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Tailoring Carbon-Based Materials for Thermoelectric  
Applications

Ana Rita Correia e Sousa

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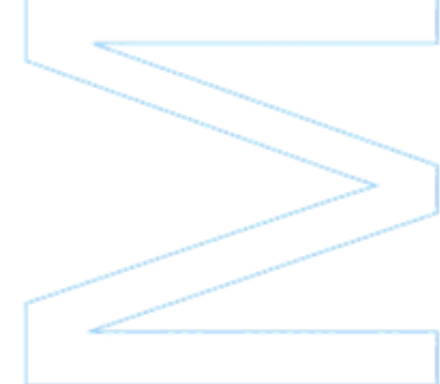
# Tailoring Carbon-Based Materials for Thermoelectric Applications

Ana Rita Correia e Sousa

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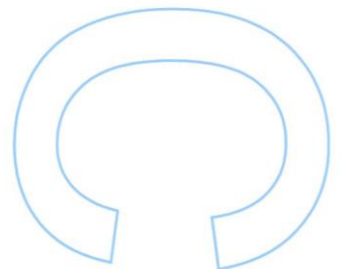
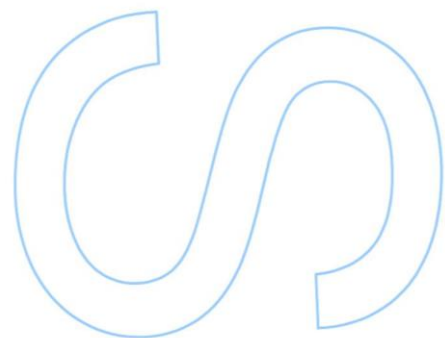
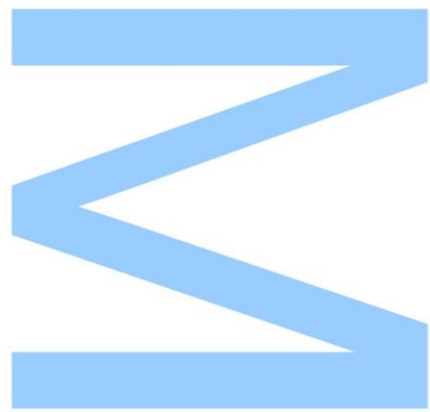
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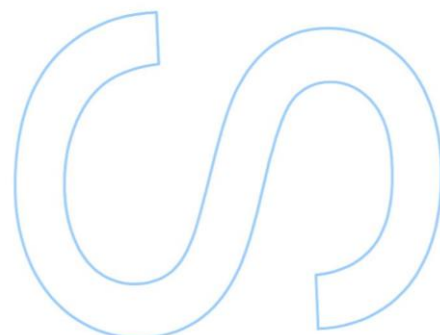
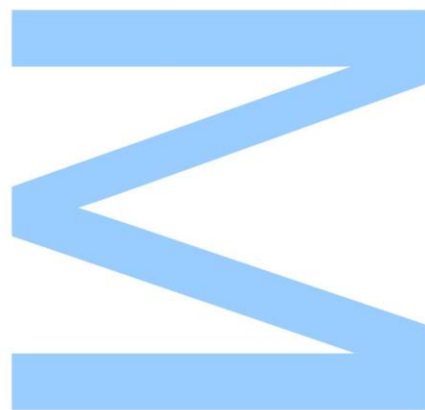




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Porto, \_\_\_\_/\_\_\_\_/\_\_\_\_



University of Porto

Faculty of Sciences

Department of Physics and Astronomy

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# **Tailoring Carbon-based Materials for Thermoelectric Applications**

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*“It is not our part to master all the tides of the world, but to do what is in us for the succour of those years wherein we are set, uprooting the evil in the fields that we know, so that those who live after may have clean earth to till.”*

*J. R. R. Tolkien*

*The Return of the King*



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## Abstract

The constant exploration for innovative means to harvest and produce alternative power energy sources have been a way of boosting the technology to new paths, namely into the Internet of Things project. An ingenious technology that allows to overcome these challenges are the Thermoelectric Generators. These engines, grant the transformation of the thermal energy into electrical energy. Following these trends, this project focuses on the use of carbon-based materials as an alternative to the mainstream inorganic materials that are used nowadays, and tailored them towards tuned transport properties. Nanocomposites, that combine the polymeric advantages with the ones that the carbon materials provide, were used to produce flexible thermoelectric devices through the use of printing techniques.

Firstly, this work addresses several strategies for tailoring carbon-based materials, focusing on graphene and MWCNT. These materials were subjected to different treatments, namely, nitric acid oxidation and nitrogen doping using melamine, heat treatments at different temperatures and mechanic treatments such as ball-milling. The modified materials were thoroughly characterized regarding their morphology, textural and surface properties as well as their transport properties. The results unveil that the treatments applied led to the ability of acting independently on the Seebeck coefficient, electrical conductivity and thermal conductivity thus allowing to tune the thermoelectric features. Moreover, the tuning of these features was promoted by the modification of other intrinsic properties of the materials such as the carrier density, the band structure and the phononic phenomena. Through the tailoring of the MWCNT, it was possible to improve the figure of merit up to 73 times, relative to the starting material, in bulk, to a value of  $55.5 \times 10^{-6}$ , using a nitric acid oxidation at 12 M and ball-milling combination.

It is presented the fabrication of nanocomposites composed of functionalized MWCNT as a filler and PVA/H<sub>3</sub>PO<sub>4</sub> as a binder. It was studied the transport properties of the nanocomposite relative to the weight concentration of filler, where it was applied a percolation model. It was also discovered that the optimal concentration goes towards the (10 – 12) wt. % of carbon material. Additionally, it was studied the nanocomposites using the functionalized MWCNT, from where it was concluded that the transport properties don't follow the same trend as the materials in bulk. Single-mode thermoelectric devices constituted by 10 stripes was produced by a printing process using the functionalized MWCNT. A maximum output power of  $105 \mu\text{Wcm}^{-2}$  was obtained for a  $\Delta T = 10 \text{ K}$ , using the pristine MWCNT, correspondent to a figure of merit of 0.0043.



## Resumo

A exploração constante de meios inovadores para colher e produzir fontes alternativas de energia é um impulsionador da tecnologia para novos caminhos, nomeadamente para o projeto *Internet das Coisas*. Uma tecnologia engenhosa que permite ultrapassar estes desafios são os Geradores Termoelétricos. Tal tecnologia, permite a transformação da energia térmica em energia elétrica. Seguindo estas ideias, este projeto concentra-se no uso de materiais à base de carbono como uma alternativa aos materiais termoelétricos convencionais e otimizá-los. Os nanocompósitos, que aliam as vantagens poliméricas às vantagens dos materiais de carbono, foram utilizados para produzir dispositivos termoelétricos flexíveis através do uso de técnicas de impressão.

Inicialmente, este trabalho explica a modificação de materiais à base de carbono, com foco no grafeno e nos MWCNT. Estes materiais foram submetidos a diferentes tratamentos, como oxidação com  $\text{HNO}_3$ , dopagem com nitrogénio usando melamina, tratamentos térmicos a diferentes temperaturas e ball-milling. Os materiais modificados foram meticulosamente caracterizados quanto à sua morfologia e propriedades texturais, assim como quanto às suas propriedades de transporte. Os resultados revelam que os tratamentos aplicados levaram à possibilidade de atuar independentemente sobre o coeficiente de Seebeck, condutividade elétrica e condutividade térmica, permitindo o ajuste das propriedades termoelétricas. O ajuste destas características foi possível através da modificação da densidade de portadores, da estrutura de banda e dos fenómenos fonónicos. A modificação dos MWCNT permitiu melhorar a figura de mérito até 73 vezes, em relação ao material original, até um valor de  $55.5 \times 10^{-6}$ , utilizando uma combinação de oxidação com  $\text{HNO}_3$  (12 M) e ball-milling.

É apresentada a fabricação de nanocompósitos compostos por MWCNT funcionalizado e PVA/ $\text{H}_3\text{PO}_4$  como material ligante. Foram estudadas as propriedades de transporte do nanocompósito em relação à concentração de MWCNT, onde foi aplicado um modelo de percolação. Também foi descoberto que a concentração ótima se encontra entre (10 – 12) wt.% de material de carbono. Adicionalmente, foram estudados os nanocompósitos usando os MWCNT funcionalizados, de onde foi concluído que as propriedades de transporte não seguem a mesma tendência que os materiais em *bulk*. Os dispositivos termoelétricos foram fabricados com 10 *stripes*, através de um processo de impressão utilizando o MWCNT funcionalizado. Uma potência máxima de  $105 \mu\text{Wcm}^{-2}$  foi obtida para um  $\Delta T = 10 \text{ K}$ , com o uso dos MWCNT originais, correspondente a uma figura de mérito de 0.0043.



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## Symbols

| Symbol     | Name                               | SI unit                          |
|------------|------------------------------------|----------------------------------|
| $\Delta T$ | Temperature Gradient               | K                                |
| $\Delta V$ | Voltage Difference                 | V                                |
| $S$        | Seebeck Coefficient                | VK <sup>-1</sup>                 |
| $zT$       | Figure of Merit                    | Dimensionless                    |
| $PF$       | Power Factor                       | Wm <sup>-1</sup> K <sup>-2</sup> |
| $\sigma$   | Electrical Conductivity            | $\Omega^{-1}\text{m}^{-1}$       |
| $\kappa$   | Thermal Conductivity               | Wm <sup>-1</sup> K <sup>-1</sup> |
| $\kappa_e$ | Electronical<br>Thermoconductivity | Wm <sup>-1</sup> K <sup>-1</sup> |
| $\kappa_l$ | Phononic<br>Thermoconductivity     | Wm <sup>-1</sup> K <sup>-1</sup> |
| $T$        | Temperature                        | K                                |
| $\eta$     | Efficiency                         | Dimensionless                    |
| $P$        | Power                              | W                                |
| $Q$        | Heat                               | W                                |
| $\lambda$  | Wavelength                         | m                                |
| $\theta$   | Angle                              | rad                              |
| $\rho$     | Electrical Resistivity             | $\Omega\text{m}$                 |
| $R$        | Resistance                         | $\Omega$                         |
| $S_{BET}$  | Surface BET Area                   | m <sup>2</sup> g <sup>-1</sup>   |



## Abbreviations

**OECD** - Organisation for Economic Co-operation and Development

**IoT** – Internet of Things

**TE** – Thermoelectric

**TEG** – Thermoelectric Generator

**DOS** – Density of States

**PGEC** – Phonon glass electron crystal paradigm

**CNT** – Carbon Nanotubes

**SWCNT** – Single Wall Carbon Nanotubes

**DWCNT** – Double Wall Carbon Nanotubes

**MWCNT** – Multiwalled Carbon Nanotubes

**m-CNT** – Metallic Carbon Nanotubes

**s-CNT** – Semiconductive Carbon Nanotubes

**vHS** – Van Hole Singularities

**FCCVD** - Floating Catalyst Chemical Vapour Deposition

**CVD** – Chemical Vapour Deposition

**BP** – Buckypaper

**PANI** - Polyaniline

**P3HT** - Poly(3-hexylthiophene)

**PEDOT** - poly(3,4-ethylenedioxythiophene)

**PVA** - Poly(vinyl alcohol)

**PDMS** – Polydimethylsiloxane

**PET** - Polyethylene terephthalate

**PEI** - Polyethyleneimine

**XRD** – X-Ray Diffraction

**SEM** – Scanning Electron Microscopy

**EDS** – Energy Dispersive X-Ray Spectroscopy

**TEM** – Transmission Electron Microscopy

**EA** – Elemental Analysis

**OA** – Oxygen Analysis

**pH<sub>PZC</sub>** – Point of Zero Charge pH

**TPD** – Thermal Programmed Desorption

**TGA** – Thermogravimetry Analysis

**GN** – Graphene Nanoplatelets

**FWHM** – Full Width Half Maximum

**BET** – Brunauer-Emmett-Teller method

**SSA** – Specific Surface Area

**NLDFT** – Non-Local Density Functional Theory

**IUPAC** - International Union of Pure and Applied Chemistry

**RBM** – Radial Breathing Mode

**TCR** – Temperature Coefficient of Resistivity

**VHR** – Variable Range Hopping

**M-VHR** – Mott Variable Range Hopping

**ES-VHR** - Efros-Shklovskii Variable Range Hopping

**FIT** – Fluctuation Inducing Tunnelling



# 1 Introduction

## 1.1 Motivation

The energetic and environmental concerns are a world problem of our society. If in one hand it is predicted an increase in the energy demand, followed by a shortage of fossil fuels, on the other hand, we have the associated issues, such as global warming, that are a threat to our planet's environment. According to the United States Energy Information reports in the International Energy Outlook 2018, it is predicted that the world energy consumption will increase  $\sim 23\%$  (relative to the year 2017) by the year 2040 from  $630 \times 10^{18}$  J to  $776 \times 10^{18}$  J in Non-OECD and OECD nations [1]. This energetic need motivate the replacement of fossil fuels by renewable energy sources [2]. However, this replacement is not enough neither in quantity nor in speed becoming a real necessity the improvement of the efficiency of the existing energy conversion processes which brings the focus on technologies that can reduce the fossil fuel usage while reducing greenhouse gases emissions and diminish the carbon footprint [3]. In this field, the Lawrence Livermore National Laboratory found that around 69% of the United States energy was wasted as heat in 2017, as illustrated in **Figure 1.1**.

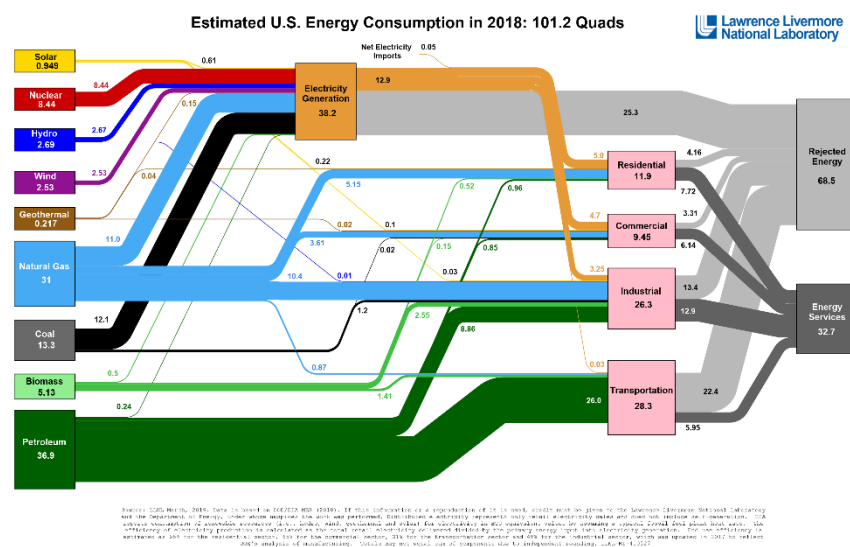


**Figure 1.1.** Estimated U.S. Energy Consumption in 2018 from the Lawrence Livermore National Laboratory [122].

From another point of view, it is also known that technology is in constant development and that the human being is also constantly searching for the next challenge that has the ability of changing and improving our current life-styles. A well-known example of such project is the Internet of Things (IoT). In this thematic, the general goal is to exclude all human intervention in the communication between devices [4]. There is a real necessity for some smart solutions in the energy field since the sensors that will be responsible for the independence of the human intervention will need to be fed and the battery replacement needs to be avoided. The IoT market is in expansion as shown in **Figure 1.2** and there are several applications that can be associated with this project such as fully automated production lines [5] and remote health care [4].

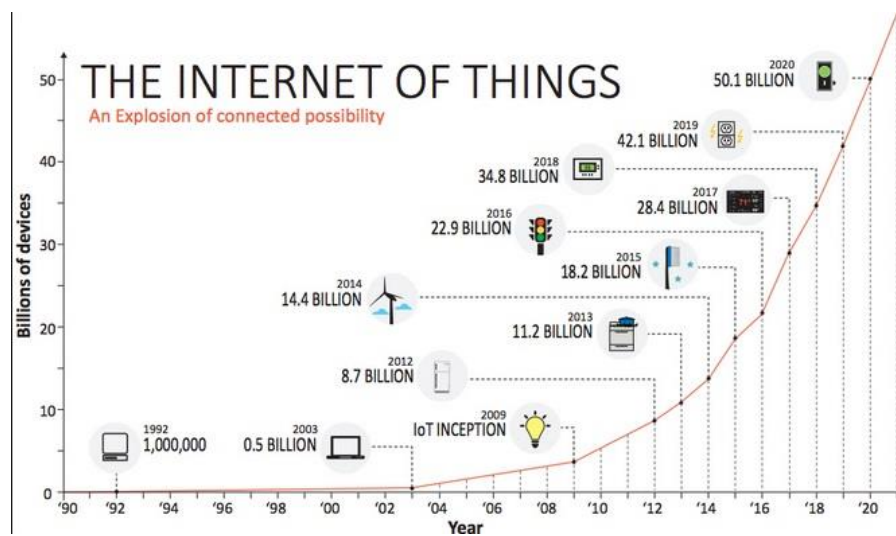


**Figure 1.2.** Prediction of the number of devices growth embedded in the context of Internet of Things [123].

If we considered the two reasons as a whole, the amount of wasted heat that can be harnessed and the needs for energy supplies brought for the emerging IoT market, were a huge opportunity for thermoelectric (TE) devices appeared.

Thermoelectric generators (TEGs) present several advantages such as pollution-free performance, no radiation, solid-state operation, no moving parts, and long lifetime [6]. However, the main issue with the use of TE materials is their reduced efficiency, that can be translated as a diminished figure of merit, making TEGs no competition for traditional generators, despite all the advantages that have been proved in their use in the low power consumption field and in remote locations. The second major problem is the high production cost owing to the fact that the most effective materials, such as tellurides and bismuth, are scarce and have a difficult processing nature not allowing thermoelectric generators to leave the niche market [3].

## 1.2 Thermoelectric Fundamentals

Thermoelectricity refers to the direct conversion of a heat flow into a current flow and vice-versa. Thomas Johann Seebeck first observed it in 1821. The experience was a compass needle near two different interconnected metal wires where a temperature gradient was applied. He observed that the compass needle deflected and that the degree of deflection was proportional to the temperature difference [7]. That was the appearance of the Seebeck effect, which can be explained as a phenomenon that appears when a temperature gradient ( $\Delta T$ ) is applied to a thermoelectric material, where it induces the movement of charge carriers which in turn provokes the production of an electrical current and a voltage difference ( $\Delta V$ ) [8]. Mobile charges tend to diffuse from the hot side (high entropy) to the cold side (low entropy) (**Figure 1.3**). The local accumulations of charges tend to generate a potential difference between both ends of the material.

The Seebeck Coefficient is given by:

$$S = - \lim_{dT \rightarrow 0} \frac{dV}{dT} \quad (1.1)$$

The Seebeck Coefficient, also known as Seebeck voltage or thermopower, is the voltage difference ( $\Delta V$ ) generated in a material for a given temperature difference ( $\Delta T$ ). This way, the Seebeck effect is based on the electromotive force and extraction of majority carriers that could be electrons or holes. The type of the majority carriers, holes or electrons, will define the type of the material, p-type or n-type, respectively.

Later, in 1834, Jean Peltier discovered that the Seebeck effect can be reversed – if a current is applied to interconnected conductors, a temperature gradient can be created at the junctions [9]. This is called the Peltier Effect and it can be used for heating and cooling.

In 1854, William Thomson, also known as Lord Kelvin, discovered that these two effects could be related in one new effect, the Thomson Effect, which could be explained as a reversible heating or cooling when there is an electrical current flowing, in the presence of a temperature gradient [10].

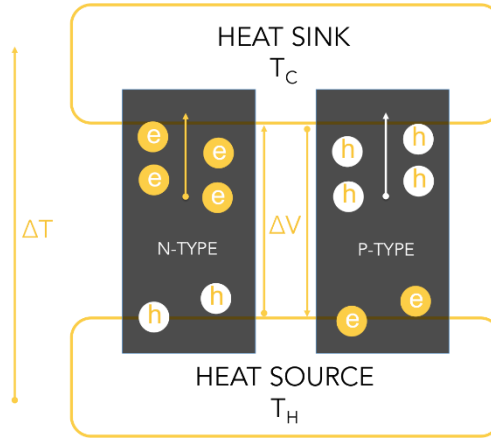


**Figure 1.3.** Schematic representation of the working principle of thermoelectric effect.

### 1.2.1 Figure of Merit

The thermoelectricity efficiency of a TE material is determined by the dimensionless figure of merit, the  $zT$ . Higher  $zT$  means higher efficiency. It can be expressed by the following equation:

$$zT = \frac{S^2 \sigma}{\kappa} T \quad (1.2)$$

where  $S$  is the Seebeck Coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity and  $T$  is the absolute temperature [11]. It is also common to quantify effectiveness of a TE material by the Power Factor, defined as PF, which is expressed by the following equation:

$$PF = S^2 \sigma \quad (1.3)$$

The sign of  $S$  will be positive for p-type materials, where the temperature gradient and the energy flow have the same direction and it will be negative for n-type materials where this direction is opposite. The relationship between the Seebeck coefficient and the carrier concentration, for 3D semiconductors, can be expressed as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \quad (1.4)$$

where  $e$  is the elementary charge,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant,  $m^*$  is the effective mass of the charge carrier and  $n$  is the carrier concentration.

The electrical conductivity can be defined as:

$$\sigma = ne\mu \quad (1.5)$$

where  $n$  is the majority charge carrier density,  $\mu$  is the charge carrier mobility and  $e$  is the elementary charge.

Heat can be carried by charge carriers and by phonons leading to the total thermal conductivity definition as:

$$\kappa = \kappa_e + \kappa_l \quad (1.6)$$

where  $\kappa_e$  refers to the electronic component and  $\kappa_l$  to the lattice component.

It should be noted that the electrical conductivity and the electronic component of the thermal conductivity are related via the Wiedemann-Franz law stated as:

$$\kappa_e = LT\sigma \quad (1.7)$$

and  $\kappa_l$  can be defined as:

$$\kappa_l = \frac{1}{3} C_v v_s \lambda_{ph} \quad (1.8)$$

where  $C_v$  is the heat capacity,  $v_s$  is the sound velocity and  $\lambda_{ph}$  is the phonon mean free path.

Looking to equation (1.2) is obvious that to improve  $zT$ , one should maximize  $S$  and  $\sigma$  while minimizing  $\kappa$ . In fact, the three principal parameters ( $\sigma$ ,  $\kappa$  and  $S$ ) are inter-related and do not have the same dependence on the carrier density (**Figure 1.4**). As so, increasing the carrier density provokes an increase in the electrical conductivity (improve  $zT$ ) and a decrease in the  $S$  (deteriorate  $zT$ ). Maximizing  $S$  can be done through two different ways: minimizing the carrier density  $n$  or increasing the effective mass  $m^*$ . These two ways are impracticable since both can affect the electrical conductivity. There are other interrelated parameters such as  $\sigma$  and  $\kappa_e$ . Improving  $\sigma$  could lead to higher values of  $\kappa$  thus deteriorating  $zT$ , as stated on equation (1.7). Looking at equation (1.8), one can see that the lattice thermal conductivity is the only parameter that is not determined by the electronic structure leading us to the conclusion that reducing the

lattice thermal conductivity is a straightforward strategy for optimizing a TE material. Minimizing  $\kappa_l$  while maximizing  $\sigma$  is known as the “phonon-glass, electron-crystal” paradigm [10], which states that for being good TE materials, they should have a facilitate charge transportation, behaving like a semiconductor crystal, while inhibiting the phononic heat transference behaving like a glass.

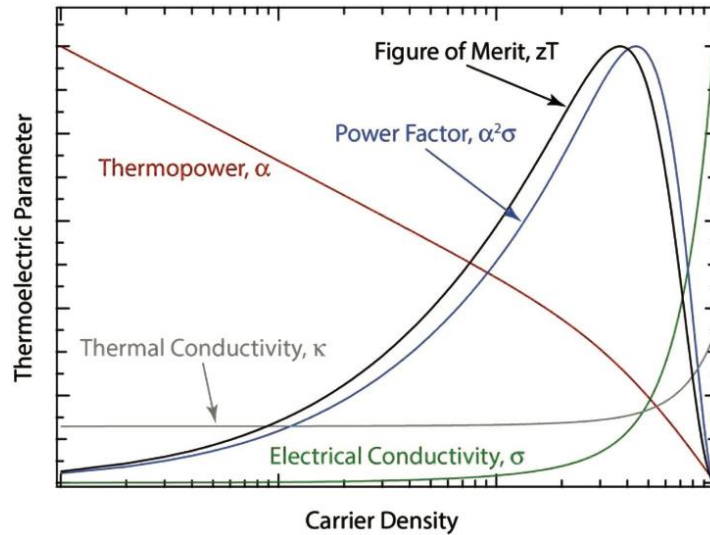


**Figure 1.4.** Schematic showing the interdependence of the various TE properties with carrier density. The individual curves are from real data on s-SWCNT [8].

In the optimization of TE materials it is important to considerate that the  $zT$  value is maximum at a particular value of carrier density (for a given temperature) and it is maximum at a particular value of temperature depending on the material.  $zT$  can be increased through the uncoupling of  $\sigma$ ,  $\kappa$  and  $S$ .

Another methodology for optimizing a TE material is nanostructuring. Nanostructuring can enhance the density of states (DOS) near the Fermi level through quantum confinement, enhancing the thermopower, and it could be a way of decoupling thermopower and electrical conductivity [12].

### 1.3 Thermoelectric Materials

Thermoelectric materials have been widely studied in the past decades. Although all materials have a nonzero thermoelectricity and there is no theoretical limit for the maximum of the figure of merit, the commercial TE materials have a relatively low  $zT$  of 1. As mentioned before, for being considered a good TE material, the material should

display high values of  $S$  and  $\sigma$  and low values of  $\kappa$ . However, other features seem to have a significant importance when choosing a TE material. For example, not being toxic and being environmentally friendly are important and relevant qualities. Having raw material availability and a large-scale manufacture potential looks like a great feature especially for lowering the production costs. Finally, stability is also important, especially high temperature stability (since TE raise efficiency with temperature) and mechanical stability properties, such as strength and toughness.

The most used TE materials are inorganic semiconductors and their alloys. There are several groups of bulk TE materials that are currently under investigation, the most promising ones are Skutterudites, lead chalcogenides (ex: PbSe, PbTe), Clathrates, Oxides (ex: ZnO) and Half-Heuslers (ex.  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ , SiGe). **Figure 1.5** displays the evolution of inorganic TE materials over time and the main events related to the TE field.

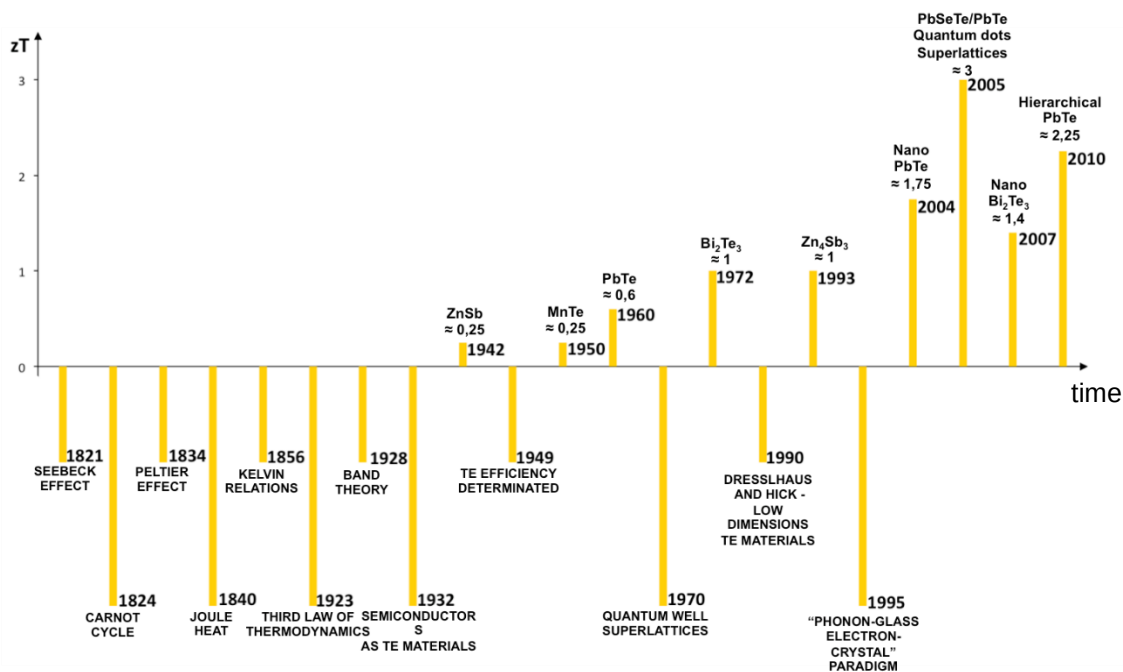


**Figure 1.5.** Schematic representation of the state of the art for inorganic TE materials as a function of the figure of merit (top) and some events relevant for a TE context, as a function of date, based on [8].

Alloying materials (site substitution) with high atomic weight is a fine way of fine-tuning the carrier concentration and improving the phonon scattering, decreasing the thermal conductivity [13]. Heavily doped semiconductors with transport properties like metals such as  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  (that can be doped with Ge, Pb and so on) are the most used TE materials since they have the highest  $zT$  ( $\sim 1$ ) near the room temperature.

The introduction of the PGEC concept as mentioned in section 1.2. arises some new materials such as Skutterudites and Clathrates. In Skutterudites, large voids are filled by heavy atoms, which remain trapped working as phonon scattering centres, reducing  $\kappa_l$

[14]. Clathrates are basically semiconductors with adjustable band gap and consist on regular lattices in which guest atoms are hosted becoming phonon–scattering centres and acting as electrical dopants [15].

Half-Heusler intermetallic alloys are also important TE materials because they are semiconductors with narrow bands that contribute to a large effective mass resulting in a large thermopower [15].

### 1.3.1 Low Structured Materials

Nanostructuring is a methodology for achieving high  $zT$  in a TE material, which suggests that it can be realized through nanoscale or nanostructured morphologies. The improvement of the TE performance of such structures relies on the classical size effect, quantum size effect and the phonon localization contributing to hinder the phonon transport [16]. The decoupling of the thermopower and the electrical conductivity can be done by enhancing the density of states (DOS) near the Fermi level via quantum confinement [17]. In heavily doped semiconductors, the mean free path ( $\lambda$ ) of electrons is shorter than the mean free path of the phonons, as so, nanostructuring is a way of introducing a large density of interfaces for phonons that can be scattered over a large  $\lambda$  more easily providing a reduction in the lattice thermal conductivity while preserving the electrical conduction and the carrier mobility [18], as it can be seen in **Figure 1.6**. This can be achieved through the preparation of nanostructures with one or two dimensions smaller than the  $\lambda$  of phonons while being larger than the charge carriers [19].

In 1993, Hicks and Dresselhaus published two papers revealing that  $zT$  could be dramatically enhanced through the substitution of 3D conventional forms for 1D and 2D structures [8]. As it can be seen in **Figure 1.5**, these publications boost a new TE era where nanoscale materials or nanoengineered interfaces nearly doubled the previous TE performances. Quantum dots, nanowires and layered structures are examples of structures that have been theoretically predicted to have much lower  $\kappa_l$  (implying higher  $zT$ ) than their bulk forms. Nevertheless, Hicks and Dresselhaus also predicted that confining electrons to 2D quantum wells of  $\text{Bi}_2\text{Te}_3$  could lead to  $zT = 6,9$  [20], which was not yet achieved.

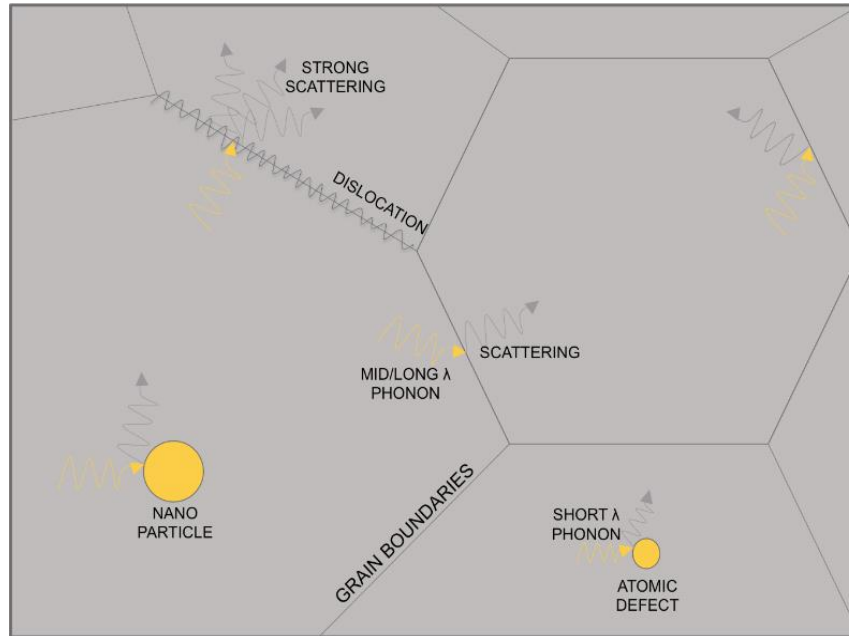


**Figure 1.6.** Schematic representation of the nanostructuring effect in phononic scattering.

### 1.3.2 Carbon-Based Materials

Most of the TE materials discussed above are expensive, scarce, toxic, and mechanically and thermal instable preventing them to be a feasible energy solution. On the other side, carbon-based materials have a range of qualities that heavily contrast with the materials mentioned above. Carbon-based materials are flexible, strong, high-temperature stable, abundant on earth and most of its allotropes are neither toxic nor heavy. The vast variety of allotropes is due to the capability of hybridization in different kinds of bonds ( $sp$ ,  $sp^2$  and  $sp^3$ ) that allow carbon to be in a 0D form (e.g. fullerene), 1D form (e.g. carbon nanotube), 2D form (e.g. graphene) or a 3D form (e.g. diamond) [21]. All these particularities make carbon-based materials of great interest and potential for TE applications.

Several carbon-based materials will be aboard in the course of this work. Some carbon-based materials that will be addressed are represented on **Table 1.1** as well as some properties and some TE relevant studies.

**Table 1.1.** General properties and relevant TE studied summarized for different carbon-based materials.

| Carbon Material  | Properties                                                                                                                                                                                                                          | Thermoelectric Studies                                                                                                                                                                         |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Activated Carbon | Small, low-volume pores;<br>Large surface area;<br>Micropores favours adsorption;<br>Neither metal nor semiconductor; There is some “hopping” of electrons between states located on the band gap; [22]                             | Few to none;                                                                                                                                                                                   |
| Carbon Black     | 95% of pure carbon with minimal quantity of oxygen, hydrogen and nitrogen;<br>Often used for coatings and inks;<br>Paracrystalline with high surface-area-to-volume ratio; [23]                                                     | Some studies used CB as filler to improve physical properties of some polymers: Improvement of $\sigma$ after the use of CB at 2wt.% and $zT$ of 1.21 at 903 K with CB nanoinclusions [24,25]; |
| Carbon Xerogel   | Synthetic material;<br>High porosity, specific surface area and pore volume;<br>Low density;<br>High electrical conductivity; [26]                                                                                                  | Few to none;                                                                                                                                                                                   |
| Graphite         | Regular hexagonal system; Infinite carbon layers $sp^2$ hybridized;<br>Good electrical conductivity due to $\pi$ orbital symmetry displacement;<br>Low thermal conductivity due to weak interlayer van der Waals interactions; [27] | Graphite nanofibers with $zT=3.55$ ; [28]<br>Nanocomposites for improving $\sigma$ , where it was obtained $3.2 \mu Wm^{-1} K^{-2}$ at 380 K with 37.2 wt % of graphite; [29]                  |

### 1.3.2.1 Graphene

Graphene is defined as a unique atomic layer of graphite in a hexagonal crystalline arrangement, as shown in **Figure 1.7.a)**. This planar sheet is formed of carbon atoms  $sp^2$  bonded. Is considered a very good thermal and electrical conductor; actually, it's one of the most conductive materials existent, which makes this material very attractive on a TE point of view. Nevertheless, it also has a very high thermal conductivity that is a major drawback for TE applications obligating scientists to look for strategies for reducing this component recurring to strategies such as nanoengineering, addiction of isotopes, vacancies, nanoholes and dislocations [21].

Graphene is a zero-bandgap semimetal, meaning that the valence band and the conduction band meet at the Dirac points as it can be seen in **Figure 1.7.b)**. Graphene should have small Seebeck Coefficient due to the cancellation of the contributions from

electrons and holes because it has gapless band structure and linear dispersion near the Fermi level. However, one could modify the band structure and move the Fermi level away from the Dirac points, in order to achieve higher values of  $S$ . There are a variety of ways of performing these changes like hole or electron doping, or architecting by cutting graphene into graphene nanoribbons [30].

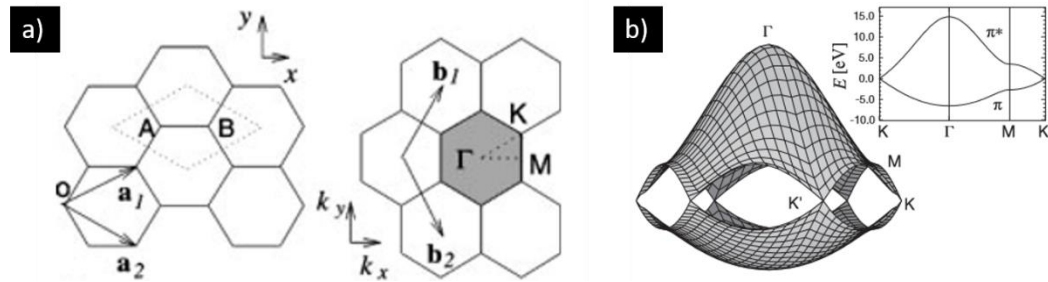


**Figure 1.7.** a) Graphene unit cell and respective Brillouin zone; b) Energy dispersion relations for 2D graphite throughout the whole region of the first Brillouin zone, adapted from [27].

There are some studies performing some type of functionalization with graphene in order to achieve higher values of the figure of merit. Structural defects such as the ones introduced by oxygen plasma treatment were found to have a constant  $zT$  with the increase of the defect concentrations until it reaches a critical value that will decrease the  $k$ , enhancing  $zT$  2.3 times [31].

## 1.4 Carbon Nanotubes (CNTs)

Carbon nanotube is another common form of carbon allotropes with the form of a cylinder. One could define it as a rolled up single, double or multilayer graphene sheet giving origin to single-walled carbon nanotube (SWCNT) double-walled carbon nanotube (DWCNT) or multiwalled carbon nanotube (MWCNT), respectively.

### 1.4.1 CNTs Properties

#### 1.4.1.1 Mechanical Properties

Carbon nanotubes are one of the strongest materials in terms of tensile strength and elastic modulus yet discovered. Their strength is a result of the covalent bond  $sp^2$  between the individual atoms of carbon. However, there are weak shear interactions

between the adjacent tubes and shells, which often decrease their effective strength [32]. CNTs are not strong under compression or bending stress due to their hollow structure [33].

#### 1.4.1.2 Electrical Properties

SWCNT electronic structure can either be metallic (m-CNT) or semiconducting (s-CNT), and it is the “roll-up vector”, or the chiral vector ( $C_h$ ), expressed by the chiral indices ( $n, m$ ) of the nanotube that defines this structure. This vector will define the nanotube chirality as it spans the circumference of the cylinder when the graphene layer is rolled up into a tube, in **Figure 1.8.a)**. There are different classifications: chiral, zigzag and armchair as it can be seen in **Figure 1.8.b)**.

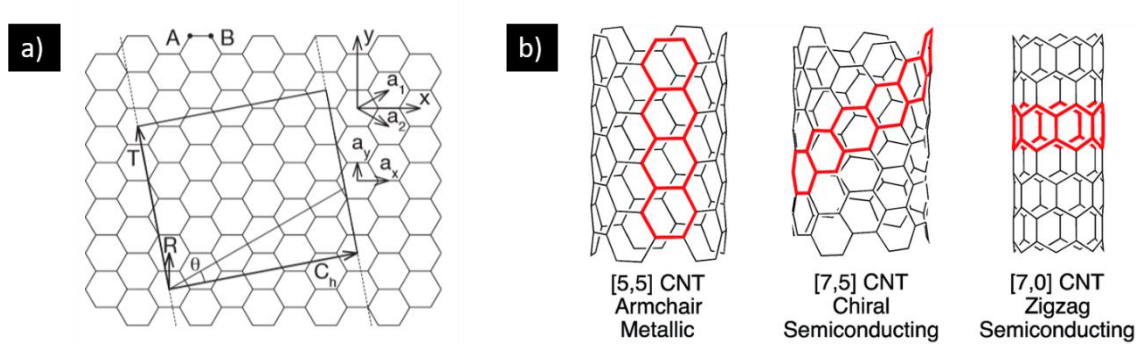


**Figure 1.8.** a) Unrolled nanotube projected on the graphene layer and the chiral vector  $C_h$ , the translational vector  $T$  along the axis and the symmetry vector  $R$ , from [27]. b) Nanotubes classifications, from [124].

If a cutting line passes through a K point of the 2D Brillouin zone placed where the  $\pi$  and the  $\pi^*$  energy bands of 2D graphite are degenerate by symmetry, it means that the 1D energy bands have a zero-band gap, and are defined as metallic. However, if there isn't a cutting line passing through the K point, then the energy gap between the valence band and the conduction band will be finite, and the CNT will be semiconductor [27], as represented in **Figure 1.9**.

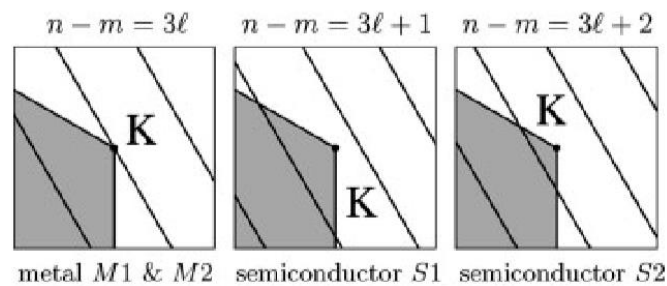


**Figure 1.9.** The different configurations of the cutting lines in the K point surroundings causing them to be metallic (first) or semiconducting (second and third), adapted from [27].

### 1.4.1.3 Thermal Properties

Nanotubes are expected to have a good thermal conductivity along the tube axis while having a good insulation lateral to the tube axis. CNTs have low mass, strong covalent bonds and low anharmonicity of the lattice that assures high  $\kappa_l$ , rendering CNTs to be inappropriate as TE materials in their raw form [34].

## 1.4.2 Functionalization of CNTs

### 1.4.2.1 Importance of the electronic structure

Van Hove singularities (vHS) are singularities in the density of states produced by quantum confinement such as 1D or 2D. Electronic bandgap could be defined as the difference between the first electron and hole vHS and the energy of these vHS will define the first reduction and oxidation potential, respectively. m-CNTs are considered to have a relatively low thermopower due to the nearly constant DOS between the vHS while s-CNTs have been experimentally found to have higher Seebeck Coefficient and the thermopower for mixed networks increased as the concentration of s-CNT increased in the network [34], **Figure 1.10**. It was found by Avery, et al. that the peak of the thermopower of s-CNT was an order of magnitude higher than the one for m-CNT and that the thermopower for s-CNT dramatically rises as the Fermi Energy is moved away from the centre of the gap [35], as implied in section 1.2.1. If the networks were completely formed by s-CNT, the conductivity would be low due to the presence of few

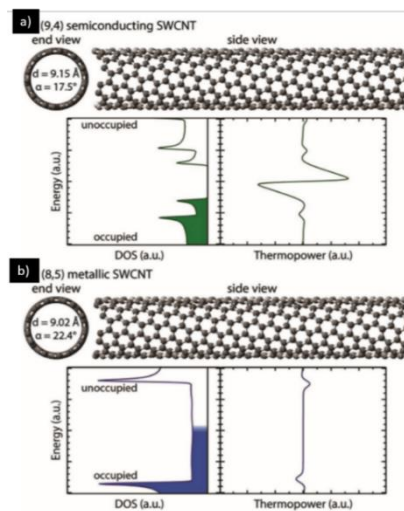


**Figure 1.10.** DOS and thermopower for a) semiconductor SWCNT and b) metallic SWCNT, adapted from [8].

carriers, and vice-versa in the case of m-CNT. Actually, doping s-CNT networks with charge transfer dopants will lead to higher conductivity values than for m-CNT [36].

Some studies predicted that the Seebeck Coefficient is maximized when the chemical potential  $\mu = \pm k_B T$  moves away from the band edges, while it vanishes near the bandgap edge. As so, appropriate doping could be a form of controlling the location of the chemical potential, maximizing the  $zT$  of CNTs [37,38].

#### 1.4.2.2 Doped Carbon Nanotubes

CNTs have both porosity and high surface area that allows accessibility in the surface for the absorption of redox molecules. CNTs have also a “locked in” morphology meaning that immersing the CNT network in a variety of solvents or dopant-containing solutions will not lead to any change in the morphology and will not lead to the creation of  $sp^3$  defects or the modification of the intrinsic band structure. CNTs also possess a  $\pi$  electron system that mediates the redox reactions meaning that there is no need for covalent bonds in order to modify the carrier density by physisorbed molecules [8]. These traits highlight CNTs in contrast to typical inorganic semiconductors.

Generally speaking, Bronsted or Lewis acids produce p-type CNTs networks while Bronsted or Lewis bases create n-type networks [39]. p-type redox dopant should have an electron affinity larger than the ionization potential of the CNT, and n-type redox dopants should have ionization potentials lower than the electron affinity of the CNT.

The carrier density and the Fermi level of CNTs can be modified using charge transfer doping. Physisorbed molecules can affect the carrier density significantly. The TE properties of air-exposed SWCNTs (physisorbed with oxygen) exhibit p-type behaviour in contrast to the degassed ones that exhibit n-type behaviour [40]. There are some concerns about the thermal and environmental stability of the physisorbed dopants since n-type dopants tend to be very unstable in air even at room temperature [8].

**Figure 1.11** represents the state of the art for doped SWCNT (p-type and n-type) in terms of their Power Factor. It should be noted that there aren't a lot of studies with MWCNTs due to their complicated networks that usually provide lower TE performances.

Floating Catalyst Chemical Vapour Deposition (FCCVD) is a method of producing CNTs that stands out by frequently providing higher Power Factor values, as it is reported in the literature. This method produces longer CNTs than the ones produced by typical solution processes that could explain the higher values of the electrical conductivity. It also has a thermal annealing composed of two steps that help with the dispersion of the

CNTs network [41]. Nevertheless, Chemical Vapour Deposition (CVD) is the most practiced method for the growth of CNT where a metal catalyst such as ferrocene is usually used, leaving, sometimes, residual catalyst particles. Buckypaper (BPs) is a preparation method that stands out as well. It is a thin sheet composed of aggregated CNTs. In this method, the CNTs are dispersed by ultra-sonication and the techniques that could be used to manufacture the BPs (e.g. hot-compression, electro-spinning) provide a better transference of stress, electrons and phonons in the network that increase the mechanic, electric and thermal properties [42].

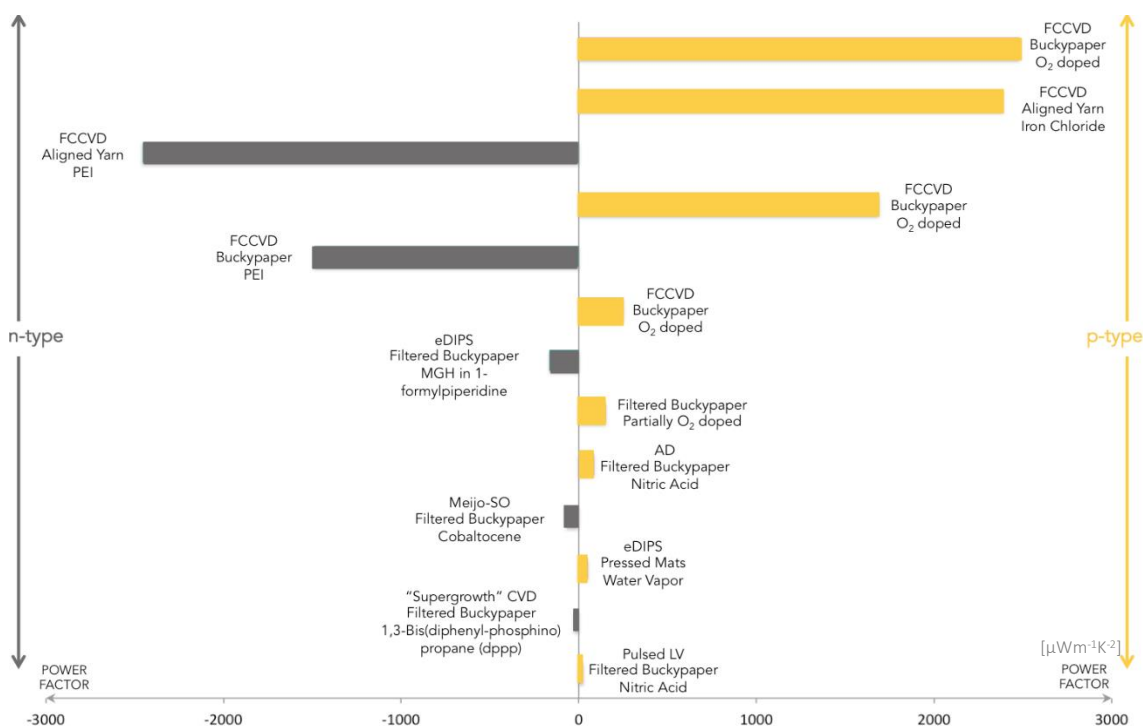


**Figure 1.11.** State of the art represented as the Power factor for treated p-type and n-type SWCNT. Based on the information gathered by Blackburn et al on *Carbon-Nanotube-Based Thermoelectric Devices* [8].

Concerning the thermal conductivity, this is the least understood component of the figure of merit and is not often reported in TE studies, especially on CNT studies due to the difficulty in obtaining an accurate measurement (this being the reason why the state of the art in **Figure 1.11** is represented in terms of the Power Factor). It is often reported that the value of  $\kappa$  is orders of magnitude higher than the value obtained for the  $\kappa_e$  by the Wiedemann Franz law (1.7) implying that the thermal transport is dominated by phonons [43,44]. Some studies even implied that the length of the SWCNTs present in the network determined the thermal conductivity, as longer nanotubes would result in fewer junctions between nanotubes, resulting in a better thermal transport [43]. Avery et

al. conducted a study for s-SWCNT networks where the main conclusions were that the thermal conductivity in SWCNTs could be largely decoupled from the electrical conductivity and that dopant molecules could affect the phonon mean free path, lowering the thermal conductivity [44].

## Acid Treatment - Oxidation

One of the most common doping processes of CNTs is using an acid treatment, especially a nitric acid treatment. This process helps with the removing of amorphous carbon and some catalyst particles that could be present as long as improves the dispersion of the CNTs [44]. Acids containing oxygen dope the CNTs making them more p-type, which could affect the Seebeck Coefficient as well. **Figure 1.12** summarizes how the Nitric Acid treatment could affect the CNTs.

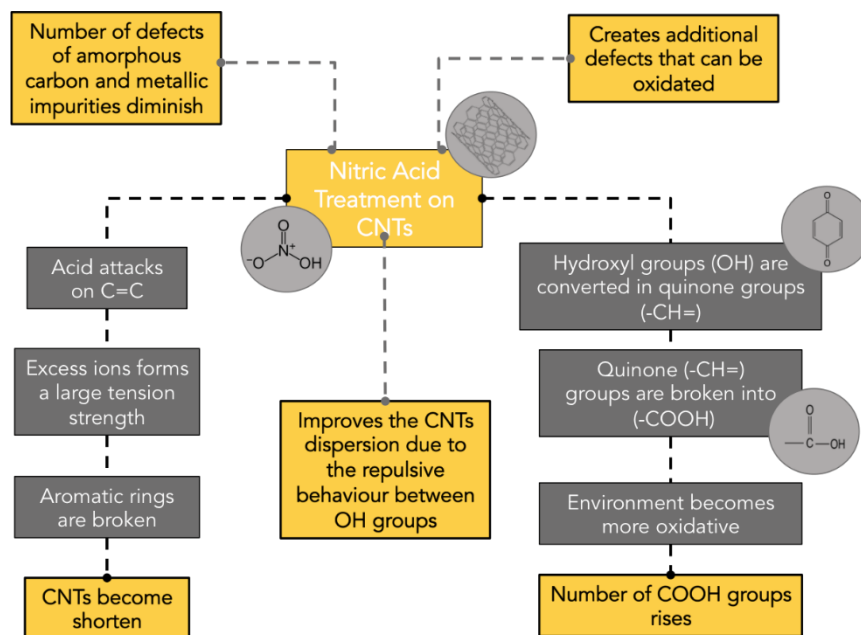


**Figure 1.12.** Diagram summarizing the effects of Nitric Acid on carbon nanotubes.

## Melamine treatment – Nitrogen Doping

It is possible to control the electronic properties by doping CNTs with heteroatoms, introducing electron acceptor or donors in the network [45,46]. Nitrogen could be inserted in the CNTs network due to the similar sizes of carbon and nitrogen atoms [46]. These nitrogen atoms are rich in electrons, providing electrons for the carbon lattice inducing a more metallic or semiconductive behaviour [47].

In a TE point of view, to date there aren't studies done with melamine, however, this type of N-doping has been studied for catalytic purposes [48].

#### 1.4.2.3 Importance of the temperature

While studying a TE material, it is important to study the temperature dependence of  $S$ ,  $\sigma$  and  $k$  aiming to discover the optimal operating temperature range.

Considering a single nanotube, the charge carriers' mobility is high, however, in the junctions between nanotubes there is appreciable resistance. As so, there is a general trend considering the resistance (and inverse for the electrical conductivity) in function of the temperature – a negative temperature coefficient for resistivity. This could be explained by the thermal energy that arises from the temperature increment that allows the carriers to overcome the barriers at the tube-tube junctions. There are some studies that report a negative temperature coefficient for the electrical conductivity above a certain transition temperature, a behaviour characteristic for metals – a phonon-limited transport at higher temperatures [48].

The reports for the Seebeck coefficient dependence on temperature shows that CNTs networks (metallic, semiconducting, mixed or doped networks) tend to increase  $S$  as the temperature increases, both below and above room temperature [49].

Previous studies on single tubes report that below room temperature, the thermal conductivity increases with the temperature and above room temperature,  $\kappa$  decreases as the temperature increases consistent with the Umklapp phonon-phonon scattering behaviour ( $\kappa \propto 1/T$ ) [50,51]. For CNTs networks, there is a decreasing or a relatively constant behaviour in  $\kappa$  as the temperature increases [52].

#### 1.4.3 Carbon- Nanotube- Based TE Composites

In the TE field, polymers have gained attention due to their cheapness, flexibility and facile processing. Regarding their TE performance, polymers are often described as not having sufficient electrical conductivity and higher values of Seebeck effect. Nevertheless, they have an inherently low thermal conductivity.

As a standalone, polymers do not have a remarkable TE performance however they could be used to form nanocomposites containing carbon as a way of dramatically

improving their TE behaviour [53]. Several studies have been conducted in the matter of using polymers (both conductive and insulating ones) and carbon materials to form nanocomposites aiming for a TE application as it can be seen in **Figure 1.13**.

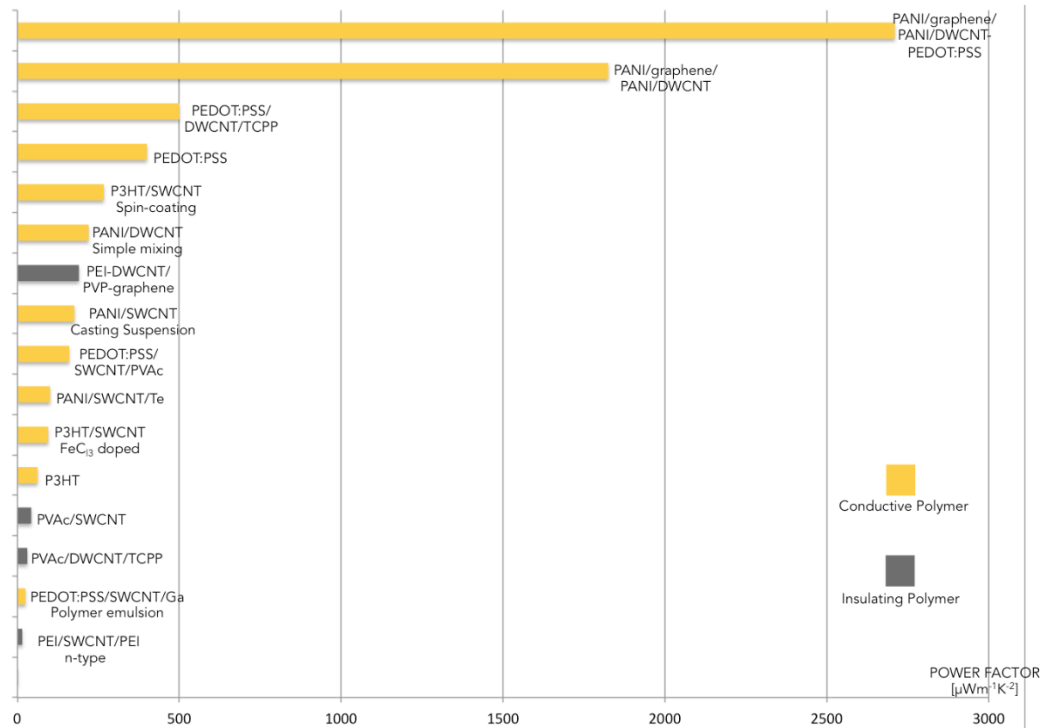


**Figure 1.13.** State of the art for carbon-nanotube-based composites with conductive and insulating polymers. Based on the work *Carbon-Nanotube-Based Thermoelectric Devices* from Blackburn et al [8].

Insulating polymers have been used as a way of improving the electrical conductivity and decreasing the thermal conductivity; however, they can often provide a low TE performance due to the insulating effect of the matrix surrounding the CNTs. **Figure 1.14** summarizes some of the advantages that the incorporation of CNTs into insulating polymers could offer.

As it can be seen in **Figure 1.13**, conductive polymers often deliver a better TE performance. The reason why is that conjugated polymers behave themselves as TE materials since they have available charge carriers and they have an efficient transport through the  $\pi$  orbitals [54]. PANI (polyaniline), P3HT (poly(3-hexylthiophene)) and PEDOT are some examples of this type of polymers.

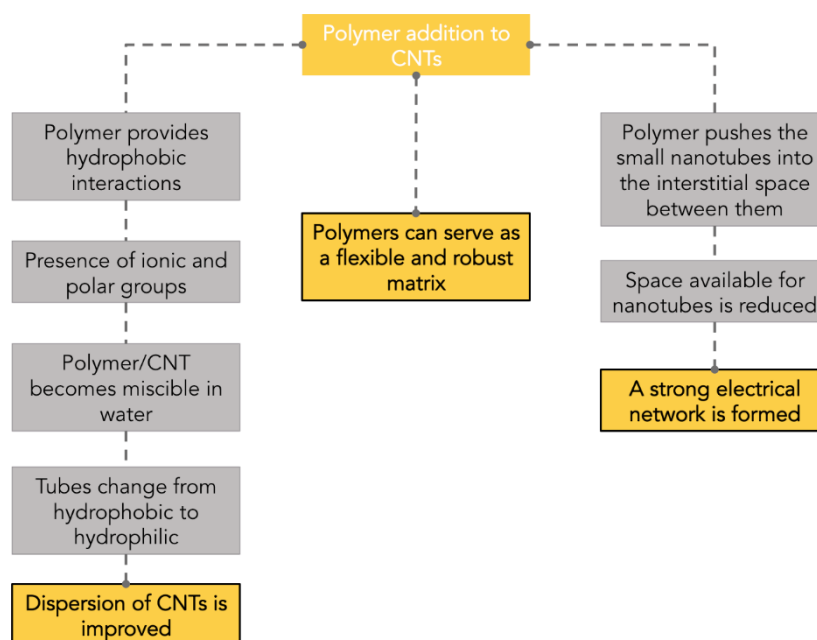


**Figure 1.14.** Diagram summarizing the effects of the polymer addition on carbon nanotubes for forming nanocomposites.

#### 1.4.3.1 Poly (Vinyl Alcohol) – PVA

PVA is one of the less explored organic polymers on a TE context. It has a semi-crystalline nature due to the presence of OH groups and hydrogen bonds. It can be seen as a crystalline polymer with an imperfect crystalline network where the voids are filled with amorphous content.

PVA may be considered as a nontoxic, recyclable, environmentally friendly, water-soluble polymer that has good adhesive properties, high tensile strength and good flexibility making it a good candidate to use as a binding agent in printed films [55]. As a non-conductive polymer, it may perform as an insulating matrix, however it has also a thermal insulating behaviour.

There are some studies of TE materials produced with PVA, mainly with inorganic materials. Some studies can be highlighted where an organic material is used such as the use of PVA in the improvement of the Seebeck Coefficient about 30% in Graphene Oxide [56] and the creation of conductive paths in a nanocomposite formed with PVA and Graphene nanoplatelets [57].

## 1.5 Devices and Applications

A typical TE module consists of an alternating leg configuration (p-type and n-type) that are connected electrically in series and thermally in parallel as can be seen in **Figure 1.15**. This configuration provides a minimal parasitic loss of electrical resistance while enables an optimized heat transference.

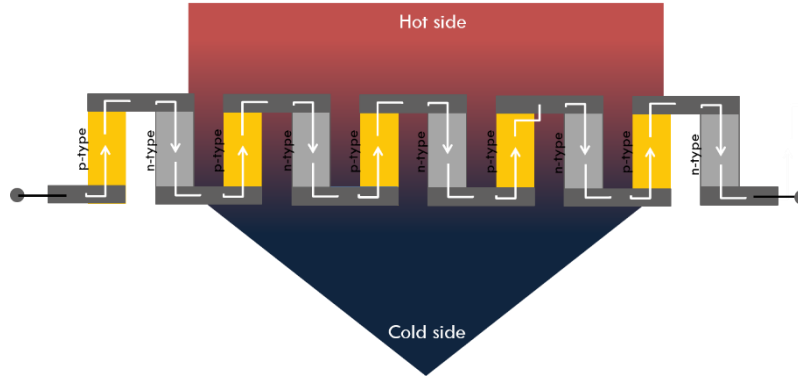


**Figure 1.15.** Schematic representation of the most effective configuration (p-n) for a Thermoelectric Generator.

The efficiency of a generator could be given by:

$$\eta = \frac{P}{Q} \quad (1.9)$$

where  $Q$  is the heat provided to the generator and,  $P$  is the power generated by the device. The efficiency is related to the Carnot efficiency through the expression:

$$\eta = \frac{\Delta T}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}} \quad (1.10)$$

where  $\Delta T$  is the temperature gradient,  $T_h$  is the hot temperature and  $T_c$  is the cold temperature.  $ZT$  is the figure of merit of the device and as so it is represented by uppercases [58].

So far, the efficiency of thermoelectric devices is not competitive with traditional mechanical power generators [59]. A material with  $zT$  of 3 or higher working on temperatures in the range of 300 K and 773 K could provide a Carnot efficiency of 50%, which would upgrade TEGs in the market [60].

There are some remarkable applications for TEGs since they are well suitable for performing in extreme environments and decentralized locations. A well-known application is the Radioisotope Thermoelectric Generator that re-uses the heat released by the decay of radioisotope materials to generate electricity that can be used in space, where other generators such as fuel cells or solar cells are not practical. Another example is the automotive waste heat recovery where the main idea is to attach a TEG module between a heat exchanger and a cooling system (radiator) and use that  $\Delta T$  to harvest energy that can be re-used in the automotive performance.

### 1.5.1 Flexible Thermoelectric Devices

The materials with higher figures of merit mentioned in the previous section are the inorganic ones and they frequently exhibit higher outputs relative to the organic ones. Nevertheless, they possess some drawbacks such as difficult processability, higher costs, toxicity and brittleness. As an opposition, organic materials offer higher flexibility, lightweight, lower costs and an easier processability. These features conceive organic materials to be attractive in the device making despite the lower performance since there is a great demand to use flexible TE devices in nonplanar surfaces. Organic-based thermoelectric materials could be pure polymer TE materials, polymer-inorganic materials or polymer-organic materials such as CNTs and graphene-based composites [61]. Carbon-based TE devices are suitable for low-grade heat energy harvesting since they are quite effective in the 300 - 400 K range. An easy application for this kind of devices would be the recovery of the human body dissipated heat for charging a small battery in low powered devices (e.g. cell phone, health sensors, etc.).

There are a wide variety of methods to fabricate portable and flexible TE devices such as the synthesis of inks and pastes for the purpose of screen printing, inkjet printing, photolithography patterning, roll-to-roll printing, dispenser printing and spray printing [62,63]. There are some commonly used substrates in flexible TE devices such as polyimide (PI), polydimethylsiloxane (PDMS) and polyethylene terephthalate (PET) [64,65].

### 1.5.1.1 Architecture of TE modules

The module performance depends not only on the TE material but also on the leg geometry and the fill factor. Changing the module geometry, such as the prolongation of the leg length or the reduction of the cross-section could lead to an increase in the temperature gradient, which could lead to an increase on the Joule heating losses. The fill factor also has an effect on the temperature gradient - a low fill factor would mean that the  $\Delta T$  is easier to maintain but would also mean a limit on the power generation due to the reduction of the elements number [66].

There are several conditions to consider when doing TE energy harvesting. For maximum heat conversion to electricity, the device should be matched to the external load both thermally and electrically and the heat exchangers should also be connected to it. The  $\Delta T$  across the TEG should be approximately 1/2 that the one between the source and ambient for occurring thermal matching. The most effective way of obtaining a  $\Delta T$  across the legs in low-cost techniques where the films are on the nanometre or micrometre range is to designing the heat transfer in the in-plane direction of the elements [67].

### 1.5.1.2 State-of-the art flexible carbon-based devices

Hong et al. have done a spray-printed organic TEG formed of a p-type CNT and P3HT polymer composite. A polyimide substrate was used, where it was patterned 41 lines of the nanocomposite ( $1\text{ mm} \times 15\text{ mm}$  each line) connected in series by dispenser printed silver electrode lines. It was obtained a  $32.7\text{ nW}$  of power with a  $10\text{ K}$  temperature gradient [68].

Kim et al. created a device with a different kind of geometry where p-type and n-type CNT films were alternately in series with insulating films of PTFE between them as can be seen in **Figure 1.16**. The modules consisted of a 72 p-type films ( $S = 97\text{ }\mu\text{VK}^{-1}$ ;  $\sigma = 110\text{ S cm}^{-1}$ ) and 72 n-type films ( $S = -86\text{ }\mu\text{VK}^{-1}$ ;  $\sigma = 52\text{ S cm}^{-1}$ , PEI and diethylenetriamine with subsequent  $\text{NaBH}_4$  treatment). The device produced an open circuit voltage of  $9.6\text{ mV}$  ( $465\text{ mV}$  with  $\Delta T = 49\text{ K}$ ) and a power output of  $1.8\text{ }\mu\text{W}$  with  $\Delta T = 32\text{ K}$  [69].

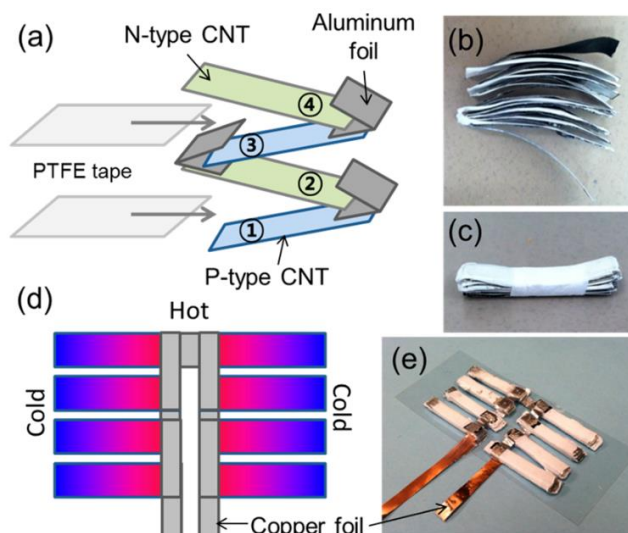


**Figure 1.16.** a) Assembly of p- and n-type carbon nanotube films. b) Each module with 9 films of each type. c) PTFE bounding the stack. d) Schematic representation of the device. e) Final TE device with 144 films is total. From [69].

Zhou et al. produced a device using SWCNT buckypapers grown directly by FCCVD. The p-type SWCNT paper was masked to make alternate 3 pairs of legs of p-type and n-type (PEI was used as a dopant for the n-type component) as it can be seen in **Figure 1.17**. This device delivered  $\Delta V \approx 3 \text{ mV}$  at  $\Delta T = 8 \text{ K}$  and  $\Delta V \approx 10 \text{ mV}$  at  $\Delta T = 27.5 \text{ K}$ , at this temperature the power produced was  $\approx 2.5 \mu\text{W}$  [70].

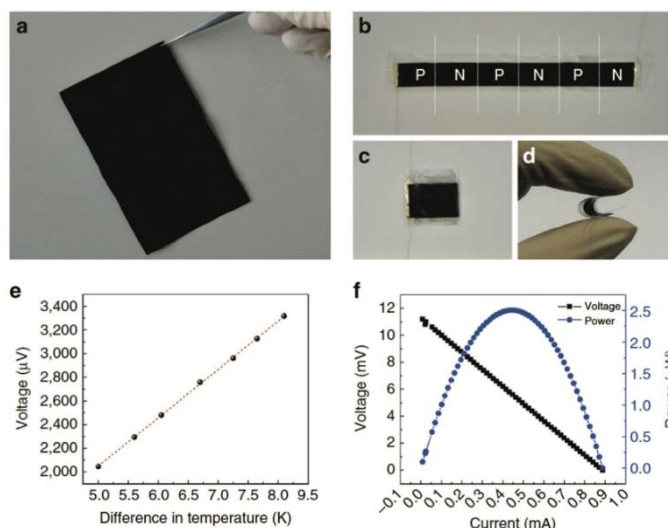


**Figure 1.17.** a-d) Pictures of the CNT film prepared by superposing multilayer. e) Voltage produce a different temperature. f) Voltage-current curve and Power-current for a  $\Delta T = 27.5$ . Adapted from [70].

## 1.6 Goals

Until now it was presented the state of the art regarding the carbon-based thermoelectric field and the flexible carbon-based devices which are the main goal of the present thesis.

Briefly, it will be presented some previous studies concerning the TE performance of a variety of carbon-based materials (activated carbon, Carbon Black, carbon xerogel, graphite, graphene and MWCNTs). Subsequently, two materials were chosen (graphene and MWCNTs) to perform posterior functionalization. These materials were functionalized through some different types of treatments (chemical, thermal and mechanic) and were evaluated relative to their TE performance. Some different characterization methods were used in order to understand the changings that were performed. The poor results with graphene lead to the choice of using MWCNTs for further investigations. MWCNTs were used to form nanocomposites with PVA and their TE performance was also evaluated.

Aiming the final goal, flexible TE devices were produced and also evaluated relative to the capability of harvesting energy at low temperature gradients.

## 2 Experimental Methodology

This chapter will present descriptions of relevant experimental methodologies applied that have given origin to the samples tested in this work. It will also give an overall explanation of the characterization techniques used to verify the extend of the alterations performed in the materials and the thermoelectric performance evaluation of such materials. As so, this chapter will be divided into four subsections: Relevant Experimental Procedures, Characterization Techniques, Transport Properties, and Device Performance Measurements.

Initially, it will be addressed some of the experimental processes that were used in this work with the purpose of sample production such as Oxidation, Ball-milling, Heat treatments, Nitrogen Doping, Sintering, Buckypaper Production, PVA doped with  $\text{H}_3\text{PO}_4$  preparation, Ink Formulation/Stencil Printing and a sample preparation summary.

The second part of this chapter will concern the description of the characterization techniques used in this work such as X-ray diffraction (XRD), Raman Spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), Thermogravimetry Analysis (TGA), Point of Zero Charge PH ( $\text{PH}_{\text{PZC}}$ ), Temperature Programmed Desorption (TPD), Elemental Analysis (EA) and  $\text{N}_2$  adsorption-desorption isotherms.

Then, it will be explained the homemade setups used to measure the Seebeck coefficient (for non-resistive and resistive samples at for room temperature and as well for lower temperature measurements), the thermal conductivity and the four-probe method used to measure the resistance that will be used to calculate the electrical conductivity.

Finally, it will be explained the benchmark tests used to obtain the device performance.

### 2.1 Relevant Experimental Procedures

#### 2.1.1 Oxidation Process

Oxidation processes were applied to the carbon materials with the goal of cleaning impurities and introducing some oxygenated surface groups onto the samples. The

samples were oxidized with nitric acid ( $\text{HNO}_3$ ) in the liquid phase with different molar concentrations (7 M and 12 M). In this process, 3 g of carbon material was placed on a round-bottom flask containing 300 mL of  $\text{HNO}_3$ , as illustrated in **Figure 2.1**. Then, the liquid was heated in a heating mantle until reaching boiling temperature. This condition was maintained for 3 hours. After, the carbon material was washed with distilled water on a macroporous plaque until reach neutral pH and dried at 110 °C in an oven for 24 hours.

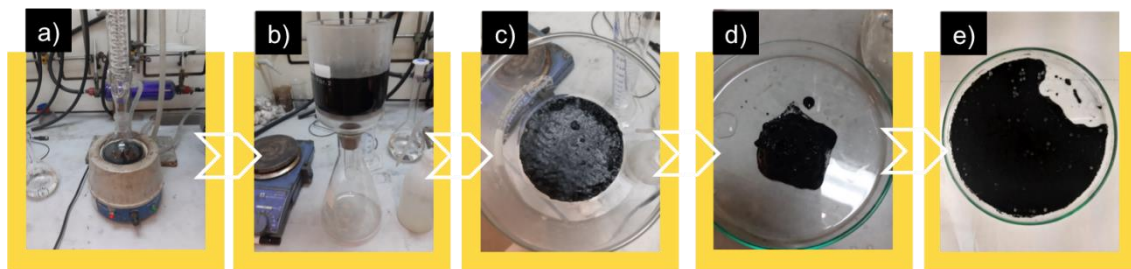


**Figure 2.1.** a) Heating of the sample on a heat mantle. b-c) Sample washing on a macroporous plaque until neuter pH. d-e) Sample after watching before and after drying

### 2.1.2 Ball milling

Ball milling is a method for modifying carbon nanotubes such as adjusting their lengths, opening closed ends, and increasing the surface areas [71]. Ball milling can also modify the nanotubes morphology by curving them [72], creating nanoparticles [73] or making them amorphous if the process is too prolonged.

In this work, the sample materials were placed on a closed flask without any gas flow in a Retsch MM200 equipment (**Figure 2.2.a**) with a frequency of 15 Hz, during 4 hours, following the same approach as Nxumalo et al. in [74]. The equipment performs radial oscillations on the horizontal position, and the grinding balls impact on the sample material with high energy, pulverizing and mixing it, as it is represented in **Figure 2.2.b**.

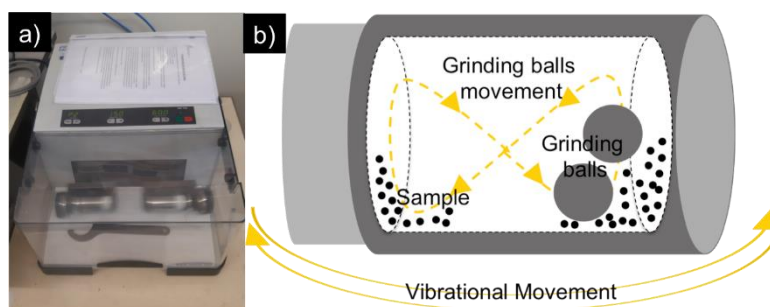


**Figure 2.2.** a) equipment used in this work. b) Schematic representation of the ball-milling process.

### 2.1.3 Thermal Treatments

Different temperature treatments were applied to the samples to help the doping processes or to selectively remove the oxygen-containing surface groups. For that, the carbon material was placed in a fused-silica tubular reactor, as illustrated in **Figure 2.3**, and heated until it reaches the desired temperature (600 °C or 900 °C) at a rate of 5 °Cmin<sup>-1</sup> under a constant flow of N<sub>2</sub> (100 N cm<sup>3</sup>min<sup>-1</sup>). The temperature was then kept for 1 hour. After that, the sample was cooled under the same atmosphere, collected, and stored.



**Figure 2.3.** Equipment used for the thermal treatments.

### 2.1.4 Nitrogen doping

Graphene was nitrogen doped through the following procedure: a solution of 0.65 g of graphene in 200mL of ethanol was left in a shaker for 24 hours; then it was filtrated and placed in an oven overnight for drying; after drying, the powder was placed on an oven for a heat treatment at 600 °C for consolidating such atoms into the graphene network.

For doping the carbon nanotubes, it was performed the ball-milling process using a melamine precursor, with the same process described on section 2.1.2. It was used two quantities of these substance, 0.36 g and 0.8 g. After this, a heat treatment at 600 °C (as described in section 2.1.3) was applied for consolidating such atoms into the nanotubes network. This process is based on the work of Soares et al. [48].

### 2.1.5 Sintering / Compression of the Powders

A sintering process consists on the compression of powders aiming to reduce the air between the particles, bringing them closer together. This process can be caused by

pressure, strengthening the interparticular bonds, transforming the bulk powder into a compact pellet.

In this work, a steel die was used for obtaining pellets from different powders samples (**Figure 2.4**). It was used a 4000-6000 Psi pressure for 60 seconds resulting in a 1.3 cm diameter pellet.

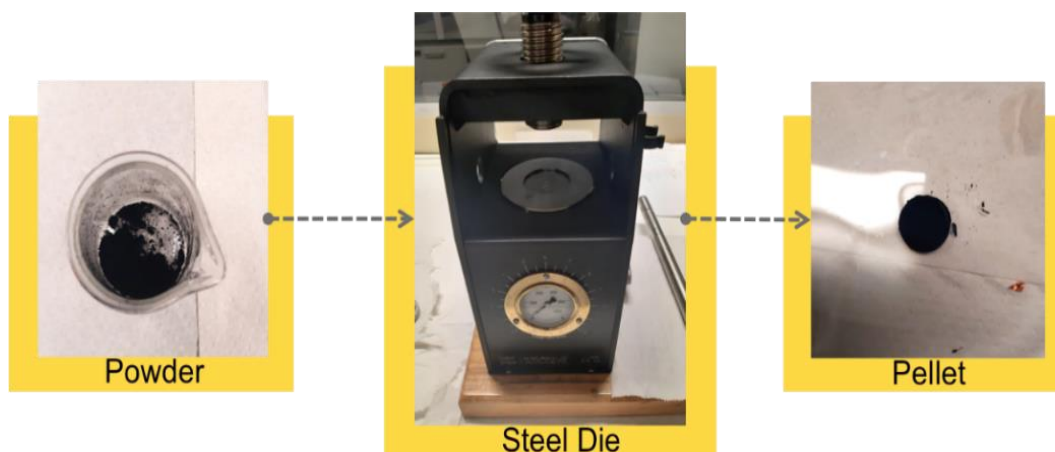


**Figure 2.4.** Schematic representation of the sintering process from powder into pellet through the use of steel die.

### 2.1.6 Buckypaper Production

Buckypaper was used as a support substrate to enable the transport properties of the carbon-based materials. This preparation was as follows (**Figure 2.5**): the carbon material was dispersed in a Millipore water and isopropanol mixture, 50 mL of each; the mixture under an ice bath was placed on an ultrasonicator at 70% for 60 minutes; after the sonication, the mixture was vacuum filtrated through a nylon filter membrane (PALL, 0.45  $\mu\text{m}$ , 47 mm) and subsequently air-dried.

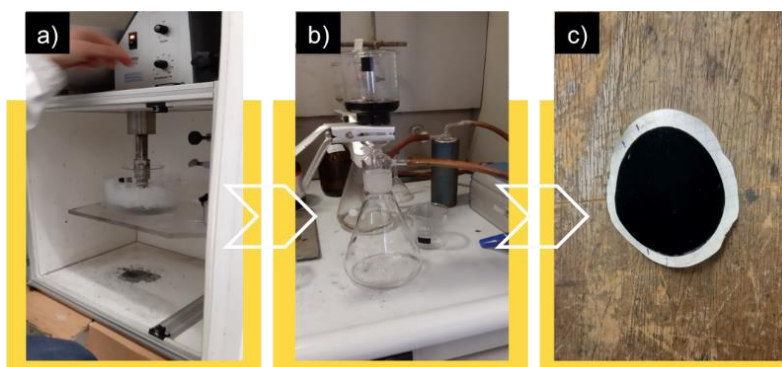


**Figure 2.5.** a) Equipment use for ultrasonication. b) Vacuum filtration through a nylon membrane. c) Buckypaper obtained after drying.

### 2.1.7 PVA doped with $H_3PO_4$ production

Regarding the polymer preparation it was used poly (vinyl alcohol) (PVA) at 99% from Sigma-Aldrich doped with orthophosphoric acid ( $H_3PO_4$ ) at 85% from Fisher Chemical. The procedure for the preparation is represented in **Figure 2.6**:  $H_3PO_4$  was solubilized in 60 mL of Millipore water, the same amount of PVA (1:1) ratio was joint into the mixture while stirring; The mixture was incubated in a silicone bath and heated until 85 °C in a hot plate and kept at this temperature and under continuous stirring for 12 hours.

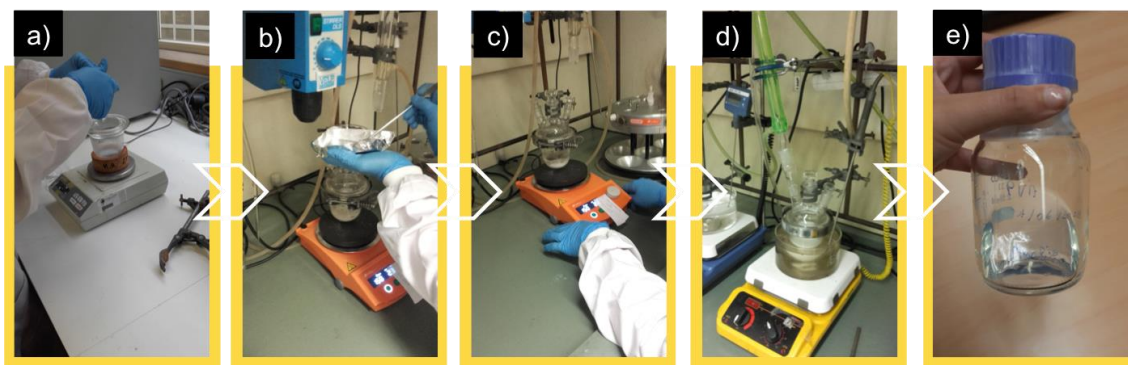


**Figure 2.6.** a) Acid weighing. b) Addition of PVA to the acid. c) Mixture of the components under stirring. c) Heating in a silicone bath. d) Doped PVA obtained.

### 2.1.8 Ink Formulation and Stencil Printing

For testing some of the tailored materials, inks or nanocomposites were formed using a carbon material and PVA (doped or non-doped with  $H_3PO_4$ ). The procedure for the formulation of nanocomposites, represented in consists on **Figure 2.7**: mixing the two materials under continuous stirring until a homogeneous paste-like material is obtained; dropping the paste in a pre-cleaned PET substrate with a rectangular vinyl mask; spread the ink; removing the mask and leaving the film air-drying overnight.

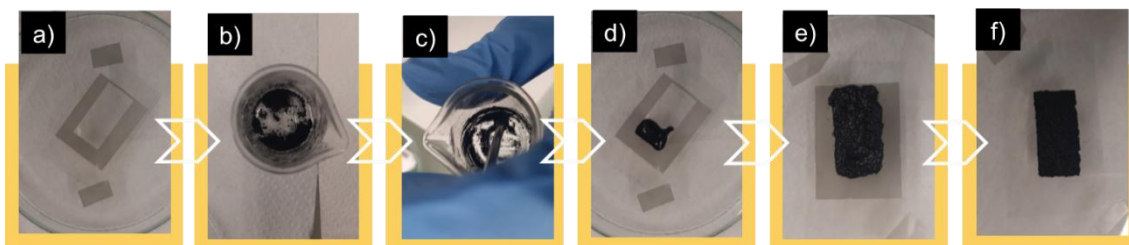


**Figure 2.7.** a) Vinyl mask over the substrate. b-c) PVA and carbon material mixing. d-e) placement of the ink over the mask and substrate set. f) Film obtained after the mask removal.

## 2.1.9 Sample preparation summarized

**Table 2.1** and **Table 2.2** summarize the treatments applied on graphene nanoplatelets (GN) and on multiwalled carbon nanotubes (MWCNT). The starting materials are described on **Table A1** on Annex A.

**Table 2.1.** Summary of the treatments applied on the functionalized graphene samples.

|               | Chemical<br>Treatment | Heat<br>Treatment      | Mechanical<br>Treatment |
|---------------|-----------------------|------------------------|-------------------------|
| GN_pristine   | ---                   | ---                    | ---                     |
| GN_WM_HT600   | Melamine (0.36 g)     | 600 °C, N <sub>2</sub> | ---                     |
| GN_HNO3       | Nitric Acid (7M)      | ---                    | ---                     |
| GN_HNO3_HT900 | Nitric Acid (7M)      | 900 °C, N <sub>2</sub> | ---                     |

**Table 2.2.** Summary of the treatments applied on the functionalized MWCNT samples.

|                        | Chemical<br>Treatment | Heat<br>Treatment     | Mechanical<br>Treatment |
|------------------------|-----------------------|-----------------------|-------------------------|
| MWCNT_pristine         | ---                   | ---                   | ---                     |
| MWCNT_BM               | ---                   | ---                   | Ball-milling            |
| MWCNT_BM_WM0.36g_HT600 | Melamine (0.36 g)     | 600°C, N <sub>2</sub> | Ball-milling            |
| MWCNT_BM_WM0.8g_HT600  | Melamine (0.8 g)      | 600°C, N <sub>2</sub> | Ball-milling            |
| MWCNT_HNO3_7M          | Nitric Acid (7M)      | ---                   | ---                     |
| MWCNT_HNO3_7M_HT900    | Nitric Acid (7M)      | 900°C, N <sub>2</sub> | ---                     |
| MWCNT_HNO3_7M_BM       | Nitric Acid (7M)      | ---                   | Ball-milling            |
| MWCNT_HNO3_12M         | Nitric Acid (12M)     | ---                   | ---                     |
| MWCNT_HNO3_12M_BM      | Nitric Acid (12M)     | ---                   | Ball-milling            |

## 2.2 Characterization Techniques

### 2.2.1 X-Ray Diffraction

X-Ray diffraction (XRD) is a technique used to determine crystal structures of crystalline materials by providing information about the structure, phases, grain size, lattice strain, and crystal defects.

The standard equipment is composed by an x-ray tube, an x-ray detector, and a sample holder. In the cathode, x-rays are generated through the projection of a high voltage electron beam into a metal target (anode), inside an x-ray tube. After suffering collimation, the x-ray beam exposes the sample, suffers diffraction, consequently giving origin to a pattern that displays a series of peaks [75].

The working principle is based on diffraction, a phenomenon that is nothing else but a constructive interference given at specific angles when radiation is scattered coherently in periodic arrays. In this technique, X-rays pass through a sample interacting with the electrons and atoms that result in Bragg reflections. These reflections are correspondent to peaks in the diffractogram, and they give information about the crystal structure. These reflections can be studied through Bragg's Law:

$$\lambda = 2d_{hkl} \sin \theta_B \quad (2.1)$$

where  $\lambda$  is the electromagnetic radiation's wavelength,  $\theta_B$  is the diffraction angle and  $d_{hkl}$  is the distance between two adjacent atomic planes, where (hkl) refers to the Miller indexes, as it can be seen in **Figure 2.8**.

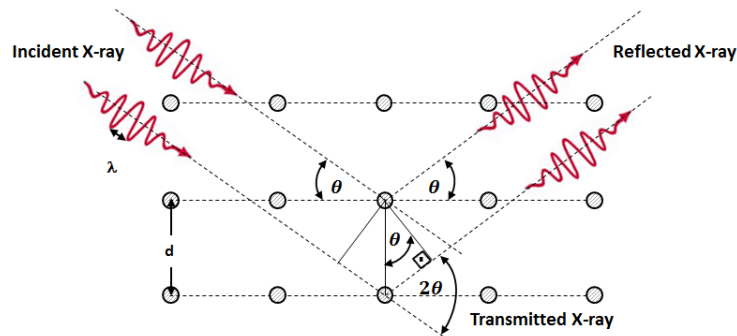


**Figure 2.8.** Schematic representation of the Bragg's relation. Adapted from [125].

The crystallite size of the samples can be calculated by using the Debye-Scherrer equation:

$$D_{hkl} = \frac{0.94\lambda}{\sqrt{B_m^2 - B_s^2 \cos \theta}} \quad (2.2)$$

where  $D_{hkl}$  is the crystalline size in the perpendicular direction to the planes of the lattice,  $\lambda$  is the source wavelength,  $B_m$  is the full-width at half-maximum (FWHM) of the maximum and  $B_s$  is the instrumental broadening [76].

The XRD technique was performed with Rigaku SmartLab® diffractometer using a Bragg-Brentano  $\theta/2\theta$  configuration using a  $Cu K\alpha$  source ( $\lambda = 1.540593 \text{ \AA}$ ).

### 2.2.2 Raman Spectroscopy

Raman Spectroscopy is a technique for analysing rotational, vibrational and other low-frequency modes in a system.

The system is composed of a laser that illuminates a sample. Electromagnetic radiation that comes from the illuminated spot passes through an optical system composed with lens and a monochromator. The collected light is dispersed onto a detector with the exception of the radiation that suffers elastic scattering at the laser's wavelength, which is filtered [77].

The laser interacts with molecular vibrations, phonons, or other types of excitation that occurs in the system. The energy shifts give out information about the vibrational modes [78]. It's based on inelastic scattering or Raman scattering of the monochromatic light as it can be seen in **Figure 2.9**.

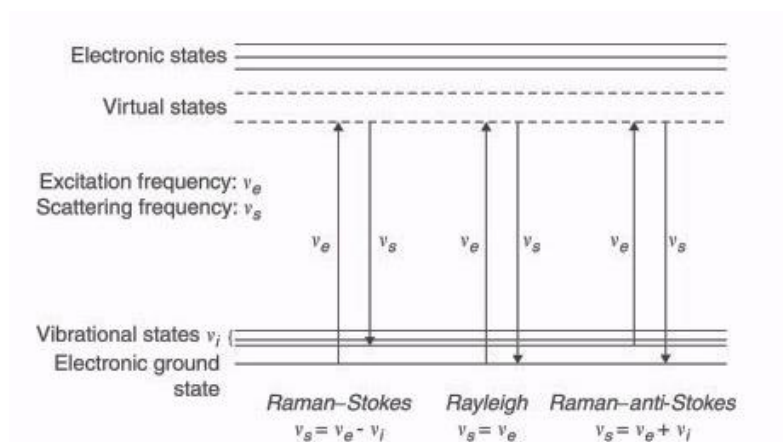


**Figure 2.9.** Schematic representation of the energy shifts for Stokes, Rayleigh and anti-Stokes scattering. Adapted from [78]

In the spontaneous Raman effect, a photon excites a molecule in a ground rovibronic state or an excited rovibronic state thus forcing the molecule in being in a virtual energy state for a short period before inelastically scattered photon results. If the scattered photon has higher energy than the incoming photon then it is called Stokes Raman scattering, if it is lower, then it's called anti-Stokes Raman scattering. Though the analysis of the rovibronic states of the molecule before and after the Raman scattering

occurrence it is possible to achieve a shift in the emitted photon's frequency, the so-called Rayleigh line.

In this work, it was used an in-Via confocal microscopy from *Renishaw* allocated at IFIMUP-IN facilities. It was used a He-Ne laser with a wavelength  $\lambda = 532 \text{ nm}$  in a frequency range from 100 to 3500  $\text{cm}^{-1}$ .

### 2.2.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a technique for structural characterization that uses high-energy electrons for reaching smaller wavelengths. The system is composed of an electron source, electromagnetic lens, sample holder, and an imaging system, as it can be seen in **Figure 2.10**. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. In TEM, the beam needs to reach a high spatial region to be transmitted throughout the sample [79]. For achieving this, the samples need to be prepared with small thickness for avoiding energy losses. There are several techniques for the preparation of specimens in order to obtain thin specimens; however, when the subjects are nanomaterials there is no need for using such techniques since they have reduced dimensions and the beam can easily pass through.

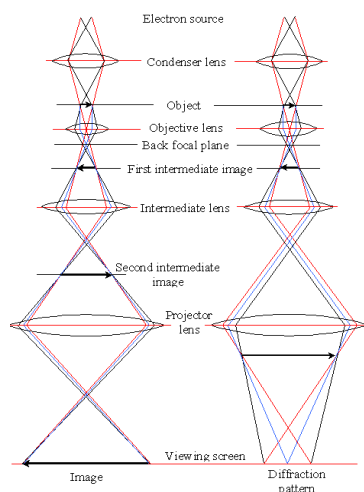


**Figure 2.10.** Schematization of the TEM setup.

In this work, it was used JEOL JEM 1400 electron microscope with an 80 kV beam voltage and a resolution between 100-200 nm, at the i3s facilities. The samples were prepared by sonicating a small piece of powder with filtrated Millipore water for 5 min then diving a copper grid in the solution and finally drying until the liquid disappear.

## 2.2.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a technique for image magnification with the purpose of obtaining information on the size, shape, composition, crystallography on the microscopic scale of a sample.

The working principle starts with the emission, from an electron source, of a focused beam composed of energetic electrons. This beam is high energy accelerated until its diameter passes through an optic apparatus (e.g. apertures, magnetic/electrostatic lens and so on), as it can be seen in **Figure 2.11.a)**. The beam is used to scan the sample in different directions (horizontal and vertical) in order to create a pattern. The interaction of the beam with the sample results in the emission of backscattered electrons (electron beam with a large fraction of the incident energy after suffering scattering and deflection by the electric fields of the atoms in the sample) and secondary atoms (beam electrons eject electrons from the sample atoms), as it can be seen in **Figure 2.11.b)**. The secondary electrons are created from the surface of the sample or adjacent to the surface regions allowing the analysis of the topography of the sample's surfaces. On the other hand, backscattered secondary electrons are created from a deepen volume region allowing the analysis of the topography but also giving information about the sample composition [80].

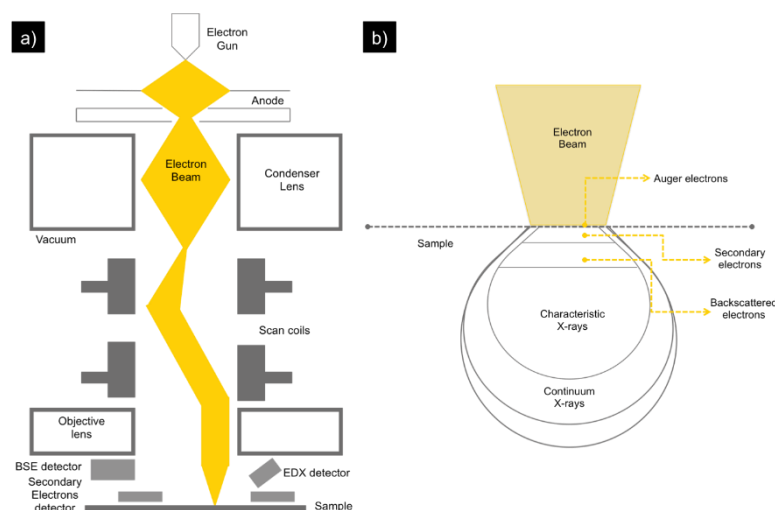


**Figure 2.11.** a) Setup of SEM equipment. b) Illustration of the multiple beam interaction with the samples.

In this work, it was used a Hitachi SEM equipment placed at the Geology department of FCUP. The samples were prepared by placing the powder in a copper tape and then it was used a carbon tape to fix the samples to the SEM sample holder.

## 2.2.5 Energy Dispersive X-Ray Spectroscopy

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a microanalysis technique for the identification and quantification of the elemental composition of a given sample, which is often used together with a SEM system.

The procedure goes as follow: an electron beam is focused on a sample provoking the excitation of an electron of the inner shell with the subsequent emission of x-rays. An electron dispersive detector receives the x-ray emissions and through the measurement of the specific wavelength of each x-ray (energy that is characteristic of each atomic transition), it is possible to perform the atomic identification of the elements that compose the sample.

In this work it was used an EDS system coupled with the SEM equipment mentioned before.

## 2.2.6 Thermogravimetry Analysis

Thermogravimetry analysis (TGA) is a destructive technique that is used to analyse the mass variation of a sample in function of the temperature or in function of the time at a controlled atmosphere and temperature. It is composed by: a precision scale, a furnace, thermocouples and a gasification system [81]. The sample is placed on an inert crucible that is taken to the furnace where the temperature and the atmosphere can be programmed for achieving different analysis.

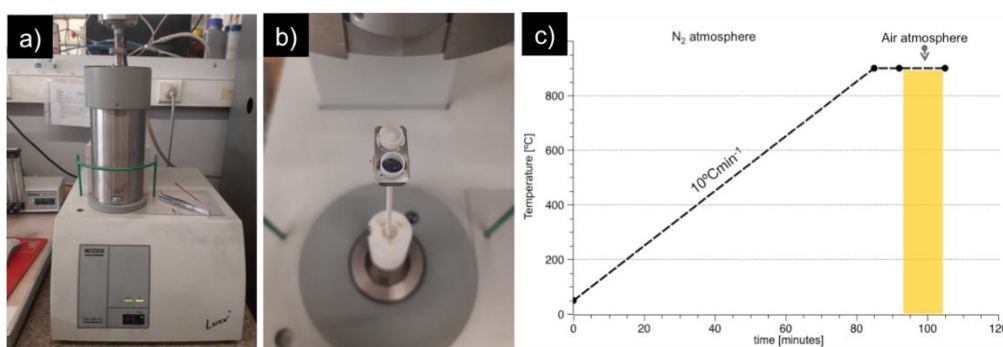


**Figure 2.12.** a) equipment used on TGA. b) detail of the sample placed on the crucible. c) Graphic representing the program used on the analysis.

For this work, a STA 409 PC/4/H Luxx Netzsch thermal analyser was used. The approximate analysis was based on the Ottaway method [82] (**Figure 2.12**): the samples

were heated at  $10\text{ }^{\circ}\text{C min}^{-1}$  from  $50\text{ }^{\circ}\text{C}$  to  $900\text{ }^{\circ}\text{C}$ , under a  $\text{N}_2$  flow; after achieving  $900\text{ }^{\circ}\text{C}$  an isotherm pass was used for 7 min under the same gas followed by 13 min in an air atmosphere for burning-off the carbon.

### 2.2.7 Point of Zero Charge pH

Point of zero charge pH ( $\text{PH}_{\text{PZC}}$ ) is a technique used to determine the acid-basic character of a sample. It is defined by the pH when the net surface charge is zero. This technique allows an estimation of the type of functional groups present on the sample surface, i.e. acidic functional groups could be carboxylic, phenolic and lactones groups and basic groups could be ketones, pyrones and chromenes on the carbon basal planes [83].

The procedure was carried out as follows (**Figure 2.13**): A solution of NaCl 0.01 M was prepared and 20 mL were placed in closed Erlenmeyer flasks; it was used HCL 0.1 M or NaOH 0.1 M to adjust the pH of the solution between 2 and 12; then, 20 mg of each sample was placed in the flasks, keeping some flasks without carbon as blank experiments (to subtract the variation of pH caused by the effect of  $\text{CO}_2$  present in the head-space); the flasks were left under stirring during 24 hours; The pH of each sample was measured and the  $\text{PH}_{\text{PZC}}$  was determined by plotting the curve of  $\text{pH}_{\text{final}}$  versus  $\text{pH}_{\text{initial}}$ ; when the curve crosses the line  $\text{pH}_{\text{initial}}=\text{pH}_{\text{final}}$ , the  $\text{PH}_{\text{PZC}}$  is achieved [84].

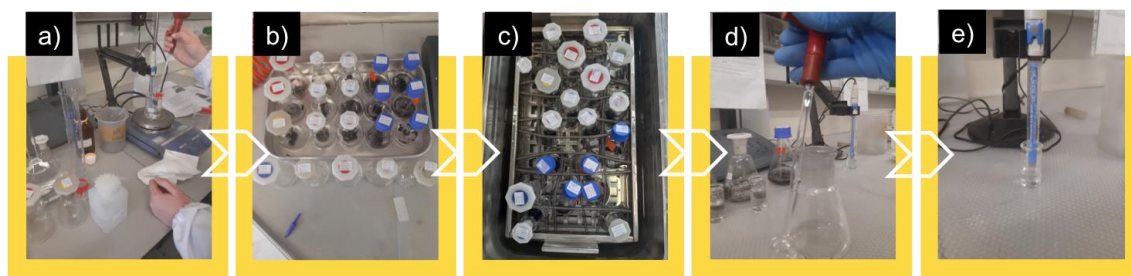


**Figure 2.13.** a) Preparation of the solution with different pH. b) Mixing the solutions with the carbon material. c) Stirring equipment used. d-e) pH measurement of the samples

### 2.2.8 Temperature Programmed Desorption

Concerning the surface chemistry, Temperature Programmed Desorption (TPD) was performed to characterize the oxygen-containing functional groups present on the surface of the samples. In TPD, there is a thermal decomposition of the oxygenated surface groups releasing  $\text{CO}$  and/or  $\text{CO}_2$  at different temperatures. Through deconvolution techniques it is possible to know the amounts of gas released (calculating the areas of the peaks) and access the nature of the groups [85], i.e., the  $\text{CO}_2$  profiles

result from the decomposition of carboxylic acid (low temperatures) and lactones (higher temperatures), phenols and carbonyl/quinone groups release CO and carboxylic anhydrides give origin to both CO and CO<sub>2</sub>.

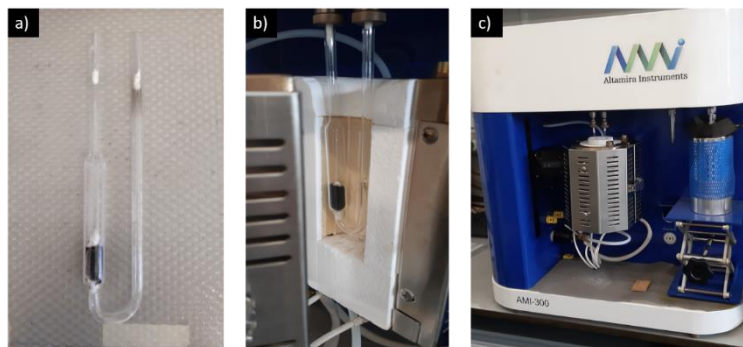


**Figure 2.14.** a) Sample preparation for TPD analysis. b) Furnace. c) TPD equipment used.

In this technique, CO and CO<sub>2</sub> spectra were obtained with a fully automated AMI 300 Catalyst characterization apparatus (Altamira Instruments) that is connected to a Dycor Dymaxion Mass Spectrometer (**Figure 2.14.c**). The samples (0.100 g) were placed in a U-shaped quartz tube (**Figure 2.14.a**) located inside an electrical furnace (**Figure 2.14.b**) and heated up from room temperature to 1100 °C at a 5 °C min<sup>-1</sup> under a constant flow rate of 25 cm<sup>3</sup> min<sup>-1</sup> of helium. A calibration of CO and CO<sub>2</sub> was carried out at the end of each analysis.

### 2.2.9 Elemental Analysis and Oxygen Analysis

Elemental analysis (EA) is a technique to analyze the elemental composition of the carbon materials. The most commonly used analysis is the CHNX analysis that refers to the mass fractions of carbon, hydrogen, nitrogen, and heteroatoms (such as halogens and sulphur). This can be accomplished through combustion analysis where the sample is burned at 1450 °C in an oxygen atmosphere while collecting the combustion products (such as CO<sub>2</sub>, H<sub>2</sub>, NO) [86]. The oxygen content can also be analyzed through Oxygen Analysis (OA) where the working principle is the pyrolytic conversion of oxygen into carbon monoxide at 1450 °C in a helium atmosphere [87].

The EA was carried out on a vario MICRO cube analyser in CHNS mode and the OA was carried out on a rapid OXY cube analyser, both from Elemental GmbH (**Figure 2.15**). Each sample, in triplicate, was placed on small boats (made of tin for EA and silver for

OA) with weights between 1.5 mg – 2 mg and analysed. A calibration was made using standard compounds prepared and analysed in a similar way of the samples.

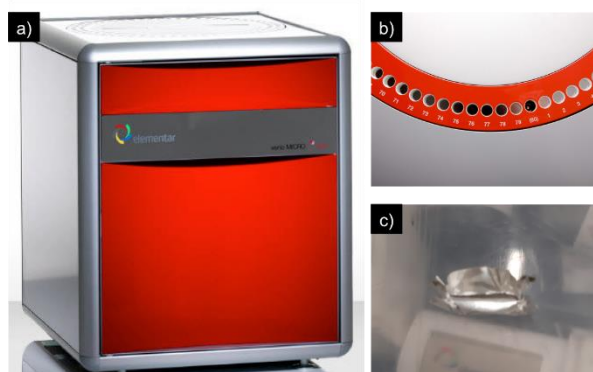


**Figure 2.15.** a) equipment used on EA. b) Sample holder detail. c) Boats used in the sample preparation. Adapted from [87].

### 2.2.10 N<sub>2</sub> adsorption-desorption isotherms

The textural characterization of the material can be obtained by performing physical adsorption of a gas on the surface of a sample at cryogenic temperature. At cryogenic temperatures, the nitrogen (most used gas in this technique) is below the critical temperature and condenses on the surface of the particles of the sample [88]. The nitrogen's volume is measured at the boiling point (-196 °C) and because its size is known, it is possible to correlate the amount of condensed (or absorbed) gas with the total surface of the material. A Brunauer-Emmett-Teller (BET) method could be used for obtaining the specific surface area (SSA) and a non-local density functional theory (NLDFT) can be applied for obtaining the pore size distribution.

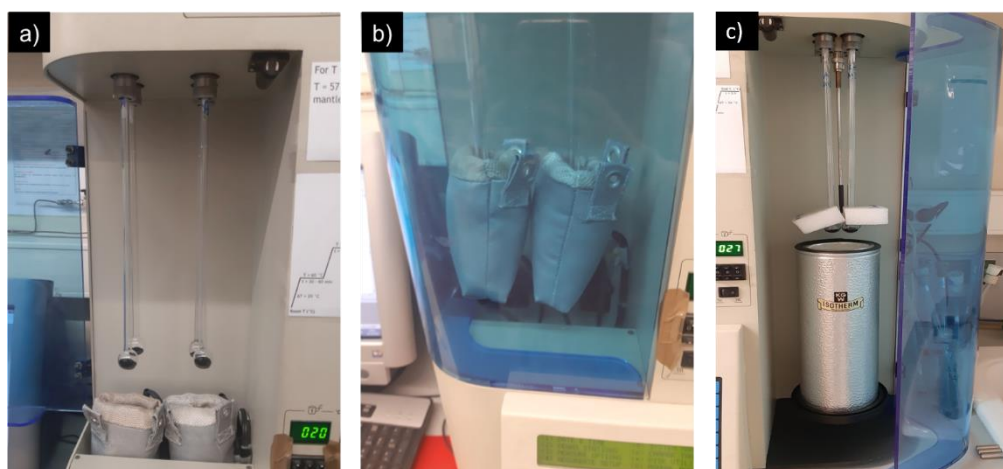


**Figure 2.16.** Equipment used on N<sub>2</sub> adsorption-desorption isotherms. a) Samples prepared for isothermal analysis. b) Degassing at 150°C process. c) Measurements at -196°C.

This technique was carried out on a multi-station Quantachrome NOVA 4200e at -196 °C (**Figure 2.16**). The samples were previously degassed at 150 °C for 3 hours. For obtaining the pore size distribution, it was used a kernel file provided by Quantachrome's data reduction software, where a cylindrical-pre model is assumed.

## 2.3 Transport Properties

The goals for the work include the optimization of the figure of merit of the carbon materials; as so, the transport properties of the produced samples were measured. The Seebeck coefficient, the thermoconductivity and the device's output measurement were performed in homemade systems allocated at IFIMUP-IN that will be described in detail in the following subsections.

### 2.3.1 Seebeck Coefficient

The Seebeck coefficient is an intrinsic property of a material that is independent of the dimension or geometry for homogeneous materials. It is established by the following equation:

$$S = - \frac{\Delta V}{\Delta T} \quad (2.3)$$

For the present work, the Seebeck Coefficient was measured at room temperature in a home-build setup represented in **Figure 2.17**. This setup is composed of two electrically isolated copper pillars where one is kept at room temperature while the other is heated using a temperature controller (lakeshore 331 TC). The temperature gradient between the two pillars is measured using K-type thermocouples placed on each pillar, which are connected to the temperature controller. It is used a nanovoltmeter (Keithley 2182) for measuring the voltage gradient between two contacts that are pressed on the top of the sample, for obtaining good electrical contact. It was used a developed LabView software where it is possible to program the different temperature gradients that are required to be measured. Only after reaching a stable gradient, the potential values are acquired by the software. It was measured the voltage gradients between 10-26 K of temperature gradients, with a 2 K step. Through the calculation of the slope through a

linear fit of the different V-T curves, it is possible to obtain the Seebeck coefficients for the different samples.

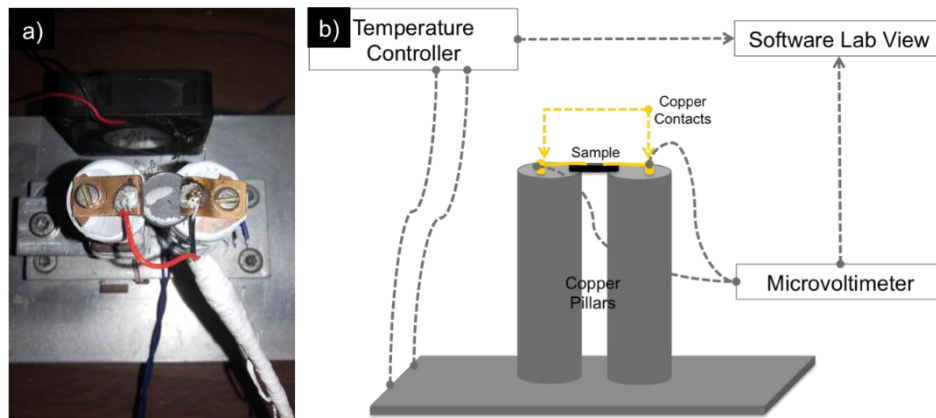


**Figure 2.17.** a) Equipment used on Seebeck at room temperature measurements. b) Schematic representation of the setup used in the experiment.

### 2.3.2 Seebeck Coefficient Setup for Resistive Materials

Some materials are too resistive to obtain a successful Seebeck Coefficient measurement from the setup described before. For this reason, it was used as an alternative setup that is based on the “zero-current” technique from Hossein-Babaei et al. [89], represented in **Figure 2.18**. This method consists of the indirect determination of the Seebeck voltage through the compensation of such voltage with an external voltage source. The setup, represented in **Figure 2.18**, has a voltage ( $V_S$ ) that is caused by the temperature difference imposed to the sample through the copper pillar system described above. The resistance inherent to the sample is represented by  $R_{AB}$  and these two components ( $R_{AB}$  and  $V_S$ ) represent the electrical behaviour of the sample. The positive side of the sample is connected to the positive terminal of the voltage source (the positive side will be the hot side for a p-type material and the cold side for a n-type material) and the negative side of the sample is connected to a variable resistance represented by  $R_1$ . The resistance is connected to the negative terminal of the voltage source and on the terminals of  $R_1$  it is placed a nanovoltmeter to measure the potential difference. The goal here is to reach the zero voltage in the  $R_1$  terminals, meaning that the voltage generated in the sample is equal to the one that is being applied by the voltage source ( $V_S$ ) which allows reaching the Seebeck voltage for the different temperature gradients, with a slight deviation caused by the current that crosses  $R_1$ .

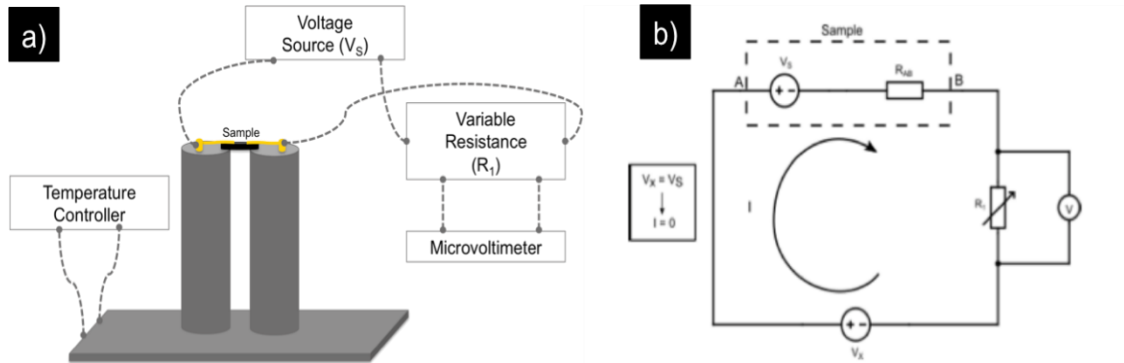


**Figure 2.18.** a) Illustration of the setup used on the Seebeck measurements for resistive samples. b) Schematic representation of the circuit used.

### 2.3.3 Electrical Conductivity

The electrical resistances of the samples were obtained by using a 4-point collinear probe method, represented in **Figure 2.19**. In this system, a current is applied in the exterior probes while the voltage is measured in the inner probes. It was used a 2410-C *SourceMeter*® from Keithley Instruments Inc. with high input impedance and accurate low current sourcing for inducing the current and acquiring the voltage data. A LabVIEW program was used for programming the current input and for the data acquisition. V-I curves are obtained and through the calculation of the slope using a linear fit and the Ohm's Law ( $V = RI$ ) it is possible to calculate the resistance.

The resistivity for parallelepiped samples was calculated using equation:

$$\rho = \frac{V A}{I s} = R \frac{A}{s} \quad (2.4)$$

where  $V$  is the voltage,  $I$  is the current,  $A$  is the cross-section area and  $s$  is the distance between the inner probes.

For cylindrical samples, it was used the following equation that considers the shape correction [90]:

$$\rho = \frac{V}{I} \frac{\pi t}{\ln \frac{\sinh(t/s)}{\sinh(t/2s)}} \quad (2.5)$$

where  $t$  is the sample's thickness. The electrical conductivity can be finally calculated by using  $\sigma = 1/\rho$ .

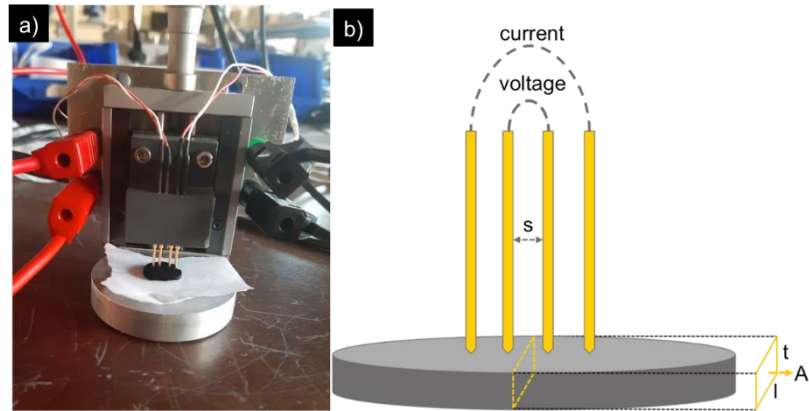


**Figure 2.19.** a) Equipment used for resistance measurements. b) Illustration of the 4-probe method.

### 2.3.4 Temperature dependence of the electrical properties

The electrical resistivity and the Seebeck Coefficient were measured as a function of the temperature for low temperatures. These measurements were performed at IFIMUP-IN.

For achieving low temperatures, it was used a closed-cycle cryostat. The sample chamber is evacuated to a pressure  $10^{-6}$  bar using an oil diffusion pump backed up by a rotary mechanical pump. A copper sample holder is protected by two radiation shields for ensuring minimal thermal fluctuations due to environment causes. In the holder, **Figure 2.20**, there are two copper blocks with internal resistances where temperature differences can be generated through joule heating and two thermocouples placed on the top of the blocks measure the thermal differences between them. The voltage across the sample and the thermocouple voltage of one block are measured by a Keithley Nanovoltmeter 281. A Keithley Nanovoltmeter 182 measures the differential thermocouple voltage of the other block. There is also thermocouple on the sample holder referenced at  $0\text{ }^{\circ}\text{C}$  and an Agilent Nanovoltmeter measures the output. LabVIEW programs are used to automate the procedures and also to collect the measurement results.

For measuring the Seebeck Coefficient, it is used a 2-probe method. The temperature of the sample holder is varied at a constant rate of  $0.5\text{ Kmin}^{-1}$ . A constant current of  $0.1\text{ A}$  is applied for heating one of the blocks while the other is kept at the same temperature as the sample holder, in order to establish a temperature difference between them. A time varying temperature difference is applied to the sample, which can be increasing or decreasing at a constant temperature rate, between  $10\text{ K}$  and  $300\text{ K}$ . The voltage across

the sample and the thermocouple voltages are instantaneously acquired, allowing to calculate the Seebeck coefficient.

It is used a 2-probe method for measuring the resistivity at low temperatures. A current of 0.2 mA is fed across two probes and the generated voltage is measured in the terminals of the probes. It was used a constant rate of 0.5 K min<sup>-1</sup> for either increasing or decreasing the temperature between 10 K and 300 K, while the voltage data is instantaneously acquired with a LabVIEW program.

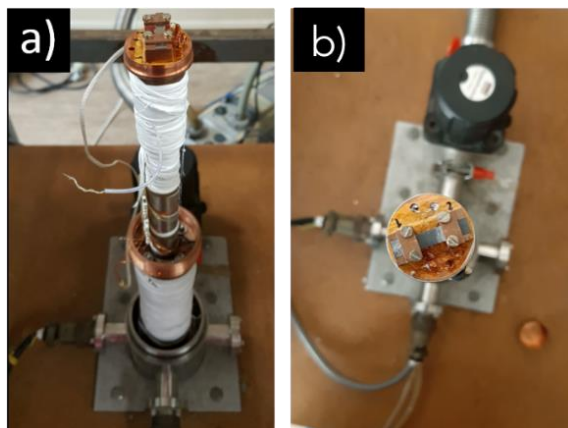


**Figure 2.20.** a) Setup used for  $S$  and  $\sigma$  measurements in function of temperature. b) detail of a carbon material buckypaper placed on the sample holder.

### 2.3.5 Thermal Conductivity

The thermal conductivity was measured on a homemade setup based on a steady-state method (**Figure 2.21**) that is built with a gold bathed copper system. The system has two pieces and each one will be in contact with the two interfaces of the sample. One of the copper pieces is heated by an internal resistance of 38  $\Omega$  that is connected to a current supply *Time Electronics 5018 Multi-Function Calibrator*. The other piece is kept cold by establishing constant flow of cooled water from the chiller. Two thermocouples ensure the temperature difference between the two interfaces of the material while a type T thermocouple is used to measure that temperature difference between both sides of the sample and it is read by an *Agilent 34420A NanoVolt/Micro-Ohm Meter*. The following equation is used to determinate the thermal conductivity ( $\kappa$ ):

$$\kappa = \frac{Qt}{A\Delta T} \quad (2.6)$$

where  $Q = VI = P$ ,  $t$  is the sample thickness,  $A$  is the area of the sample and  $\Delta T$  is the temperature gradient measured. A LabVIEW program was used to acquire the data.

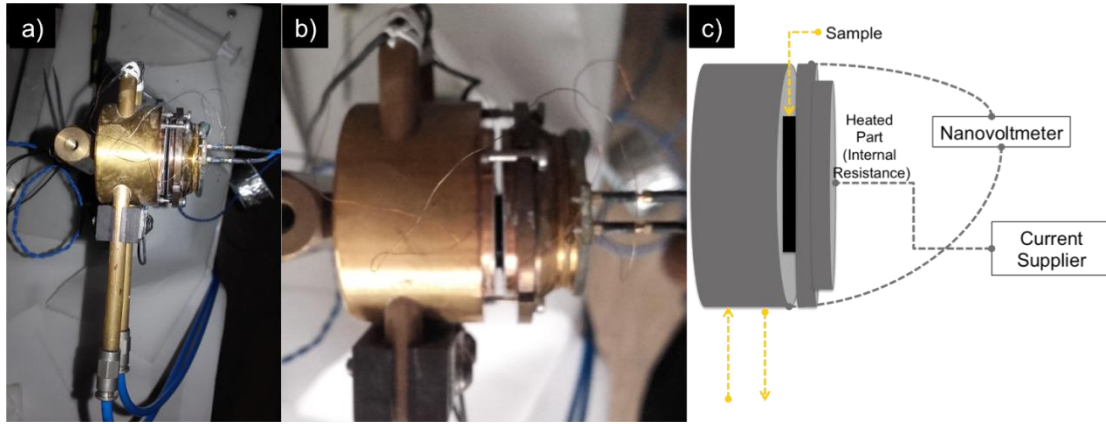


**Figure 2.21.** a-b) Equipment used for thermal conductivity measurements. c) Illustration of the setup used.

## 2.4 Device Performance Measurements

The device performance was measured using a commercial tungsten micro-probe system. The device was placed between two temperature-controlled Peltier's stages *TEC1-12706* and a temperature gradient was applied using k-type thermocouples on *TC-08 Thermocouple datalogger* from Pico Technology (**Figure 2.22**). The device was measured under different load resistances, between  $10\ \Omega$  and  $1\ \text{G}\Omega$  with the help of a circuit board and a fixed probe load. The device performance evaluation was carried out under two different configurations: open and closed circuit, for voltage and current measurements, respectively, represented in **Figure 2.22.d)**. The current was established by the Ohm's Law ( $V = RI$ ) using a probe load of  $R = 50\ \Omega$  and it is possible to obtain the output power of the device using  $P = VI$ .

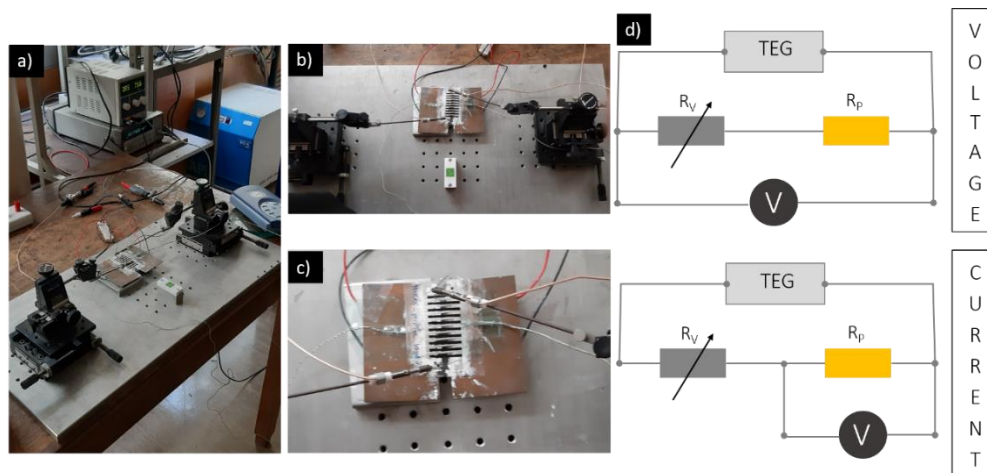


**Figure 2.22.** a-c) Overview of the homemade setup developed to measure all the TE devices produced. d) Schematic representation of the voltage and current circuits used on the measurements.

## 3 Tailoring Carbon-Based Materials

### 3.1 Carbon-Based Materials

In this section, it was performed electric transport properties tests for different samples of carbon-based materials in their original form (as cast). These tests were performed to inspect the most promising carbon-based materials relative to their TE performance and also relative to the ability of being functionalized in order to tune their  $zT$ .

The materials that were subjects of this study were Activated Charcoal, Carbon Black, Carbon Xerogel, Graphite, Graphene and MWCNTs. A **Table A1** is present in Annex A that resumes some details about the materials used in this part. These materials were submitted to the process of sintering as described in section 2.1.4, however it was not possible to transform the Activated Charcoal powder in pellet since it was too thin and the limit pressure imposed by the equipment was not sufficient to hold the material together.

#### 3.1.1 Transport Properties and TE performance

The carbon-based material samples were studied relative to their TE performance. For doing so, it was measured  $S$ ,  $\sigma$  and  $\kappa$  using the procedures of section 2.3.1, 2.3.3 and 2.3.5, respectively, at room temperature. The Carbon Xerogel sample was not possible to measure due to the inherent high electrical resistivity values. The remaining samples results concerning the electrical properties ( $S$  and  $\sigma$ ), the thermal transport ( $\kappa$ ) are represented in **Figure 3.1.a)** and **Figure 3.1.b)**, respectively.

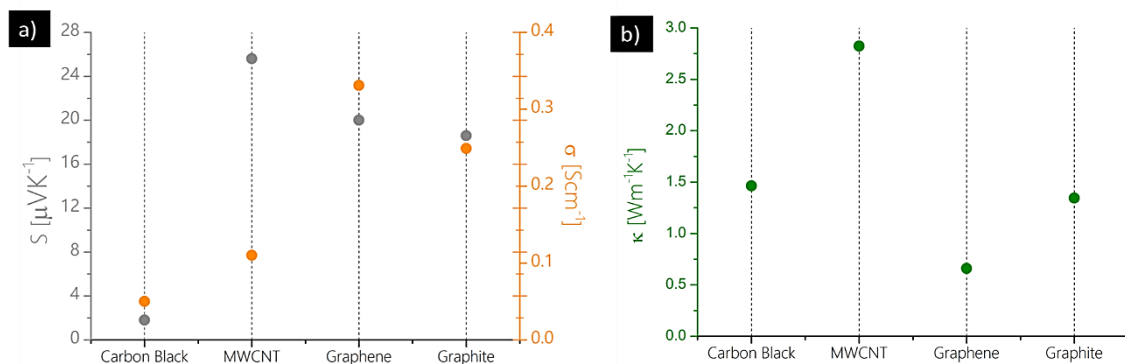


**Figure 3.1.** a) Seebeck coefficient and electrical conductivity for Carbon Black, MWCNT, Graphene and Graphite, measured in bulk in their pristine conditions. b) Thermal conductivity results for the same materials.

The Seebeck coefficient values for the carbon-based samples were all positive, which means that the materials studied were p-type at room temperature, indicating that the majority carriers are holes. The lowest  $S$  was achieved for Carbon Black ( $1.8 \mu\text{VK}^{-1}$ ). Actually, Carbon Black display generally quite poor TE properties, when compared with the remaining materials, and for that reason it was not chosen for further investigations.

The high values for  $\sigma$  on graphene ( $\sim 0.33 \text{ Scm}^{-1}$ ), are related with the remarkable electron mobility at room temperature as electrons can travel microns without suffering scattering [91,92]. The sample of graphene didn't achieved the best value reported in the literature ( $10^{-6} \Omega\text{cm}^{-1}$ ) [93], probably because the sample analysed was not a single sheet of graphene but actually Graphene Nanoplatelets, which is few-layered graphite. This explanation is corroborated by the similarities of the TE properties of graphene when compared with the graphite counterpart.

Concerning the MWCNTs, they didn't show superb TE qualities if one considers  $\sigma$  and  $\kappa$ . The Seebeck coefficient is the highest achieved for the carbon-based materials studied ( $\sim 26 \mu\text{VK}^{-1}$ ). The  $\sigma$  is lower when compared with the values from the literature, that can go up to  $\sim 512 \text{ Scm}^{-1}$  [8], however, the same literature also has a majority of reports concerning SWCNTs instead of MWCNTs. The thermal conductivity is the highest one achieved ( $\sim 2.83 \text{ Wm}^{-1}\text{K}^{-1}$ ) and this kind of behaviour is expected for MWCNTs since they demonstrate a self-supporting atomic structure and strong  $\text{sp}^2$  bonds rendering them to have a highly phonon dominated thermoconductivity [8].

The most import parameters to inspect the efficiency of the materials, as mentioned in section 1.2.1, are the  $zT$  and  $PF$ . These two parameters are displayed in **Figure 3.2**.

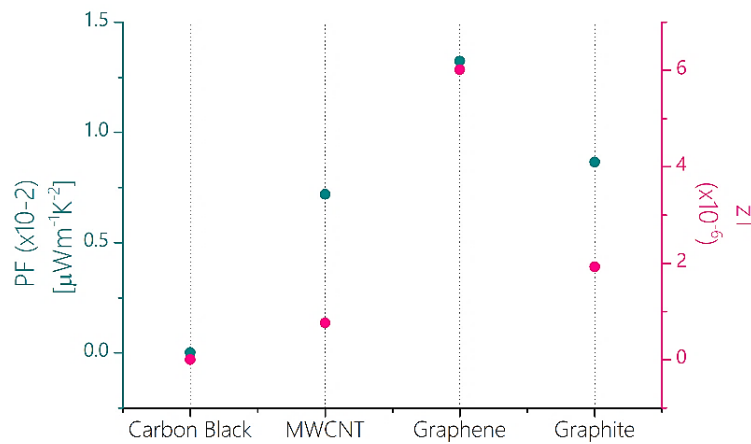


**Figure 3.2.** Power Factor and Figure of Merit results for Carbon Black, MWCNT, Graphene and Graphite measured in bulk in their pristine conditions.

It can be observed that the material that presents highest  $PF$  and  $zT$  is the graphene sample with values of  $\sim 1.32 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  and  $6.02 \times 10^{-6}$ , followed by the graphite ( $PF = 0.87 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  and  $zT = 1.93 \times 10^{-6}$ ), MWCNTs ( $PF = 0.72 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  and  $zT = 0.76 \times 10^{-6}$ ) and Carbon Black ( $PF = 0.002 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  and  $zT = 0.003 \times 10^{-6}$ ).

Considering these results, graphene is the most promising material and for that reason it was one of the materials chosen to move for the tailoring subpart. MWCNTs was the other material chosen and the reason behind it is that they have been widely studied for multiple investigators since they have a morphology highly capable of accepting different types of modifications meaning they have a better chance of progression.

### 3.2 Tailoring Graphene Nanoplatelets

Graphene Nanoplatelets (GN) was used to produce four different samples. The starting material was the same as described in **Table A1**, in Annex A. **Figure 3.3** summarizes the treatments performed on GN. The thickness of the pellets is given on **Table A2**, in Annex A.

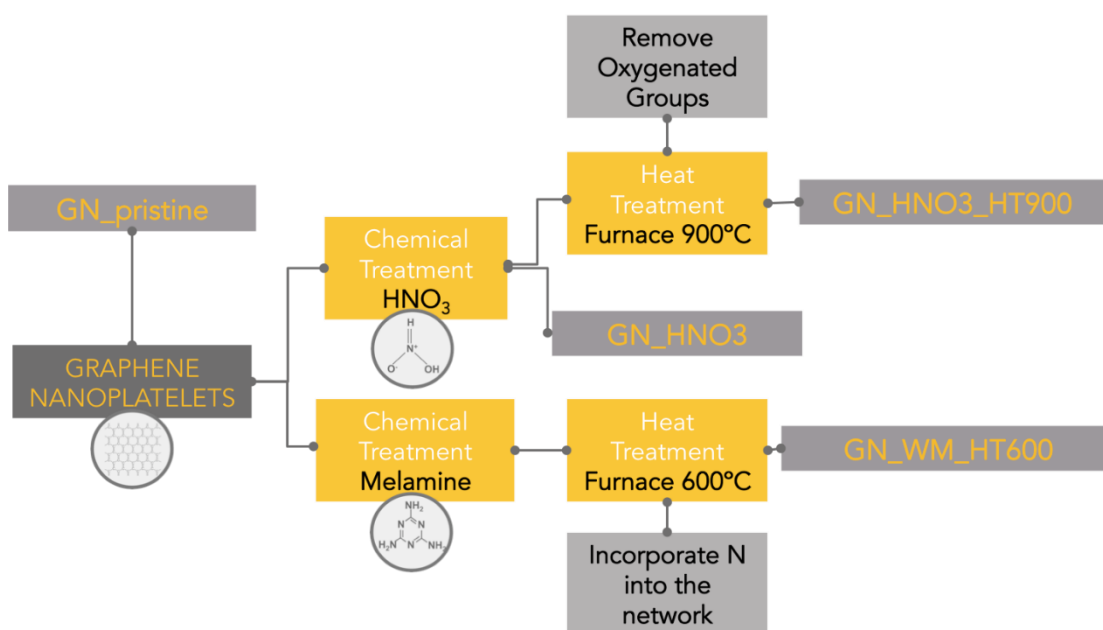


**Figure 3.3.** Schematic summary of the GN samples created and the respective treatments applied.

### 3.2.1 Morphological analysis

XRD analysis was performed to confirm the influence on the structure of the graphene samples. XRD results are shown on **Figure 3.4**.

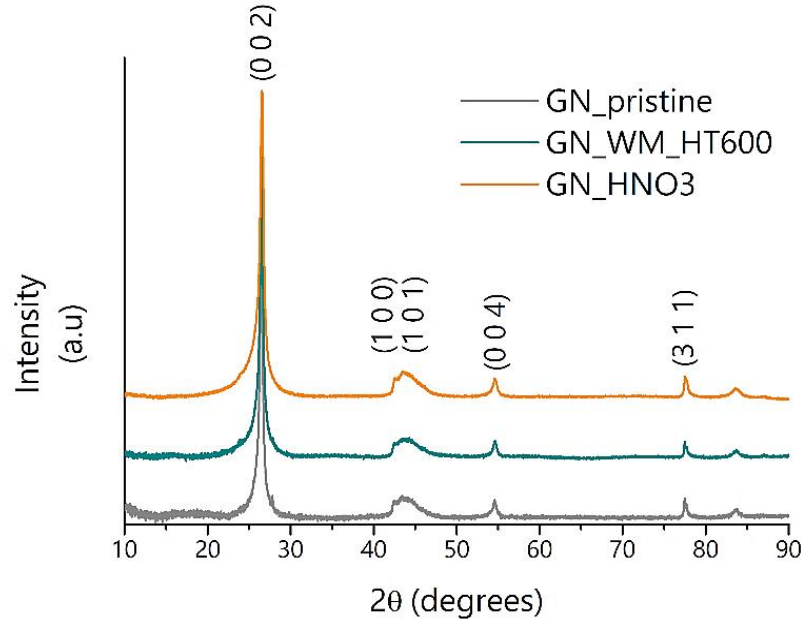


**Figure 3.4.** XRD diffraction pattern for the GN samples.

The diffraction peaks are observed at  $2\theta = 26.5^\circ, 42.5^\circ, 43.5^\circ, 54.6^\circ, 77.5^\circ$  corresponding to the planes (0 0 2), (1 0 0), (1 0 1), (0 0 4) and (3 1 1), respectively. The appearance of these reflections is mainly characteristic of the graphite since in literature the XRD of graphene should appear only one reflection around  $25^\circ$  with a large FWHM. The reflection (0 0 2) is related with the periodicity between graphene layers while the reflection (1 0 0) is related with the periodicity within the graphene layer ergo the honeycomb lattice of a single sheet [94].

**Table 3.1** shows the values of the full width at half maximum (FWHM), the crystallite size ( $L_{002}$ ), the interlayer distance ( $d_{002}$ ) and the approximate number of layers of graphene ( $N$ ) present in each sample of graphene nanoplatelets, respectively. These calculations were performed based on the (0 0 2) plane and using the Debye-Scherrer equation (2.2), the Bragg's Law (2.1) and an equation found elsewhere [95]:

$$L_{002} = (N - 1) d_{002} \quad (3.1)$$

**Table 3.1.** FWHM,  $L_{002}$ ,  $d_{002}$  and  $N^{XRD}$  for the GN samples.

| Samples     | $\theta$<br>(°) | FWHM<br>(°) | $L_{002}$<br>(nm) | $d_{002}$<br>(nm) | $N^{XRD}$ |
|-------------|-----------------|-------------|-------------------|-------------------|-----------|
| GN_pristine | 13.23           | 0.541       | 15.76             | 0.336             | 48        |
| GN_WM_HT600 | 13.26           | 0.744       | 11.46             | 0.336             | 35        |
| GN_HNO3     | 13.25           | 0.606       | 14.07             | 0.336             | 43        |

There aren't major differences in the angles between the incident ray and the scattering plans ( $\theta$ ) when the (0 0 2) peak maximize for the different samples. For that reason, the interlayer distances are the same for the different samples ( $d_{002} = 3.36 \text{ \AA}$ ) and this value is in agreement with both graphene and graphite [27]. The crystallite size is smaller in the sample where it was applied a thermal treatment, which could be due to a better atom rearrangement in the network provoked by the heat. Concerning the number of graphene layers estimated through the XRD data, the number largely differs from the value claimed by the producer for the pristine material (5-7 atomic layers as it can be seen in *Table A1* in Annex A). Even though this method doesn't give an accurate value because it doesn't consider a non-uniform distribution of the graphene thickness, the difference between the two values is large and corroborates with the conclusion that in fact we are dealing with small pieces of graphite.

Additionally, Raman Spectroscopy was performed on the GN samples. Raman Spectroscopy is a standard characterization method for graphene research. This technique is particularly useful for this material due to the information about the atomic structure and the electronic properties that came from the zero bandgap that makes all wavelength of the incident radiation resonant [96]. Raman Spectroscopy can distinguish between an amorphous carbon, a metallic nanotube and a doped graphene sample [97]. The positions, widths and intensities of the Raman peaks are a result of the variations of the electronic properties due to defects, doping, magnetic fields, edges and so on [96].

Before analysing the Raman spectrum, it is important to first know some information about the possible distinct bands that may appear in the spectrum. **Figure 3.5.a)** represents a Raman spectrum for pristine (top) and defected (bottom) graphene to set an example for this analysis.

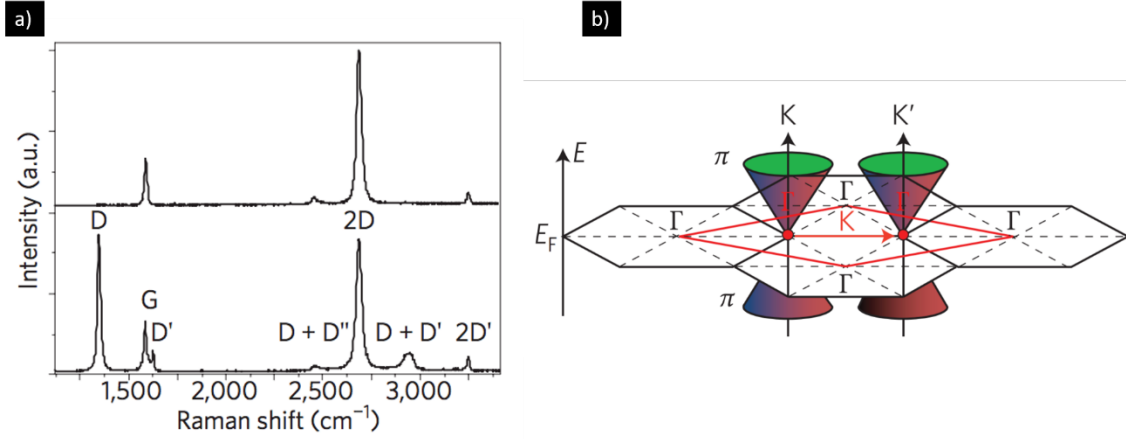


**Figure 3.5.** a) Raman spectra for pristine graphene (top) and defected graphene (bottom). b) Electronic Brillouin zones of graphene (black figures), first-phonon Brillouin zone (red rhombus) and schematic of the electronic dispersion (Dirac cones). Both adapted from [96].

The G peak is related to the high frequency phonon at  $\Gamma$  (**Figure 3.5.b**). The D peak corresponds to the breathing modes of the six-atom ring and comes from a phonon around the Brillouin zone corner K that activates double resonance. It indicates a defected morphology. The D' peak is due to the connection of two points that belong to the same cone around K (or K') also activating double resonance. Peak 2D and 2D' are always present in the spectrum because they are not caused by defects but for two opposite wave vector phonons in a process that conserves momentum. These two peaks are overtones of the D and the D' peaks, respectively. The 2D peak is also referred in the literature for G' as it is conventionally used for graphite and nanotubes [27]. The D+D'' peak is assigned to a combination of a D phonon and a phonon belonging to a phonon seen at  $\sim 1100$  cm<sup>-1</sup> that is called the D'' peak. This peak is also attributed to defects [96].

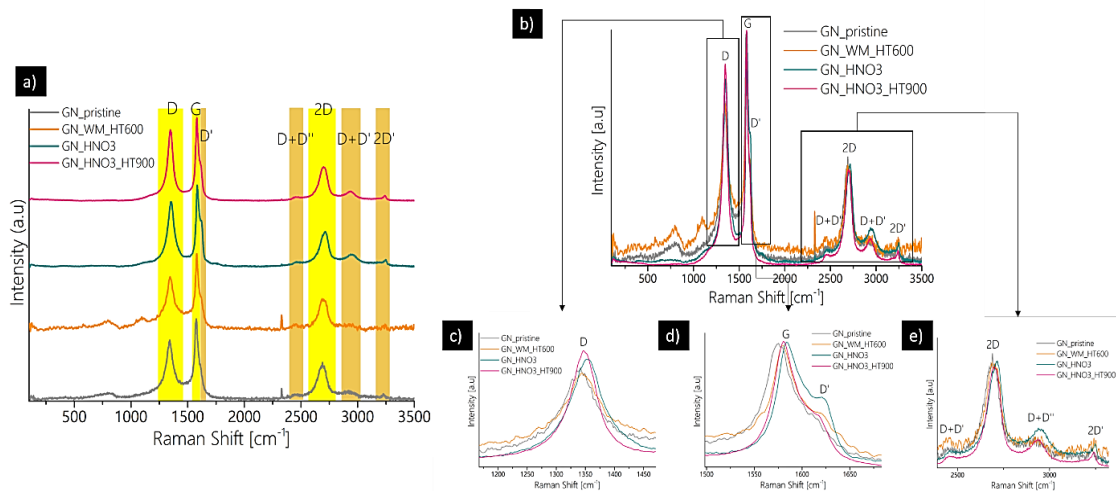


**Figure 3.6.** a-b) Raman spectra for the GN samples with the bands assigned. c) D band detailed. d) G and D' bands detailed. e) D+D', 2D, D+D'' and 2D' detailed.

**Figure 3.6** shows the Raman Spectra for the different GN samples. The peaks shifts can be seen in detail in **Table 3.2**.

**Table 3.2.** Raman prominent bands positions for the GN samples.

|               | $\omega_D$<br>[cm <sup>-1</sup> ] | $\omega_G$<br>[cm <sup>-1</sup> ] | $\omega_{D'}$<br>[cm <sup>-1</sup> ] | $\omega_{D+D''}$<br>[cm <sup>-1</sup> ] | $\omega_{2D}$<br>[cm <sup>-1</sup> ] | $\omega_{D+D'}$<br>[cm <sup>-1</sup> ] | $\omega_{2D'}$<br>[cm <sup>-1</sup> ] |
|---------------|-----------------------------------|-----------------------------------|--------------------------------------|-----------------------------------------|--------------------------------------|----------------------------------------|---------------------------------------|
| GN_pristine   | 1341.5                            | 1575.4                            | 1617.5                               | 2445.4                                  | 2689.9                               | 2924.7                                 | 3226.0                                |
| GN_WM_HT600   | 1343.2                            | 1580.3                            | 1619.1                               | 2457.0                                  | 2701.0                               | 2957.0                                 | 3241.6                                |
| GN_HNO3       | 1353.2                            | 1585.1                            | 1623.9                               | 2458.4                                  | 2714.9                               | 2944.9                                 | 3247.9                                |
| GN_HNO3_HT900 | 1346.5                            | 1580.3                            | 1617.5                               | 2452.6                                  | 2696.7                               | 2936.8                                 | 3241.5                                |

The Raman spectra follows the trend given in the literature for defected graphene samples (**Figure 3.5.a**) - bottom). It is always possible to observe the D peak in the analysed samples meaning that all samples present defects, even the pristine one.

Concerning the number of graphene layers, it is possible to do this analysis through Raman Spectroscopy. There is a C mode that appears around  $\sim 42 \text{ cm}^{-1}$  that is sensitive to the interlayer coupling. It is known in the literature that the absence of this peak would be an evidence of a single layer graphene [96]. However, the analysis of Raman Spectroscopy performed on this work started at  $100 \text{ cm}^{-1}$  thus not allowing to confirm this hypothesis.

For this reason, there was a need for finding other methods for this analysis. This is possible through the consideration of 3 bands: G band, D band and 2D band.

The G band position is highly sensitive to the number of layers. As the layer thickness increases the band position shifts to lower energy because each layer added slightly softens the bonds. The band position can be correlated to the number of graphene layers through the follow empiric relation:

$$\omega_G = 1581.6 + 11/(1 + N^{1.6}) \quad (3.2)$$

where  $\omega_G$  is the G band position in wavenumbers and  $N$  is the number of graphene layers [98]. However, to use this method the band position must be higher than  $1581.6 \text{ cm}^{-1}$  and for this reason it was only possible to calculate for the GN\_HNO3 sample (**Table 3.3**). Despite this fact, looking at **Figure 3.6.d**) it is possible to say that the layers thickness goes as follow  $\text{GN\_HNO3} < \text{GN\_HNO3\_HT900} < \text{GN\_WM\_HT600} < \text{GN\_pristine}$ .

**Table 3.3.** Number of layers from Raman data ( $N^{Ram}$ ), 2D band-G band ratio ( $I_{2D}/I_G$ ) and D band-G band ( $I_D/I_G$ ) for the GN samples.

|               | $N^{Ram}$ | $I_{2D}/I_G$ | $I_D/I_G$ |
|---------------|-----------|--------------|-----------|
| GN_pristine   | n.m.      | 0.470        | 0.741     |
| GN_WM_HT600   | n.m.      | 0.443        | 0.716     |
| GN_HNO3       | 9.6       | 0.436        | 0.797     |
| GN_HNO3_HT900 | n.m.      | 0.410        | 0.852     |

The D band is usually known as the defect band, if this band is significant it means that there are a lot of defects in the material. This band is weak in graphite and also in high quality graphene. Looking at **Figure 3.6.c)** and also to the  $I_D/I_G$  ratio (ratio between the intensity of the D peak and the G peak) it is possible to see that this band is more significant in the oxidized samples, meaning that the acid treatment introduces defects into the graphene network.

Finally, observing to the 2D band, it is caused by a resonant mechanism that is directly related to the electronic band structure, making this band sensitive to  $N$  and also to the layers orientation [96]. For doing the characterization of this band, one must look not only to the band position, but also to the band shape. A single layer graphene has a symmetric 2D peak with a FWHM of  $\sim 30 \text{ cm}^{-1}$ . The addition of graphene layers causes the 2D band to split into several overlapping modes and with this, the symmetry of the peak is lowered [98]. Looking at **Figure 3.6.e)**, it is possible to observe that the peaks from GN\_pristine and GN\_HNO3\_HT900 are the ones who present higher symmetry levels and the one for GN\_WM\_HT600 is the one that is less symmetric.

There is another method to characterize graphene as the number of layers through the ratio  $I_{2D}/I_G$ . Single-layer graphene should have a ratio of 2, double-layer graphene around 1, few-layer graphene 0.8 and multi-layer graphene around 0.5 [99]. On **Table 3.3** is given the  $I_{2D}/I_G$  for the GN sampled. From these results, it is possible to say that all the samples presented can be considered multi-layered graphene, since the ratio is  $< 0.5$ , which is in accordance with previous XRD results.

### 3.2.2 Textural and Surface Analysis

The textural properties of the samples produced were evaluated by the corresponding N<sub>2</sub> adsorption-desorption isotherms in order to qualify the modifications induced by the different treatments. **Figure 3.7** represents the results obtained from this type of technique.

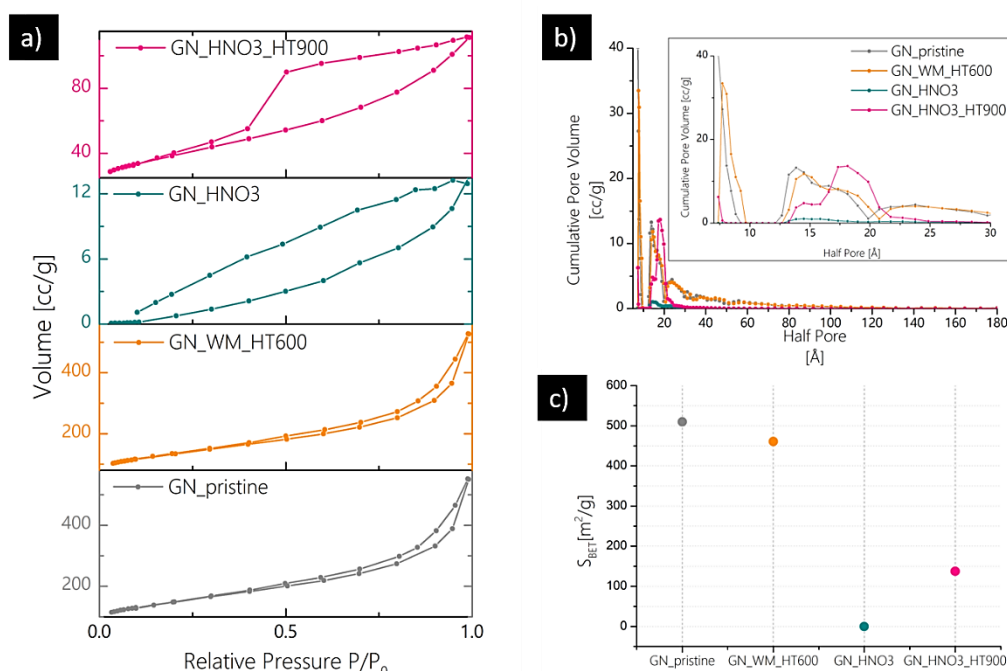


**Figure 3.7.** a) N<sub>2</sub> adsorption-desorption isotherms for the graphene materials. b) Pore volume distribution for GN samples. c) Surface BET area results.

**Figure 3.7.a)** shows the adsorption-desorption isotherms for the graphene samples. Comparing the behaviour with the IUPAC classification of physisorption isotherms, it is possible to identify that GN\_pristine and GN\_WM\_HT600 can be classified type II. This type is related to the physisorption of most gases on nonporous and microporous adsorbents [100]. The samples oxidized display hysteresis that is usually associated with capillary condensation. One may classify the GN\_HNO3 isotherm as a type H3 isotherm and the GN\_HNO3\_HT900 as a type H4. Type H3 has an adsorption similar to type II and this behaviour is typically given for plate type non rigid aggregates but also if the porous network has microporous that are not completely filled through condensation. Type H4 is a composite between type II and type III and the pronunciation that can be seen at lower pressures is due to microporous filling that are found in micro-mesoporous carbon.

Following the isotherm behaviour, GN\_pristine and GN\_WM\_HT600 also show a similar behaviour in the distribution of the pore dimensions with a slight shift of  $\sim 0.5 \text{ \AA}$  between the two half pore distributions, as it can be seen in **Figure 3.7.b)**. The main pore radius is between  $(0 - 10) \text{ \AA}$  and  $(12.5 - 20) \text{ \AA}$ . Concerning the surface area for these two samples (**Figure 3.7.c)**), there is a slight reduction for the GN\_WM\_HT600 sample that can be explained by some attraction behaviours from the introduction of the nitrogen atoms into the graphene network. A pore size reduction for the GN\_HNO3 sample should be expected due to the introduction of the surface oxygen groups however this is also accompanied with an extreme reduction of the scale in the isotherms and in the surface BET area that is less than  $5 \text{ m}^2/\text{g}$ . This suggests that the oxidation treatment provoked a relevant modification on the textural properties like a collapse of the graphene structure that may or not be caused by the elevated temperature used on the oxidation process. The heat treatment at  $900 \text{ }^\circ\text{C}$  performed on the oxidized sample not only lift the pore distribution from being almost non-existent to a  $(12.5 - 20) \text{ \AA}$  main distribution, but also increased the surface BET area, even that it remains considerably lower than the one presented by the pristine sample (loss of 73% of the surface area). This technique also revealed no presence of microporous for all the analysed samples. EA and OA analysis were also performed on the GN samples and the results are shown in **Figure 3.8.a)**.

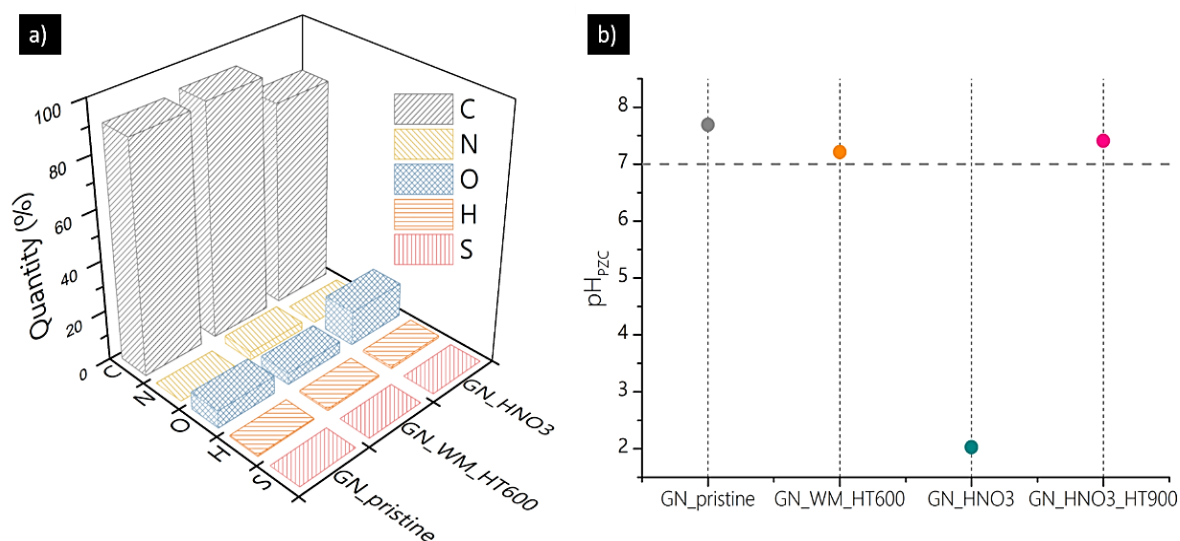


**Figure 3.8.** a) EA and OA results for the GN samples analysed. b)  $\text{pH}_{\text{PZC}}$  measured for GN samples with a grey line for neutral  $\text{pH} = 7$ .

From this analysis it is possible to understand the extent of the introduction of the functional groups in the oxidized samples and also the doping level on the melamine treated one. The melamine treatment successfully doped the GN sample, introducing ~3 % of nitrogen into the network. The oxidation treatment duplicated the oxygen quantity on the graphene sample (from ~6.9 % to ~13.8 %) indicating that oxygenated functional groups probably were attached to the graphene surface.

Considering the acid-basic character of the samples present on **Figure 3.8.b)**, the pristine sample revealed a basic-almost-neutral character ( $pH_{PZC} = 7.7$ ). GN\_WM\_HT600 maintained the neutral character and GN\_HNO3 presents an acidic character ( $pH_{PZC} = 2$ ). This acidic character suggests that the graphene surface was functionalized with acidic groups, corroborating with the results from OA. However, when the thermal treatment at 900 °C was performed on the oxidized sample, the sample revealed a return to the neutral character, suggesting that the majority of the acidic groups were removed with the heat.

TPD measurements revealed the amount of CO and CO<sub>2</sub> released with the temperature for the different samples and these results are displayed on **Figure 3.9**.

**Table 3.4** is a helpful tool for analysing the type of functional groups that can be released at the different temperatures [101].

**Table 3.4.** Functional groups liberated for the different temperatures for CO and CO<sub>2</sub> [101].

| Functional groups     | Release Temperature (T <sub>R</sub> ) | Decomposed Gas         |
|-----------------------|---------------------------------------|------------------------|
| Phenol                | 500°C < T <sub>R</sub> < 750°C        | CO                     |
| Carbonyl/Quinone      | 700°C < T <sub>R</sub> < 950°C        | CO                     |
| Carboxylic Anhydrides | 350°C < T <sub>R</sub> < 600°C        | CO and CO <sub>2</sub> |
| Carboxylic Acid       | < 450°C                               | CO <sub>2</sub>        |
| Lactones              | >600°C                                | CO <sub>2</sub>        |

The amount of CO and CO<sub>2</sub> released is higher on the GN\_HNO3 sample (in total CO = 1487 μmolg<sup>-1</sup> and CO<sub>2</sub> = 1590 μmolg<sup>-1</sup>), which is expected because the acid treatment is responsible for the introduction of additional functional groups, relative to the pristine sample. This treatment not only increased the amount of phenol, carbonyl and carboxylic anhydrides already existent on the pristine sample but also introduce some carboxylic acid and lactones as it can be seen in the CO<sub>2</sub> spectrum. Regarding the GN\_HNO3\_HT900 sample, it can be observed that the amount of gases released are

way inferior comparing with the GN\_HNO<sub>3</sub>, corroborating with the evidences found with the pH<sub>PZC</sub> results that the functional groups introduced with the oxidation were in fact mostly removed. The GN\_WM\_HT600 also revealed that almost no functional groups are present in the sample with the exception of some quantity of phenols.

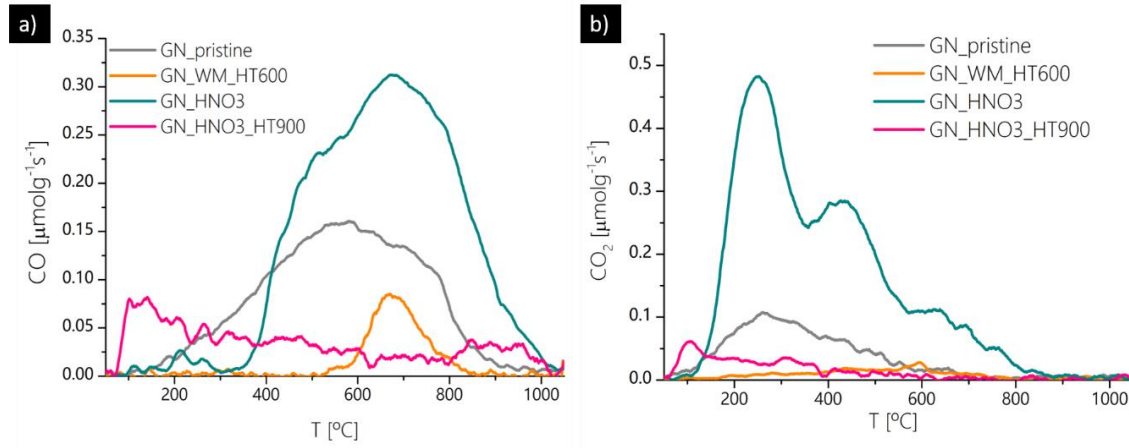


**Figure 3.9.** a) Quantity of CO liberated with the temperature for the GN samples. b) Quantity of CO<sub>2</sub> liberated with the temperature for the same samples.

The mass percentage of oxygen on the surface ( $\% m_o$ ) was calculated with base on the TPD data, assuming that all the surface oxygen is released as CO and/or CO<sub>2</sub>. These results are stated on **Table 3.5**. The base for these calculations was:

$$\% m_o = \left( \frac{CO}{2} + CO_2 \right) \times \frac{M}{10^6} \times 100 \quad (3.3)$$

where CO and CO<sub>2</sub> are the amount of gases released also stated in **Table 3.5** and M is the gases molar mass. **Table 3.5** also shows some relevant information obtain from the other techniques.

**Table 3.5.** Properties of GN functionalized samples: CO and CO<sub>2</sub> quantities and percentage of oxygen from TPD data; percentage of oxygen and nitrogen from OA and EA data; pH<sub>PZC</sub> of the GN samples; BET surface area from N<sub>2</sub> isotherms data.

|                            | CO<br>[ $\mu\text{mol g}^{-1}$ ] | CO <sub>2</sub><br>[ $\mu\text{mol g}^{-1}$ ] | $\% m_o$ | $\% O^{OA}$ | $\% N^{EA}$ | pH <sub>PZC</sub> | S <sub>BET</sub><br>[ $\text{m}^2 \text{g}^{-1}$ ] |
|----------------------------|----------------------------------|-----------------------------------------------|----------|-------------|-------------|-------------------|----------------------------------------------------|
| GN_pristine                | 803                              | 411                                           | 2.6      | 6.9         | 0.0         | 7.69              | 510                                                |
| GN_WM_HT600                | 145                              | 89                                            | 0.52     | 4.6         | 3.1         | 7.21              | 461                                                |
| GN_HNO <sub>3</sub>        | 1487                             | 1590                                          | 7.47     | 13.8        | 0.0         | 2.03              | < 5                                                |
| GN_HNO <sub>3</sub> _HT900 | 303                              | 166                                           | 1.02     | n.m.        | n.m.        | 7.41              | 137                                                |

The percentage of oxygen mass present on the surface of the samples, from TPD, follows the same trend as the oxygen content found from OA. In fact, functional groups containing oxygen are present in some degree in the pristine sample and are increased significantly with the oxidation treatment. GN\_WM\_HT600 revealed a decrease on the oxygen quantity meaning that the heat treatment applied for the incorporation of nitrogen also removed some of the oxygenated groups that were naturally attached to the surface.

Thermogravimetric analysis was also performed on the graphene samples in order to observe the thermal degradation of the materials, represented on **Figure 3.10**.

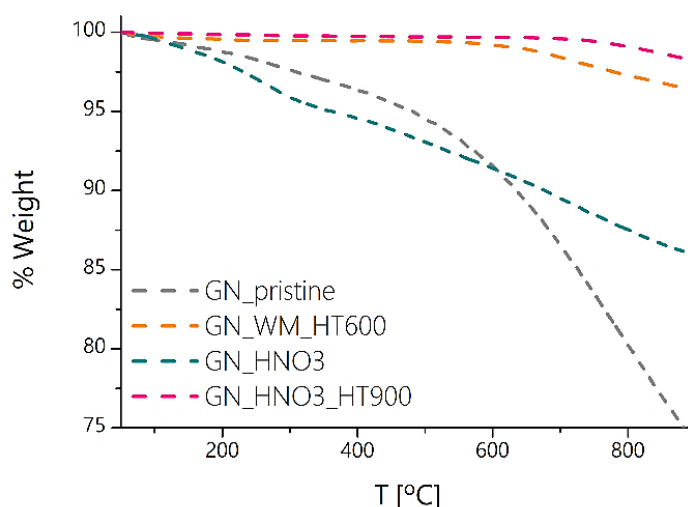


**Figure 3.10.** Thermal degradation in function of temperature for the GN samples from TG analysis.

As expected, the thermal treated materials didn't display a high level of thermal degradation. GN\_HNO3\_HT900 maintain the weight throughout the analysis losing ~1 % after 750 °C. This stability is reasonable since the material already lost the groups in the annealing at 900 °C. Following this trend, GN\_WM\_HT600 starts the weight lost around 600 °C, that is, the annealing temperature of the material. After the 500 °C, the degradation is usually due to thermal oxidation of the remaining disordered carbon [102].

In contrast, GN\_pristine and GN\_HNO3 had a considerable thermal degradation throughout the analysis, ~ 25 % and ~ 15 %, respectively. The thermal degradation is a multistage process. Up to 150 °C, it is due to the water evaporation. From 150 °C to 350 °C is attributed to the decarboxylation of the carboxyl groups [103] which corroborated with results from TPD about the existence of such carboxylic groups and also that they are more present in the GN\_HNO3, as suggested for the more accentuated slope in the TGA result for this sample. Moreover, between 350 °C and 500 °C, it is often related to the elimination of hydroxyl functionalities [104], meaning that the oxidized sample had

more hydroxylic groups, as already found before, but that they are also naturally attached to the pristine sample. After the 500 °C, the degradation is a result of the thermal oxidation of the disordered carbon. From this, it is possible to conclude that the original sample display high levels of disordered carbon and thus, that the acid treatment is a successful procedure to clean the graphitic material.

### 3.2.3 Transport Properties and TE performance

The thermoelectric performance of graphene through the application of different treatments was studied. For this reason, the transport properties of the materials were measured for the samples produced and for this purpose the powder samples were modified into pellets thus allowing for these properties to be measured. Unfortunately, it was impossible to transform the sample GN\_HNO3\_HT900 in pellet. The results for the Seebeck Coefficient, the electrical conductivity and thermal conductivity are displayed on **Figure 3.11**. An auxiliary grey line was added for the pristine sample results in order to facilitate the comparison with the values for the functionalized samples.

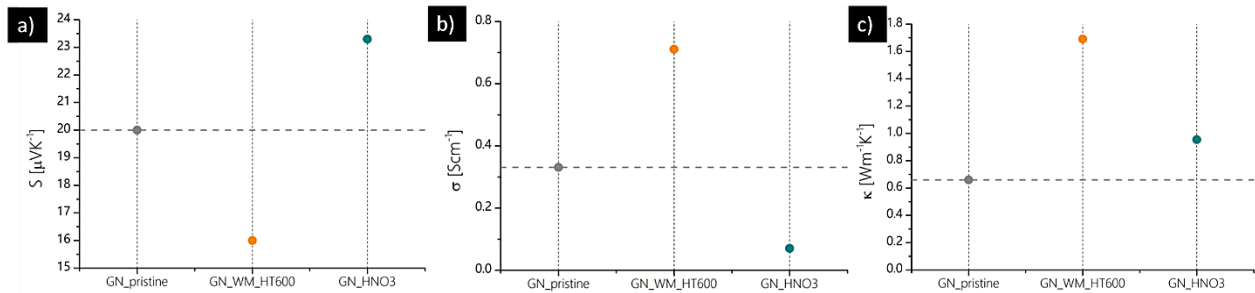


**Figure 3.11.** Transport properties for the functionalized GN samples: a) Seebeck coefficient results; b) Electrical conductivity; c) thermal conductivity. The grey line is auxiliary for comparing the developed samples with the original.

Concerning the  $S$  results, there is an improvement of 17 % relative to the pristine sample for the oxidized sample. However, the nitrogen doping was responsible for a reduction of this property around 20 %.  $S$  is affected by the band structure of the material meaning that the improvement could be due to the insertion of nitrogen which is known to induce a n-type character thus reducing the number of carriers. On the other end, the oxidation promoted an increase of  $S$  up to  $23.3 \mu\text{VK}^{-1}$ . The exact opposite happens in  $\sigma$ , GN\_WM\_HT600 perform better while GN\_HNO3 perform worst. Relative to the GN\_WM\_HT600, there was an improvement up to  $0.71 \text{ Scm}^{-1}$ , an upgrade of 115 % relative to the pristine sample. This could be explained by an increase in the carrier density. Oddly, the oxidation didn't improve this property like it was supposed to and

such fact could be easily explained by the collapse of the graphene structure that was concluded in the previous chapter through the surface BET area results. This same reason may explain the increase of the thermal conductivity since larger surface areas promote phonon scattering that reduces the phononic component of this property. GN\_WM\_HT600 also revealed a setback on  $\kappa$  of 156% relative to the pristine sample.

Power Factor and Figure of Merit were also calculated for the GN samples and the results are shown in **Figure 3.12**.

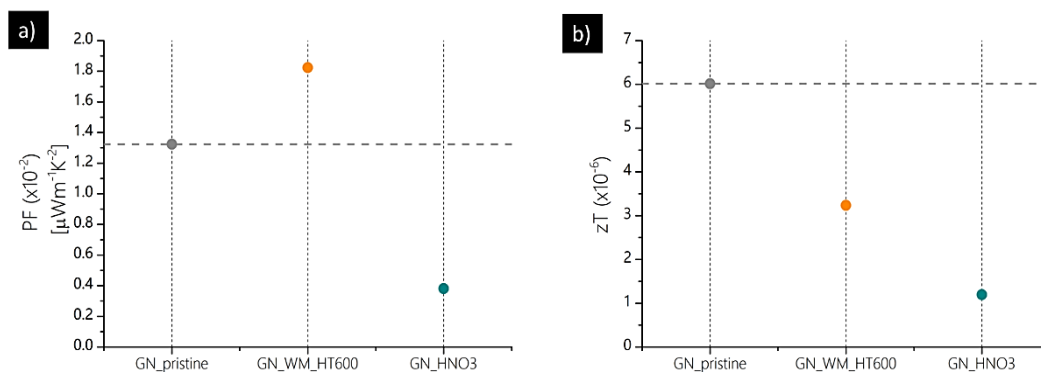


**Figure 3.12.** Thermoelectric performance of the GN samples: a) Power Factor; b) Figure of Merit.

The power factor represents the electrical properties of the materials. It was possible to improve the electrical properties of GN\_WM\_HT600 in 38 % relative to GN\_pristine, obtaining a value for this propriety of  $\sim 1.82 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ . However, the thermal transport causes the final TE performance evaluated through  $zT$  to get worst. This is a great example of how important the thermal conductivity could be in this analysis. The collapse of the graphene structure imposed by the use of elevated temperatures in the oxidation process caused the TE properties of the material to deteriorate. Unfortunately, the improvement of the TE performance of graphene was not possible for the functionalizations performed.

### 3.3 Tailoring Multiwalled Carbon Nanotubes

MWCNTs were subjected to different type of treatments. The starting material were carbon nanotubes multiwalled-type as described in **Table A1** in Annex A. The thickness of the pellets is given on **Table A3**, in Annex A. **Figure 3.13** schematizes the process that produced the nine different samples of MWCNTs.

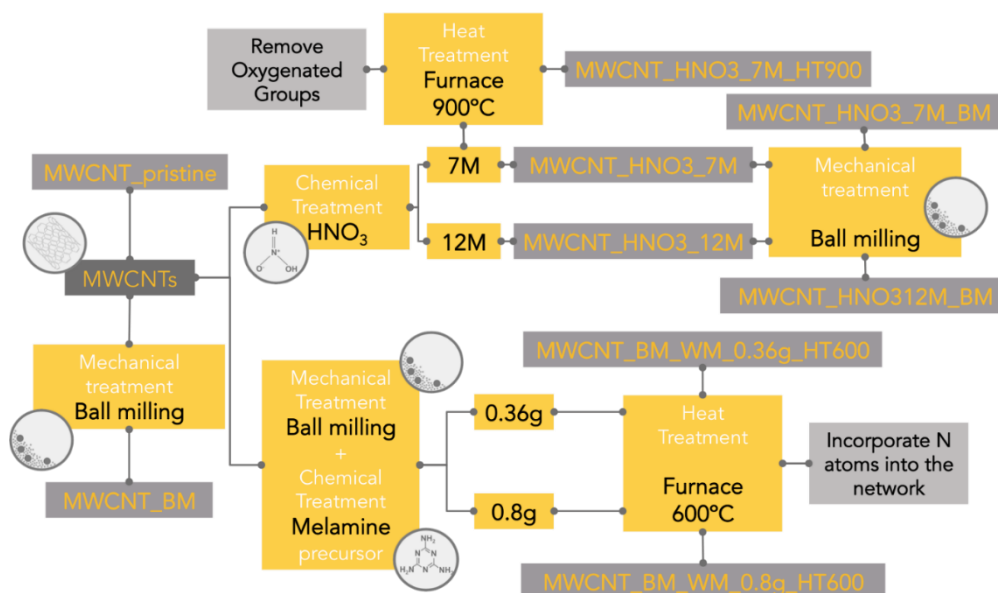


**Figure 3.13.** Schematic representation of the MWCNT samples and the processes used to obtain them.

### 3.3.1 Morphological Analysis

TEM analysis was used to qualify the differences between some of the functionalized samples. Such results are shown on **Figure 3.14**.

From TEM analysis, it was achieved a diameter size of the original nanotubes around 9 nm, consistent with the diameter disclaimed by the producers. Moreover, the average diameter doesn't seem to change upon the modifications applied (**Figure 3.15.a**).

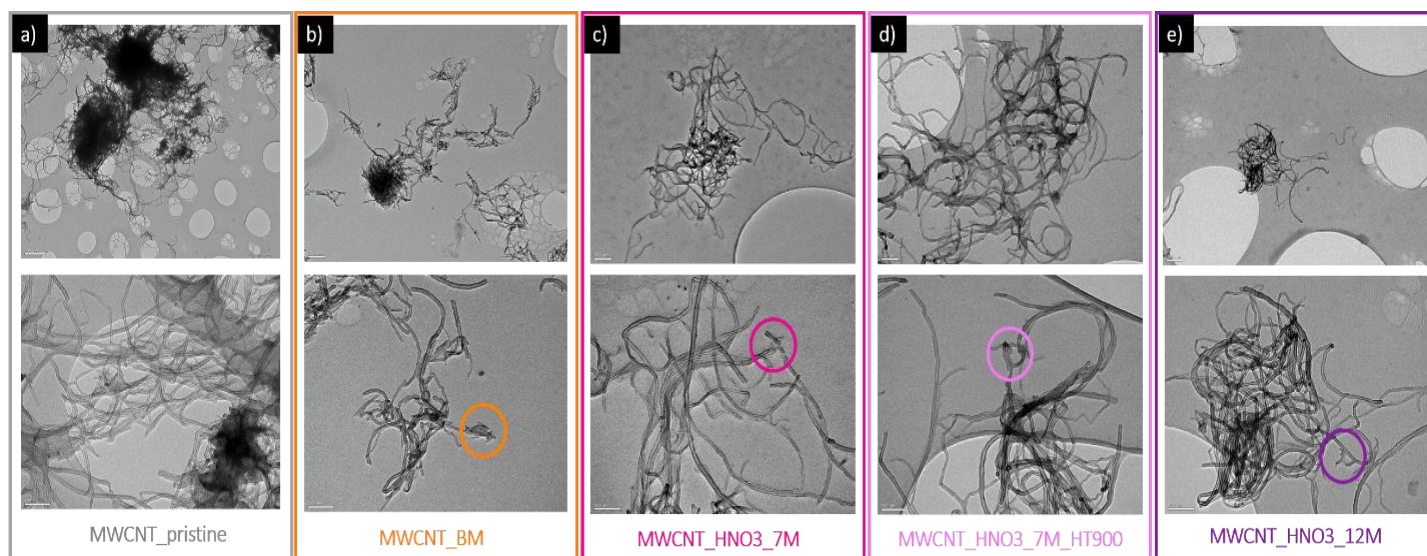


**Figure 3.14.** TEM images of the prepared samples. a) MWCNT\_pristine (top - 0.5μm; bottom - 100nm); b) MWCNT\_BM (top - 200nm; bottom - 100nm); c) MWCNT\_HNO3\_7M (top - 100nm; bottom - 200nm); d) MWCNT\_HNO3\_7M\_HT900 (top - 100nm; bottom - 200nm); e) MWCNT\_HNO3\_12M (top - 100nm; bottom - 100nm).

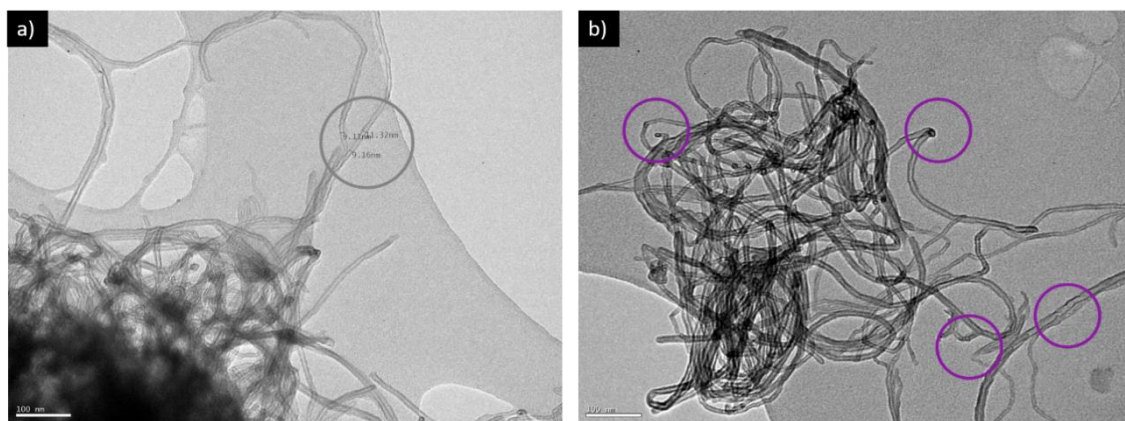


**Figure 3.15.** TEM images. a) MWCNT pristine diameters. b) MWCNT HNO<sub>3</sub> 12M defects details.

Additionally, TEM results showed that the original sample (**Figure 3.14.a**) - top) present a more agglomerated disposition of the nanotubes in contrast with the rest of the samples where it is shown a more dispersive configuration. This could be explained by the repulsions imposed by the functional groups attached to the nanotube's walls. Furthermore, is possible to observe the defects that the oxidative treatments and ball-milling caused to the MWCNTs (**Figure 3.15.b**). It is very clear that the treated samples show some cut ended-tips, folded tips, inconsistencies on the diameters over the nanotube length that could be considered as cracks on the walls and also that the nanotubes look smaller than the nanotubes of the original sample.

XRD was another technique used for characterizing the morphology of the MWCNTs samples. The results are shown on **Figure 3.16**.

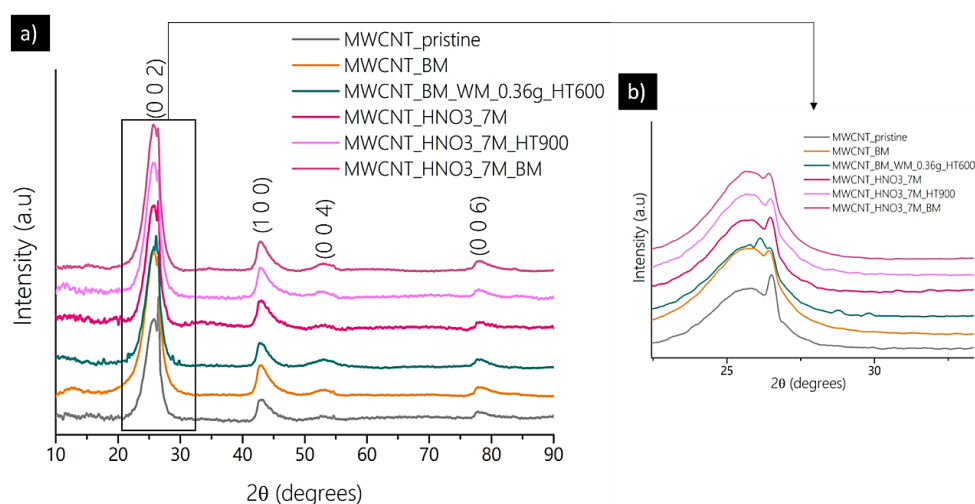


**Figure 3.16.** a) XRD results for MWCNT samples prepared with the respective diffraction peaks assigned. b) Close up on the (0 0 2) diffraction peak where it is possible to observe an extra peak.

The first conclusions that can be made are the diffraction peaks that can be observed at  $2\theta = 25.8^\circ; 43^\circ; 53.4^\circ; 77.8^\circ$  that are related to planes (0 0 2), (1 0 0), (0 0 4) and (0 0 6), respectively, an evidence of the high crystallinity that the materials present that are consistent with the ones found in the literature for this type of material [105]. An impurity peak arises for  $\sim 26.5^\circ$  as it can be seen in detail in **Figure 3.16.b)** and can be an effect from a graphitic influence. This peak is present in all spectra which means that the impurity comes from the commercial batch of MWCNT and it is not provoked by the treatments applied to the samples. Moreover, another unidentified peak is present in the MWCNT\_BM\_WM\_0.36g\_HT600 at  $\sim 26.2^\circ$ . The graphitic peaks also seem to be reduced with the treatments applied and therefore one could conclude that they promote the cleansing of the material.

The reflection on plan (0 0 2) is related with the periodicity between layers and this peak can be studied for obtaining different information. Applying the Bragg's law give information about the interlayer distance ( $d_{002}$ ) and applying the Debye-Scherrer relation give information about the crystallite size ( $L_{002}$ ). These results are shown on **Table 3.6**.

**Table 3.6.**  $\theta$ ,  $d_{002}$ , FWHM,  $L_{002}$ ,  $\delta$  for the MWCNT samples, based on the XRD data.

|                         | $\theta$<br>( $^\circ$ ) | $d_{002}$<br>(nm) | FWHM<br>( $^\circ$ ) | $L_{002}$<br>(nm) | $\delta$<br>(nm <sup>-2</sup> ) |
|-------------------------|--------------------------|-------------------|----------------------|-------------------|---------------------------------|
| MWCNT_pristine          | 12.88                    | 0.346             | 2.656                | 2.99              | 0.112                           |
| MWCNT_BM                | 12.92                    | 0.345             | 2.925                | 2.72              | 0.135                           |
| MWCNT_BM_WM_0.36g_HT600 | 12.91                    | 0.345             | 2.647                | 3.00              | 0.111                           |
| MWCNT_HNO3_7M           | 12.84                    | 0.347             | 2.528                | 3.14              | 0.101                           |
| MWCNT_HNO3_7M_HT900     | 12.85                    | 0.346             | 2.653                | 3.00              | 0.111                           |
| MWCNT_HNO3_7M_BM        | 12.85                    | 0.346             | 2.683                | 2.96              | 0.114                           |

The interlayer distance does not change dramatically between samples, which means that the interlayer distance is not a variable upon the functionalization performed. This value is always around  $\sim 0.35$  nm, which is consistent with the values found in the literature that go from 0.32 nm to 0.38 nm [106]. The crystallite size is a more variable parameter, ball-milling seems to reduce the crystallite size (about 9% relative to the pristine sample), which aligns with the demolish nature of the treatment and oxidation seems to increase the crystallite size (about 5% relative to the pristine sample), which could be explained by the introduction of the surface functional groups. Moreover, the application of the heat treatments in both samples makes them returning to the original crystallite size as it can be seen in sample MWCNT\_BM\_WM\_0.36g\_HT600 and also on sample MWCNT\_HNO3\_7M\_HT900, from these results, one must conclude that the

heat treatments promote the atomic rearrangement. The atomic dislocation factor can be calculated from the crystallite size values ( $\delta = 1/L_{002}^2$ ) and as so it can be concluded that while ball-milling promotes the atomic dislocations, the heat treatments and oxidation promotes the atomic rearrangement.

Reflection (1 0 0) also gives relevant information about the periodicity of the hexagonal lattice present in a single sheet of graphene, and, as it was not observed relevant shifts on this peak, one must conclude that this lattice periodicity was not changed with the modifications applied to the MWCNTs.

Raman Spectroscopy was another characterization technique applied to the MWCNTs samples. This technique is a powerful tool for the characterization of  $sp^2$  carbons since it can be used to evaluate the diameter, the disorders, effects in nanotube-nanotube interactions and so on [107]. A lot of progress has been made on obtaining the maxim information from the Raman data in SWCNT. **Figure 3.17.a)** is a representation of a typical spectrum for SWCNT. The characteristic bands are features than can provide complementary information about the nanotubes. The RBM band is the first band to appear and refers to the radial breathing mode where all the carbon atoms are moving in-phase in the radial direction as it can be seen in **Figure 3.17.b)**. This band is sensitive to the tube diameter and also to the (n, m) representing the nanotube chirality. The G band is due to the movement of neighbouring atoms in opposite direction along the surface of the tube, as represented in **Figure 3.17.c)**. It is an intrinsic feature of the carbon nanotube closely related with the  $sp^2$  vibrations [27]. One of the features allowed for this band is to distinguish between a semiconducting and a metallic nanotube. In SWCNT, this band shows two components,  $G^+$  and  $G^-$ , that are attributed to different phenomena: the first from vibrations along the circumferential directions and could be related to the diameter of the nanotubes; and the second one from vibrations along the G direction related with the metallicity of the CNT [96]. The D band gets the name from the fact that it represents the dispersive disorder giving an overview of the defect concentration. It should not appear in high quality materials and is a direct consequence from a break of symmetry that can be caused by different events, like vacancy defects, porous, edges and so on. The  $G'$  band is a harmonic of second order also related to the dispersive disorder. Both of these shows strong dispersive behaviour and are interpreted for the literature as a double resonance process induced by the laser where there is a resonant transition of an electron from the valence to the conductance band [107], as it is represented in **Figure 3.17.d)**. Contrarily to the D band,  $G'$  band is observed for defect-free  $sp^2$  carbon because it does not require an elastic defect-related scattering

process [108]. This band can also be a way of accessing the doping level on a sample and to a certain degree, reveal that n-doped samples shift to lower frequencies while p-doped samples shift to higher frequencies.

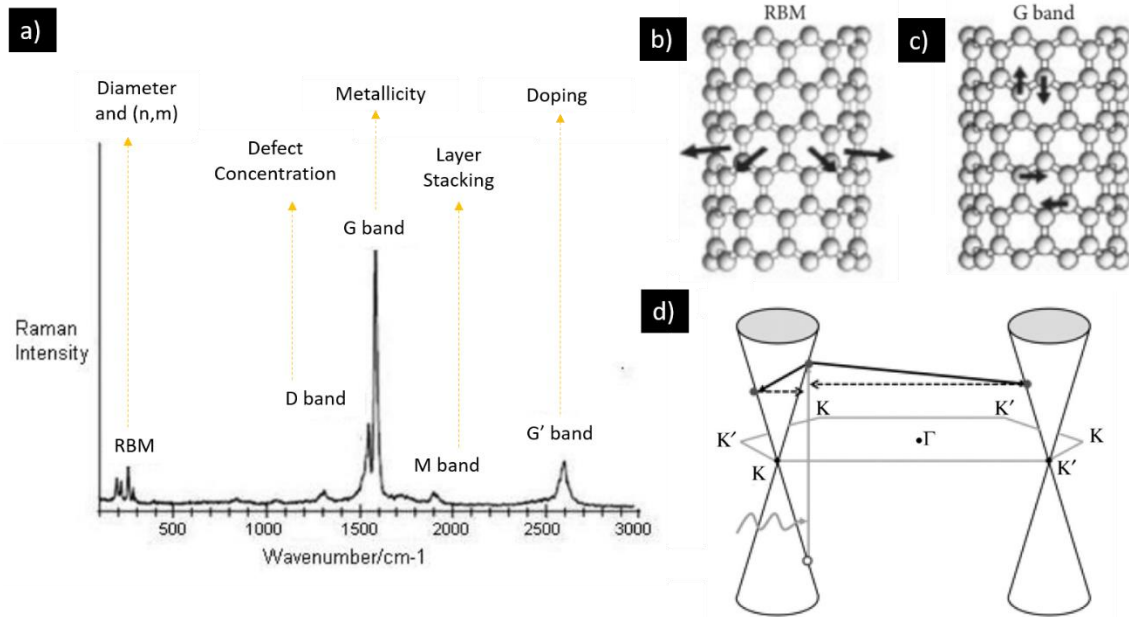


**Figure 3.17.** a) Typical SWCNT spectra with the main bands assigned and the respective features, adapted from [126]. b-c) Schematic representation of the atomic vibration for the b) RBM mode and c) G band, adapted from [27]. d) Schematic representation of the electronic dispersion near the Fermi level at the K and K' points in the hexagonal Brillouin zone. The light induced electron-hole formation is indicated by a grey arrow. The two resonant electron-phonon scattering processes associated with the D and D' bands are indicated by the black arrows. Adapted from [127].

The foundations are now settled for the analysis of the MWCNT spectra. However, one should be careful when doing these correlations because SWCNT spectrum is very different from the MWCNT. If a DWCNT has the multiple effect of two concentric nanotubes that can present 4 different configurations in total (the same but also different electrical behaviour that affect the spectrum in different ways), one can easily escalate to what the endless combinations in MWCNT could contribute for the Raman spectra. Moreover, analysing a single element is very different from having a bundle, because nanotubes interact with each other which can have a great impact on the optical properties. **Figure 3.18** shows the Raman spectra for the different MWCNT samples, where the most relevant bands are already signaled.

In general, Raman spectra follow the same trend represented in **Figure 3.18.a)** since the 3 main bands are present. However, some differences must be noticed between SWCNT typical spectrum and the ones obtained for the MWCNTs. First, in MWCNT there isn't a remarkable presence of the RBM. This absence is explained by the large diameter of the outer nanotubes that must be less than 2 nm for this effect to be visible. Other characteristic that cannot be detected is the splitting of the G band in  $G^+$  and  $G^-$  and it's due to the effect of the diameter distribution in an individual MWCNT but also to

the variation between the different nanotubes within the ensemble of MWCNT. And finally, the ratio between the D band and the G band is significantly bigger in SWCNT than it is for MWCNT, this indicates that MWCNT presents a higher quantity of structural defects as it is expected due to the effect of the multiple graphitic layers [108].

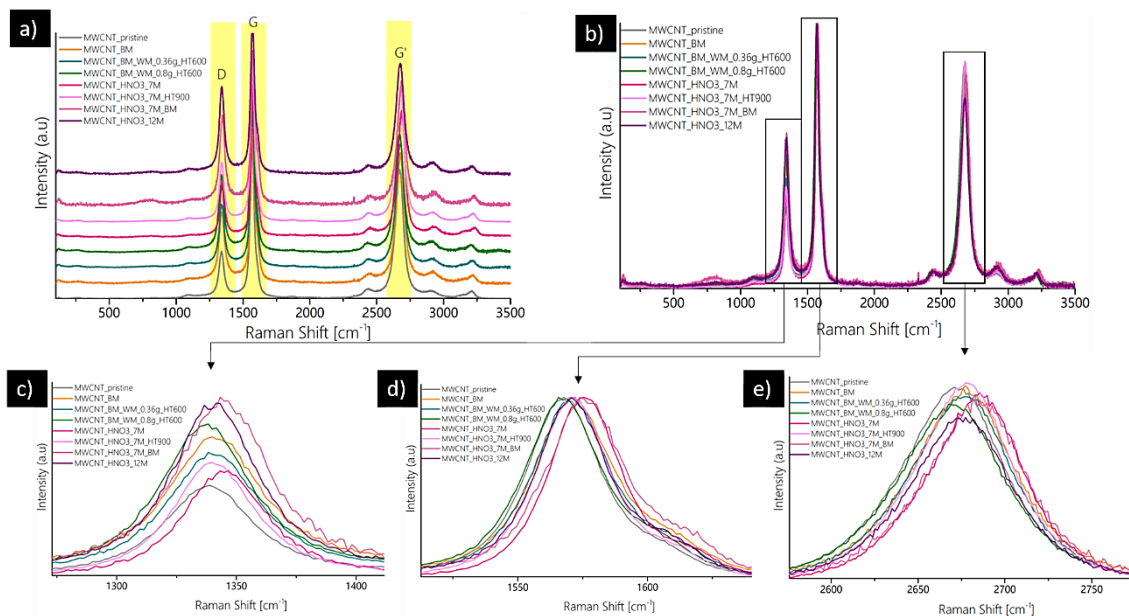


**Figure 3.18.** a-b) Raman Spectra for the MWCNT prepared samples with the main bands assigned. Close up of the c) D band; d) G band and e) G' band.

It is also very noticeable that there are shifts in the functionalized samples relative to the original sample, revealing that the treatments used affected the optical properties of the MWCNTs. **Table 3.7** shows the peaks positions for the respective main bands and the ratio between the intensities of the D band and the G band.

**Table 3.7.** D band, G and G' band positions and the ratio between the intensities of the D and G peak for the MWCNT samples.

|                         | $\omega_D$<br>[cm <sup>-1</sup> ] | $\omega_G$<br>[cm <sup>-1</sup> ] | $\omega_{G'}$<br>[cm <sup>-1</sup> ] | $I_D/I_G$ |
|-------------------------|-----------------------------------|-----------------------------------|--------------------------------------|-----------|
| MWCNT_pristine          | 1338.6                            | 1566.8                            | 2673.1                               | 0.313     |
| MWCNT_BM                | 1343.2                            | 1570.7                            | 2679.5                               | 0.457     |
| MWCNT_BM_WM_0.36g_HT600 | 1339.9                            | 1570.7                            | 2677.5                               | 0.405     |
| MWCNT_BM_WM_0.8g_HT600  | 1338.2                            | 1566.8                            | 2670.9                               | 0.504     |
| MWCNT_HNO3_7M           | 1346.6                            | 1576.0                            | 2686.5                               | 0.353     |
| MWCNT_HNO3_7M_HT900     | 1339.9                            | 1570.7                            | 2678.9                               | 0.383     |
| MWCNT_HNO3_7M_BM        | 1343.9                            | 1576.0                            | 2686.9                               | 0.576     |
| MWCNT_HNO3_12M          | 1339.9                            | 1570.7                            | 2677.4                               | 0.57      |

The  $I_D/I_G$  is a good indicator of the quality of bulk samples. The approximation of these bands (equivalent to the highest ratio) reveals a higher quantity of structural defects. For obvious reasons, ball-milling is a treatment that increases the defect concentration, as already proved by TEM analysis. This conclusion comes from the comparison between samples before and after ball milling, the case of MWCNT\_pristine and MWCNT\_BM and also between MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_BM where there is an increase of  $\sim 46\%$  and  $\sim 63\%$  of ratio relative to the samples before ball milling, respectively. The oxidative treatment is also a defect inducer factor but this factor is way more noticeable when the acid concentration is bigger (increases  $\sim 13\%$  for 7 M and  $\sim 82\%$  for 12 M of the pristine sample value). A reasonable explanation for this occurrence is that the acid causes the destruction of the graphitic integrity with the subsequent formation of small graphitic fragments which leads to an enhancement of the  $I_D/I_G$  ratio. Moreover, the increase of the quantity of melamine used in the nitrogen doped samples also increases the defect concentration since this is the only variable factor between these two samples. In the literature, there are reports that heat treatments may reduce the defect concentration and re-ordering the carbon structure, however this is only true when the annealing temperature is above 1000 °C [109]. Actually, below this temperature, the reports follow the opposite direction [110], increasing the defect level in the samples, fact that is observed for sample MWCNT\_HNO3\_7M\_HT900 relative to sample MWCNT\_HNO3\_7M where there is a humble increase of  $\sim 8\%$  in the defect concentration.

There are two ways of distinguish semiconductive behaviour from metallic behaviour from Raman Spectroscopy. One is from RBM, and the other is by analysing  $G^-$  and  $G^+$  in the G band. Unfortunately, MWCNT doesn't show neither of these features so it is impossible to correctly analyse the transport behaviour from the Raman spectra. Nevertheless, there are three distinctive trends in the G bands obtained from this technique. The first one aggregates the pristine sample and the nitrogen doped with 0.8 g of melamine around  $\omega_G \sim 1566.8 \text{ cm}^{-1}$ . The second one is the most popular configuration and is formed by the ball-milled sample, the nitrogen doped with 0.36 g, the oxidized sample with 7 M followed by annealing at 900 °C and the oxidized sample with 12 M, around  $\omega_G \sim 1570.7 \text{ cm}^{-1}$ . The final one is around  $\omega_G \sim 1576.0 \text{ cm}^{-1}$  and is formed by the oxidized sample with 7 M HNO<sub>3</sub> and also by the same sample with ball-milling. These shifts in the G band can probably be attributed to an inherent type of metallicity.

Finally, it is known that the  $G'$  band feature can give information about the doping level, for SWCNT. If the escalation for MWCNT is a possibility, then the conclusion would

be that the treatments applied imposed a more p-doping level in almost all samples due to the shift for higher frequencies relative to the original MWCNT, with the exception of the sample MWCNT\_BM\_WM\_0.8g\_HT600, where there is a shift for a lower frequency and therefore it could be promoted a more n-type doping. Samples MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_BM were the ones with larger shifts to the right, which could indicate that these samples could have a more p-type doping than the rest.

### 3.3.2 Textural and Surface Analysis

The functionalized MWCNT textural properties were evaluated by the corresponding N<sub>2</sub> adsorption-desorption isotherms in order to qualify the modifications induced by the different treatments. **Figure 3.19** shows the different types of isotherms obtained.

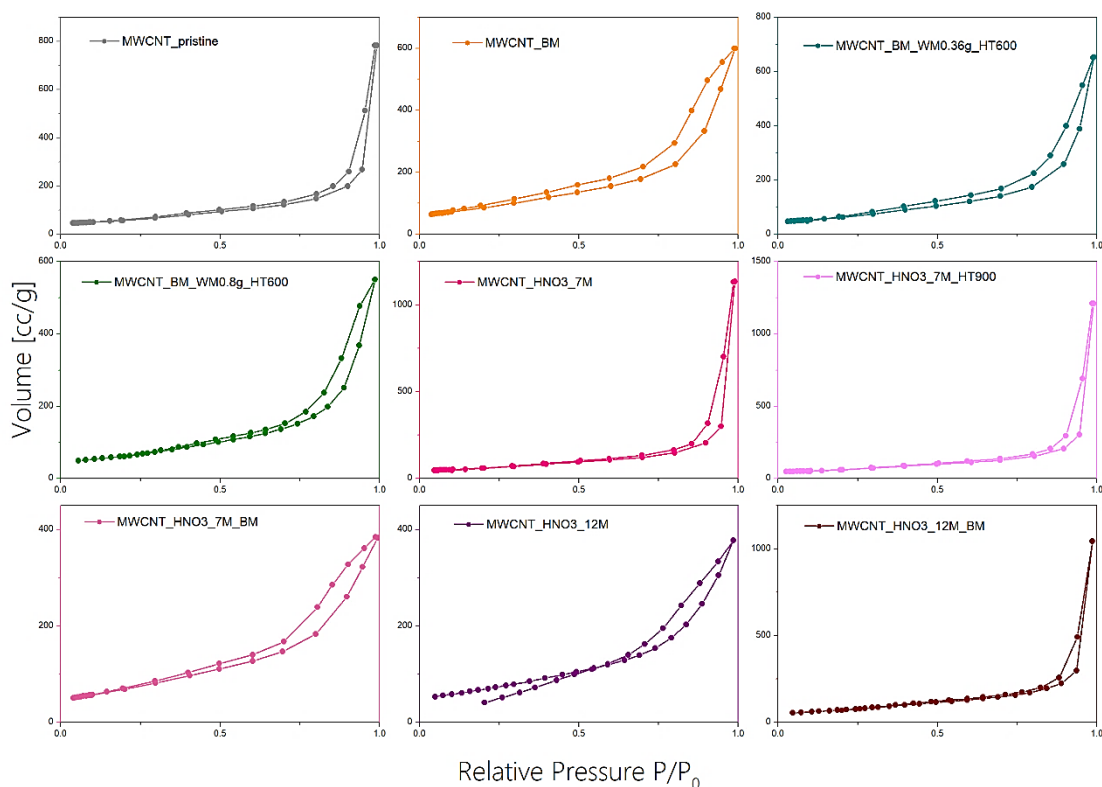


**Figure 3.19.** Adsorption – desorption isotherms for the MWCNT prepared samples.

Through the IUPAC classification of physisorption isotherms [100], it is possible to classify the samples produced. All samples could be qualified as type II which is characteristic for non-porous and macroporous materials. However, there is some hysteresis associated, especially for the samples where ball-milling was performed, therefore, type H3 could be a more accurate classification which is a classification that

resembles type II when the macropores are not completely filled with pore condensate. This delayed condensation could happen in open-ended pores (e.g. cylindrical geometry), which is the case for nanotubes.

This technique also provides information on the pore radius distribution and the superficial BET area, as it can be seen in **Figure 3.20**.

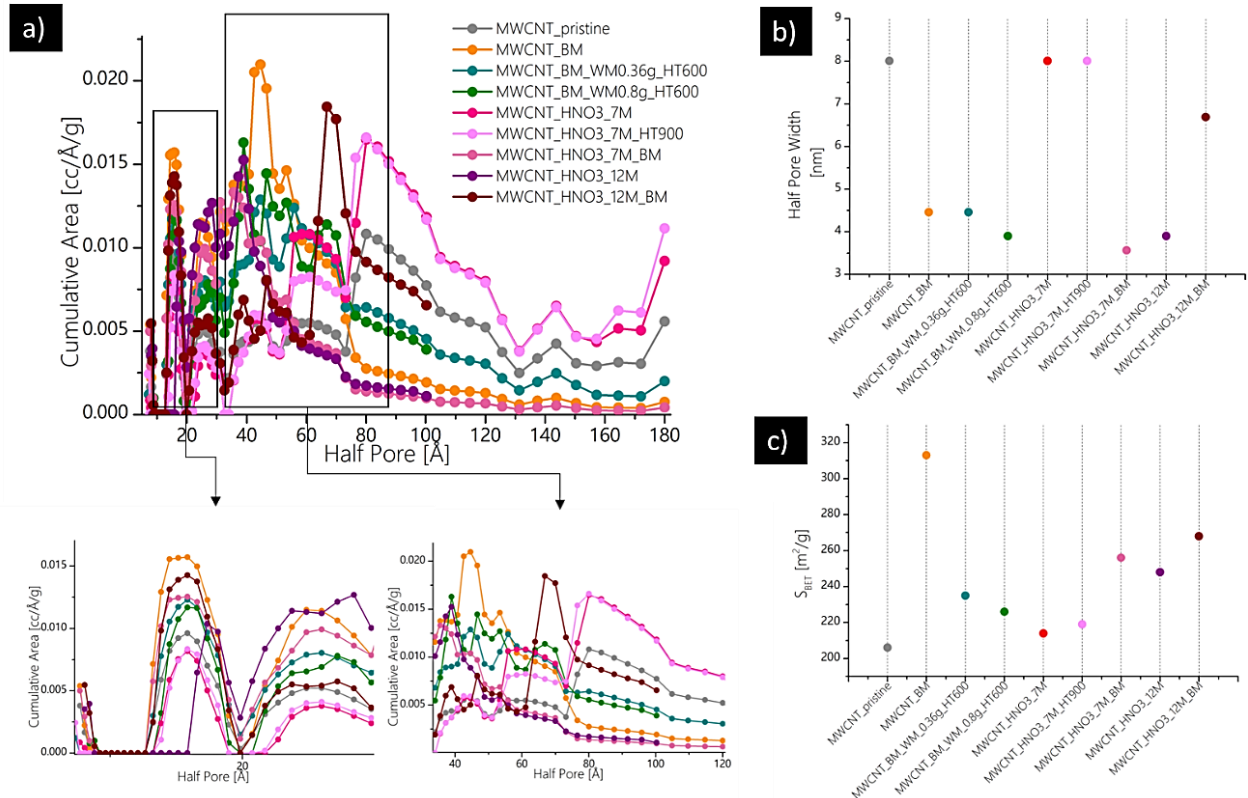


**Figure 3.20.** a) Textural properties for the functionalized MWCNT samples. a) Cumulative Area in function of the Half Pore. b) Half pore width. c) Surface BET area.

From these results, it is noticeable that different trends arise from different treatments. Samples where ball-milling was performed have enhanced cumulative area in distribution before 60 Å, and reduced cumulative area after this value, which means that this treatment reduces the pore size. Contrarily, MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_HT900, rises after 60 Å, meaning that this treatment leads to a bigger pore configuration, which could be interpreted by three different ways: the introduction of defects; the cutting of the nanotube's tips; and the arrangement of the MWCNT bundles, since the majority of pore distribution observed is due to the free space between bundles. When the concentration of the acid is 12 M, the configuration doesn't follow the exact same behaviour, having a displacement for a smaller pore configuration

caused by the utilization of more severe oxidation conditions. This conclusion for oxidative treatments is corroborated by the Raman Spectroscopy and TEM analysis where it was already concluded that the nitric acid obviously causes defects in the nanotubes.

**Figure 3.20.b)** displays this same tendency in a cleaner way, where it can be seen that ball-milling in fact reduces the pore width, oxidation maintains it with the exception when it was applied a higher acid concentration that lead to a small pore width.

The surface BET area results for the different MWCNT samples are shown in **Figure 3.20.c)**. From these results it is possible to conclude that ball-milling is responsible for an increase of the  $S_{BET}$ . Since ball-milling is a technique that can cause the length decreasing of the nanotubes as well as cutting closed ends, it is only logical that the surface area increase. Other method that can cause a rise of this parameter is the oxidation treatment, slightly revealed by the MWCNT\_HNO3\_7M sample, but undoubtedly revealed by MWCNT\_HNO3\_12M. This is evidence that the oxidation is also responsible for cutting the nanotubes.

EA, OA and  $pH_{PZC}$  results are represented in **Figure 3.21**.

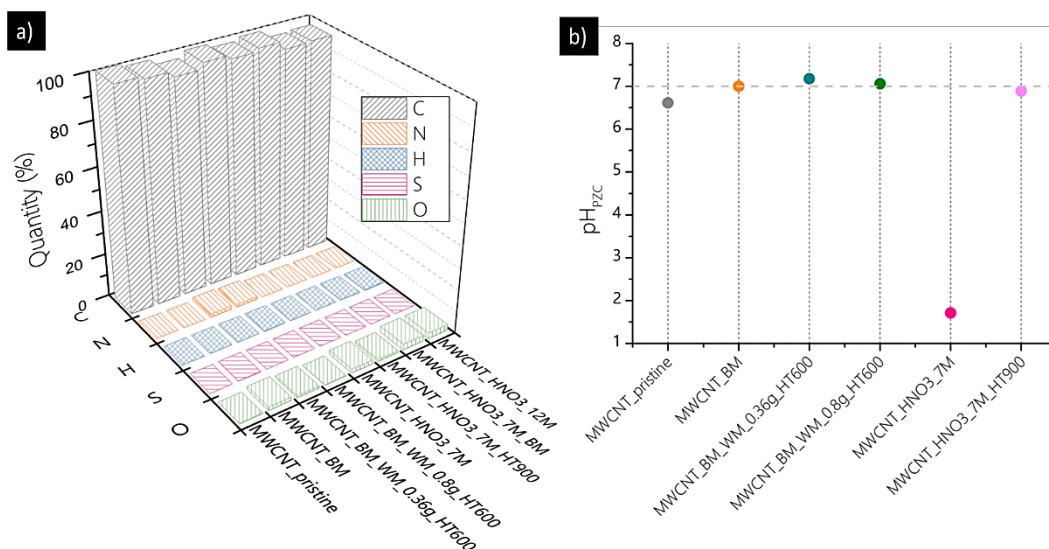


**Figure 3.21.** a) EA and OA results for MWCNT prepared samples. b) Point of zero charge pH for MWCNTs.

From EA and OA, it is possible to confirm that nitrogen was introduced with the application of the melamine treatment. The percentage introduced was  $\sim 1.5\%$  and  $\sim 1.2\%$  for MWCNT\_BM\_WM\_0.36g\_HT600 and MWCNT\_BM\_WM\_0.8g\_HT600, respectively. From these results it is possible to conclude that doing the treatment with

more quantity of melamine didn't allowed the introduction of more quantity of nitrogen into the MWCNT network, contrarily to what was intentioned. However, the oxygen level was reduced with the increase of melamine (4 times smaller). These contradictory results are also evidenced from TEM analysis, Raman Spectroscopy and also N<sub>2</sub> isotherms where it was discovered that the increase of melamine quantity upon the ball-milling treatment lead to a higher level of defect, a more n-type doping tendency and also to small pore widths.

Regarding the oxidized samples, it is possible to conclude that oxygen was introduced for samples MWCNT\_HNO3\_7M and MWCNT\_HNO3\_12M, ~ 1.8% and ~ 2.7%, respectively, revealing that increasing the acid concentration lead to a higher level of oxygen introduced, around 1.5 times higher. These results were also accompanied with an increase of the hydrogen quantity, 1.8 times higher, when the acid quantity was increased. From here, one must conclude that the oxidative treatments successfully attached oxygenated groups (e.g. hydroxyls) in the MWCNT surfaces. Additionally, the results for MWCNT\_HNO3\_7M\_HT900, revealed a decrease in the oxygen quantity, from ~ 1.8 % to ~ 0.8 % (2.25 times smaller). This could be explained by the removal of the functional groups added upon the oxidation.

OA also revealed that ball-milling was responsible to slightly increase the oxygen levels in the samples where this treatment was performed. This is possible to observe through the comparation of the samples before and after this treatment, such as MWCNT\_pristine and MWCNT\_BM, where the increase of oxygen was ~ 1.4 %, and MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_BM, where the increase of oxygen was ~0.9 %.

Concerning the point zero charge pH results, most samples revealed a neutral acid-base behaviour (pH<sub>PZC</sub> around 7). Similarly to the GN results, only the samples where oxidation was performed showed an acidic character (pH<sub>PZC</sub> <2) revealing the presence of acidic functional groups and also that the annealing at 900 °C performed on MWCNT\_HNO3\_7M returned the sample to a neutral pH, revealing that the acidic groups introduced with the oxidation were partially or totally removed.

The TPD spectra for some of the MWCNT samples are shown in **Figure 3.22**. As expected, the original material practically didn't reveal the existence of a large amount of surface groups. Additionally, MWCNT\_BM\_WM0.36g\_HT600 shows to have no surface groups released, only a few amount of CO is released between 400 °C and 600 °C. However, it is not possible to say with certainty what type of groups exist since the atomic mass is the same for CO and N<sub>2</sub>.

An increase in the amount of surface oxygen-containing groups is evidenced by the larger amounts of CO and CO<sub>2</sub> results released in sample MWCNT\_HNO<sub>3</sub>\_7M and MWCNT\_HNO<sub>3</sub>\_12M. The use of the more concentrated acid (12 M) allow the introduction of more oxygen-containing groups as evidenced by the larger areas in the TPD spectra and corroborated by the OA analysis. MWCNT\_HNO<sub>3</sub>\_7M\_HT900 revealed the removal of practically all surface groups introduced with the oxidation.

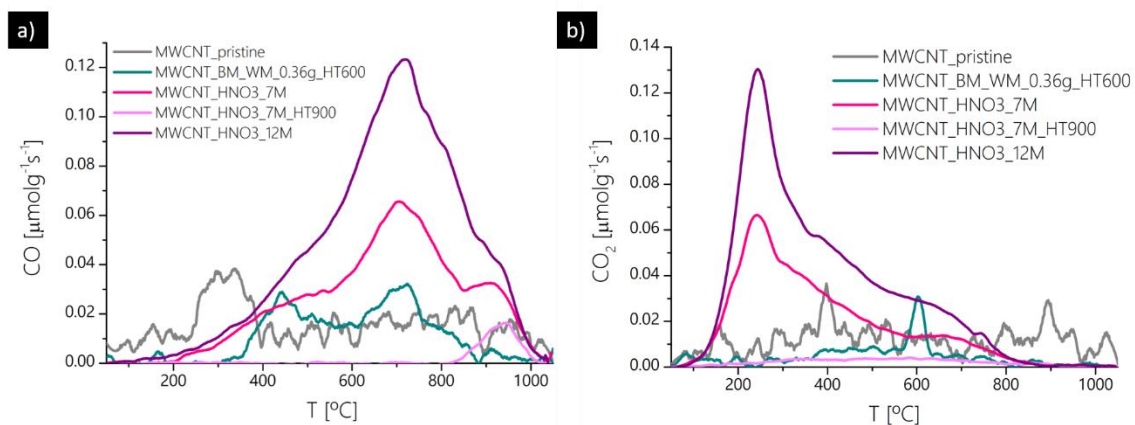


Figure 3.22. a) CO and b) CO<sub>2</sub> released on TPD analysis.

The oxidized samples have similar thermal desorption spectra. An additional analysis for determining the amount of each surface groups was performed through the deconvolution of the CO and CO<sub>2</sub> spectra. Such results are shown on **Figure 3.23**.

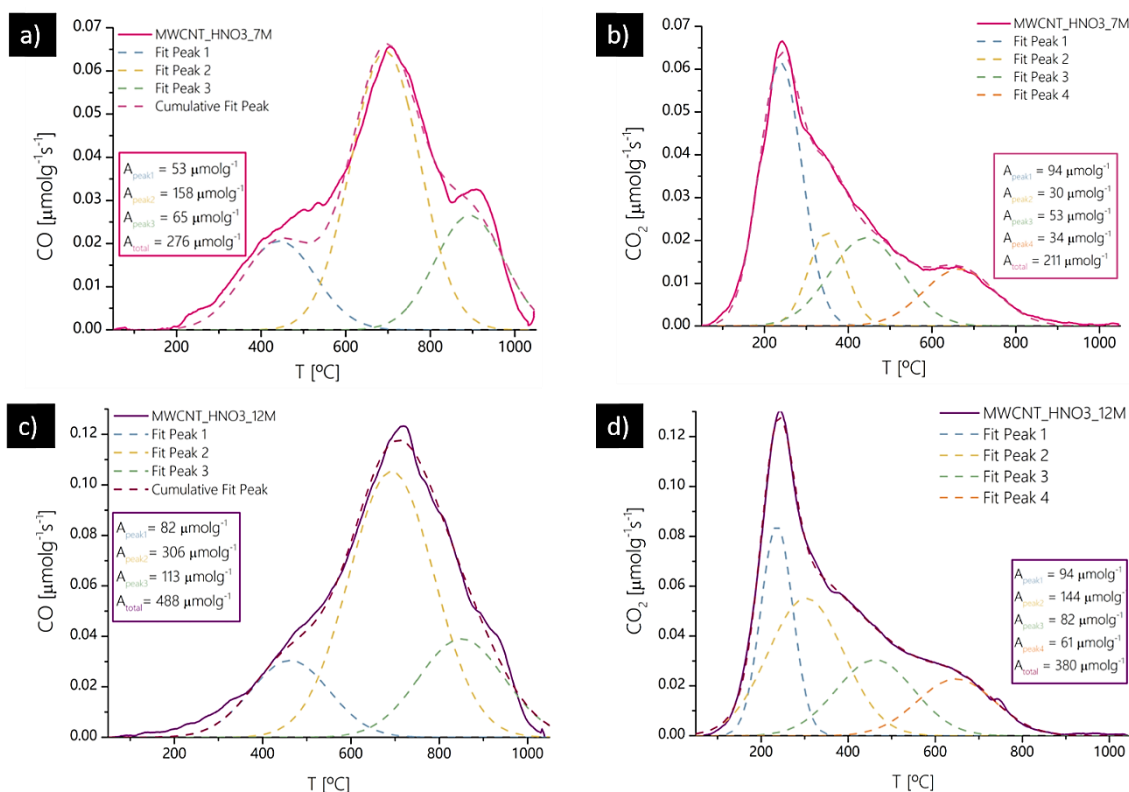


Figure 3.23. Results of the deconvolution of TPD spectra using a multiple Gaussian function. a) CO and b) CO<sub>2</sub> of MWCNT\_HNO<sub>3</sub>\_7M; c) CO and b) CO<sub>2</sub> of MWCNT\_HNO<sub>3</sub>\_12M.

Following the same rules stated in table 3.4, the CO profile reveals the existence of carboxyl anhydrides between 350 °C and 600 °C, phenols from 500 °C until 750 °C and carbonyl quinones, in the range of 750 °C to 1050 °C. The CO<sub>2</sub> spectra reveals a large amount of carboxyl acid (up to 450 °C), carboxylic anhydrides between 350 °C and 600 °C and some lactones released from 600 °C to 1050 °C.

In **Table 3.8** is represented textural and chemical characterization of the prepared materials including the mass percentage of oxygen on the surface obtained from the TPD data, and using equation (3.3).

**Table 3.8.** Textural and surface properties of MWCNT: Amount of CO and CO<sub>2</sub> released and mass percentage of oxygen on the surface, from TPD data; Quantity of oxygen and nitrogen, from EA and OA; pH<sub>PZC</sub>; and S<sub>BET</sub>, from N<sub>2</sub> isotherms.

|                        | CO<br>[ $\mu\text{mol g}^{-1}$ ] | CO <sub>2</sub><br>[ $\mu\text{mol g}^{-1}$ ] | %m <sub>O</sub> | %O <sup>OA</sup> | %N <sup>EA</sup> | pH <sub>PZC</sub> | S <sub>BET</sub><br>[m <sup>2</sup> g <sup>-1</sup> ] |
|------------------------|----------------------------------|-----------------------------------------------|-----------------|------------------|------------------|-------------------|-------------------------------------------------------|
| MWCNT_pristine         | 184                              | 142                                           | 0.75            | 0.28             | 0                | 6.6               | 206                                                   |
| MWCNT_BM               | n.m.                             | n.m.                                          | n.m.            | 1.71             | 0                | 7                 | 313                                                   |
| MWCNT_BM_WM0.36g_HT600 | 118                              | 53                                            | 0.36            | 0.89             | 1.52             | 7.2               | 235                                                   |
| MWCNT_BM_WM0.8g_HT600  | n.m.                             | n.m.                                          | n.m.            | 0.24             | 1.21             | 7.1               | 226                                                   |
| MWCNT_HNO3_7M          | 286                              | 213                                           | 1.14            | 1.82             | 0                | 1.7               | 214                                                   |
| MWCNT_HNO3_7M_HT900    | 25                               | 18                                            | 0.10            | 0.83             | 0                | 6.9               | 219                                                   |
| MWCNT_HNO3_7M_BM       | n.m.                             | n.m.                                          | n.m.            | 2.71             | 0                | n.m.              | 256                                                   |
| MWCNT_HNO3_12M         | 509                              | 382                                           | 2.04            | 2.71             | 0                | n.m.              | 248                                                   |
| MWCNT_HNO3_12M_BM      | n.m.                             | n.m.                                          | n.m.            | n.m.             | n.m.             | n.m.              | 268                                                   |

TGA results are represented in **Figure 3.24**. Similarly to the graphene results, the thermal degradation of MWCNTs is also a multistage process. Up to 150 °C, the weight loss is attributed to the evaporation of the absorbed water. This behaviour is more evidenced in the acid treated samples. From 150 °C to 350 °C, the thermal degradation is due to the decarboxylation of the carboxylic groups. This is also more evident in the acid treated samples, specially, for the sample MWCNT\_HNO3\_12M, meaning that more concentrated acid creates samples with more quantity of carboxylic groups, corroborating the TPD results concerning the two prepared oxidized samples with different concentrations. In the range between 350 °C and 500 °C, the explanation is the eliminations of the hydroxyl functionalities. Not surprisingly, the acid treated samples revealed having more quantity of these groups, as already confirmed by the OA, pH<sub>PZC</sub> and TPD. After 500 °C, the degradation is related with the thermal oxidation of the remaining disordered carbon. MWCNT\_HNO3\_12M display an odd behaviour when compared with samples where similar treatments were applied. Here the ball-milling

appeared to improve the thermal stability of the oxidized sample. The heat-treated sample at 900 °C shows thermal stability up to higher temperatures since it was already subject to a thermal decomposition stage in order to removing the surface groups.

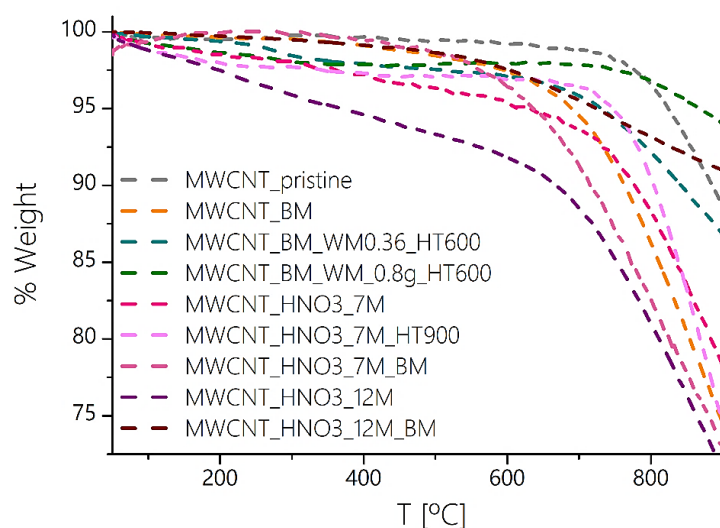


**Figure 3.24.** TGA results for the functionalized MWCNTs.

Additionally, the melamine treated samples showed a small thermal degradation  $\sim 2\%$  below 600 °C, which was already expected since the samples were already subjected to a melamine decomposition stage. After this temperature, the weight loss is more evident and can be justified by the remaining oxygen containing groups present on the MWCNT walls. Moreover, ball-milled samples consistently revealed a weight loss above 600 °C therefore ball-milling actually contain small oxygen-containing surface groups that are released above this temperature, as already revealed by OA. This behaviour is more accentuated in MWCNT\_BM\_WM0.36g\_HT600, thus, the increasement of the melamine quantity revealed to develop more stability when facing the action of the temperature.

**Figure 3.25** is a schematic representation of the nanotubes created with the oxidized sample and the melamine treated sample, based on the properties found with the surface and textural analysis.

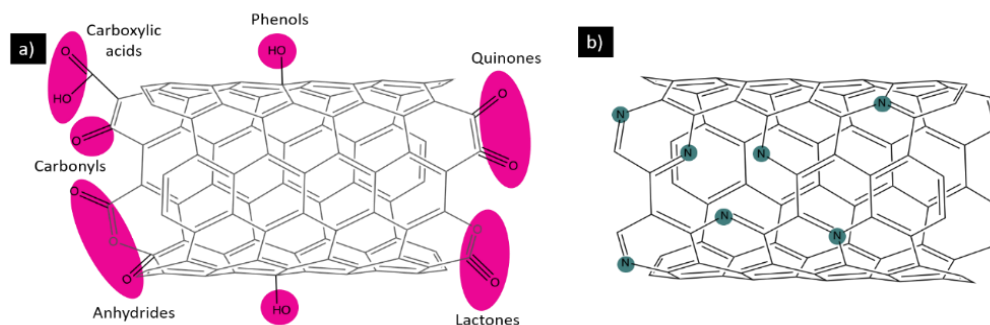


**Figure 3.25.** Schematic representation of the functionalities applied on the MWCNT for a) oxidizes samples; and b) the melamine treated samples.

### 3.3.3 Transport Properties

#### 3.3.3.1 Transport Properties and TE performance, at room temperature

The transport properties of the materials were measured for the samples prepared and for this purpose the powder samples were transform in bulk ones allowing for these properties to be measured. The results for the Seebeck Coefficient, the electrical conductivity and thermal conductivity are displayed on **Figure 3.26**, **Figure 3.28**, and **Figure 3.29**. An auxiliary grey line was added for the pristine sample results in order to facilitate the comparison with the values for the functionalized samples.

Concerning the  $S$ , two treatments revealed to be positive for optimizing this parameter: acid nitric oxidation and ball-milling. There are three different distinct groups for  $S$ . The first one is mainly composed by the oxidized samples and ball-milled ones, where the value is  $\sim 35 \mu\text{VK}^{-1}$ . The second one is composed by the pristine sample and the nitrogen doped ones, where the value goes toward  $\sim 26 \mu\text{VK}^{-1}$ . And the last one is composed by the heat treated at  $900^\circ\text{C}$  sample, where  $S$  is  $\sim 19 \mu\text{VK}^{-1}$ .

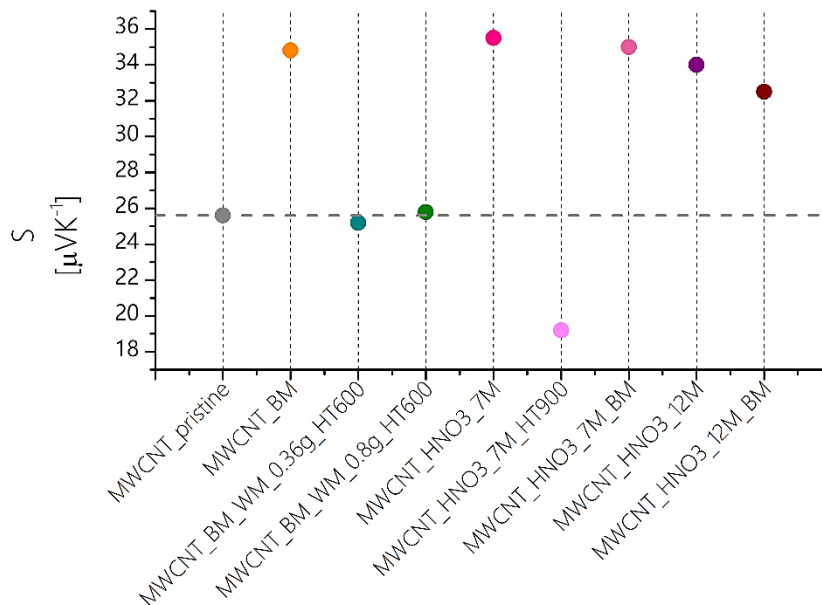


**Figure 3.26.** Seebeck coefficient ( $\mu\text{VK}^{-1}$ ) for the functionalized MWCNT samples.

These results could be justified by the oxygen quantity present in the sample that may induce a more p-type behaviour, that is related with the electron-withdrawing process, explained on **Figure 3.27**. This can be clearly observed in the difference for this parameter between sample MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_HT900, where the main difference is the absence of the functional oxygen-containing groups at the sample's surface caused by the heat treatment, and confirmed by OA and TPD

results. Additionally, the increase of surface oxygen containing groups in MWCNT\_HNO3\_12M didn't increase the Seebeck coefficient and this could indicate a limit value for how this parameter could be influenced by these groups.

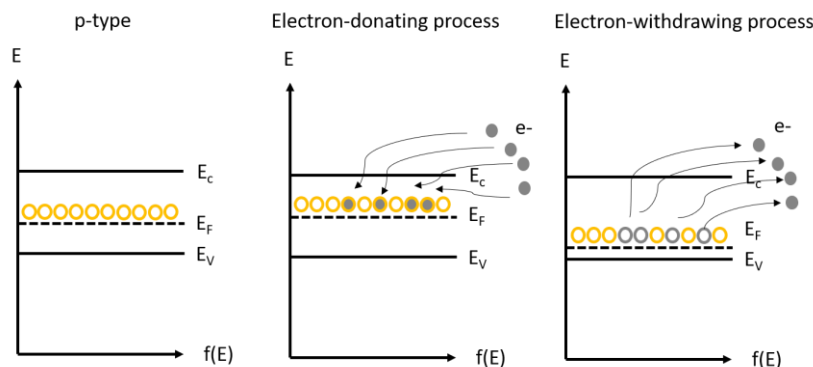


**Figure 3.27.** Schematization of the Fermi level under an electron-donating or withdrawing process in the band structure of a p-type material.

The melamine treatment doesn't change the value of  $S$ , and this could be explained by the n-type behaviour (electron-donating process on **Figure 3.27**) caused by the nitrogen doping, that would push  $S$  for negative values. However, such radical reduction doesn't happen, maybe because ball milling, that increases the oxygen content, can counteract this tendency. This fact could be confirmed by the analysis of the G' band, where it can be observed that both melamine treated samples are shifted to lower frequencies, revealing n-type doping, but the one with increased quantity of melamine is more shifted than the other. While the nitrogen content, from EA results, didn't reveal to be increased, the oxygen content, from OA results, was reduced, thus leading to the conclusion that oxygen-containing groups play an important role in the Seebeck coefficient.

Regarding the electrical conductivity results for the different samples (**Figure 3.28**), it was possible to improve this parameter for all the samples created. The maximum value obtained was  $\sigma = 1.33 \text{ Scm}^{-1}$  for MWCNT\_BM\_WM\_0.8g\_HT600, followed by the oxidized sample MWCNT\_HNO3\_12M ( $\sigma = 0.96 \text{ Scm}^{-1}$ ). The improvement relative to the pristine sample ( $\sigma = 0.11 \text{ Scm}^{-1}$ ) is considerable.

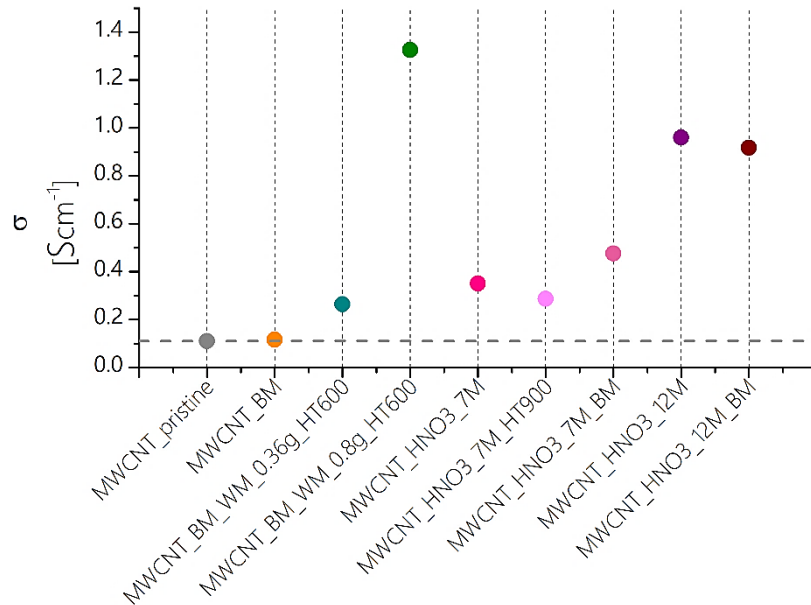


**Figure 3.28.** Electrical conductivity ( $\text{Scm}^{-1}$ ) for the functionalized MWCNT samples.

Considering the melamine treated samples, the results could be explained by the increase of the carrier density, however, the quantity of nitrogen introduced for the two melamine treated samples is similar, as revealed by EA, but the values of  $\sigma$  are very dissimilar. A relevant difference appears on the Raman spectra in the G' band, where a more n-type doping is suggested and in the  $I_D/I_G$  ratio where it is revealed a more defect concentration level, for the sample MWCNT\_BM\_WM0.8g\_HT600, and this could be a clue for explaining this improvement of  $\sigma$ .

Looking to samples MWCNT\_HNO3\_7M and MWCNT\_HNO3\_7M\_HT900, it is possible to have an idea of the influence of the functional groups. While there is a slight reduction on  $\sigma$  ( $\sim 19\%$ ) after the annealing and the subsequent removal of the groups, this difference is not enough for putting the functional groups as the main reason for the  $\sigma$  improvement, but reveals that cleaning the graphitic components with the use of acid is an important step for this parameter. Comparing MWCNT\_HNO3\_7M with MWCNT\_HNO3\_12M, the improvement for the second mentioned is large and the main differences between them are the number of surface groups, revealed by OA and TPD and the defect concentration from Raman spectroscopy. Some studies correlate the decrease of  $\sigma$  with the increased degree of damaged structural integrity as measured by Raman spectroscopy [111], however, the exact opposite behaviour is found on this results since the oxidation seems to benefit this parameter.

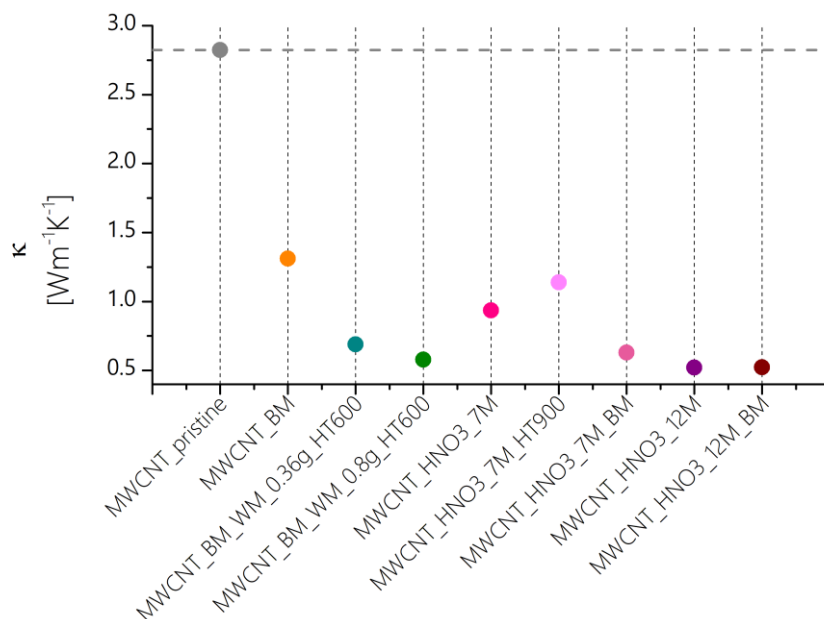


**Figure 3.29.** Thermal conductivity ( $\text{Wm}^{-1}\text{K}^{-1}$ ) for the MWCNT functionalized samples.

The thermal conductivity results for the MWCNT samples can be found in **Figure 3.29**. The functionalization of the prepared samples remarkably reduced the thermal conductivity, which is a positive occurrence in a TE context. The minimal value for this parameter obtained was  $\kappa = 0.52 \text{ Wm}^{-1}\text{K}^{-1}$  for the 12 M nitric acid samples, which is a considerable improvement when comparing with the value of the original sample of nanotubes ( $\kappa = 2.82 \text{ Wm}^{-1}\text{K}^{-1}$ ), a reduction of  $\sim 82 \%$ . These phenomena are easily explained by the mechanical damage provoked in the nanotubes such as the length decrease, the cut-ends tips, the defects in the nanotube's walls and so on, as revealed by TEM and  $S_{\text{BET}}$  results. Such defected morphology is responsible for increasing the phonon scattering and therefore reducing the lattice component of the thermal conductivity. This strategy for reducing  $\kappa$  is effective because it doesn't affect the electrical conductivity.

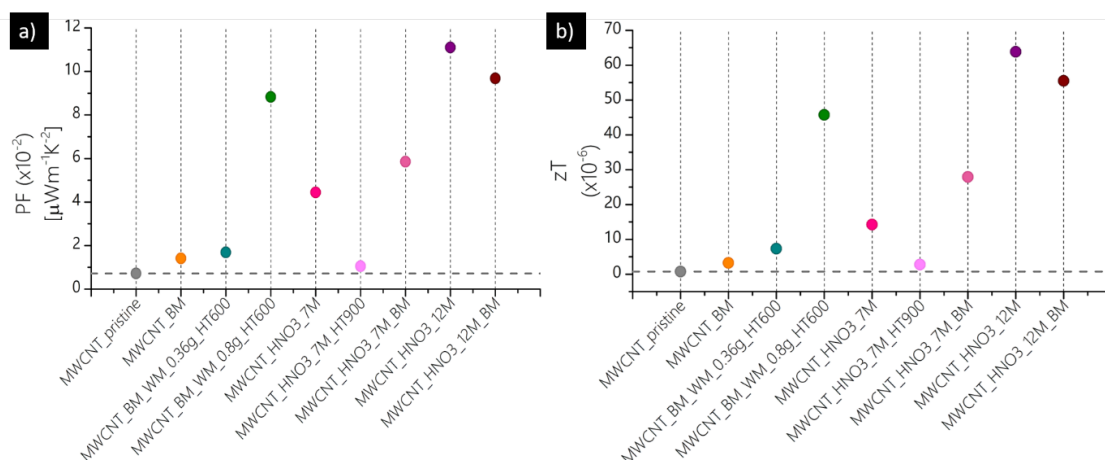


**Figure 3.30.** TE performance of functionalized MWCNT. a) Power Factor ( $\mu\text{Wm}^{-1}\text{K}^{-2}$ ); b) Figure of Merit.

The TE properties, Power Factor and Figure of Merit, are represented on **Figure 3.30.a)** and **Figure 3.30.b)**, respectively. Both show the large improvement obtained for the TE performance. The most optimized material was MWCNT\_HNO3\_12M, where it was obtained  $PF = 11 \times 10^{-2} \mu W m^{-1} K^{-2}$  and  $zT = 64 \times 10^{-6}$ . It was an improvement of 15 times and 84 times when compared with the original sample ( $PF = 0.72 \times 10^{-2} \mu W m^{-1} K^{-2}$  and  $zT = 0.76 \times 10^{-6}$ ), respectively. The nitrogen doping also revealed to be very positive for the TE performance, especially when it was used more melamine quantity. It was achieved a  $PF = 8.8 \times 10^{-2} \mu W m^{-1} K^{-2}$  and  $zT = 46 \times 10^{-6}$ .

### 3.3.3.2 Transport Properties in function of temperature, for low temperatures

In order to understanding the adjacent transport properties of the functionalized materials, it was performed a study on the electrical conductivity and Seebeck coefficient in function of temperature, for cryostat temperatures (between 20 K and 300 K). For doing so, it was created a buckypaper with the MWCNT\_pristine sample and with the MWCNT\_HNO3\_7M\_BM sample (with thicknesses  $t = 0.107 \text{ mm}$  and  $t = 0.054 \text{ mm}$ , respectively), with the procedure described on section 2.1.5. **Figure 3.31** shows the samples created.

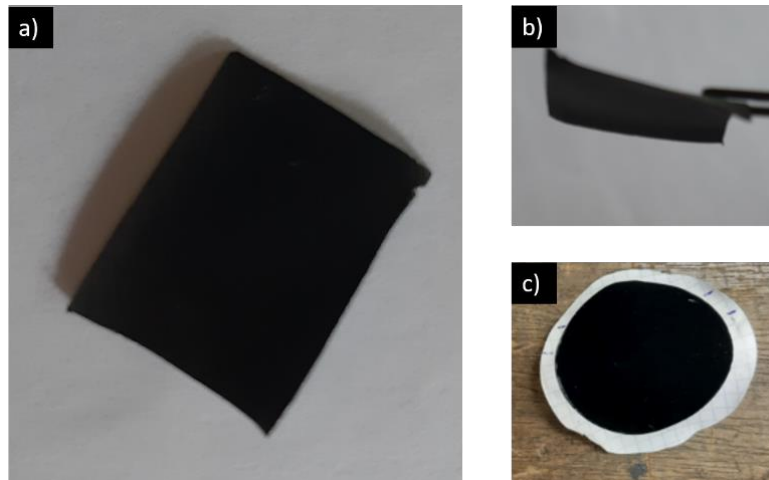


**Figure 3.31.** a-b) MWCNT\_HNO3\_BM buckypaper in a rectangular shape. c) MWCNT\_pristine buckypaper as obtained after drying.

Before measuring the electrical properties in cryo-temperatures, they were measured at room temperature. The results are shown on **Table 3.9**. The results for bulk of the same samples are also represented in order to establishing the advantages of using thin films.

**Table 3.9.** Electrical properties ( $\sigma$ ,  $S$  and  $PF$ ) for MWCNT\_pristine and MWCNT\_HNO3\_7M\_BM in bulk and buckypaper.

| Materials        | Sample preparation | Electrical Conductivity [ $\text{Scm}^{-1}$ ] | Seebeck Coefficient [ $\mu\text{VK}^{-1}$ ] | Power Factor ( $\times 10^{-2}$ ) [ $\mu\text{Wm}^{-1}\text{K}^{-2}$ ] |
|------------------|--------------------|-----------------------------------------------|---------------------------------------------|------------------------------------------------------------------------|
| MWCNT_pristine   | Bulk               | 0.110                                         | 25.6                                        | 0.719                                                                  |
|                  | Buckypaper         | 0.221                                         | 32.7                                        | 2.363                                                                  |
| MWCNT_HNO3_7M_BM | Bulk               | 0.476                                         | 35                                          | 5.849                                                                  |
|                  | Buckypaper         | 0.400                                         | 39                                          | 6.085                                                                  |

The results revealed that doing the sample preparation as buckypaper improved the electrical properties of the samples. The Power Factor increased  $\sim 230\%$  from bulk to buckypaper for the MWCNT\_pristine and  $\sim 40\%$  for the MWCNT\_HNO3\_7M\_BM. This is easily explained by the increased contact pressure between the material particles.

#### A. Electrical conductivity and transport regimes

The temperature coefficient of resistivity (TCR) shows the resistance change in function of the temperature. For metals, the TCR is positive and for insulator it is negative [112]. Nevertheless, a negative TCR can appear for metals with finite conductivity for low temperatures. The characteristic behaviour of conductivity can be described by the reduced activation energy ( $W$ ) in function of the logarithmic scale temperature. The activation energy is defined as [113]:

$$W = \frac{d[\ln\sigma(T)]}{s[\ln(T)]} \quad (3.4)$$

It is well known that metals possess high electrical conductivity ( $10^4 - 10^6$ )  $\text{Scm}^{-1}$ . This is owed to the finite DOS at the Fermi level even for low temperatures. **Figure 3.32.a)** shows the reduced activation energies for different electrical behaviours. **Figure 3.32.b)** represents the normalized resistance for the two different samples and the respective reduced activation energy (**Figure 3.32.c)**).

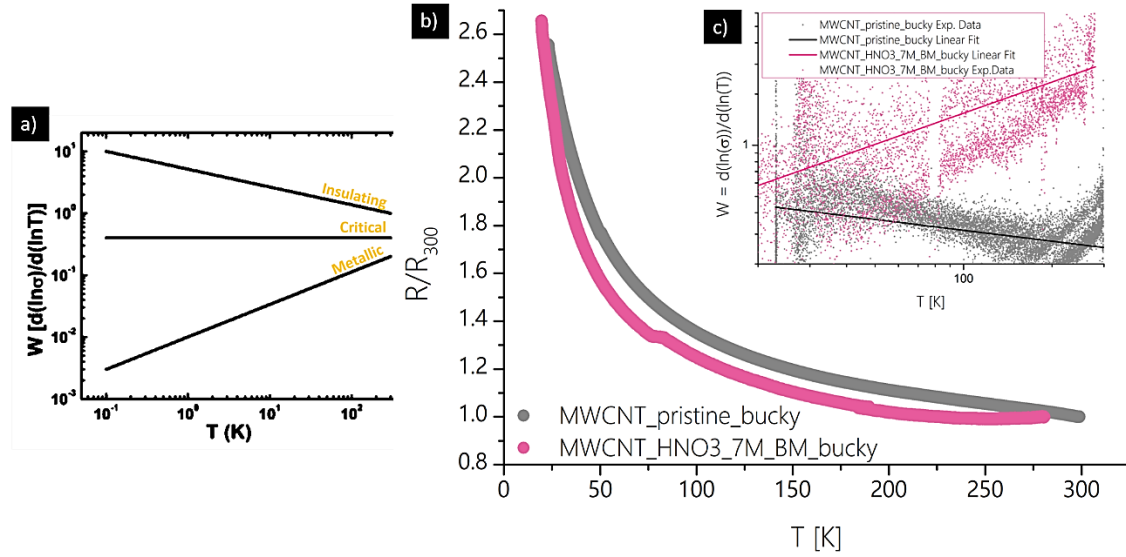


**Figure 3.32.** a) Reduced activation energy ( $W$ ) vs. temperature ( $T$ ). The negative and positive slopes of  $W$ - $T$  plot correspond to insulating and metallic regimes. In the critical regime,  $W$  is independent of  $T$ , adapted from [112]. b) Temperature dependence of normalized resistance of MWCNT\_pristine and MWCNT\_HNO3\_BM. c) Reduced activation energy ( $W$  vs.  $T$ ) for the same samples.

From the  $W - T$  plotting slopes, it is possible to conclude that MWCNT\_pristine is in the insulating regime while the MWCNT\_HNO3\_7M\_BM is in the metallic regime. These results prove that performing the nitric acid oxidation on the MWCNT improved the metallic character of the nanotubes. Allying these results to the Raman Spectroscopy results, one could speculate that shifts to higher frequencies in the G band would lead to a more metallic character of the MWCNTs.

For studying the transport regimes in these two MWCNT samples, 4 transport models were considered:

◇ Variable Range Hopping (VHR)

Is a theoretical model for strongly disordered systems with localized states, for low temperature conditions. In strongly disordered systems,  $\sigma$  approaches zero at sufficiently low temperatures. This model is expressed by:

$$\sigma = \sigma_0 \exp \left[ \frac{-T_C}{T} \right]^n \quad (3.5)$$

where  $\sigma_0$  is a factor temperature dependent,  $n$  depends on the extend of the disorder, the system's dimension, morphology and interaction between the charge carriers.  $n$  depends on the shape of density (DOS) near the Fermi Level:  $N(E) = N_0 |(E - E_F)|^\nu$ , where  $n = (\nu + 1)/(\nu + 4)$  for 3D,  $n = (\nu + 1)/(\nu + 3)$  in 2D [114].

◇ Mott Variable Range Hopping (M-VHR)

This model takes the form of VHR for  $n=1/4$ :

$$\sigma = \sigma_{Mott} \exp \left[ \frac{-T_{Mott}}{T} \right]^{1/4}; T_{Mott} = \frac{18.1}{k_B L_C^3 N(E_F)} \quad (3.6)$$

where  $T_{Mott}$  is the characteristic temperature referred as the Mott temperature,  $k_B$  is the Boltzmann constant,  $L_C$  is localization length and  $N(E_F)$  is the DOS (which is constant) at the Fermi Level [115].

◇ Efros-Shklovskii Variable Range Hopping (ES-VHR)

The VHR model takes this form when the  $N(E)$  varies quadratically near to the Fermi level ( $\nu = 2$ ) and  $n = 1/2$ :

$$\sigma = \sigma_{ES} \exp \left[ \frac{-T_{ES}}{T} \right]^{1/2}; T_{ES} = \frac{\beta e^2}{k_B L_C \kappa} \quad (3.7)$$

where  $T_{ES}$  is the characteristic temperature as Efros-Shklovskii temperature,  $\beta$  is a numerical constant equal to 2.8 in 3D and 6.8 in 2D,  $e$  is the electronic charge and  $\kappa$  is the dielectric constant of the medium. This model includes the effects of the long-range Coulomb interaction between localized states. This interaction creates a ‘soft’ gap in the DOS near the Fermi Level known as the Coulomb gap [116].

◇ Fluctuation Induced Tunnelling (FIT)

This model describes the electrical conduction for disordered materials where there is large conducting pathways separated by small insulating barriers [117,118]:

$$\sigma(T) = \sigma_0 \exp \left[ \frac{-T_1}{T_0 + T} \right]; T_1 = \frac{8\varepsilon_0}{e^2 k_B} \left( \frac{AV_0^2}{w} \right); T_0 = \frac{16\varepsilon_0 \hbar}{\pi(2m)^{1/2} e^2 k_B} \left( \frac{AV_0^{3/2}}{w^2} \right) \quad (3.8)$$

where  $\varepsilon_0$  is the vacuum permittivity,  $e$  is the electronic charge,  $2\pi\hbar$  is the Planck’s constant and  $m$  is the electronic mass.  $T_1$  is the temperature below which the conduction is dominated by the tunnelling carriers through the barrier and  $T_0$  is the temperature above which the thermally activated conduction over the barrier begins to occur. The conduction mechanism was modelled as the tunnelling electrons through a single potential barrier of width  $w$ , height  $V_0$ , and junction area  $A$ , which is the size at the point of the closest approach of two large conducting regions.

**Figure 3.33** and **Figure 3.34** represent the conductivity in function of the temperature and the 4 different models were applied with the goal of discovering which one fitted the best.

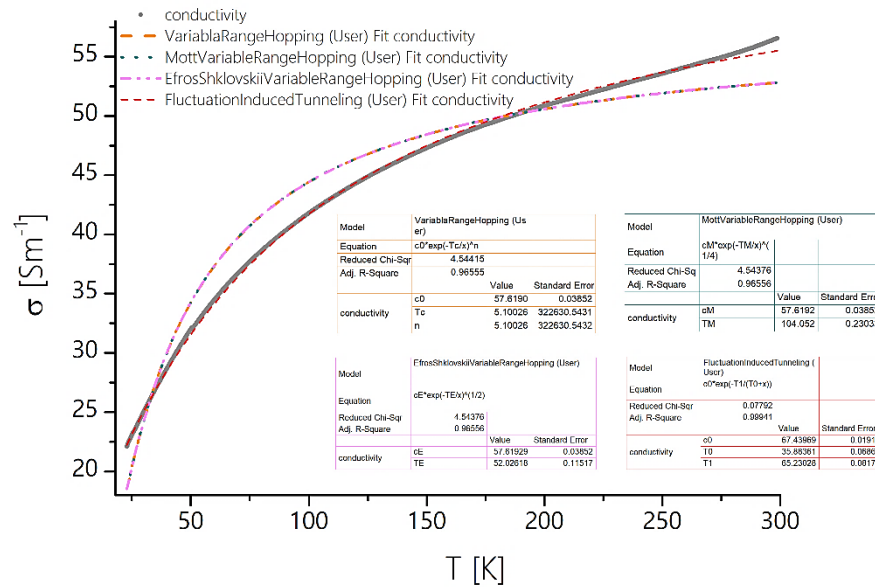


**Figure 3.33.** Electrical conductivity ( $\text{Sm}^{-1}$ ) vs. temperature (K) for MWCNT\_pristine buckypaper with 4 fitted transport models: VHR, M-VHR, ES-VHR and FIT.

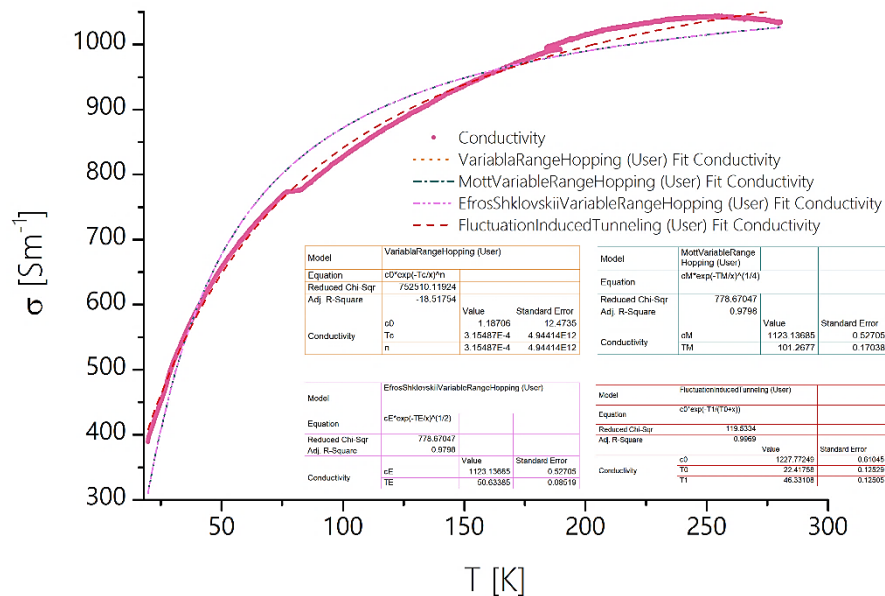


**Figure 3.34.** Electrical conductivity ( $\text{Sm}^{-1}$ ) vs. temperature (K) for MWCNT\_HNO3\_7M\_BM buckypaper with 4 fitted transport models: VHR, M-VHR, ES-VHR and FIT.

Firstly, it is possible to observe in both materials that with the increasing temperature, there is an increasement of the conductivity. This behaviour is explained by the high mobilities present within the nanotube in contrast with the resistance that is presented in junctions between nanotubes. The temperature increase provides the thermal energy necessary to surmount the barriers at the tube-tube junctions [119].

Both materials fitted better with the FIT model. The fitted parameters results are represented in **Table 3.10**.

**Table 3.10.**  $\sigma_0$ ,  $T_0$ ,  $T_1$ ,  $T_1/T_0$  and  $V_0^{1/2}w$  parameters obtained through the FIT model fitted to the  $\sigma$  vs.  $T$  for the MWCNT\_pristine and MWCNT\_HNO3\_7M\_BM.

|                  | $\sigma_0$<br>[Sm <sup>-1</sup> ] | $T_0$<br>[K] | $T_1$<br>[K] | $T_1/T_0$ | $V_0^{1/2}w$<br>(x10 <sup>-27</sup> ) [eV <sup>1/2</sup> m] |
|------------------|-----------------------------------|--------------|--------------|-----------|-------------------------------------------------------------|
| MWCNT_pristine   | 67.44                             | 35.88        | 65.23        | 1.818     | 5.58                                                        |
| MWCNT_HNO3_7M_BM | 1227.77                           | 22.42        | 46.33        | 2.066     | 6.35                                                        |

From these results, one can conclude that the conduction above the barrier is activated for lower temperatures when the MWCNT are oxidized. Moreover, the conduction stops being dominated by tunnelling carriers at lower temperatures for the same sample. Even though both materials follow the same model, it is obvious that MWCNT\_HNO3\_7M\_BM has a much more efficient electrical conductivity. The potential barrier ( $V_0^{1/2}w$ ) seems to be larger for the MWCNT\_HNO3\_7M\_BM which could be explained by the smaller length and more dispersive behaviour that both ball-milling and acid nitric cause in the nanotubes.

## B. Seebeck Coefficient

The Seebeck coefficient in function of the temperature for MWCNT\_pristine and MWCNT\_HNO3\_7M\_BM is represented in **Figure 3.35**.

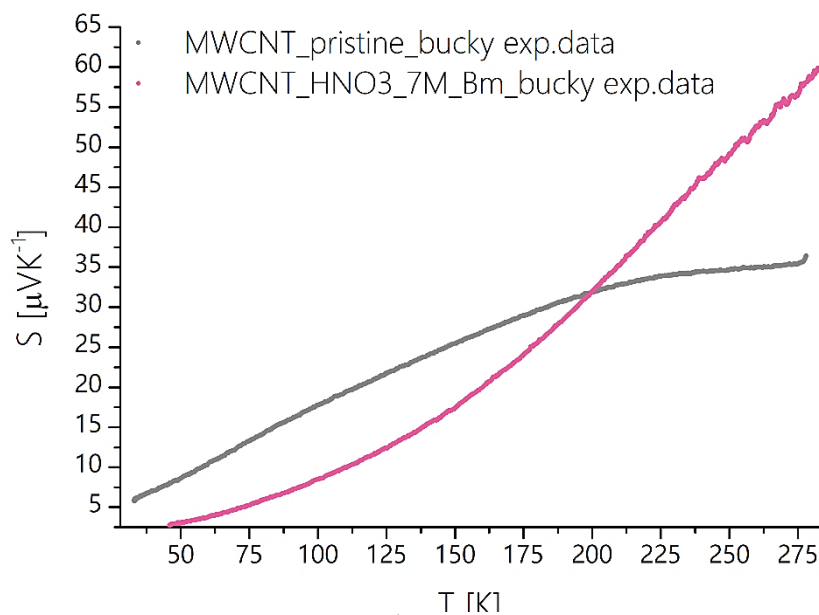


**Figure 3.35.** Seebeck coefficient ( $\mu\text{VK}^{-1}$ ) vs. Temperature (K) for MWCNT\_pristine buckypaper and MWCNT\_HNO3\_7M\_BM buckypaper.

The results show that the pristine material has a higher  $S$  below 190 K. However, above this temperature,  $S$  of MWCNT\_HNO3\_BM is higher. When the temperature goes closer to the room temperature, the oxidized sample performs better and this conclusion is confirmed by the Seebeck coefficient values measured at room temperature, for both bulk and buckypaper configurations. Actually, the general trend is for an increase of the Seebeck coefficient with increasing temperature for both temperatures below and above room temperature, which is a behaviour displayed by semiconductors, metallic and hybrid materials [119]. The linearity above 175 K showed by the oxidized sample is also a proof of their metallic behaviour. Finally, it can be concluded that the functionalization substantially modifies the driving bands and thus has a huge impact on the transport properties.

## 4 MWCNT nanocomposites and TEG prototypes

In this chapter, it was produced a flexible thermoelectric generator using these materials. To produce the stripes in this TEG it will be used a nanocomposite that is composed with the carbon material and also a polymer as a binder. An important step is to study the optimal concentrations of carbon material relative to the quantity of polymer. A percolation model is applied in order to understand the phenomena under these nanocomposite's properties. This chapter addresses all these concepts aiming for the best device's configuration possible.

### 4.1 MWCNT nanocomposites

A study was carried out to investigate the influence of different concentrations of PVA and carbon material relative to the transport properties but also to the mechanical properties in order to obtain a material capable of being used in the development of the device.

It was used undoped and doped PVA with  $\text{H}_3\text{PO}_4$  and different ratios between the organic polymer and the carbon material were tested on a PET substrate. Two carbon materials were tested relative to the percolation, MWCNT\_pristine and MWCNT\_HNO3\_12M\_BM. It was used two different carbon materials to observe if the percolation model is valid to all the functionalized materials. An additional study was performed to the complete set of prepared materials using the same weight ratio for obtaining the most optimized material to employ in this application.

#### 4.1.1 MWCNT\_pristine bended with doped and undoped PVA nanocomposites

Firstly, it was used the original MWCNTs bended with doped and undoped PVA with  $\text{H}_3\text{PO}_4$  on a PET substrate. The method used to produce these films was the one described in section 2.1.7, and the samples produced are shown in **Figure 4.1**.

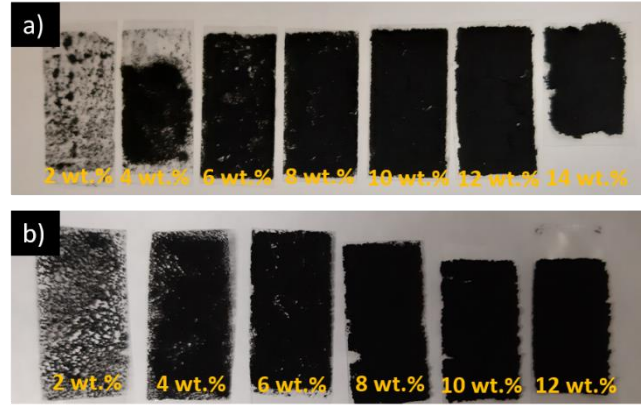


**Figure 4.1.** Nanocomposites of different weight percentages of MWCNT\_pristine and a) doped and b) undoped PVA.

At naked eye, it is observable the lack of unification between the nanotubes for lower carbon-material concentrations. As the concentration of MWCNT starts to increase, it is observed that the polymer acts like a binder, connecting the particles, resulting in a more compact and uniform film. Nevertheless, it is also visible the number of defects and cracks that the nanocomposites present. The nanocomposites start losing the adhesion to the substrate after the 12 wt.% and the films display a denser composition.

The transport properties ( $S$ ,  $\sigma$  and  $PF$ ) in function of the weight percentage of carbon material are shown in **Figure 4.2**.

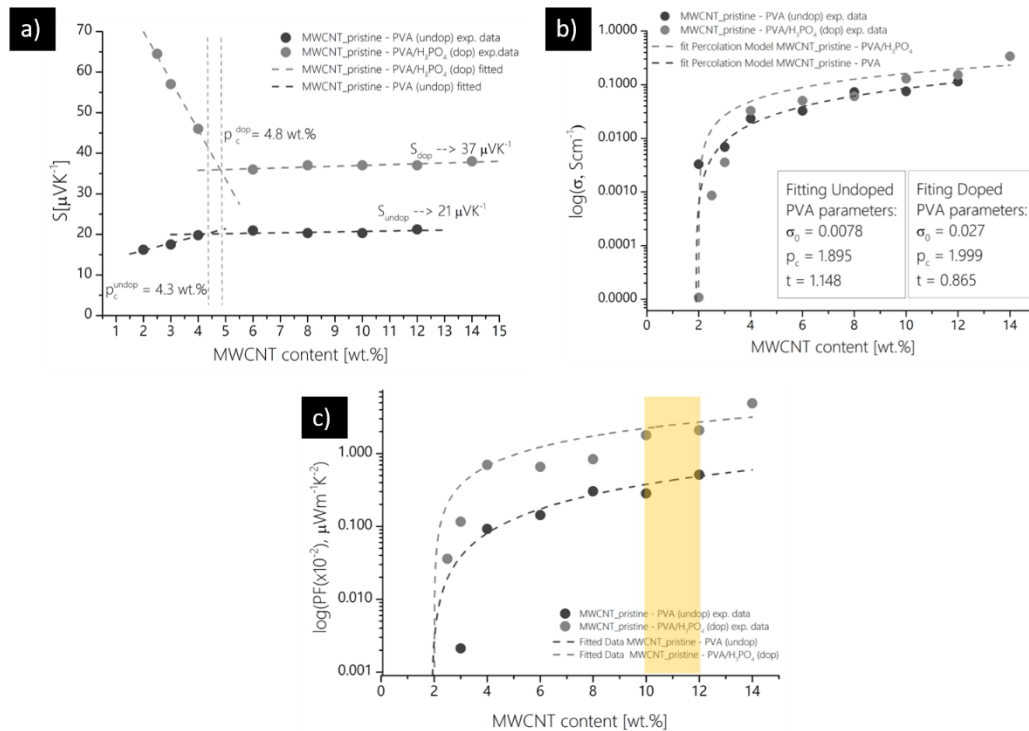


**Figure 4.2.** Transport properties of the MWCNT-PVA nanocomposites for doped and undoped PVA, in function of the weight load of carbon material. a) Seebeck Coefficient; b) Electrical conductivity with the fitted percolation model; c) Power Factor.

It is notorious the importance of doping the PVA with  $H_3PO_4$  in the Seebeck coefficient since is increased the p-type behaviour through electron-withdrawing process induced by the use of the acid. It also slightly increases the electrical conductivity, culminating in an optimized power factor.

The room temperature electrical properties of CNT reinforced polymer composites are governed by classical percolation theory [120]. This theory is based on the electrical conductivity dependence on the content of the conducting filler material. The general trend is the abruptly increase of the conductivity as the filler content increases, until this load crosses a particular value called percolation threshold ( $p_c$ ) and then the conductive path is established within the polymeric matrix, which is called the electrical percolation. Above this value, further addition of the filler material induces the conductivity to increase and saturate at high loading. This phenomenon is described by:

$$\sigma = \sigma_0(p - p_c)^t \quad (4.1)$$

where  $t$  is a positive constant.

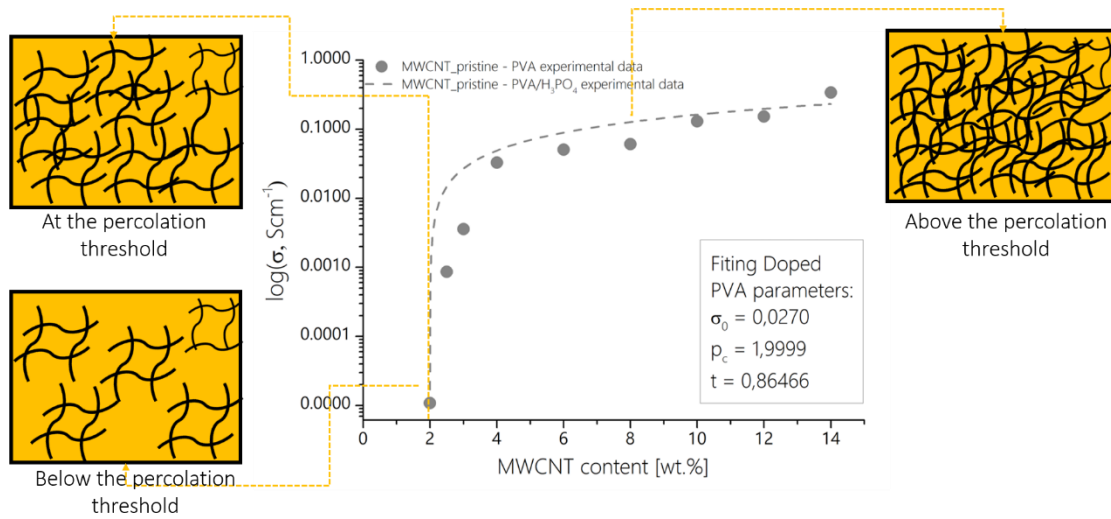


**Figure 4.3.** Schematic representation of the percolation threshold adapted to the  $\sigma$  vs. binder content (wt. %) with the nanocomposites formed with PVA/ $H_3PO_4$  and MWCNT\_pristine.

**Figure 4.3** is a schematic representation of the electrical percolation. The percolation is achieved at  $\sim 2$  wt. % for both doped and undoped PVA (**Figure 4.2.b**).

Concerning the Seebeck coefficient, this value is reduced in the doped polymer and increased in the undoped polymer until reaching a plateau of  $\sim 37 \mu VK^{-1}$  and  $\sim 21 \mu VK^{-1}$ , respectively, where the filler load is  $\sim 4.3$  wt. % and  $\sim 4.8$  wt. %. This value could be associated with a percolation threshold for  $S$  and was determinate with an interpolating linear fit (**Figure 4.2.a**). This value is slightly different from the value obtain

from the electrical percolation. Nevertheless,  $S$  is a good parameter for estimate the critical concentration since it does not depend on the shape of the sample.

The power factor results are represented in **Figure 4.2.c)**. It was also added a trend line by joining the two percolation models and subsequent fitted parameters. The maximum power factor was obtained for the filler was for doped PVA at the concentration of 14 wt.% ( $PF \sim 4.9 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ ). However, the defined optimum concentrations for these nanocomposites was obtained between 10 wt.% and 12 wt. % (marked in yellow in the **Figure 4.2.c)**) since above 12 wt.% the adhesion of the material to the substrate is lost. The power factor obtain for these vales of concentration are between  $\sim(1.8 - 2.1) \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ .

#### 4.1.2 MWCNT\_HNO3\_12M\_BM bended with PVA/H<sub>3</sub>PO<sub>4</sub> nanocomposites

In order to verify if the percolation theory is adaptable to the functionalized samples mentioned on chapter 3, it was also performed the same study with the sample MWCNT\_HNO3\_12M\_BM, that was the second best in terms of TE performance for bulk. It was not used the MWCNT\_HNO3\_12M because it would be interesting to study the ball-milling effects on the nanocomposite formation. The samples produced are shown on **Figure 4.4**.

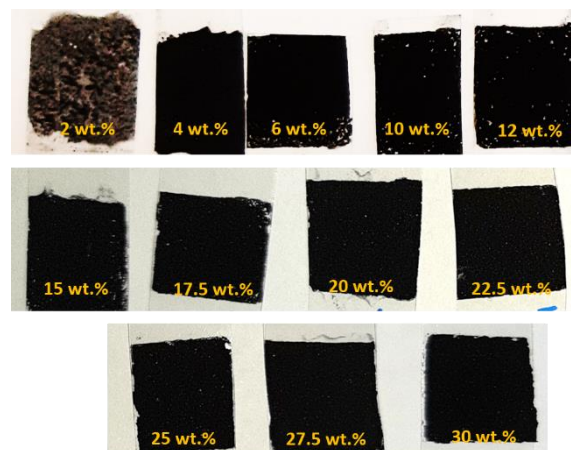


**Figure 4.4.** Nanocomposites o different weight percentages of MWCNT\_HNO3\_12M\_BM and PVA/H<sub>3</sub>PO<sub>4</sub>.

It is visible the more homogeneous appearance of the nanocomposites when compared with the MWCNT\_pristine composites. The mixture formed with this material and the PVA has a more ink-type texture which facilitates the process of stencil printing.

**Figure 4.5** shows the electrical properties of the MWCNT\_HNO<sub>3</sub>\_12M\_BM and PVA/H<sub>3</sub>PO<sub>4</sub> for different carbon material loads. It is observable that the material follows the same percolation model as the MWCNT\_pristine. The percolation is achieved at  $\sim 6$  wt. % for the Seebeck coefficient and  $\sim 1.9$  wt. % for the electrical conductivity. From these results it is possible to develop the conclusion that the different MWCNT follow the same percolation model and that after the 2 wt.% the material is already percolated.

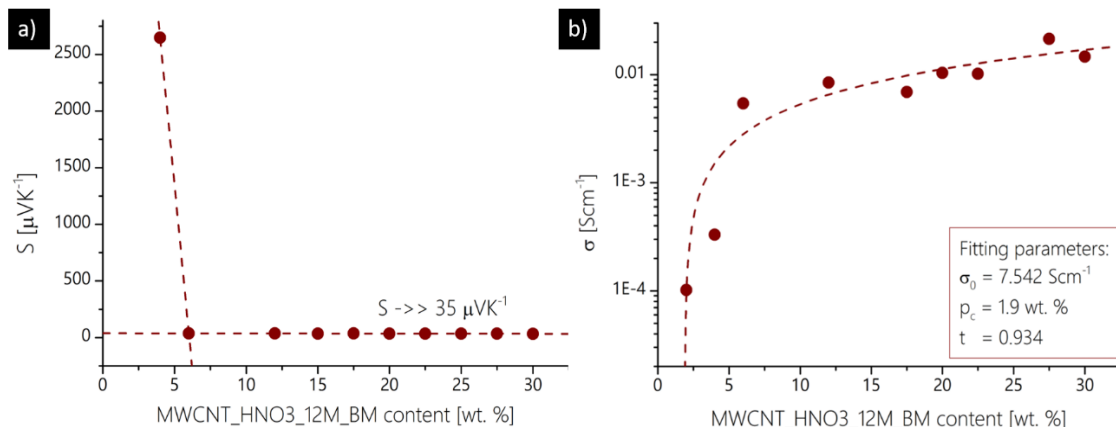


**Figure 4.5.** Electrical properties of MWCNT\_HNO<sub>3</sub>\_12M\_BM and PVA/H<sub>3</sub>PO<sub>4</sub> nanocomposites with different weight concentrations. a) Seebeck effect; b) Electrical conductivity with the respective fitted percolation models.

#### 4.1.3 Electrical properties of functionalized MWCNT and PVA/H<sub>3</sub>PO<sub>4</sub> at 12 wt. %

Since it was observed that for the functionalized material and the pristine carbon nanotube, the behaviour is similar, different nanocomposites were prepared with PVA/H<sub>3</sub>PO<sub>4</sub> and the functionalized MWCNT samples for the weight percentage of 12 wt.% that is a representative concentration of the nanocomposite already percolated and also belonging to an optimal concentration for the improved electrical properties. The results are shown in **Figure 4.6**.

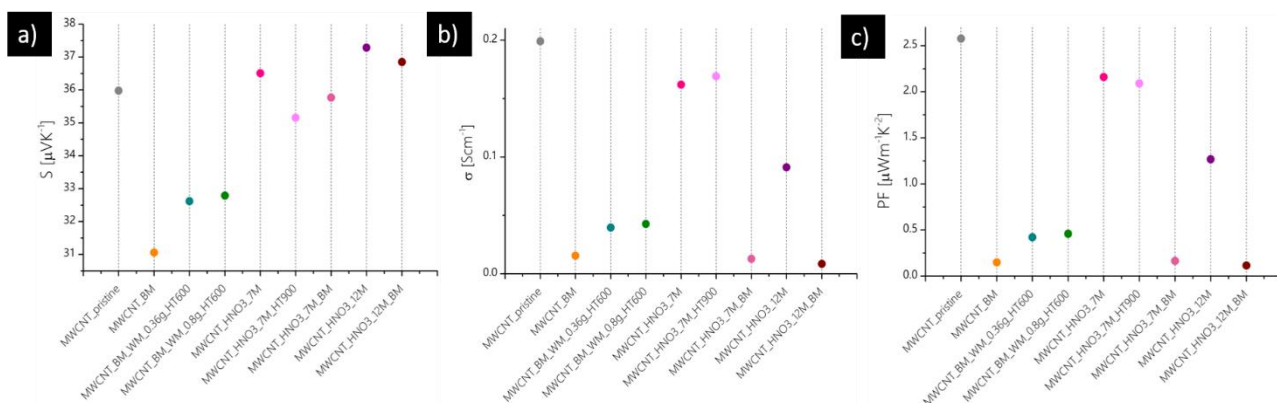


**Figure 4.6.** Electrical properties of the functionalized MWCNT samples and PVA/H<sub>3</sub>PO<sub>4</sub> nanocomposites. a) Seebeck coefficient; b) Electrical conductivity; c) Power Factor.

The electrical properties of the nanocomposites don't follow the same behaviour of the bulk samples. Nevertheless, the Seebeck coefficient resembles the same value as the maximum value obtain for the bulk samples ( $\sim 35 \mu\text{VK}^{-1}$ ), unveiling that it is the polymer the responsible for affecting the electrical conductivity. Concerning the values obtained in  $S$ , it was achieved for the oxidizes samples,  $\sim 37 \mu\text{VK}^{-1}$  whereas it is the original nanotubes that present the highest electrical conductivity ( $\sim 0.2 \text{ Scm}^{-1}$ ). The balance between both coefficient unveil that maximum  $PF$  obtained was for the nanocomposite with the original sample  $\sim 2.6 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  that actually has a better performance when compared with bulk counterparts ( $\sim 0.72 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ ). Concerning the functionalized samples, the MWCNT\_HNO3\_7M\_HT900 also present a better  $PF$  in nanocomposite that in the bulk form with a  $PF \sim 2.09 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$  as opposed to bulk ( $\sim 1.05 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ ). The other nanocomposites revealed to be better in the bulk form.

Notice that, attaching functional groups onto ends or side walls of carbon nanotubes have been reported to improve the solubility and compatibility of carbon nanotubes, especially when linked to also functionalized polymer [121]. However, there is a limitation in the oxidation conditions since they could introduce a large concentration of acid groups on their surfaces which can damage the  $\text{sp}^2$  network severely and may greatly shorten the length of carbon nanotubes [121]. In fact, as revealed by TEM and Raman spectroscopy, pristine nanotubes demonstrate having larger lengths and less defect concentration. This hypothesis is also corroborated by the results for the oxidized samples, since the material where it was used less aggressive oxidation conditions, MWCNT\_HNO3\_7M, revealed to performed better than MWCNT\_HNO3\_12M, where it was used a more concentrated nitric acid. Melamine treated sample also show to be less effective to form the nanocomposite since they were also subjected to ball-milling and therefore also possess defects and reduced lengths.

## 4.2 TEG Flexible Devices

Considering the abovementioned results, the chosen composite concentration to produce the device was 10 wt.% of carbon material with doped the polymer. It was chosen three different materials to produce the devices: MWCNT\_pristine since it had the best performance in film; MWCNT\_HNO3\_HT900 because of the performance in film

and also the improvement from bulk to nanocomposite; MWCNT\_BM\_WM0.8g\_HT600 in order to understanding the effects of a N-doped sample and also a representation of ball-milled material that is more malleable for the ink production.

The device was produced with the same procedure described in section 2.1.8, recurring to a PET substrate and two different vinyl masks, one for imprinting the contacts with Ag ink and other with 10 equidistant stripes. The devices produced were in single mode, meaning that it only operates with p-type instead of a combination of n-type and p-type. The weight percentage used was 10 wt.% instead of 12 wt.% as initially intended because the mechanical properties didn't allow an effective stencil process. The average thickness of the stripes was  $t = 0.255$  mm.

A representation of the vinyl masks used and the produced TE devices are represented in **Figure 4.7**.

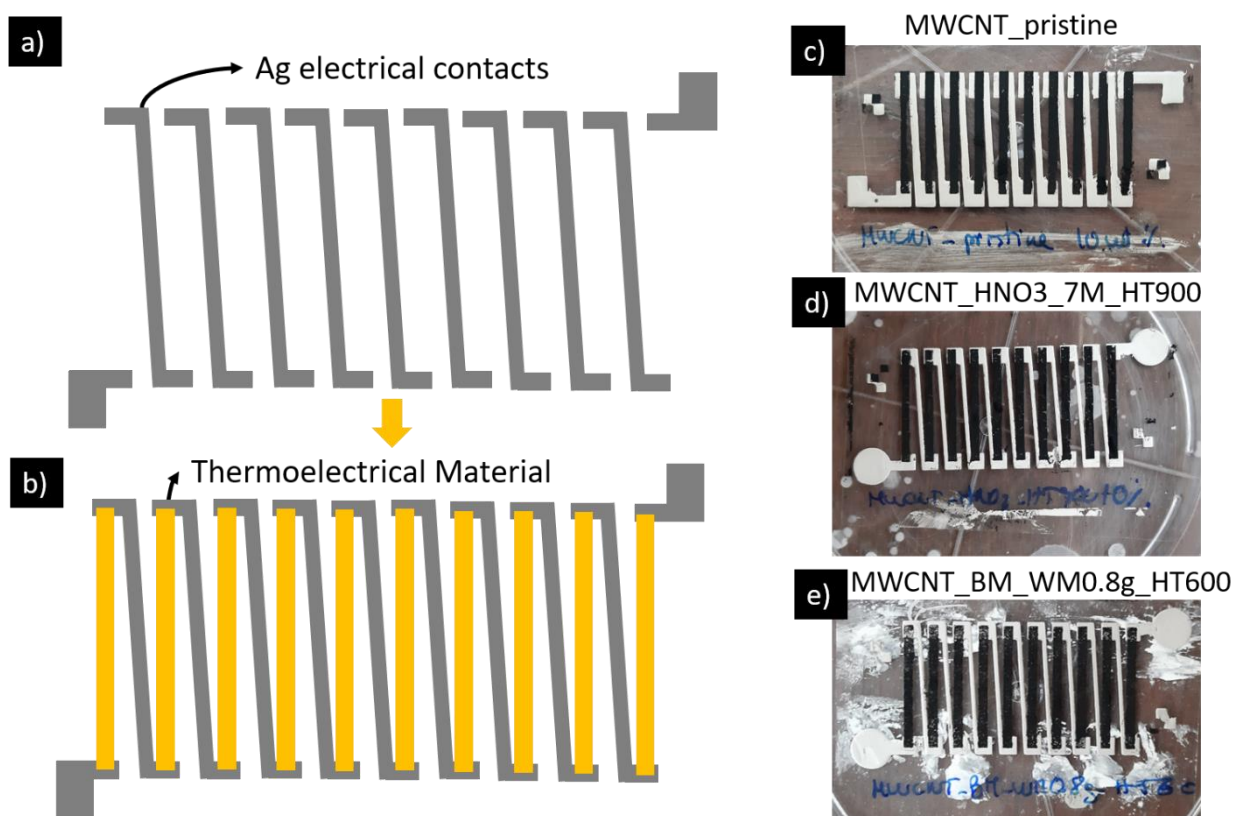


**Figure 4.7.** TE devices produced; a) Silver ink electrical contacts. b) Thermoelectrical stripes; c) TE device using MWCNT\_pristine; d) TE device using MWCNT\_HNO3\_7M\_HT900; e) TE device using MWCNT\_BM\_WM0.8g\_HT600.

The TE performance of the devices was measured with the methods described in section 2.4, with temperature gradients between 0 K and 30 K. The results for the open circuit voltage ( $V_{OC}$ ) in function of the temperature gradient ( $\Delta T$ ) are shown in **Figure 4.8**.

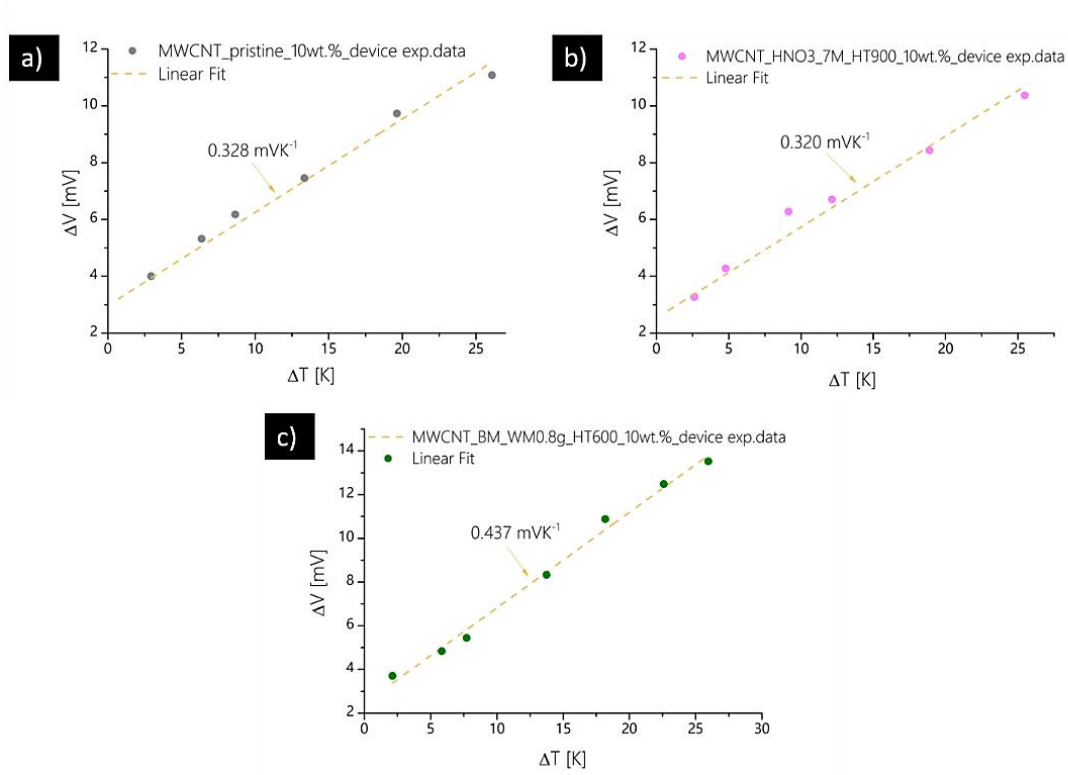


**Figure 4.8.** Output voltage at the open-circuit in function of the temperature gradient for the devices with a) MWCNT\_pristine; b) MWCNT\_HNO3\_7M\_HT900 and c) MWCNT\_BM\_WM0.8g\_HT600.

Linear slopes were achieved for the different produced devices with values of  $0.328 \text{ mVK}^{-1}$  for MWCNT\_pristine,  $0.320 \text{ mVK}^{-1}$  for MWCNT\_HNO3\_7M\_HT900 and  $0.437 \text{ mVK}^{-1}$  for MWCNT\_BM\_WM0.8g\_HT600. It must be noticed that there is a correlation between these slopes and the Seebeck coefficient of the TE composite. The obtained results are in accordance with the films produced since the sum of  $S$  of each leg is the value of the slope, thus, dividing the slope for 10 legs it is obtained values of  $32.8 \mu\text{VK}^{-1}$ ,  $32 \mu\text{VK}^{-1}$  and  $43.7 \mu\text{VK}^{-1}$  for the TE materials produces using MWCNT\_pristine, MWCNT\_HNO3\_7M\_H900 and MWCNT\_BM\_Wm0.8g\_HT600, respectively. Those values are in the same range of the values obtained for the nanocomposites ( $36 \mu\text{VK}^{-1}$ ,  $35 \mu\text{VK}^{-1}$  and  $33 \mu\text{VK}^{-1}$ , respectively) but are slightly different which could be due to the contributions of the silver paint from the electrical contacts.

Notice that the output voltage at the open-circuit didn't pass in zero (at the origin), as it was expected, and that could be explained by the sensitivity for temperature fluctuations presented by the devices.

To determine the maximum output power, it was used different loads of resistances in two different configurations, as explained on section 2.4. These measurements were made for a constant 10 K temperature gradient (**Figure 4.9**) that was assured by two thermocouples placed behind the stipes in both cold and hot side.

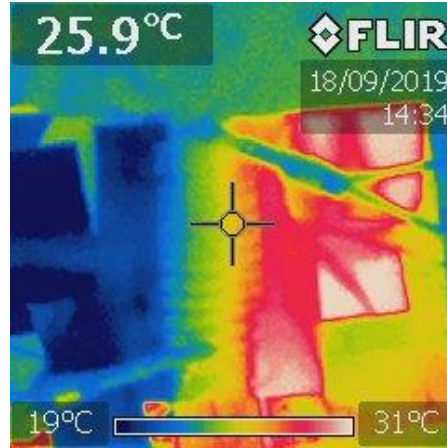


**Figure 4.9.** Infrared image of the measurement at  $\Delta T = 10$  K (representative).

The typical  $I$  and  $V$  curves as a function of the different load resistances in the two different configurations for the produced devices are presented in **Figure 4.10-top**. The resulting output power ( $P_{output}$ ) as a function of the load resistance is displayed in **Figure 4.10- bottom**.

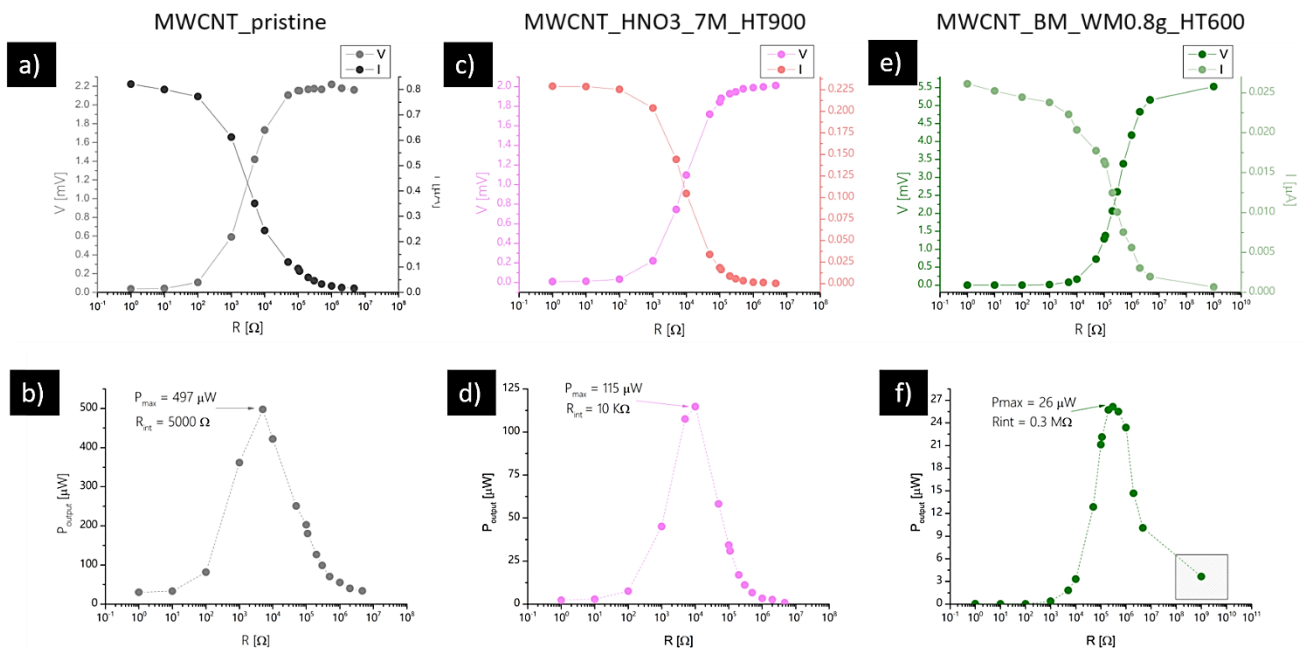


**Figure 4.10.** Electrical characterization of the TEGs produced in this work: a-b) MWCNT\_pristine; c-d) MWCNT\_HNO3\_HT900; e-f) MWCNT\_BM\_WM0.8g\_HT600. On top (a), c), e)) is the current-voltage as a function of the electrical resistance. On bottom (b), d), f)) is the maximum output power as a function of the load resistance for  $\Delta T=10$ K. Dashed lines are guides to the eyes.

From these results, the generated power obtained for  $\Delta T = 10\text{ K}$  and the correspondent internal resistances were:  $P_{\text{output}} = 497\text{ }\mu\text{W}$  correspondent to  $R_{\text{int}} = 5\text{ K}\Omega$  for the MWCNT\_pristine legged device;  $P_{\text{output}} = 115\text{ }\mu\text{W}$  and  $R_{\text{int}} = 10\text{ K}\Omega$  to the device produced with the MWCNT\_HNO3\_HT900 nanocomposite; and  $P_{\text{output}} = 26\text{ }\mu\text{W}$  with  $R_{\text{int}} = 0.3\text{ M}\Omega$  for the MWCNT\_BM\_WM0.8g\_HT600 device. It is possible to determine  $R_{\text{int}}$  for the devices through the linearization of  $V$  vs.  $I$ . With this method it is obtained  $3035\text{ }\Omega$  for MWCNT\_pristine,  $8757\text{ }\Omega$  for MWCNT\_HNO3\_7M\_HT900 and  $0.27\text{ M}\Omega$  for MWCNT\_BM\_WM0.8\_HT600. The values obtain for this parameter are similar, however, it should be acquired more data around the device's  $R_{\text{int}}$  in order to be possible to correctly access this parameter through the  $P_{\text{output}}$  curve and thus, measuring the internal resistance from the linearization is more accurate.

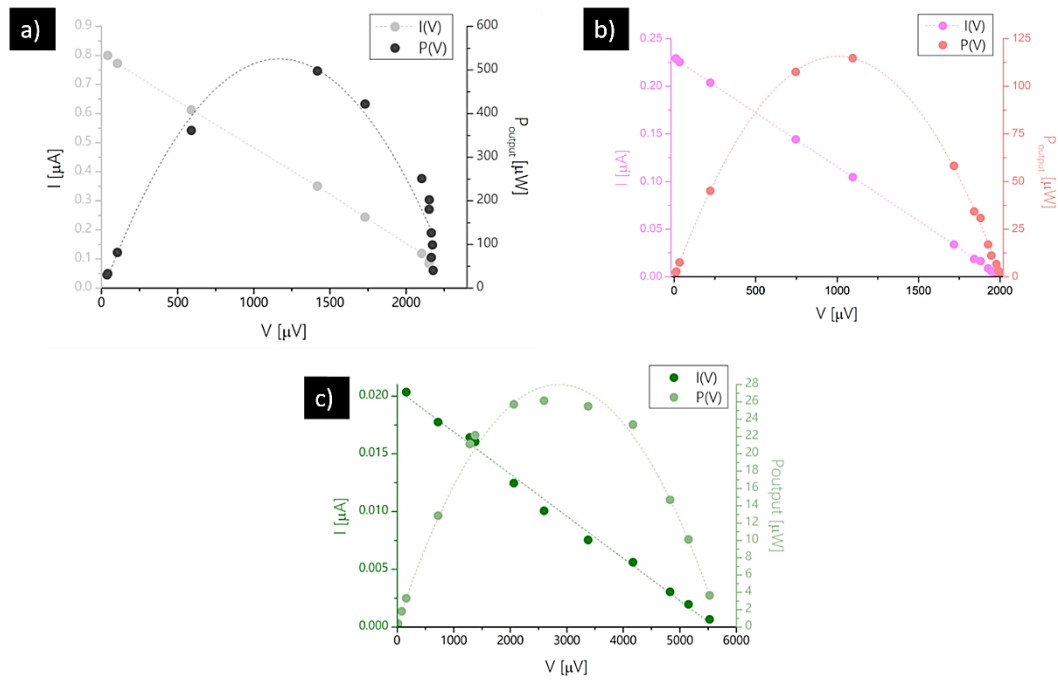


**Figure 4.11.**  $I(V)$  curves and output power achieved for  $\Delta T = 10\text{ K}$  for the devices formed with the TE materials based on a) MWCNT\_pristine; b) MWCNT\_HNO3\_7M\_HT900; c) MWCNT\_BM\_WM0.8g\_HT600.

In **Figure 4.11** is represented the superimposed  $I(V)$  curves and the generated output power for  $\Delta T = 10\text{ K}$ . The maximum power outputs were normalized by the section area of active material perpendicular to the heat gradient. It was obtained  $P_{\text{output}} = 105\text{ }\mu\text{Wcm}^{-2}$  for the device produced with MWCNT\_pristine,  $P_{\text{output}} = 23.2\text{ }\mu\text{Wcm}^{-2}$  for the device produced with MWCNT\_HNO3\_7M\_HT900 and  $P_{\text{output}} = 5.6\text{ }\mu\text{Wcm}^{-2}$  for the device produced with MWCNT\_BM\_WM0.8g\_HT600. It is also possible to calculate the

maximum efficiency of the generator and the maximum figure of merit of the device (ZT), for the same temperature gradient, using equations **(1.9)** and **(1.10)**, respectively. The results are shown on **Table 4.1**. Considering these results, the best TEG produced was the one where it was used the original MWCNT as a filler, which corroborates with the results obtained for the nanocomposites. One could see that the efficiency is extremely low for all the devices and in the case of the oxidizes MWCNTs, the efficiency is on order of magnitude lower when compared with the pristine when used at room temperature.

**Table 4.1.** TE properties of the devices produced for a temperature gradient of 10 K.

| TE material used on the<br>Device | Maximum Power output<br>$P_{output,max} (\mu W cm^{-2})$ | Efficiency<br>$\eta$ (%) | Figure of Merit<br>$ZT$ |
|-----------------------------------|----------------------------------------------------------|--------------------------|-------------------------|
| MWCNT_pristine                    | 105                                                      | 0.0463                   | 0.0043                  |
| MWCNT_HNO3_7M_HT900               | 23.2                                                     | 0.0054                   | 0.00057                 |
| MWCNT_BM_WM0.8g_HT600             | 5.6                                                      | 0.0025                   | 0.00026                 |

## 5 Conclusions and Future Work

In the course of this work, several aspects from Physics Engineering were covered, from the use of distinctive characterization techniques, printing techniques until reaching the ultimate goal of producing a device as a proof of concept. As science is not limited by boundaries, Chemical Engineering concepts were brought together for the preparation and characterization of functionalized carbon materials.

Firstly, it was studied different carbon-based material from where graphene revealed to be a promising material for thermoelectric applications, with a  $zT$  of  $\sim 6 \times 10^{-6}$ , at room temperature and MWCNTs were chosen when taking into account the price aiming to produce in massive scale.

The several treatments applied to both graphene nanoplatelets and MWCNT, through nitric acid oxidations, nitrogen doping, ball-milling and annealings, revealed that carbon materials are very band sensitive on the carrier transport properties when subjected to the physic and chemical processes. It outcomes that these treatments were responsible to perform alterations in the electronic states when compared to the pristine sample, promoting changes in the carrier densities, modification the band structures or messing with the phononic transport.

Concerning the graphene results, it was possible to optimize the Seebeck coefficient in 17% with the oxidative treatment ( $S \sim 23 \mu\text{VK}^{-1}$ ), relative to the pristine sample. It was also possible to duplicate the electrical conductivity with the melamine treatment, obtaining  $\sigma \sim 0.71 \text{ Scm}^{-1}$ . Unfortunately, the other parameters of the figure of merit for the different samples prepared didn't improved, revealing that the tailoring performed on graphene, produced an overall negative effect on the TE efficiency. Nevertheless, it is possible to observe that the functionalizations either changed the band structure revealed by the alterations on the Seebeck coefficient or changed the carrier density revealed by the modifications performed on the electrical conductivity.

Regarding the tailoring of the MWCNT, it was achieved promising improvements, in a TE perspective, with the treatments applied. Relative to the Seebeck coefficient, it was possible to enhance this property through the use of acid treatments and also through ball-milling. The maximum value obtain was  $35 \mu\text{VK}^{-1}$ , for MWCNT\_HNO3\_7M which was an improvement of 35 % when compared with the pristine counterpart. Throughout the detailed characterization, it was inferred that the modifications done on the materials were on the band structure via an electron withdrawing process. The electrical

conductivity was also improved with all the procedures used. The best material prepared for this parameter corresponds to a nitrogen doping (MWCNT\_BM\_WM0.8g\_HT600) with the value of  $1.33 \text{ Scm}^{-1}$ , 12 times larger than the value for the pristine sample. This was possible thanks to the increase in the carrier density provoked by the nitrogen atoms. An additional study on the transport properties in function of temperature, for low temperatures, was performed from where it was discovered that the materials fitted well in a fluctuation induced tunnelling model and that the oxidative treatment induced a more metallic behaviour to the carbon nanotubes. Concerning the thermal conductivity, all the treatments applied improved this parameter due to the effects of ball-milling and oxidations on the nanotube's length. As a consequence, it was provoked phonon confinement that reduced the lattice component of the thermal conductivity. The most reduction induced on this parameter was for the MWCNT\_HNO3\_12M in the value of  $0.52 \text{ Wm}^{-1}\text{K}^{-2}$ , 5.4 times smaller relative to the pristine sample. This is attributed to the use of a more concentrated acid that aggressively affected the nanotubes morphology. Finally, the sum of the results of these parameters result in larger figures of merit, at room temperature, up to  $55.5 \times 10^{-6}$ , for MWCNT\_HNO3\_12M\_BM, 73 times larger than the value obtained for MWCNT\_pristine.

Considering the nanocomposites formed with PVA and the functionalized carbon materials, it was possible to conclude that the  $\text{H}_3\text{PO}_4$  doping had a positive effect on the polymer by increasing the Seebeck coefficient. A percolation model was successfully applied to the composites from where it was discovered that material percolate above 2 wt.% of carbon material for the electrical conductivity and above 4 wt.% for the Seebeck coefficient. It was also presumed that the model was applicable to nanocomposites formed with the different produced MWCNT. An optimized range for the weight concentration of the filler relative to the polymer relies between 10 wt.% and 12 wt. %, considering both the transport properties and mechanical properties. A study on the functionalized materials mixed with the polymer for a 12 wt.% was implemented from where it was determined that the pristine sample performed better relative to the remaining changed MWCNT due to the larger length of the nanotubes and less defected morphology. For this nanocomposite it was obtained a power factor of  $2.58 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ , that is actually better than the power factor obtained for the same sample in bulk ( $\sim 0.72 \times 10^{-2} \mu\text{Wm}^{-1}\text{K}^{-2}$ ), an evidence of the positive effects of the polymer for constructing a TE material, aside of the advantages in terms of mechanical properties.

As a proof of concept, single-mode thermoelectric devices constituted by 10 stripes were produced recurring to a printing process and using PVA/ $\text{H}_3\text{PO}_4$ , a PET substrate

and three different material as a filler in the nanocomposite: MWCNT\_pristine, MWCNT\_HNO3\_7M\_HT900 and MWCNT\_BM\_WM0.8g\_HT600. A maximum power output was obtain using MWCNT\_pristine in the value of  $105 \mu\text{Wcm}^{-2}$ , correspondent to a figure of merit of 0.0043, for the temperature gradient of 10 K.

All things considered, some future guidelines can be taken into account, to further optimizing the results obtained.

In respect of the graphene results, it would be interesting to perform the oxidation treatment at room temperature in order to not obtain a collapsed graphene structure that would certainly improve the electrical properties of the material.

Concerning the functionalized MWCNT, information is very important to understand the modifications performed on the materials, and as so, an extensive study could be done in this matter such as X-ray photoelectron spectroscopy in order to obtain a more chemical characterization about the N configurations (e.g. pyridinic, pyrrolic...), intel on the binding energies and also Raman Spectroscopy at different laser wavelengths and starting at lower frequencies to complement the information already obtained. Further investigations on the surface modifications or doping either through electron-withdrawing or electron-donating species would be interesting in order to tune the TE properties could be done. It could also be created hybrid materials, either by using different combinations of carbon materials (e.g. MWCNT and graphene) or by joining organic and inorganic (e.g. MWCNT and  $\text{Bi}_2\text{Te}_3$ ). Measuring of the transport properties at high temperatures should be carried out, since these properties improve with the increase of the temperature and carbon materials are stable at high temperatures.

On nanocomposites, based on our experiment work, it is probably the point that should be more tackled. As a first point, the use of a conductive polymer (e.g. PANI, PEDOT...) would be a good strategy to help the electrical conduction and compared with the one used in the present case. Since the drastic change of  $PF$  of the nanocomposites, are related to the polymer, the burning of the polymer could also be an interesting approach. Another interesting addition would be the use of surfactants (e.g. Gum Arabic...) to improve the dispersion of the nanotubes that could also be a way of overcoming the setbacks encountered for the use of functionalized MWCNT in nanocomposites.

Considering the prototypes fabrication, different configurations could be tried. For example, using buckypapers instead of nanocomposites could eliminate the negative effects of the use of the polymer, improving certain TE properties such as the electrical conductivity. Different architectures could also be tried, such as an n-p type configuration

that has been considered the most efficient TE configuration. And finally, the production process could be escalated by using, for example, screen printing. Additionally, stress tests could be made with the devices in order to evaluate their mechanical stability.

Given the innovative results of the present thesis, one must conclude that carbon materials are promising materials to use on the TE field and that the results appropriate set a path for the fulfilment of the needs for innovative energetic solutions and also in the context of the Internet of Things (IoT).

## Appendix A

In this chapter, auxiliary information will be given.

**Table A1.** Properties of the pristine carbon-based materials as disclaimed by the producers.

|                       |                                                     |                  |                                                                                                                                                                                                                                                                              |
|-----------------------|-----------------------------------------------------|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Carbon Based Material | Product And Producer                                | ✓<br>✓<br>✓      | Relevant specifications (as disclaimed by the producer)                                                                                                                                                                                                                      |
| Activated Charcoal    | Sigma Aldrich®<br>NORIT® GAC 1240<br># M - 1368     | ✓                | Rod form                                                                                                                                                                                                                                                                     |
| Carbon Black          | Carbon Black<br>Printex® G                          | ✓<br>✓<br>✓      | Powder<br>Average particle size = 51 nm<br>$S_{BET} = 32 \text{ m}^2\text{g}^{-1}$                                                                                                                                                                                           |
| Carbon Xerogel        | Produced by the<br>LCM/LSRE at FEUP                 | ✓<br>✓<br>✓      | pH = 6.9<br>$S_{BET} = 572 \text{ m}^2\text{g}^{-1}$<br>$S_{micro} = 290 \text{ m}^2\text{g}^{-1}$                                                                                                                                                                           |
| Graphite              | Sigma Aldrich®                                      | ✓<br>✓           | Powder<br>< 20 $\mu\text{m}$                                                                                                                                                                                                                                                 |
| Graphene              | Graphene Nanoplatelets<br>Aggregates<br>ALFA AESAR™ | ✓<br>✓<br>✓<br>✓ | Powder<br>Surface Area = 500 $\text{m}^2/\text{g}$<br>Sheet resistance $10 \frac{\Omega}{sq}$ (for a 25 $\mu\text{m}$ film)<br>Raman D/G and D/D': 0.28 and 5.0 (The 2D band shape indicates the presence of few-layer graphene flakes with an average of 5-7 atomic layers) |
| MWCNTs                | Thin MWCNT<br>Nanocyl®<br>NC3100™                   | ✓<br>✓<br>✓<br>✓ | 95+%C purity<br>Produced via CCVD process<br>Average diameter = 9.5 nm (from High Resolution TEM analysis)<br>Average length = 1.5 $\mu\text{m}$ (from TEM analysis)                                                                                                         |

### Additional Properties of the functionalized graphene and MWCNT.

**Table A2.** Thicknesses of the functionalized graphene pellet samples.

| Samples        | GN_pristine | GN_WM_HT600 | GN_HNO3 |
|----------------|-------------|-------------|---------|
| Thickness (mm) | 1.194       | 0.751       | 1.871   |

**Table A3.** Thicknesses of the functionalized MWCNT pellet samples.

| Samples        | MWCNT_<br>pristine | MWCNT_<br>BM | MWCNT_<br>BM_WM_<br>0.36g_HT600 | MWCNT_<br>BM_WM_<br>0.8g_HT600 | MWCNT_<br>HNO3_7M | MWCNT_<br>HNO3_<br>7M_HT900 | MWCNT_<br>HNO3_<br>7M_BM | MWCNT_<br>HNO3_<br>12M | MWCNT_<br>HNO3_<br>12M_BM |
|----------------|--------------------|--------------|---------------------------------|--------------------------------|-------------------|-----------------------------|--------------------------|------------------------|---------------------------|
| Thickness (mm) | 2.347              | 1.120        | 0.871                           | 0.486                          | 1.619             | 1.236                       | 0.751                    | 0.744                  | 0.625                     |

## Appendix B

In this chapter, other not so relevant results will be given. SEM and EDS showed some non-conclusive or conflicting results, this being the reason why they are shown in this chapter instead of chapter 3.

SEM analysis was performed on samples MWCNT\_HNO3 and MWCNT\_HNO3\_HT900 and the results are shown on **Figure B1**. Unfortunately, the limited resolution of the equipment didn't allow a good view of the details of the nanotubes.

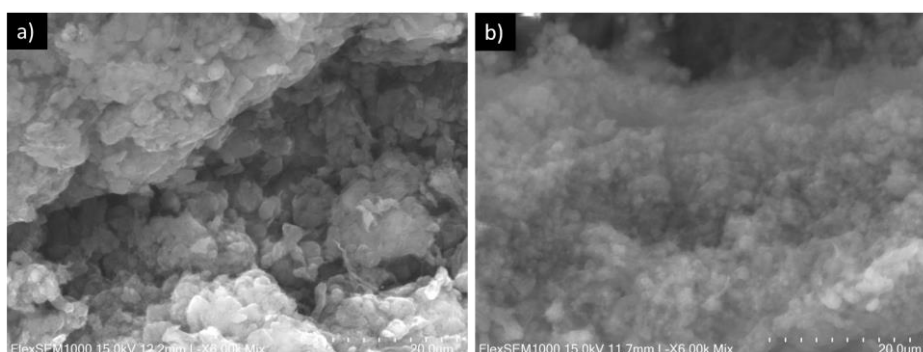


**Figure B1.** SEM results for a) MWCNT\_HNO3\_7M and b) MWCNT\_HNO3\_7M\_HT900.

EDS can give an overview of the elemental analysis and it was performed on the previous samples and also on MWCNT\_BM\_WM\_0.36g\_HT600. This technique was performed in vacuum at 15 kV by scanning a small piece of the sample surface. The results are shown in **Figure B2**.

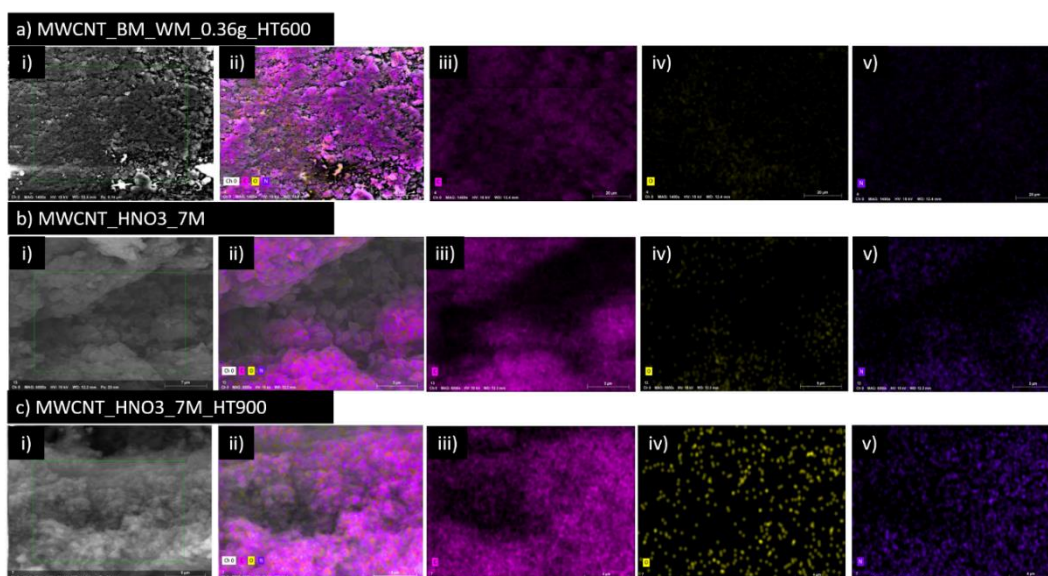


**Figure B2.** EDS results for a) MWCNT\_BM\_WM\_0.3g\_HT600; b) MWCNT\_HNO3\_7M and c) MWCNT\_HNO3\_7M\_HT900. i) SEM image; ii) Scanning of C, O and N; iii) C; iv) O; v) N.

These results are accompanied by the respective mass percentage of each element analysed obtained from the EDS analysis, represented on **Table B1**.

**Table B1.** Mass percentage of C, N and O, from EDS scanning data.

|                      | C (Wt. %) | N (Wt. %) | O (Wt. %) |
|----------------------|-----------|-----------|-----------|
| MWCNT_WM_0.36g_HT600 | 75.57     | 21.03     | 4.41      |
| MWCNT_HNO3_7M        | 75.73     | 22.26     | 2.01      |
| MWCNT_HNO3_7M_HT900  | 86.22     | 12.96     | 0.82      |

Unfortunately, these results are far from the truth since it is impossible for EDS to detect such high values of nitrogen in the analysed samples even for the nitrogen doped one. Oxygen level also cannot be higher in MWCNT\_BM\_WM0.36g\_HT600 sample than for the samples where oxygen functional groups were introduced even though these results could be explained by the analysis in profundity that is given by the x-rays as an opposition of the introduction of such groups at the material's surface.

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