Amonia plasma functionalization of carbon nanotubes for supercapacitor applications

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Abstract: The modification of the surface of carbon nanotubes grown by plasma enchanced chemical vapour deposition with a plasma treatment allows the alteration of their supercapacitor properties. The modified nanotubes show a noteworthy increase in their specific capacitance from 4.2 mF up to 8.2 mF using cyclic voltammetry at a scan rate of 50 mV s^{-1} in a Na_2SO_4 solution. Furthermore, the increased capacitance of the nanotubes was also studied in galvanostatic charge-discharge experiments, which showed a capacity increment from 1.9 mF up to 3.2 mF.

I. INTRODUCTION

The recent and speedy development of nanotechnology and material science has opened up a wide range of opportunities to explore new applications and treatments for nanomaterials. Nowadays, carbon nanotubes (CNTs) are considered a fundamental contributor in current nanotechnology and possess an extensive scope of utilizations, including conductive and high-strength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices [1]. As far as this study concerns, the use of carbon nanotubes has facilitated the progression of micro-electrochemical capacitors, permitting flexible and adaptable devices to be made [2].

The above-mentioned applications are well justified when considering the unique properties of this material. Carbon nanotubes consist of empty cylinders of graphite sheets. They can be understood as single molecules, in relation to their small size ($\sim$ nm in diameter and $\sim \mu$m length). There are infinitely many ways to roll a sheet into a cylinder, resulting in different diameters and microscopic structures of the tubes. CNTs can be classified as single-wall (SWCNTs) or as multi-wall carbon nanotubes (MWCNTs). SWCNTs consist of tubes made of a single graphite layer rolled up into an empty cylinder, while MWCNTs are tubes comprising several, concentrically arranged cylinders. [3] CNTs may behave either as a metal or as a semiconductor with ballistic conduction, and MWCNTs have a band gap of 0 eV. CNTs have a Young's modulus of around 1 TPa, possess an extremely high tensile strength and are up to 100 times stronger than steel [4].

In order to take profit of the properties of this material, it is important to take into account the generation of amorphous carbon as a byproduct during the growth of CNTs, which can appear as an obstacle for some applications. This non-desirable byproduct can be evaded and eliminated by modifying the surface. These treatments must be careful with their impact, as they should only modify the CNTs surfaces. Some previous studies have implemented a great variety of treatments, such as plasma oxidation [4] [5], photooxidation, ozone oxidation and electrowetting [6].

There are various methods of growing CNTs, such as Chemical Vapor Deposition (CVD), arc discharge, Pulsed Laser Deposition (PLD) and Plasma-Enchanced Chemical Vapor Deposition (PECVD). This one is the one used in our study. The CVD technique exploits a carbon font (CH_4, CO_2, C_2H_2) in the gas and plasma phases or a resistively high-temperature coil, in order to transmit the energy to the gas carbon molecules. The mechanism breaks the molecule and permits the obtaining of atomic carbon. Then, due to a diffusion process, this atomic carbon reaches the substrate, previously heated and covered with a metal catalyst, and gets attached to it. Some important parameters in the CVD method are the temperature, the pressure, and the volume and concentration of carbon fonts.

Regarding to PECVD method, this includes a glow discharge in a reaction compartment through a high-frequency voltage applied to both of the electrodes. In the PECVD technique, a substrate is introduced on the grounded electrode. With the goal of forming a regular film, the reacting gas is introduced from the opposite plate. By sputtering (or by CVD technique), catalytic metals like iron, cobalt or nickel are inserted in Si or SiO_2. Subsequently, when the introduction of the metal particles is finished and a substrate is formed, on the metal substrate CNTs are grown by the glow discharge produced by a high-frequency power source. A gas which contains carbon, like C_2H_2, CH_4, C_4H_2, C_4H_6 or CO is introduced to the closed compartment throughout the glow discharge. Some important parameters in the PECVD method are the catalytic material, the growth temperature, the temperature gradient between the catalytic particle and the plasma technological parameters. [9]

As far as this study concerns, plasma treatments are a good option to eliminate the amorphous carbon from CNTs because of its effectiveness. Also, they are a good option as this method has the benefit to be nonpolluting, which is valuable for an industrial production. The

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FIG. 1: Picture of the PECVD reactor used to create the CNTs involved in this study. The arrows show, from left to right: the place to introduce the sample inside the closed compartment and three different heads; one for iron sputtering, one for silicon sputtering and one for heater and PECVD reaction. [9]

effects on the surface and bordering zones can be controlled with the intensity of the plasma. The excited species found in the plasma, such as radicals, electrons and ions can interact with the particles in the surface of CNTs, and are able to have a variety of consequences as breaking the carbon bonds and creating sites where new radicals are bonded.

In this study MWCNTs were altered with ammonia (NH_3) plasma. Previous studies have carried on experiments involving MWCNTs with nitrogen plasma or water plasma treatments. [4][5]. In those, the plasma treatment was controlled with the operational parameters of the plasma pressure and the plasma power.

II. EXPERIMENTAL

A. Production of VA-MWCNTs

Vertically aligned MWCNTs were grown by PECVD technique over a graphite substrate. The steps in order to grow the VA-MWCNTs were the following:

- Cathode sputtering by iron magnetron process using an argon flow, which is equivalent to an iron layer of 2 nm.
- Annealing process, involving an hidrogen atmosphere
- PECVD process: two different (acetylene and ammonia) plasmas were used in this process.

The growth parameters in the three processes are shown at Table 1.

Sputtering parameters	Value
Ar flow	135 sccm
Plasma power	50 W
Time	50 s
Pressure	0.02 mbar
Annealing parameters	**Value**
Time	750 s
Final temperature	750 ^{o}C
Pressure	2 mbar
H_2 flow	100 sccm
PECVD parameters	**Value**
Pressure	1 mbar
Time	900 s
C_2H_2 flow	100 sccm
NH_3 flow	50 sccm

TABLE I: VA-MWCNTs growing parameters.

B. VA-MWCNTs plasma treatment

In order to remove amorphous carbon from the surfaces of CNTs and to functionalize them with chemical groups present in ammonia, VA-MWCTs were treated with an ammonia plasma. The plasma treatment parameters are shown at Table 2.

Parameter	Value
Plasma treatment time	30 s
NH_3 flow	50 sccm
Pressure	135 Pa
Discharge power	10 W

TABLE II: VA-MWCNTs ammonia plasma treatment parameters.

C. VA-MWCNTs characterization

The morphology of untreated VA-MWCNTs samples were studied by the Field Emission Scanning Electron Microscopy (FE-SEM) technique.

Raman spectroscopy technique was used in order to study the quality of the CNTs in both treated and untreated samples. The Raman spectrum of CNTs essentially shows three typical bands: the tangential stretching G mode (at 1500 - 1600 cm^{-1}), the D mode (at 1330 - 1360 cm^{-1}) and the radial breathing modes (at 100 - 400 cm^{-1}), nonetheless, this last band is not shown at MWCNTs. On the other hand, MWCNTs may also show an extra Raman band at $\approx 1615 cm^{-1}$ named D' that relates with the imperfections on the walls of CNTs. The ratio

of intensities between the D and G bands is defined as:

$$R = \frac{I_D}{I_G} \tag{1}$$

It can be understood as the proportion of structural defects present in the CNTs.

One of the main questions throughout this study is whether the capacity of MWCNTs is modified as a consequence of the ammonia plasma treatment. In order to solve this question, cyclic voltammetry (CV) experiments with treated and non-treated samples were carried out. CV is an electrochemical method that measures the current that occurs in an electrochemical cell with bound conditions where voltage is in excess of that predicted by the Nernst equation. CV is effectuated by cycling the potential of a working electrode, and measuring the resulting current. MWCNTs were used as an electrode, whereas the other electrode used as a reference was one made of silver / silver chloride (Ag/AgCl, 3M KCl). Another electrode consisting on a platinum ring was also used as an auxiliary electrode. The scan rate for CVs was set to 50 mV/s in a 0.1 M Na_2SO_4 bath.

With the goal of obtaining more information about the capacity behaviour among untreated and ammonia plasma treated samples, galvanostatic cyclic charge - discharge experiments were effectuated. These galvanostatic cyclic charge - discharge experiments consist in the application of a constant current to the samples with the intention to charge and discharge between bounded voltage limit values. This allows to calculate the capacity of the samples.

When galvanostatic charge - discharge experiments are analysed in ideal capacitors, the charge and discharge V(t) behaviours must be lineal as the capacity and intensity are constant (the last one because of working in a galvanostatic mode):

$$\frac{dV}{dt} = \frac{I}{C} \tag{2}$$

Thereby, the charge-discharge cycles in ideal capacitors have a triangular shape. In this study, the charge - discharge intensity of the cyclic voltammetries was set to 500 μA.

III. RESULTS AND DISCUSSION

A. FE-SEM images

The FE-SEM images allowed having an insight of the morphological characteristics of non-treated VA-MWCNTs

B. Raman spectroscopy

The G and D bands for treated plasma CNTs show a higher intensity and a downshift in their frequencies. The causes of this downshift are diverse, such as the evacuation of amorphous carbon or a decrease in the diameter of the ammonia plasma treated nanotubes due to plasma etching. The incorporation of nitrogen functional groups is also an agent that causes this downshift.

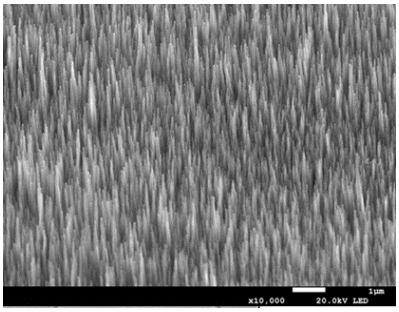

FIG. 2: FE-SEM image of MWCNTs before ammonia plasma treatment.

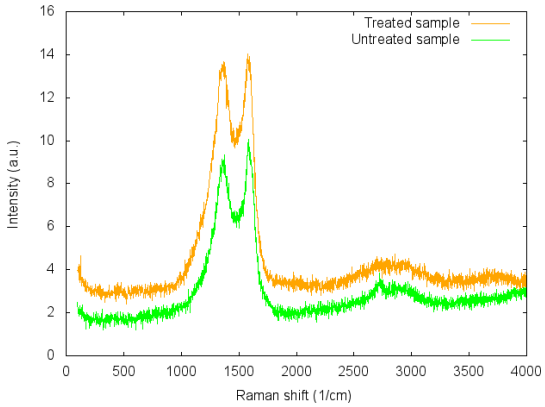

FIG. 3: Raman spectra of untreated and NH_3 plasma treated CNTs samples. In the untreated sample, the D band, the G band and the R ratio had the following values: 1369 cm^{-1}, 1581 cm^{-1} and 0.911. On the other hand, in the treated sample, the D band, the G band and the R ratio had the following values: 1363 cm^{-1}, 1576 cm^{-1} and 0.983.

The R ratio increment is related with an increase of the structural disorder and a presence of nitrogen functional groups in the CNTs, as a result of the effect of the plasma treatment in the nanotubes surface.

There are studies that also altered MWCNTS with an ammonia plasma treatment, [7] [8]. Those have found that the modified MWCNTs present imine, amine, nitrile, and amide groups due to the ammonia plasma treatment, so it is probable that the studied treated samples have had an incorporation of those functional groups.

C. Cyclic Voltammetry

As can be seen at Fig 4, the voltammogram for the untreated sample shows less area than the ammonia plasma treated sample indicating that the capacity is increased

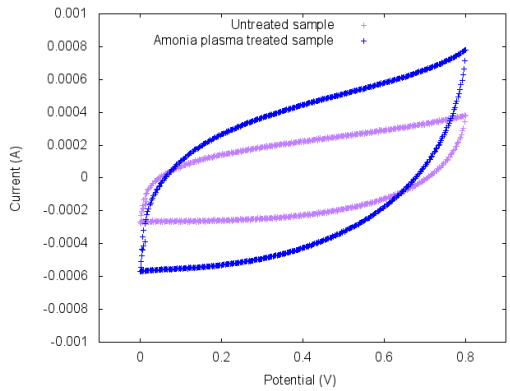

FIG. 4: Cyclic voltammograms of ammonia plasma treated and non-treated samples MWCNTs at a scan rate of 50 mV/s in a 0.1 M Na_2SO_4 solution

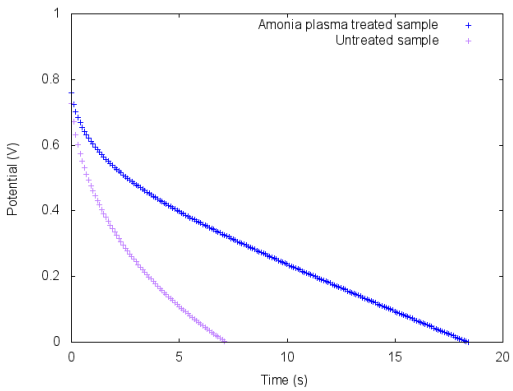

FIG. 5: Comparison between a discharge curve from a charge - discharge experiment involving ammonia plasma treated and non-treated samples MWCNTs with a current set to 500 μA.

with the treatment.

In order to calculate the samples capacities utilising the cyclic voltammetry data, the following mathematical procedure was used:

$$\Delta Q = \frac{\sum I \cdot \Delta t}{2} \tag{3}$$

$$C = \frac{\Delta Q}{\Delta V} \tag{4}$$

The 1/2 factor in the first fraction is caused by the fact that the collected data showed all the cycle and in order to calculate the capacity only half cycle is needed. The voltage was set to $\Delta V = 0.8\,V$.

Sample	Capacity (μF)
Untreated	4166
Treated	8211

TABLE III: Capacitance comparison between non-treated and treated MWCNTs samples using the cyclic voltammetry data.

Table IV shows the values of the capacitances for untreated and treated MWCNTs samples. The capacitance increases from 4.2 mF for untreated MWCNTs up to 8.2 mF for ammonia plasma treated MWCNTs. This growth of the capacity can be explained as a consequence from the introduction of nitrogen functionalities to the MWCNTs walls.

Accordingly to this, functional nitrogen groups, received from the ammonia plasma treatment, boost the charge storage capacities of MWCNTs. Furthermore, this increase in the capacity is also a consequence of the removal of the amorhpous carbon of the MWCNTs.

D. Galvanostatic charge - discharge analysis

As can be seen at Fig 5, it is shown that the discharge curve of the ammonia plasma treated sample is less pronounced than the one of the untreated sample. Qualitatively, the faster the fall of the discharge curve, the less the capacitance, thereby the capacitance is higher in the ammonia plasma treated sample.

As MWCNTs are not ideal capacitors, their discharge V(t) behaviour is not lineal. When this occurs, there may be series resistors, and/or superficial reactions that cause a modification in the measured current.

With the intention of calculating the capacities of both samples, the linear regression of the first 10-15 points was calculated in order to find the slope (which is negative and has units of V/s).

With the calculated value of the slope "$\Delta V/\Delta t$" it is easy to find the capacity using:

$$C = \frac{1}{\Delta V/\Delta t} \cdot I \tag{5}$$

Where I has the value of $I = -0.0005\ A$. With this reasoning, the capacity values obtained are:

Sample	Capacity (μF)
Untreated	1897
Treated	3245

TABLE IV: Capacitance comparison between non-treated and treated MWCNTs samples using the galvanostatic charge-discharge data.

As it happened with the cyclic voltammetry experiment, an increase of the capacitance value of ammonia plasma treated sample is obtained.

Precisely, in the galvanostatic charge-discharge experiment, the capacitance of the untreated sample had a value of 1.9 mF and the capacitance of the ammonia treated sample had a value of 3.2 mF.

Once again, this increase in the capacity of the treated sample is a result of the introduction of functional nitro-

gen groups in the MWCNTs walls and also of the removal of the amorphous carbon from them.

Though the magnitude order for the capacities obtained for both experiments is the same, it is remarkable to meditate the causes of the different values for the same samples. One of the most probable cause is the one related to the fact that they are different methods. Though both methods are evaluating the same physical characteristic, capacitance can show variations depending on the rhythm of the charge injection, which is different in these two methods.

Nonetheless, in the cyclic voltammetry experiment the capacitance increased in a 1.9 factor, while in galvanostatic charge - discharge experiment, this factor has a value of 1.7. Though they are not the same values, one can conclude that generally, the capacity of VA-MWCNTs is increased with the ammonia plasma treatment.

Previous studies carried on similar experiments using MWCNTs untreated and treated with different plasmas (water and nitrogen) [4][5]. They concluded that those treatments produce an increase of the MWCNTs capacity, related to an increase in the structural disorder and to the introduction of new functional radicals. Furthermore, in these articles, as a result of the analysis of Raman spectroscopy, it was found that the diameter of MWCNTs was reduced after the treatment. With this information, we can assume that plasma treatments in MWCNTs generally produce an increase of their capacities.

IV. CONCLUSIONS

VA-MWCNTs were grown by the PECVD method and functionalized by ammonia plasma treatment. This treatment allowed the introduction of different functional groups and the removal of amorphous carbon.

The Raman spectroscopy allowed an insight in the MWCNTs' diameter and in the possible the introduction of functional groups:

- The downshift in the frequencies of G and D bands indicated the evacuation of amorphous carbon, a decrease in the diameter of the treated nanotubes and the incorporation of nitrogen functional groups.

- The increase in the R ratio for treated samples also indicated an increase of the structural disorder and the presence of nitrogen chemical groups.

The cyclic voltammetry experiment showed an increase of the capacity from 4.2 mF for non treated samples up to 8.2 mF for treated samples.

The galvanostatic charge-discharge study also displayed an increase of the capacity. In this case, the capacity goes from 1.9 mF for non treated samples up to 3.2 mF for ammonia plasma treated samples.

Though the values are not the same for these different techniques, a capacity increase is shown in both (by a 1.9 factor in CV and by a 1.7 factor in galvanostatic charge-discharge).

Acknowledgments

I would like thank both of my advisors, Dr. Roger Amade Rovira and Dr. Cèsar Ferrater Martorell for the guidance and knowledge given me throughout this study.

I would also like to thank my beloved family and friends, who have given me a priceless support during all studies in this past years.

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