Abstract:
The present invention relates to a method for the synthesis and in-situ doping of carbon nanotubes (CNT). The method of the invention enables the manufacture of nanotubes in an economically viable way and free from amorphous carbon, resulting in that their purification is performed only by the catalyst, which process requires just a few washes with low-concentration commercial acid. Also, this process allows the in-situ doping of carbon nanotubes with different doping elements during and after growth.
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Methods for the preparation of carbon nanotubes doped with different elements

Field of the invention.
The present invention relates to a method for the synthesis and doping of carbon nanotubes (CNTs). The technique used in this process enables the economically viable production of nanotubes free from amorphous carbon using only a catalyst purification, which requires just a few washes with low concentration commercial acids. Similarly, the process allows the doping of nanotubes with different elements during or after their growth.
The purpose of the present invention is to synthesize carbon nanotubes (CNTs) using methane as carbon precursor, dope them in-situ with different elements such as phosphorus, aluminum and potassium, or any desired dopant element. The theoretical modeling and experimental characterization have been performed before and after doping, to identify the possible effects of this type of functionalization on said carbon systems.

Background of the invention.
Nanotechnology is a field of applied science, which entails the manipulation and control of matter at the nanometer level. The prefix *nano* indicates a billionth, and therefore a nanometer is a billionth of a meter. To facilitate views at this scale, it is possible to make initial comparisons with the dimensions of material elements with which we act in everyday life. For example, the eye's ability to observe objects starts in the scale of 1,000,000 nm, while the diameter of a human hair is 75,000 nm wide. The size of *E. coli* bacteria is 2,000 nm, and the size of a virus is 50 nm. In turn, the diameter of a nanotube can be from 1.3 nm to 100 nm, and finally, as a comparison, the hydrogen atom has a radius of about 0.1 nm.
However, it is difficult to determine and define the term nanotechnology. It has, however, very marked features including:

a) Nanotechnology involves the research and development between 1 to 100 nm.

b) Nanotechnology creates new structures with different properties from bulk materials resulting from their small size and provides applications in new fields of science.

c) Nanotechnology is based on the ability to manipulate and control bodies in an atomic scale.

In recent years, the research conducted has made on nanotechnology one of the most popular topics in various fields of chemistry, physics, and materials science today. Because of their size, nanomaterials exhibit new and unexpected electronic, optical, transport, photochemical, magnetic, electrochemical, and catalytic properties, very different from those of bulk materials, and thus enabling their potential application in various technological fields.
Nanotechnology, among many other things, has succeeded in advancing transistors. In this field, the predecessor of the vacuum tube produced in 1897, worked with a filament, which had three terminals instead of two. One of the disadvantages was the overheating of the apparatus. Some 50 years later, the solid-state transistor was built with an operating mechanism that alternated an on-off switch and combined the characteristics of metallic and semiconducting materials, being more durable than vacuum tubes.

In 1998, carbon nanotubes transistors were developed, resulting more efficient than the previous devices, as they consume less power and dissipate less heat. Aside from the CNTs, semiconductor nanoparticles, metal nanoparticles and fullerenes are other examples of nanomaterials. The manipulation of these materials at nanometric scale, has led to the manufacture of microscopes with higher resolution, as well as the manufacture of nanomachines to study their properties.

Moreover, several patent documents report different methods for obtaining nanotubes of various materials other than carbon, such as boron nitride, titanium dioxide, and molybdenum disulfide nanotubes among others.

Patent US7754183 discloses the manufacture of carbon nanotubes by chemical vapor deposition wherein the precursor materials may include one or more dopant sources (preferably boron, nitrogen, or sulfur), and wherein the carbon source, the dopant source and the catalytic source are injected into the system as liquids, or the catalytic source is located on a substrate and the synthesis process is carried out on silicon wafers.

The patent application WO2007057501 relates to functionalized carbon nanotubes with fullerene-like molecules covalently bound to the surface of the nanotubes.

Patent application CN101717983 describes a method for the preparation of titanium dioxide nanotubes doped with sulfur and fluorine, which involves preparing 0.5M H₂SO₄ + 0.5% by weight of HF in electrolyte, using an electropositive oxidizing method, which involves a titanium plate as a positive electrode and a nickel plate as a negative electrode, allowing the growth of the titanium dioxide nanotubes on the titanium plate and subsequently calcined in a heating furnace at 673-973 °K to finally obtain the material.

The patent document CN10161001 describes a method for preparing TiO₂ nanotubes doped with Pd, comprising the steps of anodizing a Ti pre-treated pure sheet, to prepare a preliminary product of the first stage, to wash the initial product with deionized water and performing ultrasonic vibration in alcohol to procure a second preliminary product of the second stage.

The patent document CN101433828 describes a method for preparing a visible and light catalyst, and titanium dioxide nanotubes doped with aluminum, which comprises the steps of
adding powdered aluminum oxide and titanium oxide in hydroxide sodium aqueous solution, stirring and heating to its final reaction. The resulting mixture was cooled at room temperature and washed until obtaining a pH value between 6.5 and 7.5, upon which the catalyst is procured. The patent document EP1998385 describes a method for doping carbon nanotubes, wherein p-doped carbon nanotubes are obtained using an electrode, a device or solar cell that includes carbon nanotubes.

These documents and others existing in the state of the art of the prior art do not disclose the subject that is matter of the present invention, mainly because the method for the synthesis and doping of carbon nanotubes of the invention allows the manufacture of highly pure and crystalline nanotubes in an economically viable way and free from amorphous carbon, wherein the purification is only for the catalyst and only requires a few washes with commercial low-concentration acid to remove the traces of the catalyst. Similarly, this process allows the synthesis of carbon nanotubes using methane as a carbon precursor, and the doping of carbon nanotubes with different doping elements during and after their growth, such as phosphorus, aluminum, and potassium.

**Brief description of the invention.**

The present invention provides methods for the synthesis and doping of carbon nanotubes *in-situ*.

The present invention also relates to the optimization of the carbon nanotubes (CNTs) synthesis using methane as carbon precursor, different catalytic mixtures, and, by doping CNTs with different elements such as P, S, Al and K, procuring different structures and configurations of carbon nanotubes.

**Brief description of the drawings.**

**Figure 1** shows the substitutional positions for dopant atoms on a graphene sheet.

**Figure 2** shows the steps outline for preparing the catalyst by the Sol-Gel method according to the present invention.

**Figure 3** shows the synthesis of CNTs with Ni at 50%, without purification (left) and purified (right), thereby confirming that they were free from amorphous carbon and metal particles after the method of the invention.

**Figure 4** shows CNTs produced by the method of the invention with Co as catalyst at 5 nm (left) and 100 nm (right).

**Figure 5** shows CNTs doped with aluminum by the method of the invention.
Figure 6 shows CNTs functionalized with potassium by the method of the invention.

**Detailed description of the invention.**

The technology we use in everyday life (cell phones, CD players, camcorders, i-pods nano, etc.) is the result of the process of miniaturization of electronic components. Today’s devices are smaller, but more efficient than those used in previous years. Among the materials used today are the nano devices based on carbon nanotubes (CNTs). These new materials consist of one-dimensional structures formed by graphene sheets. One of the main features of CNTs and a reason for their great scientific interest arises from their electronic properties. Unlike graphite, CNTs vary their electronic properties depending on the orientation of the hexagons forming their structure. A key point regarding these properties is that introducing artifacts to the network, or elements other than carbon can change them. Graphene is able of conducting electricity because electrons are free to move (electron derealization). The electronic configuration of carbon has four electrons in its last layer (2s22p2). As to graphite, a sp2 hybridization occurs, in which each atom is uniformly connected to three carbons (120°) in the xy plane, and a weak π bond is present at the z axis. The sp2 C-C bond has a length of 1.42 Å. The shape of the network is typically hexagonal and the spacing between the carbon layers is 3.35 Å. The pz orbital is responsible for Van der Waals interactions. This phenomenon elucidates why graphite can conduct electricity. The diamond, however, behaves as an insulator because all electrons are localized in the bonds within the sp3 structure.

The similarity of CNTs to graphene has aroused great interest in elucidating its electronic properties. According to theoretical studies, by introducing different elements into the carbon, these properties display interesting changes that widen application of these systems.

The current trend in electronics is the miniaturization of devices to improve properties such as increased speed, density, and efficiency. In this widely demanded process traditional silicon technologies are reaching the minimum size that can be achieved, assuring proper operation. CNTs can play the same role as silicon in electronic circuits, but at the molecular scale where silicon and other semiconductors stop working. CNTs are expected to become a basic piece in "molecular electronics" which uses molecules as building blocks for manufacturing devices. Electronics at the molecular level will not only facilitate the manufacturing of smaller conventional devices, but also create new ones that take advantage of the quantum effects that characterize the nanoscale in which they operate. Another contribution of CNTs to electronics is that they can be excellent heat conductors, making them ideal heat sinks produced in electronic systems.
An important feature of the electronic devices integrating CNTs is the increase in their useful life, mainly resulting from the mechanical (mechanical strength, hardness, toughness, flexibility, and elasticity) and thermal properties (good heat conduction and structural stability at high temperatures) of nanotubes.

The CNTs properties depend greatly on the diameter of the structure and the chiral angle that display properties that can be intrinsic to the growth process of the CNT, or be modified, subsequently generating defects in the hexagonal lattice.

The electronic properties of CNTs depend on their electronic structure. Their behavior has a wide range, as CNTs can behave as semiconductors, or, in some cases, as superconductors. CNTs doping is one route to modify their electronic, vibrational, chemical, and mechanical properties, replacing some of the carbon atoms by other elements. CNTs have presented significant changes in their electronic properties resulting from the presence of the excess or deficiency of electrons. Studies have been done mainly with boron and nitrogen, as they contain less or one more electron, compared with carbon, and their properties do not differ much because they are located in the same period in the periodic table. If the boron replaces some atoms in a graphene sheet, the electronic structure is likely to contain vacuums, which are responsible for generating p-type conductor materials, while substituting a carbon atom of nitrogen is achieved forming an n-type material.

We have theoretically analyzed different possibilities of doping CNTs. Due to the search of new semiconductor materials for applications in gas sensors and hydrogen storage, has been proposed doping CNTs with aluminum.

CNTs are used in a wide range of applications such as nanocircuits, interconnectors, diodes, field effect transistors, flat screens, luminescent lamps and tubes, optoelectronic memories, spintronics and sensors among others.

An important contribution to the present invention is the prediction and study of the vibrational properties of CNTs.

One embodiment of the present invention is to procure low-energy structures, and obtaining the links between C and the doping elements, the electronic location after doping, the density of electronic states, the band structure and characteristic modes of vibration with and without doping.

Another embodiment of the present invention is the economic production of doped carbon nanotubes free from amorphous carbon.

Another embodiment of the present invention consists of having determined the optimal technical characteristics in the preparation of CNTs.
There are many processes to produce CNTs, among others: arc discharge, laser ablation, pyrolysis, microwave, gas phase, Chemical Vapor Deposition (CVD). One of the major processes used in the synthesis of CNTs is the arc discharge in which two graphite rods are connected to a voltage source, forming plasma from the carbon vaporization. The other two processes are laser ablation and CVD, the latter being the more economically viable technique, and which is used in the present invention. The CVD technique employs carbon sources in liquid or gaseous phase, and external heating; e.g., a resistor. The carbon precursors most commonly used are: methane, carbon monoxide, acetylene, acetone, and alcohol (hydrocarbon derivative). In this process the heat (energy) within the reactor breaks the molecule containing carbon and for the latter to diffuse into the substrate, which has been previously coated with a catalyst. The CVD technique is a method that allows a higher production at lower cost, while also creating nanotubes with few impurities at relatively low reaction temperatures. Generally, the transition metals are used as catalyst in the growth reaction of CNTs. These metals can often be recovered chemically unchanged after the growth reaction. It is important for the catalyst particles to have a controlled size and a good distribution on the substrate. It has been shown theoretically that the electronic structure of CNTs is tightly bound to the diameter and its chirality. The diameter at the same time, is related to the size of the catalyst particles and the size of the pores of the substrate. When the catalyst has a particles with a size of a few nanometers, are formed single-walled nanotubes (SWCNTs), whereas particles larger than 10 nm favors the formation of multi-walled nanotubes (MWCNTs).

Furthermore, MWCNT are produced at lower temperatures (600-900°C) compared with SWCNT (900-1200°C). Therefore, the free energy for the formation of MWCNT is lower. It should also be noted that the growth conditions could vary depending on the combination catalyst-carbon precursor. Carbon precursors that have proven to be the most efficient in the growth of MWCNTs are acetylene and benzene; these compounds are unstable at high temperatures and eventually deposit large amounts of carbonaceous compounds. Among the most efficient catalysts, it has been found that transition metals such as iron, cobalt, and nickel are good catalysts for the growth of CNTs. However, the catalyst must be of nanometer size to generate a greater surface area and active sites to produce the nucleation and growth of CNTs. The main parameters that determine the catalytic properties are: the composition, morphology, preparation method, support, and pre-treatment (pre-reduction of metal oxides). The materials that have shown to be better substrates for the growth of CNTs are: SiO₂, MgO, zeolites, and porous minerals. Therefore, the combination of the type of carbon precursor, the catalyst, and the
growth temperature determine the formation of different types of CNTs (SWCNTs, DWCNTs, MWCNTs, and CNTs bonds as X and Y formations).

The preparation of the catalyst is one of the crucial points for the growth of CNTs. There are different routes for preparing the catalyst. Among the most used techniques are the sol-gel process, the impregnation process, Metal Organic Chemical Vapor Deposition (MOCVD), and physical deposition.

The sol-gel process is used mainly to produce particles with nanometric sizes. This process has advantages over other methods not only to achieve homogeneous mixtures of cations at atomic scale, but also to form films and fibers onto gels. The main objective of the sol-gel process is the preparation of a homogeneous catalyst support, from which a semi rigid gel may be isolated with an atomic level of homogeneity. In the synthesis by sol-gel process the soluble catalyst support is hydrolyzed to form a dispersion of colloidal particles in a solvent. Moreover, the reaction forms bonds between particles (soles), generating an infinite network of particles called gel. Subsequently, the gel is subjected to a thermal process for procuring metal oxides from transition metals, to be used as catalysts. There are two variants of the sol-gel process, and they differ mainly by the initiators of the sol: 1) sol-gel process using alkoxides, and 2) polymeric initiator process.

In the present invention the depositing of catalyst particles on the substrate is performed by immersion-removal method (dip coating), which is normally used for obtaining films. The above method is an effective and low cost technique for coating various materials. The substrates are introduced into the liquid contained in any container (sol-gel catalyst particles), and subsequently removed at a controlled speed, continuing the evaporation of the solvent. The removal speed is a critical factor for success and directly affects the thickness variations of the formed layer. A slow extraction is better, because it produces uniform thickness; in turn, a rapid extraction produces coatings that are thinner at the top and thicker at the bottom. Finally, the material is obtained by heat treatment.

Preparation of nickel oxide by sol-gel method. The use of different synthesis routes for nickel oxide (NiO) (II) has been of great significance in the preparation of new materials. These methods can produce marked differences in some parameters such as the particle size, morphology, crystallinity, and surface area of NiO. The sol-gel process is a reliable and popular method to prepare metals such as metal oxides with small particle sizes, uniform, and with various morphologies. The main interest in materials derived from these materials is their application as catalysts. For the catalyst particles, the alkoxide is mixed to prepare the silica
catalyst precursor salts in aqueous solution. Subsequently, the support is contacted with the prepared solution, whereby the catalyst is deposited on or inside (for a porous support) the substrate. The solvent, which is mixture of water and alcohol, is then evaporated, consolidating the mixture catalyst/substrate. When the catalyst is introduced by impregnation, the impregnation time depends on the type of substrate and process used; it can vary from 15 minutes up to 7 hours for substrates such as MCM41.

Metal organic chemical vapor deposition (MOCVD). A metalorganic precursor is evaporated and fed into the reaction zone by a carrier gas. The heating in the reaction zone causes the decomposition of the catalyst and its deposition on the substrate. It is also possible to use a mixture of carbon precursor and the catalyst precursor, achieving the growth of structures aligned on quartz substrates.

Physical deposition. The metal is evaporated to deposit on the substrate. If deposited at room temperature, it is usual to obtain a thin film of amorphous material on the substrate.

Characterization. The catalysts used for the growth of CNT in this invention were characterized by X-ray diffraction and scanning electron microscopy (SEM), while the CNTs were characterized by Micro-Raman spectroscopy, scanning electron microscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy issued (XPS), TGA (thermogravimetric analysis), and DSC (differential scanning calorimetry).

X-ray diffraction. X-ray diffraction is based on scattering, a phenomenon whereby a portion of the incident radiation (photon) is diverted from its original propagation direction with equal or lower energy (elastic scattering and inelastic scattering), resulting from the collision with an electron irradiated material. By using this technique each atom in a crystal can disperse in all directions at an X-ray beam that impinges on it. X-ray diffraction is used for qualitative and quantitative identification of species, the approximate amount of each, and for the determination of crystal structures.

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). SEM microscope is an instrument for the observation and surface characterization of organic and inorganic materials. The most important applications of SEM include the study of the
microstructure, determining the degree of crystallinity, morphology of the samples, defects, and their aggregation states, and in-situ microanalysis, among others. The main features of SEM are high resolution (~ 100 Å), a great depth of field that gives a three-dimensional effect to images, and simple sample preparation.

Raman spectroscopy. Raman spectroscopy is a useful tool for the characterization of carbonaceous materials. The analysis of molecular vibrations can provide information about the structure of the material, allowing its identification. When a beam irradiates a molecule, energy can be transmitted, absorbed or scattered. Raman spectroscopy is based on one of the many phenomena of light scattering.

Transmission electron microscopy (TEM). The transmission electron microscope, unlike other microscopes, does not scan surfaces; on the contrary, the electron beam is incident and goes through the observed sample, and the shadow of fine details is captured on a screen with light-emitting properties, located on the bottom of the column. For the structural study of CNTs this technique is necessary for determining the number of layers with a multi-walled NT, the inner and outer diameter, and the existence of impurities in the material.

X-ray issued photoelectron spectroscopy (XPS). The XPS technique has its origin in the investigations of the photo electric effect discovered by Hertz in 1887, in which X rays are used as the excitation source. The XPS technique is considered a powerful tool for chemical analysis and is a semi-quantitative spectroscopy of low spatial resolution commonly used to estimate the stoichiometry, chemical state, and electronic structure of the elements existing in a material. Because of the short length of the photoelectrons excited by the solid, the XPS technique has a large specific surface. Once the sample is irradiated, the energy emerging from it is captured by a concentric hemispherical analyzer, producing a spectrum with a series of peaks corresponding to the photoelectrons emitted. The energy for this peak is characteristic of each element; therefore, the XPS provides information about the chemical bonds. This technique is mainly applied in the invention reported here to identify the doping elements in CNT.

Thermogravimetric analysis (TGA). Thermogravimetric analysis is based on the measurement of the variation of the mass in a sample when subjected to temperature changes in a controlled
atmosphere. The mass change can be a loss or a gain, depending on the treatment atmosphere. This technique is applied for stability studies or thermal decomposition, and for the determination of impurities, moisture, and kinetic studies. This analysis is used in the samples obtained in the present invention, to quantify the percentage of CNTs obtained. The determination of this variable is relatively easy, since it depends on the decomposition temperatures of the different components of the sample. These components are: amorphous carbon, highly crystalline carbon (CNTs), silica (support), and a catalyst if the samples were not purified. In preliminary studies it is known that the approximate temperature of decomposition of the nitrates ranges between 70 and 100°C, the temperature of amorphous carbon oxidization occurs from 300 to 400°C, whereas the oxidization of CNTs is between 600 and 800°C. The loss of these materials in an oxidizing atmosphere is shown by the appearance of a downward slope (step) in a mass loss curve in time. Therefore, the difference in weight provided by these steps it is possible to determine the loss amount of each element and subtract it from the total weight (initial) of the sample so that the remaining weight is that of the CNTs produced. With this data can be determine the weight percentage of the CNTs obtained.

In the present invention the samples were analyzed on a Mettler Stare SW 8.0, injecting a flow of 50 ml/min of air. The analysis was performed in a temperature range of 25 to 900°C with a heating ramp of 10°C/min.

Following examples are presented for illustrating the invention and are not intended to limit the scope of it.

**Example 1. Doping of graphene.**

Theoretical analysis of the electronic structure provides a good description and a quantitative approach to many phenomena. To make a first approximation of the properties that could appear in CNTs once doped; we researched the study of a graphene sheet. We primarily made the theoretical study of doping atoms of different elements to see if substitutional doping type were possible or not and to determine the most energetically stable structures (lowest energy of formation).

The graphene sheets were characterized by molecular dynamics code from first principles Car Parinello Molecular Dynamics, which is based on the so-called Density Functional Theory (DFT), and in which the orbitals are expanded in plane waves. This code uses standard pseudo potentials, considering only the valence electrons in performing calculations and leaving out the core electrons. To determine the exchange-correlation energy, we used the BLYP approximation (Becke-Lee-Yang-Parr). In this first approach, we performed geometry optimization, and
characterization of electronic structure; we also made stability calculations and obtained the Wannier functions of the molecular structures analyzed.

We considered periodic conditions along the graphene plane (x, y), and a great distance between plates in the z axis to prevent interaction between them. For this, we used a distance of 8Å on such axis. Calculations were performed with and without spin influence, using LSD approximation (local spin density) for the latter case, and LBFGS algorithm (limited memory Broyden-Fletcher-Goldfarb-Shannon method) for optimization of the ions position. We used a cutting 60Ry energy, since it is considered suitable for carbon systems, and a convergence criterion of 0.01eV/Å. We used a sheet of graphene with 72 carbon atoms, with dimensions a = b = 14.826Å, which showing a cell parameter of 2.471Å, which is very close to the experimental and theoretical studies earlier reported. The C-C bond distances obtained theoretically were compared with the experimentally reported bond length for a network of graphene with a value of 1.421 Å.

To obtain the lowest energy configuration, different positions were proposed for substitutional dopant atoms as shows figure 1; the position labeled with the letter A is the dopant atom when the doping is performed with a single atom. This position is also considered as a reference point for the doping with 2 and 3 atoms. The possible combinations for doping with 2 atoms are: AB, AC, and AD, while for 3 atoms are: ABC, ABD, ABE, and BGF. Except for these cases, we also considered pyridine sites; these sites are formed when tearing a carbon atom from the network; therefore, the configuration would be BGF, but without the central atom (position A).

Wannier functions were obtained through unitary transformations of the Kohn-Sham orbitals minimizing the extended wave function (min <r^2>), according to the description given by Berghold et.al. The localization of the Wannier centers provides information about the existence of bonds and their form, defining the type of bond formed. Another useful tool for the identification of bonds in the system and the location of unpaired electrons is the electron localization function (ELF), which was also used in the present invention. Finally, the formation energy of defects was calculated from equation 1:

\[ E_f = E_T + \eta \mu_C - E_g - \eta \mu_i \]  

(1)

where \( E_T \) is the total energy of a graphene sheet after the doping, \( n \) denotes the number of carbon atoms substituted by the dopant element. \( E_g \) is the total energy of the graphene sheet without doping, while \( \mu_C \) and \( \mu_i \) are the chemical potentials of the carbon atoms and the impurities respectively. The chemical potential of carbon was obtained from the ratio E/N, where N is the
number of carbon atoms in the super cell (N= 72 in the case here reported). The chemical potential of the doping elements was calculated from the atomic energies of the dimers at gas phase \( S_2 \) y \( P_2 \) (\( \mu_i = E_i - m_i \alpha / 2 \), being \( i = S \) or \( P \)).

Example 2. Doping of carbon nanotubes.

For calculations of carbon nanotubes doping, we used the Vienna ab initio simulation package (VASP), which like CPMD is based on DFT. This code uses plane-waves and provides pseudo potentials type PAW (Projected Augmented Waves). The energy cutoff used for the calculation was of \( E_{cut} = 470 eV \), while the approach used to determine the exchange-correlation energy was the generalized gradient (GGA). For doping of armchair nanotubes, we used one nanotube (5.5) using 3 unit cells (60 atoms, 20 atoms per unit cell), while for the doping of zigzag nanotubes we used one nanotube (8.0), and only 2 unit cells (64 atoms, 32 per unit cell). Single wall nanotubes were doped with phosphorus (P), aluminum (Al), and potassium (K). The integrations of the Brillouin zone for the calculation of one armchair nanotube (5.5) and zigzag nanotube (8.0) were performed using a Monkhorst-Pack grid with 12 and 10 \( k \) points respectively in the direction \( z \) (1 x 1 x 12, and 1 x 1 x 10 respectively), while the convergence criterion used was 0.003 eV/\( \text{Å} \). Finally, the energy necessary for forming the defect was calculated from the equation (1).

Example 3. Catalyst preparation.

The procedure developed allows synthesizing industrial structures, SWCNTs, MWCNTs, in addition of doping with any element you wish to introduce into the carbon nanotube network.

The catalyst synthesis was developed using sol—gel; the goal is to find metallic nanoparticles available of uniform size to accommodate the growth of carbon nanotubes. For this we used Ni, Fe, Co, and Mo precursors, and each can be used according to the characteristics needed for the application of the CNTs.

The synthesis was developed in a tubular furnace using methane as a carbon source. Employed temperatures were between 700 and 800°C, the reducing gas was a mixture of hydrogen: nitrogen, while the synthesis times will be short since they vary between 20 and 40 minutes once started the growth of the CNTs.

As catalyst, we prepared nickel particles from high purity \( \text{Ni(0}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (Baker Company). Based on the weight of silica per milliliter of solution (0.126 g/ml), we calculated the amounts necessary to introduce different percentages of catalyst to the silica obtained. The technique used for the preparation of the catalyst was the sol-gel process. The nickel nitrate was dissolved in water and mixed during the preparation of the silica.
For the preparation of the films, we used quartz and silicon as substrates for the catalyst support. Both substrates were subjected to surface treatment prior to depositing the catalyst to grow preferentially the NTs. The treatments are described below.

**Example 4. Modification of substrate.**

*Sand Blast method.* The surface modification by Sand Blast method consists in the bombardment of the substrate with silica particles. These particles are projected onto the substrate using an air gun at a pressure of 60 psi. The substrate was placed at a distance of approximately 10 cm of the air gun, and the modification time was 5s. The diameter of the silica particles ranges between 180 and 300 μm.

*Striping method.* This method involves scratching the quartz substrate using a diamond tip to generate parallel lines on its surface.

*Roughing.* The roughing on the surface of quartz was performed with 180-grit sandpaper, generating parallel lines uniformly throughout the surface.

*Hydrofluoric acid attack.* The surface of both substrates was attacked with hydrofluoric acid at 1% by volume. The attack time was 10 min, generating nano-rugosities.

**Example 5. Generation of metal catalyst oxides.**

For the generation of nickel oxides, we prepared 100 ml of catalyst solution using a molar ratio of tetraethylorthosilicate (TEOS): ethanol: water 1:4:4; with different weight percentages of nickel nitrate hexahydrate to obtain theoretical compositions of 10, 30, 40, and 50% wt of NiO respect for silica, as shown in table 1. All reactions were accelerated by an acid, which unbalances the reaction and fragments the silica and the catalytic metal. In the preparation process we first mixed the TEOS and ethanol for approximately 8 to 20 min and separated the nickel nitrate dissolved in distilled water. Subsequently, we combined both mixtures and continued stirring the solution until obtaining the desired phase of the catalyst solution. Once the precursor solution was obtained, we placed it in a drying oven at 60°C to remove the solvents. Subsequently, the sample was calcined at 650°C for two hours. Figure 2 illustrates the route of preparation of the films and powders of nickel oxides by sol-gel.
Table 1. Weight ratio of reactants for the preparation of 30 ml of the catalyst solution by sol-gel process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEOS (g)</th>
<th>Ethanol (g)</th>
<th>Water (g)</th>
<th>Ni(NO$_3$)$_2$·6H$_2$O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>11-12</td>
<td>10-11</td>
<td>4-5</td>
<td>0.5-2</td>
</tr>
<tr>
<td>30</td>
<td>11-12</td>
<td>10-11</td>
<td>4-5</td>
<td>4-7</td>
</tr>
<tr>
<td>40</td>
<td>11-12</td>
<td>10-11</td>
<td>4-5</td>
<td>5-8</td>
</tr>
<tr>
<td>50</td>
<td>11-12</td>
<td>10-11</td>
<td>4-5</td>
<td>12-14</td>
</tr>
</tbody>
</table>

Example 6. Preparation of catalyst solutions from 0.1 M, 0.2 M, 0.3 M, and 1 M Ni(NO$_3$)$_2$·6H$_2$O.

Another method of preparation of the catalyst solutions was from 0.1 M, 0.2 M, 0.3 M and 1 M Ni(NO$_3$)$_2$·6H$_2$O, using distilled water as solvent. This procedure was carried out for the preparation of catalyst particles applied on the growth of CNTs by PLICVD method. The substrates were superficially modified by the methods described above and then immersed in the nickel nitrate solution for one minute, extracted at a rate of 0.36 cm/s. The substrates were dried at 95°C for 15 min and subjected to heat treatment for one hour at 450°C, producing nickel oxides.

The procedure allows synthesizing industrial structures, SWCNTs, and MWCNTs, besides the doping with any element you want to introduce into the carbon nanotube network.

Example 7. PLICVD (Pulsed liquid injection chemical vapor deposition) growth process.

The operating principle behind the PLICVD process is based on the instantaneous evaporation of the liquid carbon precursor at 280°C in small micro-doses. This fluid is pulse injected through a nozzle. Through this process, we tested the growth of CNTs using acetone and ethanol. Each precursor was injected at 2 pulses per second, while maintaining a pressure of 3.9 to 4.1 Torr.

Once the substrates with the catalyst particles (films) are placed in the reaction chamber of the furnace tube (oriented vertically), the vacuum is generated and is passed an Ar stream until the temperature rises to 600°C. After this, the catalyst is reduced in an atmosphere of 90% v/v of N$_2$ and 10% v/v of H$_2$ for 45 min (see table 2 for the optimal conditions of the reduction process).

The operating principle is to provide the carbon precursor through pulse injectors with frequencies between milliseconds to seconds. This frequency is monitored and adjusted by a computer. There is a diffusion of the reactive gases to the surface of the substrate, which should
be preheated to simplify de adsorption of the reactive species, creating active sites because of the increased volume of said surface. The equipment has three injectors to deposit thin films of composite materials or multilayer. It is important to generate a vacuum in the reaction chamber and to have a liquid nitrogen trap to prevent its contamination. The equipment is operated at a temperature of 300 to 1000°C at a pressure of 665 Pa.

**Table 2. Operating parameters during the reduction process of the catalyst oxides**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (Torr)</td>
<td>2.83 Torr</td>
</tr>
<tr>
<td>Temperature</td>
<td>600°C</td>
</tr>
<tr>
<td>Reaction gas</td>
<td>Mixture N2-H2</td>
</tr>
<tr>
<td>Gas flow (l/min)</td>
<td>0.4 l/min</td>
</tr>
<tr>
<td>Reduction time (minutes)</td>
<td>45 minutes</td>
</tr>
</tbody>
</table>

When the temperature rises to 900°C, starts the growth of CNTs by the principle of operation of this equipment. The total amount of carbon precursor injected was approximately 95 ml. Table 3 summarizes the operation conditions for the growth of CNTs.

**Table 3. Operating parameters during the growth process of carbon nanotubes**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>900°C</td>
</tr>
<tr>
<td>Transport and evaporator temperature</td>
<td>280°C</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>3.9-4.1 Torr</td>
</tr>
<tr>
<td>Frequency of injection (ms)</td>
<td>500 ms</td>
</tr>
<tr>
<td>Pulse length (ms)</td>
<td>4 ms</td>
</tr>
<tr>
<td>C Precursor</td>
<td>Acetone</td>
</tr>
<tr>
<td>Carrier gas flow (l/min)</td>
<td>0.8 l/min</td>
</tr>
<tr>
<td>Time of growth (minutes)</td>
<td>90 minutes</td>
</tr>
</tbody>
</table>

**Example 8. Process for growth by chemical deposition gas.**

The operating principle of the growth process by chemical deposition gas is based on the exposure of the catalyst material to a carbon-saturated atmosphere in a sealed tube furnace. The oven temperature is raised, so that carbon is deposited on the substrate by the catalytic effect. Once the substrates with the catalyst particles have been placed in the reaction chamber of the furnace horizontally oriented, the vacuum is generated and is passed a stream of N₂ until the temperature rises to 700°C. Subsequently, the catalyst is reduced in an atmosphere of 90% v/v of
N₂ and 10% v/v of H₂ for 30 min. The growth of CNTs starts after the reduction time according to the principle of operation of this equipment.

**Example 9. Carbon nanotubes growth equipment.**

The operation principle of this equipment is very simple. The first sample is placed in the oven; once inside, the temperature is raised to 600°C with a nitrogen flow of 1 L/min; when reaching the desired temperature, a reducing atmosphere is generated and maintained for 30 min in the presence of a vacuum. Subsequently, the temperature is raised to 800°C, and the growth process occurs under a controlled flow of the carbon precursor gas (methane).

Table 4 shows the optimal parameters used for the growth of CNTs by the technique of chemical deposition gas. This table contains the optimum type of catalyst and the percentage respect to silica, as well as the temperatures, reduction, and growth times. The whole process was automated and programmed electronically through LabView.

<table>
<thead>
<tr>
<th>Table 4. Optimal parameters for the growth of CNT on a gas chemistry deposition equipment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel oxides percentage (%)</td>
</tr>
<tr>
<td>Reduction temperature (°C)</td>
</tr>
<tr>
<td>Reduction time (minutes)</td>
</tr>
<tr>
<td>Vacuum (Torr)</td>
</tr>
<tr>
<td>Temperature of growth (°C)</td>
</tr>
<tr>
<td>Time of growth (minutes)</td>
</tr>
<tr>
<td>C Precursor</td>
</tr>
<tr>
<td>Carbon precursor flow (l/min)</td>
</tr>
</tbody>
</table>

**Example 10. Carbon nanotubes doping.**

The doping of CNT was carried out during the growth thereof. To do this, we used an Ultrasonic Nebulizer NEBUCOR E-303, coupled to the furnace tube. Within the nebulizer, a known amount of the dopant element was placed and injected by pulses. The nebulized dopant element is carried into the reaction zone through a gas with a flow of 0.2-0.5 l/min. The parameters used for doping are shown in table 4, including the injection of the dopant and the carrier gas flow. The solutions were introduced to the nebulizer at 1% by volume. The precursors used for doping were orthophosphoric acid for doping with phosphorus, aluminum nitrate for doping with Al and acid phthalate of potassium for doping with potassium.
Example 11. Purification.

This process is not performed within the reactor to remove traces of the catalyst when used in solid form. Regarding catalysts used in film or liquid forms, this procedure may be omitted, reducing the consumption of acids for the purification of CNT.

To remove traces of the catalyst and silica (carrier), we used a purification method based on washing the sample with different acids and taking advantage of the magnetic character of the nanoparticulated catalytic metals using washings with hydrochloric acid (1-3%) and hydrofluoric acid (1-3%) with stirring in a magnetized container, and after that, performing the washing several times with distilled water. The final drying is performed at a temperature of 60°C for 12 hr.

The first component removed from the sample is silica, which acts as a support of the catalyst particles. For this step, we added 2% HF and the solution was stirred for 30 minutes. Subsequently, we washed it several times to completely remove the HF, and added HCl at 2M, stirring for another 30 minutes, washing again the sample several times to finally subject it to a drying treatment at 80°C.

The purification system operates in a simple manner. Once the CNT are placed inside the container, the acids are added under mechanical stirring at a constant speed. The system includes a magnet, which serves to separate metallic particles that are not removed with HCl.

According to the results obtained, the density of electronic states (DOS) once the CNT have been doped, show a change from metallic character to semiconductor, depending the type of dopant. This and other results, make these materials a promise for its application in gas sensors or strengthening of polymeric materials among others.
Claims

1. A method for the synthesis and doping of carbon nanotubes, characterized because comprising:
   a) Preparing a sol-gel support, which contains an oxide of a catalytic transition metal;
   b) Growing carbon nanotubes;
   c) Doping the carbon nanotubes with a dopant element; and
   d) Purifying.
2. The method of claim 1, characterized because the oxide of a catalytic transition metal is prepared using alkoxides.
3. The method of claim 2, characterized because the preparation of the oxide of a catalytic transition metal using alkoxides comprises:
   a) The mixture of tetraethylrhomosilicate (TEOS) and ethanol;
   b) Separately dissolving a catalytic metal salt in distilled water;
   c) The combination of the solutions a) and b);
   d) Adding acid with stirring, and
   e) Drying and calcining.
4. A method for the synthesis and doping of carbon nanotubes, characterized because comprising:
   a) Providing a solution containing an oxide of a catalytic transition metal;
   b) Providing a substrate and modify its surface;
   c) Depositing the catalyst solution by dipping the substrate;
   d) Doping the carbon nanotubes with a dopant element, and
   e) Purifying.
5. The method of Claim 4, characterized because the surface modification of the substrate is performed by sandblasting, scratching, grinding, or hydrofluoric acid attacks.
6. The method according to claims 1 and 4, characterized because the catalytic transition metal is selected from Ni, Fe, Co and Mo.
7. The method of claim 6, characterized because the catalytic transition metal is Ni.
8. The method according to claims 1 and 4, characterized because the doping is performed by nebulizing a dopant element using injection pulses.
9. The method according to claims 1 and 4, characterized because the dopant element is carried into the reaction zone by a carrier gas.
10. The method according to claim 9, characterized because the dopant element is selected from de P, S, Al and K.
11. The method according to claims 1 and 4, characterized because the purification is performed by washing the sample using acids and magnetic attraction.

12. The method of claim 11, characterized because the acids are hydrochloric acid and hydrofluoric acid.

13. The method according to claims 1 and 4, characterized because the growth and doping of carbon nanotubes occur in a single step.

14. Doped carbon nanotubes manufactured according to the procedure of claims 1 or 4.

15. Doped carbon nanotubes according to claim 14, characterized because they are multi-walled and/or helical geometry.
Figure 2

The diagram illustrates the process of preparing nickel oxide using the alcoholic method. The process begins with the reactants Ni(NO₃)₂ • 6H₂O, distilled water, ethanol, and TEOS. These reactants are mixed to form a precursor solution. From the precursor solution, powders and films are obtained. The powders are then transformed into a gel through drying and heat treatment, leading to nickel oxide. The films undergo substrate washing and immersion removal to produce nickel oxide.