

Synthesis and electrical characterization of graphene nanowalls electrodes

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Abstract: The aim of this project is to study the electrochemical properties of manufactured electrodes based on graphene nanowalls (GNWs) grown on stainless steel (SS310) by inductively coupled plasma vapor deposition (ICP-CVD). In order to improve the electrochemical characteristics of the electrode, a Mn-oxide/GNWs/SS310 system was deposited by magnetron sputtering (MS) from a target of MnO_2 . The morphology of GNWs electrode and the electrode decorated by Mn-oxide was evidenced by electronic microscopy. In addition, the samples were characterized electrochemically by cyclic voltammetry (CV) and galvanometric charge-discharge cycles (CDG). As a result, a specific capacitance of 0.21 mF/cm^2 was obtained on the GNWs/SS310 electrode and 1.74 mF/cm^2 on the MnO_2 /GNWs/SS310 electrode.

I. INTRODUCTION

Carbon structures have been studied for several years, some of them since their recent discovery due to their vast applications. The main carbon structures are graphite, diamond, amorphous carbon and graphene.

Among the novel materials we have graphene. Graphene is a 2D monolayer structure with a hexagonal form and a distance between carbon atoms of 0.142 nm [1,2]. These graphene monolayers can be stacked up to ten times and it will continue exhibiting the main characteristics of graphene. Graphene is primarily known for its promising optical, electrical, and mechanical properties. The first time graphene was isolated, was separating layers of graphene from a graphite structure. The technique used to separate the graphene layers was stripping Scotch tape previously attached on a pyrolytic graphite block. The graphene monolayers stayed glued to the Scotch tape detached from the graphite structure.

Graphene nanowalls (GNWs) are 2D structures made of graphene layers grown on a substrate. These GNWs appear vertically arranged on the substrate and they have characteristic dimensions of the order of few micrometres of height and a thickness of only a few nanometres [3,4]. One of their interesting features is their large surface area in comparison to their volume. GNWs also have numerous and unique mechanical, chemical, electronic, and optical properties. They are known for being highly hydrophobic, with very low reflectance or for their high specific absorbance. Their extremely high electron conductivity and high specific area make them very promising to produce new super capacitors, which could replace or supplement traditional batteries in a near future [5].

II. DEPOSITION TECHNOLOGIES

A. Chemical Vapor Deposition by Inductively Coupled Plasma

The main method used to synthesize GNWs is chemical vapor deposition (CVD), which involves a mixture of hydrocarbon and hydrogen gases to this purpose. These gases are used as source gases for the growth because they

decompose at high temperatures used in CVD. There are mainly two phenomena involved in the growth of graphene layers: diffusion and segregation, which occur during the annealing and cooling of the sample. The solubility of the graphene on the metal substrate is an important parameter to control the adsorption or desorption of the carbon atoms as well as the crystallographic orientation. For that reason, using different metals as substrates can lead to different graphene morphologies.

The main advantage of CVD method is its capability to produce large amounts of graphene structures, but the use of toxic and flammable gases is the main drawback if they are not removed properly, due to their hazardous properties.

The need of high temperatures limits the CVD application because some substrates can be damaged. Plasma enhanced chemical vapor deposition (PECVD), solves this problem. In a PECVD process, the energy from the power source is transferred to free electrons, so they are in very high temperatures because of their lightness. The neutral atoms remain at the ambient temperature. The collision of the electrons with the neutrals induce excitation, decomposition, and ionization. It is important to be conscious that the geometry of the reactor directly affects the process [6].

There main reported forms of growing GNWs through PECVD are microwave plasma, inductively coupled plasma (ICP), capacitively coupled plasma (CCP) with H radical injection, very high frequency or VHF plasma with H radical injection, electron beam excited plasma and DC plasma.

The method used to grow GNWs in the present work was radio frequency ICP-CVD at 13.56 MHz on a stainless steel SS310 substrate. The reactor is composed by a tubular furnace to heat the samples, a quartz tube, a vacuum system, and a RF coil surrounding the quartz tube inside the furnace

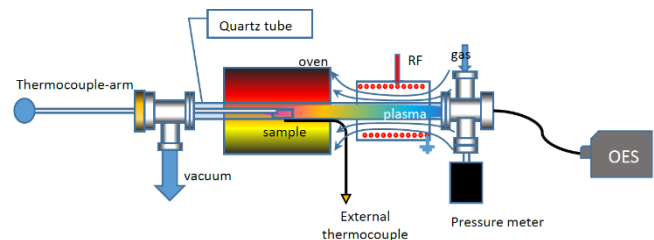


FIG. 1: Schematic figure of the chemical vapor deposition inductively coupled plasma system used in the present work [14].

(Fig. 1). The coil is made of a copper tube (5 mm diameter) with a total length of $\lambda/4$. The antenna was connected to an RF power supply and a matching box made of capacitors and inductances. Its purpose is to induce the plasma generation by creating an induced electric field inside the quartz tube. The reason why the length of copper tube is $\lambda/4$ is to produce a steady wave in a resonance configuration. The imaginary impedance of the matching box is variable and must be tuned (automatically reached) in order to achieve that the impedance of the set plasma and the antenna ($Z_p = R_p + iX_p$), together with the impedance of the matching box, has an input impedance of 50Ω , thus avoiding reflected power back to the power supply.

Firstly, a hydrogen plasma of 30 s was done to clean the surface of the substrate. Then, a 30 minutes methane plasma was done at $750 \text{ }^\circ\text{C}$. Finally, an oxygen plasma was done to activate the hydrophilic properties of the GNWs. The sample was horizontally positioned with an inclination of 5° against the incoming gas flow.

B. Magnetron Sputtering

Magnetron sputtering (MS) process is widely used to make coatings and thin film depositions. It is a technique that is classified as physical vapor deposition (PVD). The sputtering process consists on a target (cathode) bombarded by energetic ions from a plasma. The bombardment generates erosion on the target and ejection or “sputtering” of atoms from itself. These ejected particles condense and form a thin film on the substrate, located in front of the target. Secondary electrons are also created, and they help to keep the ionization process into the plasma. In early sputtering processes they were limited by their slow deposition rates, low ionisation efficiencies in the plasma and overheating of the substrate [7].

The use of a magnetron behind the cathode establishes a system of confinement of the movement of the secondary electrons in the vicinity of the target attached to the cathode. One of the most common magnetron configurations consists of a magnet positioned at the central axis of the target forming a pole and the other pole is formed by a ring of magnets around the edge of the target. The confinement of secondary electrons increases the probability of an ionising collision between an electron and a neutral atom. As a result, the density of the plasma in the target region is significantly higher than in basic sputtering, enhancing the deposition rates at the substrate as well as allowing lower operating pressures and lower operating voltages [7].

The sputtering process was made at room temperature, with a RF power supply (set to 13.56 MHz) of 125 W with a duration of 400 s with 9 cm of distance between substrate and target. The gas used to produce the plasma was Argon at a pressure of 1.0 Pa, kept constant by using a motorized conductance valve controlled by a capacitive pressure meter.

III. CHARACTERIZATION TECHNIQUES

To characterise the samples two electrochemical measurements were conducted: cyclic voltammetry (CV) and galvanostatic charge/discharge (CDG). High resolution electronic microscopy and a Raman spectroscopy were also conducted. Both electrochemical techniques use the same experimental measurement system. Three electrodes are immersed in a solution or electrolyte. One of the electrodes is the working electrode that consists on the material that is being tested. There is also a counter electrochemical electrode (Pt ring) for passing the current and a reference electrode (Ag/AgCl 3M KCl) with fixed potential throughout the measurement. To characterise the sample known potential or current is applied to the working electrode, and the corresponding response (current or potential) is measured. In both measurements the electrolyte used was 1M Na_2SO_4 at room temperature.

A. Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique that consists on cycling the potential of a working electrode and measuring the resulting current. The potential of the working electrode is compared against the reference electrode whose potential remains constant. During the cyclic voltammogram the current through the working electrode is measured. Ideal capacitors have a rectangular shaped voltammetry and capacitors with resistivity have a tilted rectangular shape. The presence of peaks is related to redox reactions and/or a pseudocapacitor (PS) behaviour, namely surface redox reactions at the electrode/electrolyte interface. The specific capacitance per area unit, C_s , can be obtained using the following equation:

$$C_s = \frac{q_a + |q_c|}{2A\Delta V} \quad (1)$$

Where q_a and q_c are the anodic and cathodic charges in C respectively, A the surface of the sample in cm^2 and ΔV the potential window applied in V.

B. Charge/Discharge Galvanometry

A charge/discharge galvanometry (CDG) is an electrochemical technique that consists on maintaining a constant current through the working electrode to measure the charge and discharge cycles. The potential of the working electrode is measured during these cycles as well as the time. On electrochemical double-layer capacitors (EDLCs), due to the lack of surface redox reactions the discharge cycle has a linear response. In PS the contribution of surface redox reactions to the overall capacitance is higher so the response has a curvature. The general criteria to calculate the specific capacitance is to only consider the first half of the discharge cycle.

$$C_s = \frac{I}{(\Delta V/\Delta t)A} \quad (2)$$

Where I is the current applied during the charge in A, ΔV is half the voltage difference in V during the discharge process, Δt the discharge time in s during ΔV and A is the area of the sample in cm^2 .

C. High-Resolution Transmission Electron Microscopy

High-resolution transmission electron microscopy (HRTEM) is based on a regular transmission electron microscope (TEM) but specialized on imaging the atomic structure of the sample.

TEM basic pieces consist on a vacuum chamber, an electron gun, and magnetic lenses. The vacuum chamber purpose is to increase the mean free path of the electrons from the gun to avoid them to collide residual gas or other particles. The electron gun emits electrons directly into the sample and a sensor under the sample measure the transmitted electrons through the studied material. The magnetic lenses are made to emulate optical lenses and they focus the electron beam into the sample. Electron microscopy is widely used in submicron systems it does not have the limitations associated with the long wavelength of optical microscopes.

D. Raman spectroscopy

Raman spectroscopy is based on the inelastic scattering of a monochromatic light source, usually a laser. The sample scatters elastically and inelastically the radiation from the laser. When the radiation is scattered elastically is called Rayleigh scattering and if it is scattered inelastically it is also known as Raman scattering. Raman scattering can occur with vibrational, rotational or energy molecule changes. Most of the scattered radiation is elastic so the Raman radiation is weak. When the Raman radiation interacts with the sample it changes its energy to a higher (Stokes Raman scattering) or lower level (anti-Stokes Raman scattering). This energetic change is used to characterise the sample and obtain its "fingerprint" [8]. This spectroscopy is complementary with the infrared spectroscopy.

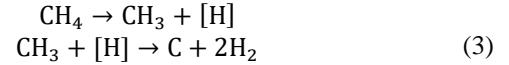
Raman spectroscopy basic pieces consist on a laser, a Rayleigh filter, and a spectrograph. The Raman signal comes from symmetric lattice vibrations unlike infrared spectroscopy which only picks up signal from asymmetric vibrations. For this reason, it is said that both spectroscopies are complementary. Raman spectroscopy is highly sensitive to carbon materials and able to provide information of their structure. It can discern even slight changes in structure making it a very valuable tool in the characterization of carbon nanomaterials [9].

IV. GROWTH MECHANISM OF GNWs AND GNWs/MnO₂

A. Growth of GNWs

Firstly, the substrate absorbs the hydrocarbon radicals, as a result of the decomposition of methane as a consequence of

the high temperature and the plasma. A very thin layer of amorphous carbon is formed. Ion irradiation induces the formation of nucleation sites and enhance the absorption of CH_x (1-3) and C_x (1-3) radicals [10].



The absorbed carbon species diffuse and condense on tiny islands. Graphene nanolayers start growing and nucleating at these islands with random orientations. The reactive carbon particles continue bonding to the edge of these vertically grown layers, growing into the same direction of the radicals' diffusion and perpendicular to the substrate. While the high sheets keep growing, the low-lying graphene layers do not receive as much as radicals as the high sheets do. In consequence the amount of carbon radicals they receive is significantly lower, so they stop growing while the larger ones keep growing [11].

B. MnO₂ deposition

GNWs are very promising as supercapacitor electrodes due to their high power density and high energy density values. Several studies have been conducted last years about their great performance as electrodes for electrochemical double-layer capacitors or EDLC.

There are three types of supercapacitors: electrochemical double-layer capacitors (EDLC), pseudocapacitors (PC) and hybrids. EDLC electrostatic electrodes use the formation of an electric double layer at the interface between the solid electrode and the ions of the electrolyte, where ions can be reversibly absorbed at the electrode interface. In general, EDLCs are made of carbon material. On the other hand, electrochemical pseudocapacitors use electrodes with rich redox behaviour near the surface region involving electrolyte ions in fast and reversible redox reactions. They are generally made of metal oxides or polymers and have larger specific capacitance than EDLCs. The third group are hybrid capacitors which combine one faradaic electrode as energy source with another capacitive electrode as power source. In general hybrid capacitors have much greater energy density than EDLCs but their limited cyclability is a major drawback [12,13].

V. RESULTS AND DISCUSSION

Two samples were studied and characterised: GNWs and GNWs/MnO₂.

The parameters to grow GNWs in the ICP-CVD were extracted from Arevik Musheghyan work [14] (Table 1). Firstly, a H_2 plasma to clean the surface of the substrate (stainless steel SS310 plate) was done. Then, a plasma with CH_4 was generated to do grow the GNWs. Finally, a O_2 plasma was done to activate the hydrophilic properties to conduct the electrochemical measurements. It is important to

mention that between the CH₄ plasma and the O₂ plasma the sample was cooled down at room temperature.

	Power (W)	Pressure (Pa)	Plasma time (s)	Temp. (K)
Plasma H ₂	400	56	30	293
Plasma CH ₄	400	56	1800	1023
Plasma O ₂	400	56	30	293

TABLE 1: Basic parameters of the plasmas done to the sample.

The power source was a RF power supply with a frequency of 13.56 MHz and the sample was tilted 5°. Before the deposition was done the mass and the dimensions of the substrate were measured. Then the mass was measured again to know the mass of the deposited GNWs. The thickness of the GNWs were also measured using a profilometer. As a result, 2.9 mg of GNWs with a thickness of 653.2 nm were grown on a stainless steel (SS310) foil 0.10 mm thick and 38.3 mm × 50.8 mm.

To check that the deposited element was really graphene Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) (JEOL2100 with an accelerating voltage of 200kV) were conducted. The Raman spectroscopy shows the typical peaks for GNWs, the D band at 1346 cm⁻¹, the G band at 1582 cm⁻¹, and the D' at 1621 cm⁻¹. We can also find the 2D band at 2700 cm⁻¹ related to the presence of few layers of graphene and a G+D band at 2959 cm⁻¹ (Fig. 4) [15].

On the other hand, the HRTEM images (Fig. 3) show an interplanar distance of 0.345 nm and knowing that the characteristic interplanar distance on graphene is 0.335 nm [16] it confirms that it is graphene indeed. The difference between the two numbers is attributed to a wrong microscope focus and calibration.

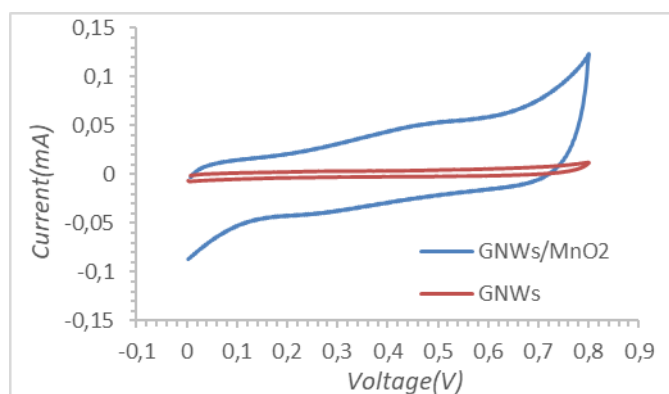


FIG. 2: Cyclic voltammetry of GNWs and GNWs/MnO₂ samples at a scan rate of 50mV·s⁻¹

The substrate with the GNWs was cut into to identic squares, one of them to be deposited with MnO₂ in the magnetron sputtering. The sputtering was done following the parameters of the Michał A. Borysiewicz paper [17].

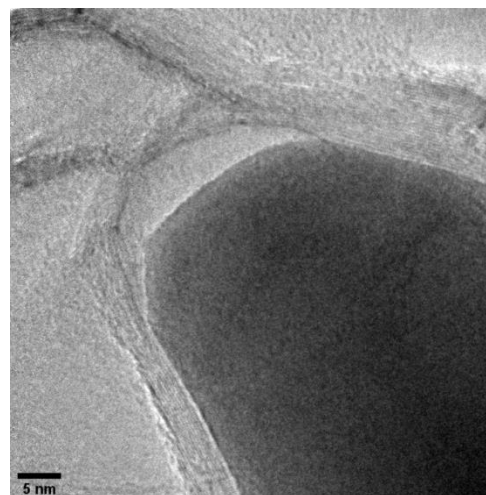


FIG. 3: Image of the GNWs made by HRTEM. It can be seen an iron particle as well as the nanowalls. From the HRTEM we can estimate the thickness of the wall.

The power source was a RF power supply at 13.56 MHz set to a power of 125W at a pressure of 1 Pa and the gas used to create the plasma was Argon with a mass flow of 10 sccm. The unit measure sccm or standard cubic centimetres per meter corresponds to the volume at room temperature and at 1 atm pressure. The plasma was performed at room temperature with a pressure of 1 Pa during 400 s. The distance between the MnO₂ target (attached on cathode) and the sample was 9 cm.

After the sputtering process was done, the mass of the square with GNWs/MnO₂ was 0.3005 g while the mass of the square done before with only GNWs was 0.2939 g.

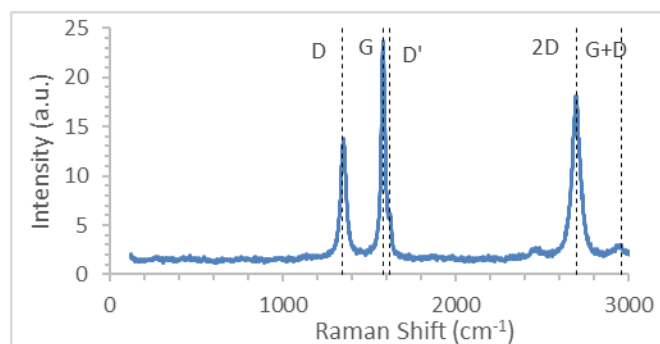


FIG. 4: Raman spectroscopy of the GNWs sample

A. GNWs

A CDG and a CV were performed on the sample to measure the specific capacitance of the GNWs sample. The CDG was performed with a current of 10 μA and the capacitance was calculated only from de discharge curve because the charge-discharge cycle is asymmetric. As a result, a capacitance of 0.21±0.03 mF/cm² was obtained combining the data from the two electrochemical characterizations. Capacitances were calculated through equations (1) and (2).

B. GNWs/MnO₂

A CDG and a CV were also performed on the GNWs/MnO₂ sample to measure its specific capacitance. The CDG was performed with a current of 50 μ A and the capacitance was calculated only from the discharge curve for the same reason as GNWs sample. As a result, a capacitance of 1.74 ± 0.36 mF/cm² was obtained combining the data from the two electrochemical characterizations. Capacitances were calculated through equations (1) and (2).

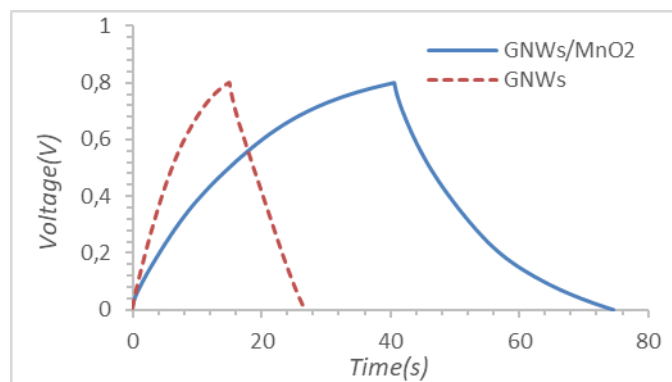


FIG. 5: CDG cycle of GNWs at 10 μ A and GNWs/MnO₂ at 50 μ A

VI. CONCLUSIONS

An electrical study focused on the capacitance of the GNWs and GNWs/MnO₂ samples was done by growing the GNWs with ICP-CVD and depositing the MnO₂ with a MS. An important result was obtained, and it is that the presence of thin layer of an oxide such as MnO₂ on a EDLCs such as GNWs enhances the specific capacitance. MS is a great technique to control the parameters of the MnO₂ deposition and the thin films have high purity. Compared to other techniques such as electrochemical deposition MS deposition rate is slow, but MS capability of great control of the deposition parameters and its high-purity thin films make it an interesting alternative.

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- [1] Koshino M. «Interlayer screening effect in graphene multilayers with ABA and ABC stacking» *Phys. Rev. B* 81, 760-762, 2010
- [2] Lui CH, Li ZQ, Chen ZY, Klimov PV, Brus LE, Heinz TF, «Imaging Stacking Order in Few-Layer Graphene», *Nano Lett.* 11, 164–169, 2011
- [3] Kondo S. and Hori M. «Highly reliable growth process of carbon nanowalls using radical injection plasma-enhanced chemical vapor deposition», *Journal of Vacuum Science & Technology*, 26, 1294-1300, 2008
- [4] Ni, Z.; Wang, Y.; Yu, T.; Shen, Z. «Raman spectroscopy and imaging of graphene» *Nano Res.*, 1, 273–291, 2008
- [5] Somnath Bharech and Richa Kumar, «A Review on the Properties and Applications of Graphene», *Journal of Material Science and Mechanical Engineering*, 2, 70-73, 2015.
- [6] Olayinka O., Esther T., Oluseyi P, Stephen A. and Albert U. «Overview of thin film deposition techniques», *AIMS Materials Science*, 6(2), 174–199, 2019
- [7] P.J. Kelly, R.D. Arnell «Magnetron sputtering: a review of recent developments and applications» *Vacuum* 56, 159-172, 2000
- [8] Smith E, Dent G, «Modern Raman Spectroscopy- A Practical Approach», *John Wiley & Sons Ltd, Chichester*, 835-835, 2005
- [9] Joe Hodkiewicz, «Characterizing Carbon Materials with Raman Spectroscopy», *Thermo Fisher Scientific*, 1-5, 2010
- [10] Denysenko IB, Xu S, Long JD, Rutkevych PP, Azarenkov NA and Ostrikov K, «Inductively coupled Ar/CH₄/H₂ plasmas for low-temperature deposition of ordered carbon nanostructures», *J. Appl. Phys.*, 95, 2713, 2004
- [11] Mineo H., Hiroki K. and Masaru H, «Graphene Nanowalls», *InTech*, 237-255, 2014
- [12] Guihua Yu, Liangbing Hu, Michael V., Huiliang W., Xing Xie, James R. McDonough, Xu Cui, Yi Cui, and Zhenan Bao, «Solution-Processed Graphene/MnO₂ Nanostructured Textiles for High-Performance Electrochemical Capacitors» *Nano Lett.*, 11, 2905–2911, 2011
- [13] Sheng Chen, Junwu Zhu, Wiaodong Wu, Qiaofeng Han, and Xin Wang «Graphene Oxide MnO₂ Nanocomposites for Supercapacitors» *ACS NANO*, 4(5), 2822-2830, 2010
- [14] Arevik M. «Synthesis and characterization of multilayer graphene nanostructures», *Universitat de Barcelona*, 2019
- [15] Hiramatsu M., Shiji K., Amano H., Hori M. «Fabrication of vertically aligned carbon nanowalls using capacitively coupled plasma-enhanced chemical vapor deposition assisted by hydrogen radical injection» *Appl. Phys. Lett.*, 84, 4708–4710, 2004
- [16] Dresselhaus MS, Dresselhaus G, Avouris Ph, «Carbon nanotubes», *Topics Appl. Phys.*, 80, 287-327, 2001
- [17] Michał A. Borysiewicz, Marek Wzorek, Marcin My_sliwiec, Jakub Kaczmarek, Marek Ekielski «Superlattices and Microstructures» *Elsevier*, 100, 1213-1220, 2016