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Synthesis and characterization of functionalized carbon nanotubes employing cobalt nitrate and acetone by using spray pyrolysis deposition technique

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Introduction

Due to hexagonal atomic structure of carbon nanotubes, exhibit interesting mechanical and electrical exceptional properties. For this, several procedures to synthesizing the carbon nanotubes were developed in order to obtain these materials with a desired structure. Several carbon sources have been reported in Literature for the synthesis of NTCs. As acetylene [1-4], Toluene [5], n-hexane, benzene and cyclopentadiene [6], etc., and after has been used alcohol [7-13]. Montoro et al. [13] showed in a comparative study that the acetone is the good candidate to synthesize multi-walled carbon nanotubes (MWCNTs) based in this type of analysis.

Respect to catalysts used, in the synthesis of the MWNTC some ceramics like alumina were used impregnated in some salts like cobalt nitrates - nickel, acetates of cobalt and manganese. Also pure metals of transition like Iron, Cobalt, Zinc, Ruthenium/Palladium, Co Na-Y, are used. Inoue et al. [9], explain that the cobalt in comparison with the iron, exhibits a poor interaction with the carbon but allows decompose better than ethanol. Also is observed certain preference in catalysts for the nucleation and growth according to Huh et al [14, 15], as well as the particle size. On the other hand Hanming et al. [16] made composites based of polyamide and functionalization of MWNTCS.

Considering the properties of low strength, high electrical conductivity and low toxicity of carbon nanotubes, various researchers have conducted experiments using these nanomaterials in interfaces for stimulation and recording of nerve cells. Single carbon nanotubes and multi-wall have been used as scaffolds for growing and neuro-regeneration and repair [Fabbro et al.] and for culturing nerve or nerve cells isolated from brain and spinal cord tissue [17-21]. Studies by Vladimir Purpura [22] showed that there is neuronal growth with carbon nanotubes functionalized multi-walled. They also highlight the work done by Laura Ballerini and colleagues who cultivated explants of spinal cord and neural circuits, demonstrating that carbon nanotubes may be suitable to promote neuronal growth and strengthening of synaptic circuits between neurons. The properties of biocompatibility and low toxicity of carbon nanotubes have been widely exploited for growing cells, including culturing stem cells in different species, routing this experimental approach to regenerative therapy and tissue engineering [23-25]. Shin et al. recently reported that the association of carbon nanotubes reinforced hybrid microgels, for cell encapsulation can be used for transplantation. Carbon nanotubes alone or in various composites allow cultivation and differentiation of human neural stem cells [23], proliferation and differentiation of pluripotent stem cells [26] and the development and absorption of mesenchymal stem cells - cortical neural stem cells [27].

Vittorio et al. have conducted research very relevant with carbon nanotubes multi-walled associated to stem cells. In addition to the ability of carbon nanotubes to promote neuronal growth, these materials have also been used for monitoring and biosensing of living cells [24-26]. Carbon nanotubes have been used as biosensors for glutamate and were able to measure in real time the flow of neuronal glutamate [28]. Schrlau et al. used carbon nanopipettes for intracellular injection [28]. Raffa et al. have made the permeation of cells without use of cables, using carbon nanotubes to stash and capture of genetic material [29]. Most recently has been reported the use of carbon nanotubes multi-walled for glucose monitoring [30]. Have been suggested that Carbon nanotubes as modulators of ion channels in excitable cells can be specific membrane ion channel blockers. Jakubek et al. reported that the physiological solutions containing carbon nanotubes single wall, inhibit Ca^{++} current through the calcium channel voltage-dependent neurons with an

IC50 of 1.2 $\mu\text{g} / \text{ml}$. However, it was shown that blocking is not due to the action of the nanotubes, is the presence of contaminating material present in the nanotubes [31]. In another interesting study, Xu et al. showed that carbon nanotubes multi-walled suppress currents to K⁺ channels, IK1 IK type, present in PC-12 cells [32].

This chapter will briefly discuss some procedures for carbon nanotubes synthesis and characterization of its structure.

Background

Graphene, a single atomic layer of carbon atoms bonded in a hexagonal lattice, is one of few materials that are stable in two dimensions and free-standing when suspended. This unexpected stability, combined with its exotic band structure and other unusual physical properties, has led to a considerable amount of experimental research. Of the many theoretical studies of graphene, a substantial portion are devoted to the physics of grapheme edges, whose structure in narrow graphene ribbons is predicted to have a major impact on their electronic properties. Experimental studies of the graphene edge have lagged behind, mainly due to the difficulty of atomically resolving and characterizing the boundaries of graphene sheets, but would give insight into the one-dimensional (1D) interface of a purely 2D structure.

The SWCNTs are semiconducting materials with different band gaps and can be applied in electronic or bio sensing endings. SWCNTs within specific diameter ranges with suitable band gaps have revealed superior transistor performances. For photovoltaic applications, SWCNTs of single chirality show better performances compared to SWCNT mixtures of metallic and semiconducting chiral species. For biomedical applications, chirality enriched SWCNTs demonstrate much brighter photoluminescence emissions, leading to lower SWCNT doses and less toxicity concerns. With these advantages to offer, it has been a long-standing goal to selectively obtain single chirality SWCNTs for potential applications ranging from electronics to medicine.

Some methods to grow CNT

Electric arc discharge: Electrophysical method

Carbon nanotubes were first observed in 1991 by physicist Sumio Iijima [33] produced using an arc-discharge evaporation method [34-39]. Arora and Sharma [34] conducted a complete compendium of types of carbon nanotube synthesis using an electric arc. The principle of this method of synthesis is based on sublimation of an electrode, commonly made in graphite that is used as carbon source. The sublimation is carried out by applying an AC, DC or Pulsating potential in function of intensity of voltage, current and frequency. Then, the vaporized carbon, high temperatures in presence with catalyzer is decisive to produce carbon nanotubes.

A DC electric potential in the electrodes generates a constant electric field causing the carbon sublimation in the graphite and then a high speed movement of electrons to the anode and ions of carbon to the cathode occurs. If the diameter of the cathode electrode is smaller than the anode, a difference in current density takes place and so generating a gradient temperature to form plasma.

This causes the carbon sublimation in graphite and in the presence of precursors (catalysts), carbon nanotubes growing begins. (Fig. 3.1A)

With an electric current alternating periodically (AC), deposition takes place outside the electrodes. The plasma escapes from the area where the arc occurs and due to thermal effects of the plasma the growing of carbon nanotubes begins. (Fig. 3.1B)

With pulsed electric arc, the formation of nanotubes is presented in discrete form. The pulse strikes the anode surface, the carbon sublimation begins and the deposition occurs in the cathode. (Fig. 3.1C)

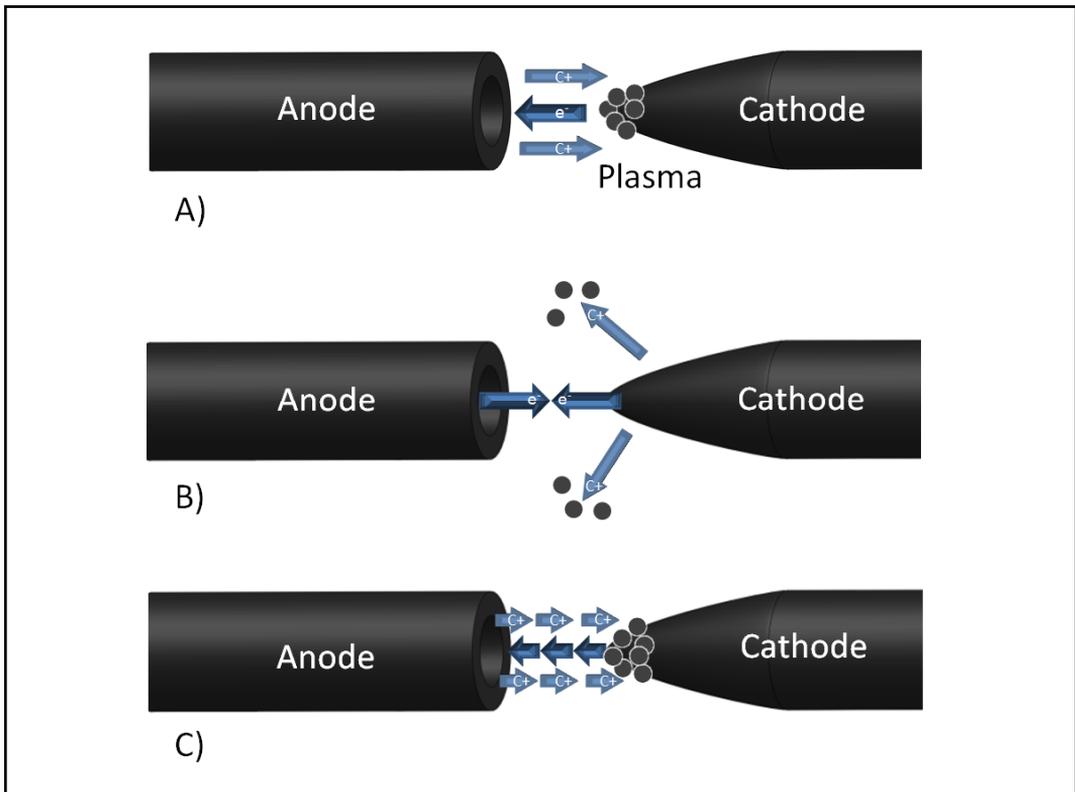


FIGURE 3.1

Effects of the different electric currents types forming electric arc: a) DC, b) AC, and c) Pulsed. *Image from reference [34]*

Effects of the electrical parameters in the growing of carbon nanotubes

Voltage effect: A voltage is applied to the electrodes and an electrical breakdown of the gas dielectric is produced. A sudden change of the arc voltage, results in the formation of bamboo-like structures.

Current effect: This affects the quality, performance and size of the nanotubes.

Frequency: This parameter affects the quality deposition. The AC voltage produces high quality carbon nanotubes monolayer. It has been found that with frequencies below 50Hz, best growth is obtained. And at frequencies above 400 Hz, the concentration of amorphous carbon (soot) increases.

Electrohydrodynamic atomization: Electro spraying

An electric field is applied to a liquid pumped through a fine capillary and directed towards a metal plate [40]. After achieving the onset voltage which is dependent on the capillary radius, the capillary-plate distance and the surface tension of the liquid produce an aerosol with the formation of a Taylor cone. Jet and spray as illustrated in figure 3.2.

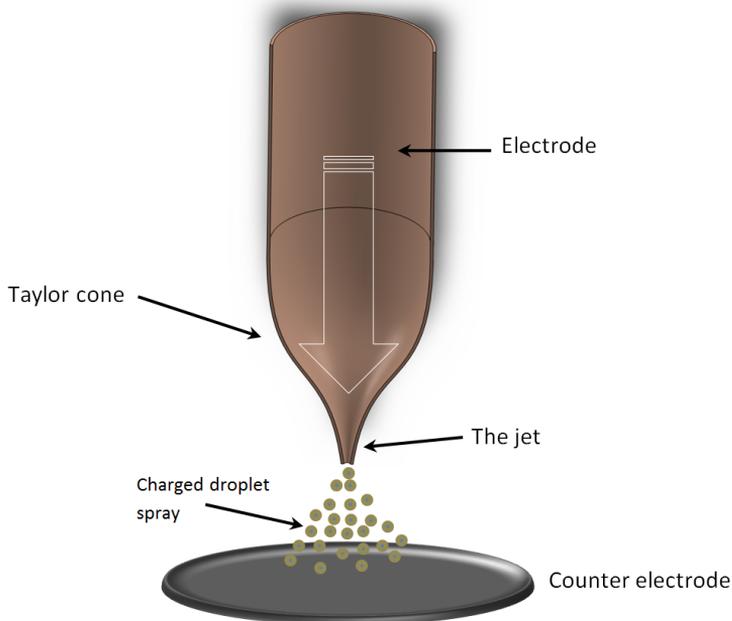


FIGURE 3.2

Scheme of electrodeposition equipment. Spray flow of carbon precursor is supplied in the equipment and the synthesis temperature is obtained by means of an electric field that generates the plasma point. *Image from reference [42]*

A capillary with external diameter of 230 μm was used, the capillary-plate distance was 6mm and the solvent was n-propanol pumped at a rate of 0.0021 sccm. A hole in the ground plate is to allow some of the spray pass through and a gas inlet port was connected in a gas-tight manner to a flanged silica furnace tube for use in the gas phase synthesis of carbon nanotubes.

Carbon nanotubes have been synthesized by radio frequency plasma generator (RF Plasma). Yabe et al. [41] did an iron film deposition with an electro-deposition equipment (sputtering) over a

(100) silicon wafer. Bouanis et al. [42] used tungsten heater resistances to achieve the high synthesis temperatures required for carbon nanotubes.

SPRAY PIROLISIS, CVD

Catalyzer under subtract

This synthesis process is based on heating the catalyst that has been deposited over MgO substrate, Al₂O₃, anodized aluminum, Zeolite [43], etc. The carbon supply commonly used is a gas hydrocarbon as methane (CH₄) [44] ethine (C₂H₂) [45-46], polypropylene in solid state [47] and as liquid in microdrops form [48]. By means of a carrier gas they are conducted to the place where the reaction occurs. The synthesis temperature for carbon nanotubes is from 600°C to 1000°C [44]. At this stage the decomposition of the carbon source occurs and the catalyst particles serve as seeds for nanotubes growing. The catalyst can be deposited on the substrate in different ways (Patterned).

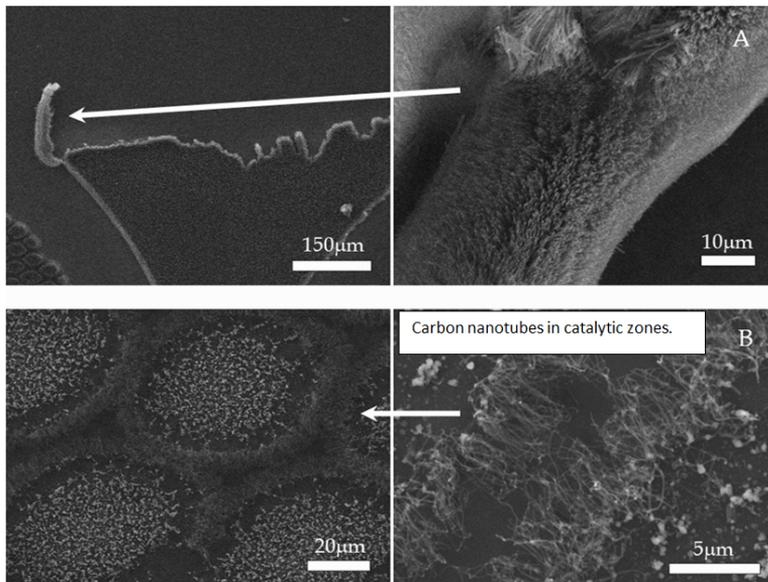


FIGURE 3.3

A) Carbon nanotubes grown over a piece of cobalt thin film detached from silicon substrate B) Carbon nanotubes growth among catalyst zones at carbon nanotubes grown by lithography

Chemical vapour deposition (CVD)

This process as in the catalyzer under subtract method, the catalyst is dissolved in the liquid solution of the carbon precursor. For example, Aguilar et al. [49] used a ferrocene/toluene solution and Gómez et.al [50] used an Acetone/cobalt nitrate solution by means of incomplete pyrolysis, the carbon nanotubes caused that functional groups occupy the graphite structure of carbon nanotubes.

Carbon nanotubes can be produced by different CVD methods such as thermally activated CVD, plasma enhanced CVD, aerosol-assisted CVD and fluidized bed CVD. Parametric studies have been reported for several CVD methods to provide better understanding of the influence of the manufacturing factors on geometrical and structural properties of CNTs. Direct chemical vapor deposition (CVD) by co-feeding hydrocarbon and catalyst vapors has been used successfully to synthesize CNTs on quartz substrates and resulted in population densities as high as 10^{10} cm^{-2} . The reaction mechanism depends of the activity catalytic growth of carbon nanotubes. A great variety of catalyst supports (silica gel, zeolite materials, alumina, etc.) with different pore diameter.

Synthesis Method of Carbon Nanotubes Using The Spray Pyrolysis Technique

Case of study I: Synthesis method of functionalized carbon nanotubes employing cobalt nitrate and acetone by spray pyrolysis.

In this study has been selected the acetone like carbon source and cobalt nitrate like catalyst, which will analyze its performance in the synthesis of MWCNTs with spray pyrolysis. Also will be analyzed the groups ketone and nitrate product of the decomposition of these compounds on the MWCNT functionalization. Figure 3.4 shows the pyrolytic system employed for the synthesis of the multilayer carbon nanotubes (MWCNT).

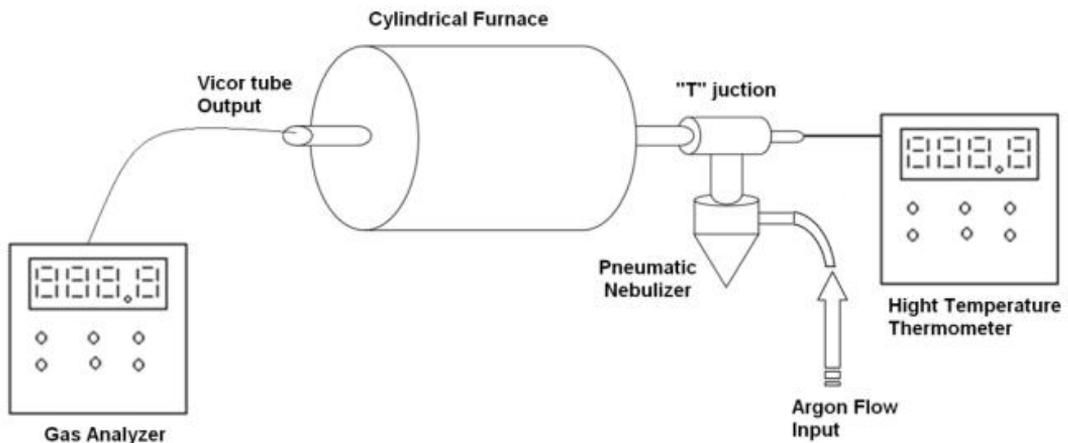


FIGURE 3.4
Spray pyrolysis system used to obtain the SWNTC

For the synthesis of nanotubes were selected four temperatures 700°C , 800°C , 900°C , and 1000°C and kept constant during the synthesis phase. During the preheating phase, an 800 sccm argon flow is applied. Once the synthesis temperature had been reached, 20 mL of acetone/catalyst solution was applied through a spray device with an argon flow to 2,500 sccm. Once the solution has been finished, the heating system was turn off. The assembly was allowed to cool to room temperature keeping during this process a flow of argon 800 sccm.

The vicor tube was cut into four sections to be named. These sections of the analysis phase were each one of 7.5 cm in length and was named in according to its position like upstream zone, first and second downstream zone Isothermal zones. In order to observe the growth of carbon

nanotubes a small segment of each of these parts has been extracted and analyzed using a scanning microscope JEOL JSM-7401F. Subsequently each one of these segments was separately immersed in an acidic solution (1 : 3) nitric/sulfuric and extracted carbon nanotubes from the substrate by vicor ultrasonic treatment. To remove acid residues were washed with distilled water and tri-several rinses in acetone. Finally in the cleanup phase, the specimens of each section were suspended in acetone in order to be characterized. The experimental setup appears in figure 3.4. Figure 3.5 shows the vicor tube image identifying the different zones.

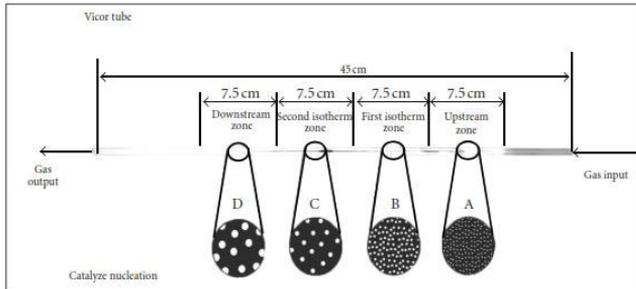


FIGURE 3.5

Vicor tube with measurements and zones

Figure 3.6a illustrates the forest of carbon nanotubes obtained in the upstream zone at 900°C, where is observed the orderly growth. Also is observed a good homogeneity of them in size and shape.

Case of study II. Spray pyrolysis by using ferrocene and toluene as principal reagents

These nanotubes were prepared as follows. As first step a solution of 0.25 g of ferrocene in 25 mL of toluene was prepared. After the solution was heated in a tubular oven at 800°C in an Ar flux of 360 sccm. Finally a quartz substrate was inserted and reduced the flux up to 2 sccm.

Figure 3.6b displays a SEM image of MWNTC obtained by using toluene and ferrocene as reagents. As we can see these nanotubes have a better distribution and homogeneity than those obtained in the above mentioned method (case of study I). In order to have an idea of their physical dimensions a zoom of dispersed MWNTC was done. In Figure 3.6c we observe different sizes and lengths of the nanotubes.

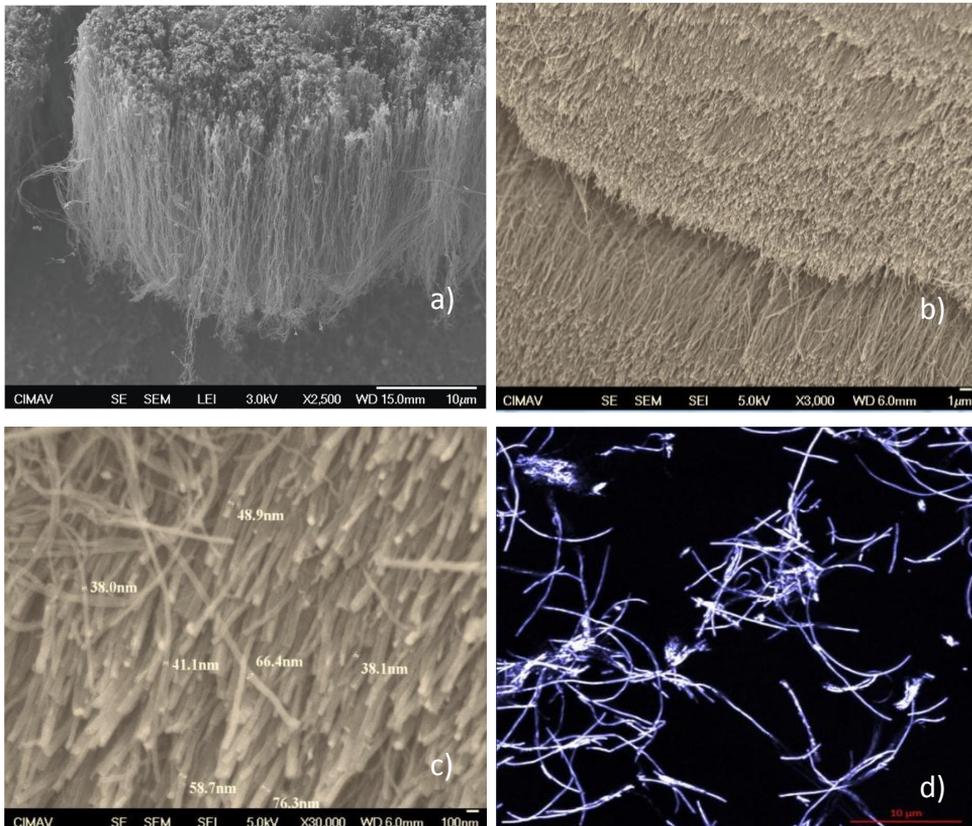


FIGURE 3.6

Images of carbon nanotubes obtained by mean of a) SEM obtained by the spray pyrolysis technique, b) FESEM obtained by using ferrocene and toluene as reagents, c) SEM at higher magnification, d) Confocal, used as representative image used in biosciences

A confocal micrograph was taken of the same sample (Figure 3.6). This image is very representative because we are only seeing the nanotubes and its distribution. This technique is very useful in biosciences.

On the other hand, the way to know if we have good quality of MWNTC, is Raman spectroscopy. Raman technique has the capability to detect those very weak signals in where the coherent light strikes on a sample. Thus, the detected vibrations are part of the finger print of the sample.

Figure 3.7 shows the Raman spectra of the MWNTC taken directly of the synthesized sample. In this Figure we observe the characteristic G, G' lines of the MWNTC. The D line represents the amorphous state and the ratio IG/ID give us the quality of a pure sample.

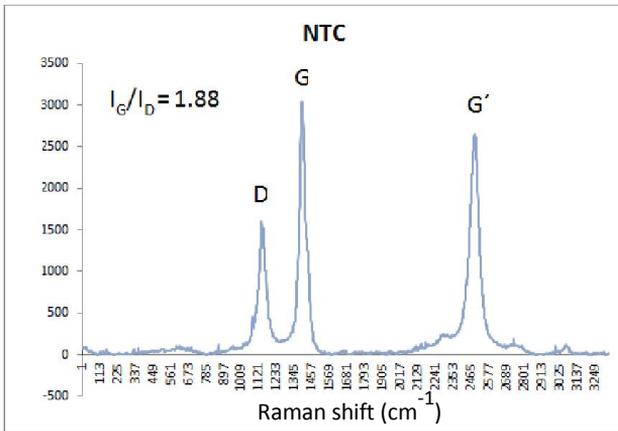


FIGURE 3.7
Raman spectrum of MWNTC

Functionalization

The graphene structure of carbon nanotubes can interact with certain functional groups on the surface in order to solubilize, to get alloys or give them a magnetic character. Unal et al. [51] performs an oxidation of the carbon nanotubes with an acid treatment of H_2SO_4 y HNO_3 at this way assembled functional groups of CoFe_2O_4 via a bridge $-\text{COOH}$ toward the nanotube (Fig. 3.8). The CoFe_2O_4 gives the nanotube magnetic behavior, together the intrinsic percolative character, can also obtain materials with electrical properties.

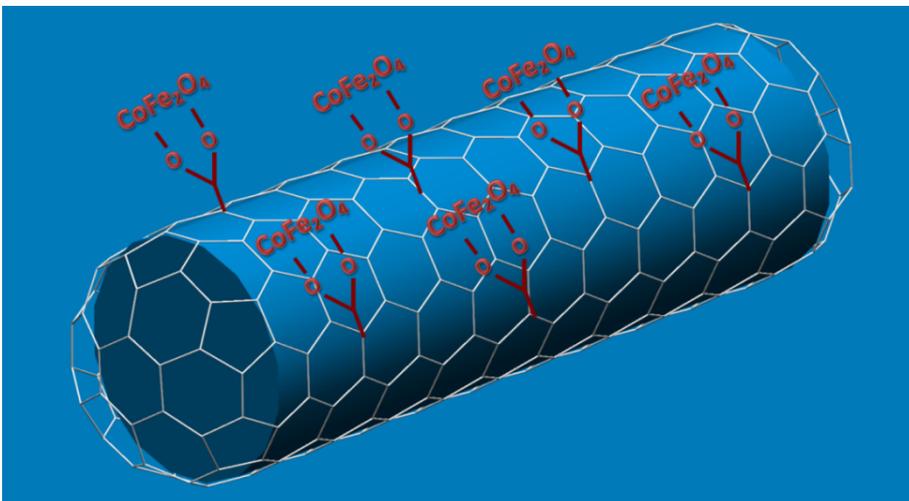


FIGURE 3.8
Simplification of the functionalization of carbon nanotubes with groups CoFe_2O_4 y $-\text{COOH}$ used as a bridge.
Image from reference [51]

Biocompatibility

The development of new field effect transistors (FET) has evolved considerably. These transistors are manufactured using doped silicon crystals, but recently an interest has taken to research new materials for these transistors, like graphene (GFET), Ion Selectivity (ISFET), carbon nanotubes, etc [52]. These materials could be developed as biosensors for applications in various types of cancers, cholesterol, hemoglobin, glucose oxidase, etc.

The scheme of a biosensor based on a FET transistor is shown in figure 3.9. Drain, Source and Gate terminals are shown.

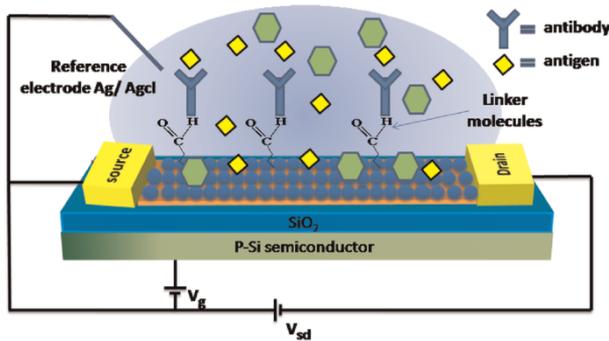


FIGURE 3.9

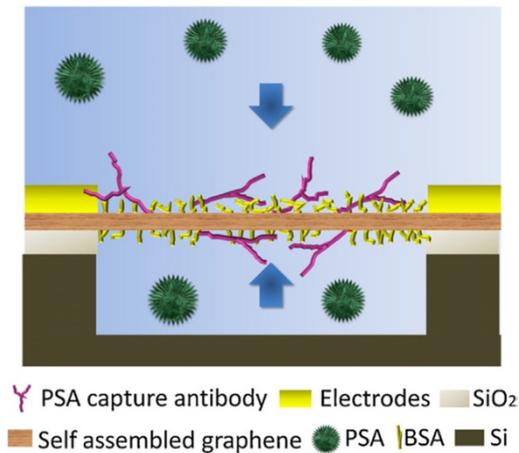
Scheme of a biosensor based on a FET transistor. Courtesy of Nehra, K.P. Singh Biosensors and Bioelectronics74 [52]

ISFET transistors type incorporate layers of enzymes, chains of DNA and antibodies to be used in detection of various elements. Among the nanomaterials that have been used for making the Gate terminal of the FET-based biosensors are magnetic nanoparticles, silicon nanowires (SiNW), titanium dioxide, zinc oxide, gallium nitride, carbon nanotubes, and graphene. Applications are broad and some of these are:

pH Sensors: Is a device SiNW FET for to detect the analytes through a pH solution. This transistor is made of a cover of oxide SiNW functionalized. This material gives a higher detection sensitivity for pH and with different biological receptors can selectively detect biological entities in solution.

Protein sensors: Regonda et al. [53]. Developed a sensor Si nano-grating (SiNG) used in insulin detection. Puppo et al. developed a sensor based on SiNW Functionalized with glycidoxypopyl trimethoxysilane (GPTS) bound to a rabbit antibody. This device can detect exogenously antigens of human breast tumors.

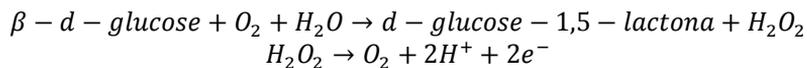
Have been developed other sensors to detect Prostate-specific antigen (PSA) based on nano-composites of alternated layers (layer by layer) of grapheme and poly (styrene sulfonate)/ (PDDA) [54]. After the sensor is functionalized by means of antibodies PSA on the surface (fig. 3.10). Once the biosensor grapheme modified with antibodies is in the solution of PSA, immunoreaction will take place on both sides of graphene suspended and the graphene conductance is modified due to the absorption of PSA on the surface of the graphene.

**FIGURE 3.10**

Simplification of the functionalization of carbon nanotubes with groups CoFe_2O_4 y $-\text{COOH}$ used as bridge. Image from [54]

Cholesterol sensor: Ahmad et al. [55] made a cholesterol sensor based on nanorods of ZnO vertically aligned with an enzyme that dissolves the cholesterol which in turn causes a variation in sensor conductance. On the other hand, Lawal [56] developed a biosensor with graphene and nano particles of platinum (GR/PtNP) and sensing is based on variations in conductivity due to the immobilization of the cholesterol esterase and cholesterol oxidase and also with the surface interaction of GR/PtNP.

Glucose sensors: This sensor is based on a hybrid of a film of polypyrrole and carboxylated graphene (C-PPy). The operation is by reducing graphene oxide (RGO) / C-PPy. The graphene sheet has ohmic contact with the electrodes. When reacts with glucose causes an increase in conductivity of graphene. The glucose oxidation is as follows.



Estimated growing mechanism

The catalyst is used to facilitate the hydrocarbons decomposition used as carbon source in the synthesis of carbon nanotubes. The metal must have solubility for carbon and react chemically but should not be a strong carbide former as it happens. [57].

In the case study model, the CNT growth nanotube process was partitioned into four main steps. At the first step, the pyrolyzed hydrocarbon products were adsorbed on the surface of catalyst particles, which decomposed into the carbon atoms due to the presence of catalyst and carbon atoms realigned on a certain catalytic crystal face, as is shown in Fig. 3.11a, the shape realigned exhibiting tubular figure. The second step might be the formation of C–C chemical bond. The carbon atoms around the tube were combined to form chemical bonds, and the tube would gradually grow, as is shown in Fig. 3.11b. The third step is the deactivation of catalyst and formation of seal. The carbon atoms in the open tip of tube were integrated to form seal owing to

the close spacing of carbon atoms in inner nanotube, as is presented in Fig. 3.11c. Then the residual finite carbon atoms around tube were provided to the growth of tube outer layers. Finally all tube layers were sealed, and CNT growth stopped, and the CNT reached its maximum length, as is exhibited in Fig. 3.11d.

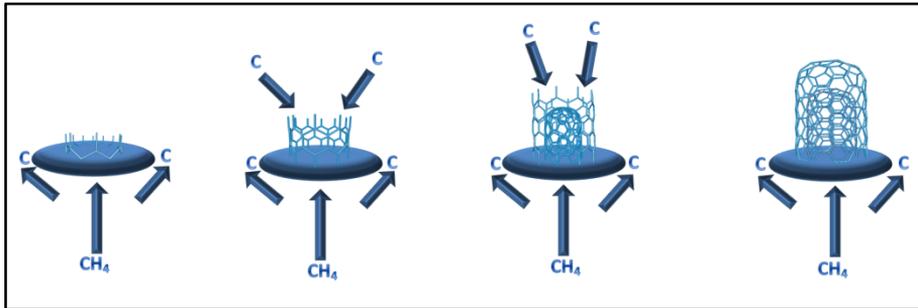


FIGURE 3.11
Growing steps of MWNTC in the spray pyrolysis system

Conclusions

The synthesis of carbon nanotubes by using both reagents, ferrocene with toluene or cobalt nitrate in the method of spray pyrolysis system resulted as very simple methods, in addition to the carbon source and metallic cobalt as a catalyst, water and CO to remain in the good condition formation of carbon nanotubes. We considered that an incomplete decomposition reaction of these two compounds resulted in several functional groups adhered to the graphene structure of the nanotubes. The water produced by the same cobalt nitrate participates in the formation of CO from CO decomposition product of acetone is proposed where additional work is controlled hydration of cobalt nitrate to observe the effect of growth and quality of carbon nanotubes. In addition to change the way of collection of catalyst particles to increase the production of multiwall carbon nanotubes, we most control the use of the reagents. Finally it is very noticeable that the use of a solution of ferrocene diluted on toluene gives us a very good quality MWNTC.

Acknowledgments

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