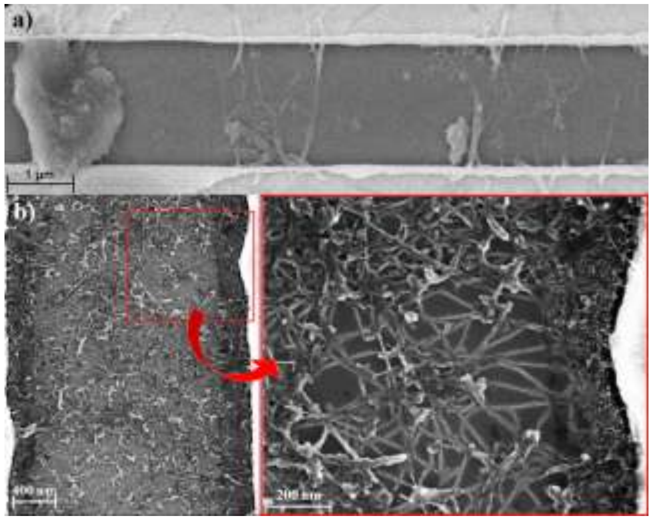

Figure 3 – a) PE6800 with 0,1mg/ml of CNT at 10MHz and 10Vpp bias: region of CNT filled with impurities. **b)** Dichlorobenzene with 0,1mg/ml of CNT at 10MHz and 10Vpp bias.

Frequency: The increased frequency of the AC electric field to 16 MHz (figure 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 (10Vpp with $4V_{DC}$) a sudden but substantial distortion in the orientation of the membrane and a greater number of impurities (as well as CNT) appeared (figure 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 15MHz, the CNT between the electrodes are still in a huge amount (Figure 7a) as in the test at 15MHz 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.

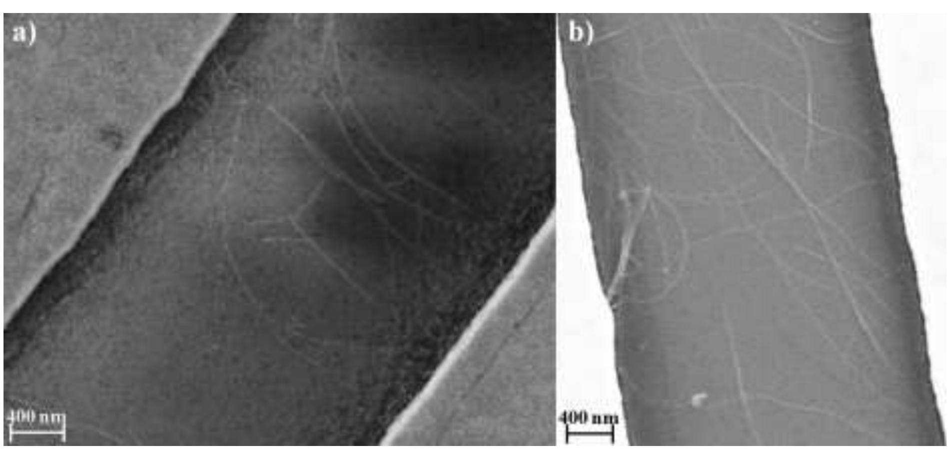

Figure 4 – a) SDS at 16Vpp bias and **b)** PE6800 at 20Vpp bias.

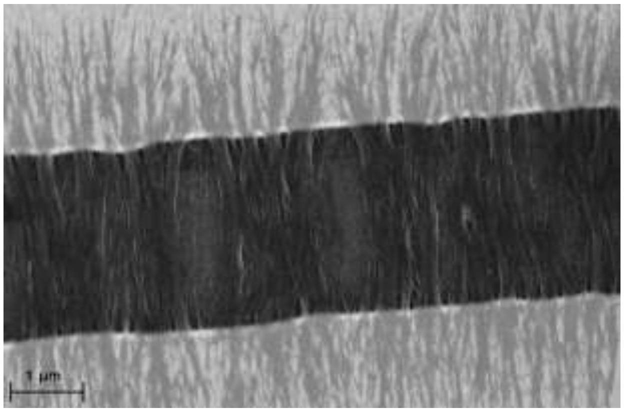

Figure 5 – SDS at 16MHz (0,1mg/ml of CNT at 10Vpp bias). Several “ropes” of well aligned CNT, apparently overlaid at different heights.

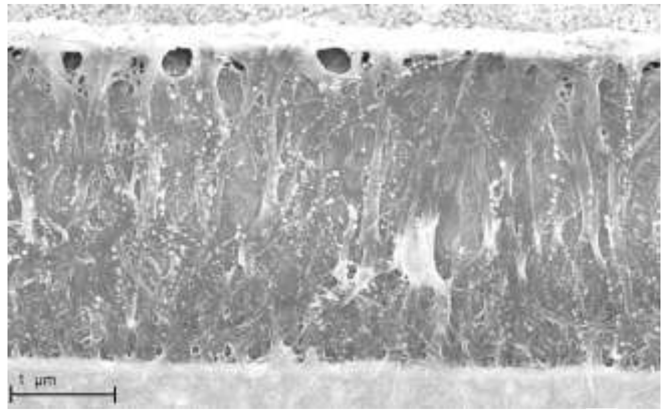

Figure 6 – SDS with 0,1mg/ml of CNT at 10Vpp/4V_{DC} bias and 10MHz.

A further frequency increase to 20MHz (keeping a 10Vpp/2V_{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 (Figure 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".

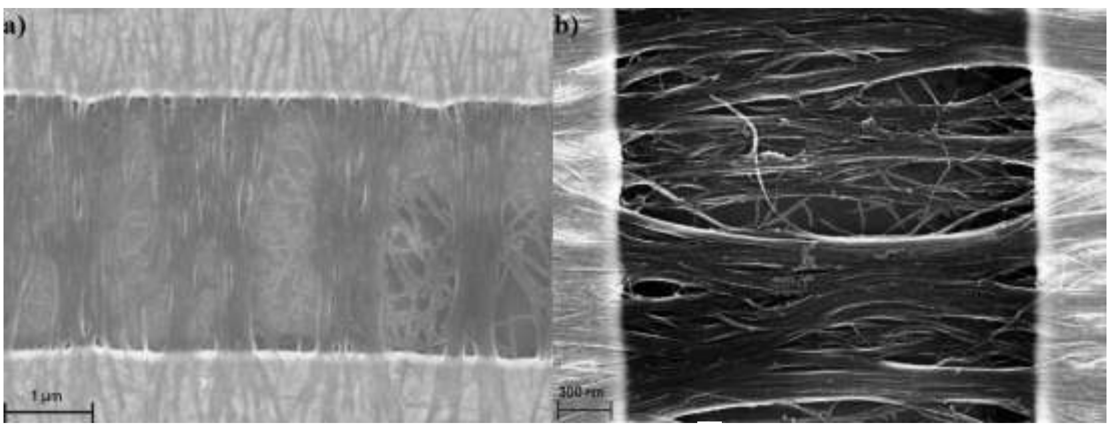

Figure 7 – a) SDS with 0,1mg/ml de CNT at 10Vpp/2V_{DC} and 15MHz bias in a 2µm; **b)** Larger but still thin “ropes” (SDS with 0,1mg/ml of CNT at 20MHz and 10Vpp/2V_{DC} bias).

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 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. 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]:

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