Biotin molecules on nitrogen-doped carbon nanotubes enhance the uniform anchoring and formation of Ag nanoparticles

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Abstract

An efficient method for anchoring silver nanoparticles (Ag-NPs) on the surface of nitrogen-doped multi-walled carbon nanotubes (CN_x-MWCNTs) is reported. The process involves the attachment of biotin molecules on the surface of CN_x-MWCNTs (both, pristine and acid treated) that act as a reducing agent for AgNO₃, thus generating an efficient and homogeneous coating of Ag-NPs (~3 nm in diameter). The reduction of AgNO₃ on either pristine CN_x-MWCNTs or acid treated CN_x-MWCNTs (without biotin) results in Ag-NPs of large diameters and size distribution, in addition to a low anchoring efficiency. We confirmed that the use of biotin substantially improves the Ag-NPs anchoring efficiency, especially on acid treated CN_x-MWCNTs. In order to elucidate the mechanism whereby Ag-NPs strongly bind to the surface of CN_x-MWCNTs, density functional theory (DFT) calculations were carried out. These revealed the existence of covalent bonds established between one side of the biotin molecule and the CN_x-MWCNT surface through oxygen atoms, leaving accessible the exposed sulfur atoms at the other end, which further provided an excellent interaction with the Ag-NPs via S-Ag bonds. Finally, we demonstrate that these Ag-NPs coated CN_x-MWCNTs could be used as efficient sensors of CS₂.

Keywords: Biotin, silver, nanoparticles, nitrogen-doping, nanotubes.

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1. Introduction

Carbon nanotubes (CNTs) have attracted the attention of numerous scientists due to their possible applications in different areas such as mechanical reinforcement in polymer composites [1], as active materials in gas sensors [2,3], bio-sensors [4,5], and drug deliverers [6]. However, CNTs (e.g. MWCNTs) exhibit an almost chemically inert surface, which complicates their interaction with different atomic species. Therefore, surface functionalization of CNTs is necessary in order to improve its interaction with their surroundings. There are several routes used to increase the CNT reactivity. While most of them use acid treatments, the tube surface of CNTs gets partially damaged, thus giving rise to vacancies, dangling bonds, and diverse radicals and functional groups on the nanotubes' surface. Other methods involve the doping of CNTs by introducing diverse hetero-atoms such as B, N, Si, P, etc. within the nanotube's lattice [7-9]. Doping in carbon nanotubes with nitrogen, phosphorus, and boron, generally induces charge redistribution along the defective area enhancing diverse electronic features and improving the surface reactivity [8-11]. However, the extensive literature, simple and inexpensive synthesis procedures used to obtain large amounts of N-doped nanocarbons, additionally to the higher nitrogen incorporation, controllable doping configurations [12], improved biocompatibility [13-15] and substrate reactivity for particle depositions [16-18] makes them an excellent candidate for diverse applications. This is not the case for B-doped nanocarbons, where dangerous and expensive reagents are used [8,19], also the low incorporation of heteroatoms and less diversity on doping configurations limits the usability of these doped systems. In addition, nitrogen-doped multi-walled carbon nanotubes (CN_x-MWCNTs) have proved to be an excellent material for various applications, when compared to undoped MWCNTs [10-13].

In the case of nanoparticles (NPs) decorating CNTs, sensitive hybrid devices could be fabricated in which the metal nanoparticles act as reactive sites for the adsorption of chemical and/or biological species. The decoration of CNTs with metal NPs are of potential interest for catalysis involving fuel cells [20], hydrogen storage [21], photo-electrochemical cells [22], and sensing devices [23], in which the interaction between NPs and the CNT surface might occurs via covalent or non-covalent bonding [24]. In particular, carbon nanotubes decorated with silver nanoparticles (Ag-NPs) have specific interest in the study of surface enhanced Raman spectroscopy (SERS) [25,26], antimicrobial agents [27], pH and gas sensors [28,29], fuel cells [30], and water purification systems [31], among others.

The functionalization and subsequent anchorage of NPs on carbon nanotubes can be improved through the use of thiolated groups that provide an ideal driving force for the self-assembly of NPs, thus improving the homogeneity and NP size reduction. Examples of nanotube decoration using these groups can be observed in Pd NPs where benzyl mercaptan [32] was used, Au with alkanedithiols [33], Pt with the thiolation of carbon nanotubes [34], and the use of thiophene for ZnO NPs [18]. Although, there are some reports on the functionalization of CNTs with biotin [35-37], where the biotin contains a thionyl group, to the best of our knowledge there are no reports on using this biomolecule to efficiently anchor Ag-NPs to CN_x-MWCNTs.

In this work, we present an efficient method to obtain small Ag-NPs (*ca.* 3 nm) with narrow size distribution on CN_x-MWCNTs using biotin as a molecular linkers. The effect of acid treatment on the CN_x-MWCNTs and its role on the deposition efficiency are also investigated; additionally we tested our hybrid material as a CS₂ gas sensor.

2. Experimental procedures

Material preparation: The Ag decorated CN_x-MWCNTs are prepared using the following procedure: First, CN_x-MWCNTs are synthesized via CVD as described in Ref. [38]. Acid treated CN_x-MWCNTs are prepared using an acidic solution (3:1 in volume) of sulfuric acid (H₂SO₄) and nitric acid (HNO₃) in an ultrasonic bath for 5 hours. Subsequently, the CN_x-MWCNTs are filtered and washed with a 0.01 M solution of sodium hydroxide (NaOH) and rinsed with distilled water. The biotinized CN_x-MWCNTs are prepared by adding CN_x-MWCNTs (as produced or acid treated) and biotin powder (3:1 in weight) in a solution containing 4 ml of dimethyl sulfoxide (DMSO) and 36 ml of ethanol (EtOH), the suspension is sonicated for 30 minutes. Afterwards, the suspension is kept for 48 hours at room temperature. Finally, the biotinized samples are filtered and washed with distilled water to remove non-bonded biotin. Once the biotinized CN_x-MWCNTs are obtained, the Ag-NPs deposition is performed by adding 5 mg of CN_x-MWCNTs and 83.3 µl of silver nitrate solution (0.1 M of AgNO₃) in deionized water. The suspensions are magnetically stirred for 30 min at 50°C, and then filtered and washed with deionized water. We have compared the Ag deposition with non-biotinized nanotubes.

Gas sensors: Four different sensing devices were fabricated on silicon substrates ($\sim 1 \text{ cm}^2$) by dip coating, using an aqueous suspension ($\sim 1 \text{ mg/mL}$) of (1) CN_x -MWCNTs, (2) Ag-NPs on biotinized CN_x -MWCNTs, (3) acid treated CN_x -MWCNTs, and (4) Ag-NPs on acid treated CN_x -MWCNTs. The suspensions are obtained by sonication with an ultrasonic tip for 5 minutes. Afterwards, the silicon substrates are heat treated for 24 hrs. at 80°C , and the electrical junctions are made through silver paint and copper wires.

Material characterization: The samples were characterized using a micro Raman spectroscopy (Renishaw) with laser excitation lines of 514 nm and 633 nm. The electron microscopy was carried out using a scanning electron microscope (SEM) (XL30 SFEG FEI operated at 10-20 kV), transmission electron microscope (TEM) at 300 kV (FEI TECNAI F30 STWIN G2), atomic force microscope (AFM, JEOL equipment JSPM 5200) in tapping mode, and thermogravimetric analysis (TGA) (Perkin Elmer 6000STA) system heating from 50°C to 900°C with a rate of 10°C/min under an air flow of 20 mL/min . The sensing measurements are carried out using a Sourcemeter (Keithley) with Labview® environment. The sensing capacity is tested by placing the samples inside a quartz tube with a controlled temperature and atmosphere. Two channels are used for introducing the CS_2 and the argon gas, which is also used to purge the chamber and clean the nanotubes films. Two different exposure intervals are used: 80s for sensing the CS_2 gas and 100s to purge with argon gas; this process is repeated for five cycles at least.

Computational details: First-principles calculations were performed using the density functional theory (DFT) [39,40] as implemented in the SIESTA code [41] within the generalized gradient approximation (GGA-PBE). Norm-conserving pseudopotentials were used to represent the core electrons [42] and the wave functions were expanded in terms of a numeric pseudo-atomic simple-zeta basis, as described by Junquera *et al.* [43] a real space mesh equivalent to an energy cutoff of 200 Ry was used for the electrostatic potential integrals. In order to simulate the doping of the nanotube, a single nitrogen substitutional doping site was created on a three different carbon nanotubes, a metallic (5,5), a semi-metallic (9,0) and a semiconductor (10,0), the corresponding supercell contains 160, 180 and 200 atoms, respectively. A vacuum region of at least $20 \text{ \AA}$ between nanotubes in neighbouring supercells is kept to avoid lateral interactions. Given the system's size, gamma point calculations were carried out. In order to simulate adsorption, the molecules of interest were initially positioned $\sim 2.5 \text{ \AA}$ from the doped site, and the structure is then geometrically relaxed by conjugate gradient geometry optimization until residual forces are $< 0.04 \text{ eV/\AA}$. The thermal

stability of the adsorption process was verified by molecular dynamics (MD) using a time step of 1 fs for the integration of the equations of motion, for a minimum of 1000 steps. The temperature of 50 and 300 K was controlled by the Nose thermostat, using a Nose mass of $10.0 \text{ Ry} \cdot \text{fs}^2$ [44].

3. Results and discussion.

The SEM micrographs of Ag decorated CN_x -MWCNTs are shown in Figure 1, where the biotinized CN_x -MWCNTs (Figure 1a) exhibit relatively small Ag-NPs, however the Ag-NPs possess different sizes and are distributed non-homogeneously on the surface of nanotubes. Figure 1b displays the pristine CN_x -MWCNTs (without biotin or acid treatment) mixed only with DMSO, yielding a poor formation of Ag-NPs. Due to the low decoration efficiency, we pre-functionalized the carbon nanotubes by an acid treatment (before the biotinyzation process), in order to increase the anchoring sites on the nanotubes surface. As a result, diverse types of defects are created within the nanotubes lattice, thus improving their chemical activity. Afterwards, the biotinyzation process and the anchoring procedure are repeated, the results are shown in Figure 1(c-d). We observe that non-biotinyzied CN_x -MWCNTs, neither pristine nor acid treated, exhibit lower amounts of Ag-NPs on their surface (Figure 1b and d) when compared with biotinyzied CN_x -MWCNTs (Figure 1a and c).

Fig.1. SEM micrographs of Ag-NPs anchored on different CN_x -MWCNTs. **a)** Biotinized CN_x -MWCNTs. **b)** pristine CN_x -MWCNTs. **c)** acid treated CN_x -MWCNTs with biotin. **d)** Acid treated

CN_x-MWCNTs. Note the smaller diameter and improved distribution of Ag-NPs in c).

In order to confirm the presence of Ag in our tube material, energy dispersive X-ray (EDX) analyses were carried out and the results are shown in [Figure 2](#). Note that biotinized composites (biotinized CN_x-MWCNTs and acid treated CN_x-MWCNTs with biotin. Figure 2b and 2d) exhibit considerable quantities of Ag, corresponding to 11.6 wt% and 31.0 wt% of Ag (from EDX analyses), respectively. Interestingly, the presence of Ag is minimal on the non-biotinized composites. X-ray powder diffraction (XRD) studies reveal a well crystalline structure corresponding to a face-centered cubic (fcc) phase for Ag-NPs (see [Figure 3](#)). Due to the outstanding nanoparticle decoration of biotinized nanotubes, we focused our study on biotinized CN_x-MWCNTs and acid treated CN_x-MWCNTs with biotin. High resolution electron microscopy (HRTEM) images are shown in [Figure 4](#). Here it is possible to observe that in both systems Ag-NPs are anchored on the nanotubes surfaces; the NPs exhibit a spherical-like shape with diverse diameters. For biotinized CN_x-MWCNTs the average nanoparticle size is *ca.* 12 nm ([Figure 4a-b](#)), while the acid treated CN_x-MWCNTs with biotin ([Figure 4c-d](#)) exhibit a much smaller diameter of *ca.* 3 nm, with a well-defined crystalline structure, as suggested by XRD analysis (see [Figure 3](#)). It is also notable the excellent coverage of small Ag-NPs along the nanotubes surface, [Figure 4d](#) clearly shows that Ag-NPs are anchored to the nanotubes' surface.

Fig. 2. Energy dispersive X-ray spectroscopy (EDX) spectra of Ag-NPs deposited on different CN_x-MWCNT samples. **a)** CN_x-MWCNTs, **b)** Biotinized CN_x-MWCNTs, **c)** acid treated CN_x-MWCNTs, and **d)** acid treated CN_x-MWCNTs with biotin. The corresponding SEM images are shown in [Figure 2](#). Note that both biotinized samples (a and c) exhibit significant quantities of silver of 11.6 and 31.0% wt, respectively.

Fig 3. X-ray diffraction patterns of **a)** CN_x-MWCNTs. **b)** Ag-NPs deposited on biotinized CN_x-MWCNTs, **c)** acid treated CN_x-MWCNTs and **d)** Ag-NPs deposited on acid treated CN_x-MWCNTs. Note that the Ag-NPs exhibit a well defined face-centered cubic (fcc) crystalline phase.

Fig. 4. TEM images of Ag-NPs deposited on biotinized CN_x-MWCNTs. **a-b)** correspond to biotinized CN_x-MWCNTs. **c-d)** correspond to acid treated CN_x-MWCNTs covered with biotin. High resolution micrograph in **d)** reveals that the Ag-NPs are crystallographically ordered, as suggested by XRD.

Size distributions of Ag-NPs for both biotinized composites are depicted in Figure 5; the distribution is obtained by measuring at least 250 nanoparticles from diverse TEM micrographs. Here, we clearly observe the synergistic effect of the acid treatment and biotin passivation on decreasing considerably both particle diameter and size distribution, when compared with the nanotubes without the acid treatment. The average particle size for acid treated and biotinized nanotubes is 3 ± 1.06 nm, which is four times smaller when compared with the sample without acid treatment (particle size equal to 12 ± 4.76 nm). These results are consistent considering that nanotubes without acid treatment have fewer anchoring sites and poor interaction with biotin, and thus the excess of silver in the solution promotes larger nanoparticles. On the other hand, acid treated nanotubes exhibit a considerably number of defects, and an improved interaction with biotin, all these will later contribute to improve the nanotube decoration and growing smaller nanoparticles.

Fig. 5. Size distribution of Ag-NPs deposited on CN_x-MWCNTs. **a)** Sample corresponding to acid treated CN_x-MWCNTs with biotin, the Ag-NPs exhibit a diameter equal to 3 ± 1.06 nm. **b)** Biotinized CN_x-MWCNTs, here the particles exhibit wider size distribution with average diameter equal to 12 ± 4.76 nm.

We have analyzed the Raman spectra of the different samples considered in our study, the results are shown in Figure 6. In general, we observe that the D- and G-bands in Raman spectra are upshifted after the biotinylation process (see the vertical dashed line in Figures 6a and Figure 6b), indicating slight structural modifications on the nanotubes. Biotinized CN_x-MWCNTs exhibit a D- and G-bands upshift equal to 11 and 5 cm⁻¹, respectively. Similarly, the D- and G-bands of biotinized acid-treated nanotubes are upshifted by 21 and 3 cm⁻¹, respectively. This effect could be related by charge transfer between biotin and carbon nanotubes via p-type doping [45]. We have also analyzed the D- and G-bands intensity ratio (I_D/I_G). We noted that the I_D/I_G of biotinized CN_x-MWCNTs slightly decreases after the biotinylation process, from 0.737 to 0.613 for non-biotinized and biotinized nanotubes, respectively. Similar results were obtained for CN_x-MWCNTs treated with acid in the Figure 6b. However, in this case we observed an increase in the I_D/I_G ratio, from 0.777 to 0.891 after biotinylation. This increase indicates a decrease in the degree of crystallinity induced by the presence of biotin molecules on the tubes' surface [46] (see Figure 6b). In general, these defects are chemically active, and promote the anchoring of different molecules on the tubes's surface.

Fig. 6. Raman spectra for different samples considered in our study. The signals correspond to CN_x-MWCNTs in different conditions: **a)** CN_x-MWCNT and biotinized CN_x-MWCNTs, **b)** acid treated CN_x-MWCNTs and acid treated CN_x-MWCNTs with biotin. Notice that the spectrum of biotinized nanotubes exhibits an upshift with respect to non-biotinized nanotubes (see vertical dashed lines). Regarding acid treated CN_x-MWCNTs, the ratio between the D- and G-peak intensities increases suggesting disorder in the nanotube's lattice. The black line is used for biotinized composites, and blue line for non-biotinized materials.

Theoretical description of Ag-CN_x-MWCNTs composites.

In order to gain insight into the decoration mechanism and investigate the role of biotin in our experiments, we have performed *ab initio* calculations using density functional theory (DFT). Our DFT analysis suggests that the possible anchoring mechanism is conducted via a biotin bridge between the nanotubes and Ag-NPs surfaces, thus promoting considerably the anchoring efficiency. We initiated our DFT analysis by placing a biotin molecule at ~ 2.5 Å above a nitrogen-doped (5,5) single-walled carbon nanotube ((5,5)-CN_x-SWCNT), see details in computational methods, and then geometrically optimized. We found that the most favorable adsorption configuration exhibit the oxygenated “tail” of biotin directly attached to the nanotube's wall by a direct bonding to a C atom near the doping site, a result which is in good agreement with previous publications in which atoms surrounding the doping site exhibit higher chemical reactivity [47]. The optimized structure of the adsorbed biotin molecule on the (5,5)-CN_x-SWCNT via an oxygen atom is shown in Figure 7a. Now, when using the structure shown in Figure 7a as the starting geometry, we studied the adsorption of single Ag₁₃ cluster with icosahedral geometry; note that due the small cluster size with

an icosahedral geometry is preferred over the cuboctahedral [48]. Figure 7b depicts the optimized structure of the biotinized Ag_{13} -(5,5)- CN_x -SWCNT system. It is important to point out that after the biotin adsorption (Figure 7a), the sulfur atom of the biotin molecule is unsaturated and acts as a strong anchoring site for Ag_{13} clusters. This is also in good agreement with recently results reported by Gracia-Espino *et al.* [32], where a sulfurized molecule is used as a linker between the carbon nanomaterial and the metallic nanoparticle; the sulfur atom plays a key role in the anchoring process and results in enhanced anchoring efficiency and smaller nanoparticle diameter. We performed additional calculations using a semiconducting (10,0) and a semi-metallic (9,0) carbon nanotubes. The results suggest that the anchoring mechanism is performed similarly to the (5,5) nanotube, and that apparently the Ag deposition is chiral independent, the optimized geometries after biotin and Ag-cluster adsorption for both (9,0)- and (10,0)- CN_x -SWCNT can be seen in supporting information, Figure S4.

Fig.7. Optimized geometries of the (5,5)- CN_x -SWCNT under different conditions. **a)** Adsorption of biotin on (5,5)- CN_x -SWCNT. **b)** adsorption an Ag_{13} icosahedral cluster using a biotin molecule as a linker to the (5,5)- CN_x -SWCNT surfaces.

Gas sensing applications of Ag- CN_x -MWCNTs composites.

The excellent distribution and small diameter of Ag-NPs of our systems makes them an interesting material for diverse applications, such as gas sensing. In this context, we have complemented our studies by analyzing the CS_2 sensing capabilities of the Ag- CN_x -MWCNTs hybrid composites. The sensor fabrication and set-up details are present in the methodology section. We prepared four different types of sensor devices, and then recorded the electrical resistance as a function of time

during the CS₂ gas exposure and the results are depicted in Figure 8. We observe that the adsorption of CS₂ gas decreases the electrical resistance of the nanotube film. The reduction of electrical resistance (ΔR) upon the presence of CS₂ gas strongly depends on the hybrid system, in which the values of ΔR are observed as follows: Ag-NPs-acid treated CN_x-MWCNTs (8.93%) > Ag-NPs-biotinized CN_x-MWCNTs (6.35%) > CN_x-MWCNTs (3.17%) > Acid treated CN_x-MWCNTs (1.98%). All hybrid CN_x-MWCNTs decorated with Ag-NPs exhibit an improved response when compared to CN_x-MWCNTs without Ag NPs, showing in all the cases a small chemisorption in the sensor response. Interestingly, the material with the best performance is the Ag-NPs-acid treated CN_x-MWCNTs, and not the Ag-NPs-biotinized CN_x-MWCNTs, as depicted in Figure 8c and 8d. In both cases, the carbon nanotube structures are damaged creating several types of defects which are potentially important for nanoparticles attachment, as TEM and HRTEM characterizations demonstrate. However, as our results indicate, in the Ag-NPs-biotinized CN_x-MWCNTs composite, the biotin molecules passivate the Ag-nanoparticles, improving the homogeneity and decreasing the particle size, but also covers most of its surface and thus difficult the interaction between the Ag-nanoparticles and CS₂ gas. This excessive passivation might minimize the CS₂ gas adsorption causing a considerably reduction in the sensor sensitivity.

Fig.8. Electrical resistance in presence of CS₂ for **a)** CN_x-MWCNTs, **b)** Ag-NPs deposited on biotinized CN_x-MWCNTs, **c)** acid treated CN_x-MWCNTs and **d)** Ag-NPs deposited on acid treated CN_x-MWCNTs.

4. Conclusions

CN_x-MWCNTs covered with biotin molecules and Ag-NPs were synthesized and characterized using different techniques. Raman spectroscopy demonstrated that biotin molecules are indeed anchored to the nanotube's surface through defects (possibly vacancies and other functional groups). In addition, shifts in the D- and G-bands were observed for biotinized CN_x-MWCNTs, thus indicating that the vibrational modes of CNTs were modified due to the interactions with biotin. SEM, TEM and AFM characterization revealed that when the CN_x-MWCNTs are treated with acid and then biotinized, the Ag-NPs exhibit smaller average diameter and they are homogeneously distributed along the nanotubes surface. DFT calculations demonstrated that Ag clusters are stable and well attached to the surface of nitrogen-doped carbon nanotubes where the biotin is used as molecular linker. It is noteworthy that CN_x-MWCNTs have shown enhanced biocompatibility when compared to pristine and other types of doped MWCNTs. Therefore, the materials produced here might find unprecedented applications as bactericides, composites, bio-sensing and other bio-oriented devices and applications.

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References

1. Liu, Y. Kumar, S. *Polymer/Carbon Nanotube Nano Composite Fibers—A Review*, *ACS Appl. Mater. Interfaces*, 2014; 6: 6069–6087.
2. Tasca, F. Gorton, L. Wagner, JB. Nöll, G. *Increasing Amperometric Biosensor Sensitivity by Length Fractionated Single-Walled Carbon Nanotubes*. *Biosens. Bioelectron* 2008; 24: 272-278.
3. Tasis D, Tagmatarchis N, Bianco A, Prato M. *Chemistry of carbon nanotubes*. *Chem. Rev.* 2006; 106: 1105-1136.
4. Balasubramanian K, Burghard M. *Biosensors based on carbon nanotubes*. *Anal. Bioanal. Chem.* 2006; 385: 452–468.
5. Besteman K, Lee JO, Wiertz FGM, Heering HA, Dekker C. *Enzyme-coated carbon nanotubes as single-molecule biosensors*. *Nano Lett.* 2003; 3: 727-730.
6. Bianco A, Kostarelos K, Prato M. *Applications of carbon nanotubes in drug delivery*. *Curr. Opin. Chem. Biol.* 2005; 9: 674-679.
7. Jiang H, Zhang D, Wang R. *Silicon-doped carbon nanotubes: a potential resource for the detection of chlorophenols/chlorophenoxy radicals*. *Nanotechnology* 2009; 20: 145501.
8. Hashim DP, Narayanan NT, Romo-Herrera JM, Cullen DA, Hahm MG, Lezzi P, Suttle JR, Kelkhoff D, Muñoz-Sandoval E, Ganguli S, Roy AK, Smith DJ, Vajtai R, Sumpter BG, Meunier V, Terrones H, Terrones M, Ajayan PM. *Covalently bonded three-dimensional carbon nanotube solids via boron induced nanojunctions*. *Scientific Reports* 2012; 2: 363.
9. Cao Y, Yu H, Tan J, Peng F, Wang H, Li J, Zheng W, Wong NB. *Nitrogen-, phosphorous- and boron-doped carbon nanotubes as catalysts for the aerobic oxidation of cyclohexane*. *Carbon* 2013; 57: 433–442.
10. Terrones M, Filho AGS, Rao AM. *Doped carbon nanotubes: synthesis, characterization and applications in carbon nanotubes: advanced topics in the synthesis, structure, properties and applications*. *Topics of Applied Physics*. Jorio A, Dresselhaus G, Dresselhaus MS, Springer 2008; 531–566.
11. Cruz-Silva E, Lopez-Urias F, Muñoz-Sandoval E, Sumpter BG, Terrones H, Charlier JC,

- Meunier V, Mauricio T. *Electronic Transport and Mechanical Properties of Phosphorus- and Phosphorus–Nitrogen-Doped Carbon Nanotubes*. *ACS Nano* 2009; 3: 1913–1921.
12. Sharifi T., Hu G., Jia X., Wågberg T., *Formation of Active Sites for Oxygen Reduction Reactions by Transformation of Nitrogen Functionalities in Nitrogen-Doped Carbon Nanotubes*. *ACS Nano*. 2012; 6: 8904–8912.
 13. Castle AB, Gracia-Espino E, Nieto-Delgado C, Terrones H, Terrones M, Hussain S. *Hydroxyl-functionalized and n-doped multiwalled carbon nanotubes decorated with silver nanoparticles preserve cellular function*. *ACS Nano* 2011; 5: 2458–2466.
 14. Elías AL, Carrero-Sánchez JC, Terrones H, Endo M, Laclette JP, Terrones M. *Viability Studies of Pure Carbon- and Nitrogen-Doped Nanotubes with Entamoeba histolytica: From Amoebicidal to Biocompatible Structures*. *Small* 2007; 3: 1723–1729.
 15. Carrero-Sánchez JC, Elías AL, Mancilla R, Arreguín G, Terrones H, Laclette JP, Terrones M. *Biocompatibility and Toxicological Studies of Carbon Nanotubes Doped with Nitrogen*. *Nano Lett.* 2006; 6: 1609–1616.
 16. Jiang KY, Eitan A, Schadler LS, Ajayan PM, Siegel RW, Grobert N, Mayne M, Reyes-Reyes M, Terrones H, Terrones M. *Selective Attachment of Gold Nanoparticles to Nitrogen-Doped Carbon Nanotubes*. *Nano Lett.* 2003; 3: 275–277.
 17. Zamudio A, Elías AL, Rodríguez-Manzo JA, López-Urías F, Rodríguez-Gattorno G, Lupo F, Ruhle M, Smith DJ, Terrones H, Díaz D, Terrones M. *Efficient anchoring of silver nanoparticles on N-doped carbon nanotubes*. *Small* 2006; 2(3): 346–350.
 18. Gracia-Espino E., López-Urías F., Terrones H., Terrones M., *Self-Assembly Synthesis of Decorated Nitrogen-Doped Carbon Nanotubes with ZnO Nanoparticles: Anchoring Mechanism and the Effects of Sulfur*, *J. Phys. Chem. C*, 2015; 119: 741–747.
 19. Panchakarla, L.S. Govindaraj, A. Rao, C.N.R. *Boron- and nitrogen-doped carbon nanotubes and graphene*, *Inorganica Chimica Acta*, 2010; 363: 4163–4174
 20. Santhosh P, Gopalan A, Lee KP. *Gold nanoparticles dispersed polyaniline grafted multiwall carbon nanotubes as newer electrocatalysts: Preparation and performances for methanol oxidation*. *J. Catal.* 2006; 238: 177–185.
 21. Costa PMFJ, Coleman KS, Green MLH. *Influence of catalyst metal particles on the hydrogen sorption of single-walled carbon nanotube materials*. *Nanotechnology* 2005; 16 (4), 512–517.
 22. Zhang GQ, Zhang XG, Wang YG. *A new air electrode based on carbon nanotubes and Ag-MnO₂ for metal air electrochemical cells*. *Carbon* 2004; 42: 3097.
 23. Wu ZY, Chen LG, Shen GL, Yu RQ. *Platinum nanoparticle-modified carbon fiber*

- ultramicroelectrodes for mediator-free biosensing. Sens. Actuators B* 2006; 119: 295-301.
24. Wang T, Hu XG, Qu XH, Dong SJ. *Noncovalent functionalization of multiwalled carbon nanotubes: application in hybrid nanostructures. J. Phys. Chem. B* 2006; 110, 6631-6636.
25. Chen YC, Young RJ, Macpherson JV, Wilson NR. *Single-Walled Carbon Nanotube Networks Decorated with Silver Nanoparticles: A Novel Graded SERS Substrate. J. Phys. Chem. C* 2007; 111: 16167-16173.
26. Zhao Q, Buongiorno NM, Lu W, Bernholc J. *Carbon nanotube-metal cluster composites: A new road to chemical sensors?. Nano Lett.* 2005; 5: 847-851.
27. Yuan W, Jiang G, Che J, Qi X, Xu R, Chang MW, Chen Y, Lim SY, Dai J, Chan-Park MB. *Deposition of silver nanoparticles on multiwalled carbon nanotubes grafted with hyperbranched poly(amidoamine) and their antimicrobial effects. J. Phys. Chem. C* 2008; 112:18754-18759.
28. Zhao L, Shingaya Y, Tomimoto H, Huang Q, Nakayama TJ. *Functionalized carbon nanotubes for pH sensors based on SERS. Mater. Chem.* 2008; 18: 4759-4761
29. Espinosa, EH, Ionescu R, Bittencourt C, Felten A, Erni R, Van Tendeloo G, Pireaux JJ, Llobet E. *Metal-decorated multi-wall carbon nanotubes for low temperature gas sensing. Thin Solid Films* 2007; 515: 8322-8327.
30. Guo DJ, Li HL. *Highly dispersed Ag nanoparticles on functional MWCNT surfaces for methanol oxidation in alkaline solution. Carbon* 2005; 43:1259-1264.
31. Gunawan P, Guan C, Song X, Zhang Q, Leong SSJ, Tang C, Chen Y, Chan-Park MB, Chang MW, Wang K, Xu R. *Hollow FiberMembrane Decorated with Ag/MWCNTs: Toward Effective Water Disinfection and Biofouling Control. ACS Nano* 2011; 5: 12: 10033-10040.
32. Gracia-Espino E, Hu G, Shchukarev A, Wagberg T. *Understanding the Interface of Six-Shell Cuboctahedral and Icosahedral Palladium Clusters on Reduced Graphene Oxide: Experimental and Theoretical Study. J. Am. Chem. Soc.* 2014; 136: 6626-6633.
33. Park S, Kim HR, Kim J, Jung C, Rhee CK, Kwon K, Kim Y. *Assembly of strands of multiwall carbon nanotubes and gold nanoparticles using alkanedithiols. Carbon* 2011; 49 (2): 487-494.
34. Kim Y.-T, Mitani T. *Surface thiolation of carbon nanotubes as supports: A promising route for the high dispersión on Pt nanoparticles for electrocatalysts. J. Catal.* 2006; 238: 394-401.
35. Chen R, Zhang Y, Wang D, Dai H. *Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization. J. Am. Chem. Soc.* 2001; 123: 3838-3839.
36. Shim M, Wong N, Shi K, Chen RJ, Li Y, Dai H. *Functionalization of carbon nanotubes for biocompatibility and biomolecular recognition. Nano Lett.* 2002; 2: 285-288.

37. Star A, Gabriel JCP, Bradley K, Gruner G. *Electronic detection of specific protein binding using nanotube FET devices*. *Nano Lett.* 2003; 3:459-463.
38. Terrones M, Terrones H, Grobert N, Hsu WK, Zhu YQ, Hare JP, Kroto HW, Walton DRM, Kohler-Redlich Ph, Ruhle M, Zhang JP, Cheetham AK. *Efficient route to large arrays of CNx nanofibers by pyrolysis of ferrocene/melamine mixtures*. *Appl. Phys. Lett.* 1999; 75: 3932–3934.
39. Hohenberg P, Kohn W. *Inhomogeneous Electron Gas*. *Phys. Rev.* 1964; 136: B864.
40. Kohn W, Sham LJ. *Self-Consistent Equations Including Exchange and Correlation Effects*. *Phys. Rev.* 1965; 140: 1133-1138.
41. Soler JM, Artacho E, Gale JD, Garcia A, Junquera J, Ordejon P, Sanchez-Portal D. *The SIESTA method for ab initio order-N materials simulation*. *J. Phys-Cond Matter* 2002; 14:2745-2779.
42. Troullier N, Martins JL. *Efficient pseudopotentials for plane-wave calculations*. *Phys. Rev. B* 1991; 43:1993-2006.
43. Junquera J, Paz O, Sanchez-Portal D, Artacho E. *Numerical atomic orbitals for linear-scaling calculations*. *Phys. Rev. B* 2001; 64: 235111.
44. Nose S. *A unified formulation of the constant temperature molecular-dynamics methods*. *J. of Chem. Phys.* 1984; 81 (1): 511-519.
45. Rao AM, Eklund PC, Bandow S, Thess A, Smalley RE. *Evidence for Charge Transfer in Doped Carbon Nanotube Bundles from Raman Scattering*. *Nature* 1997; 388: 257-259
46. Assael MJ, Metaxa I, Arvanitidis J, Christofilos D, Lioutas C. *Thermal conductivity enhancement in aqueous suspensions of carbon multi-walled and double-walled nanotubes in the presence of two different dispersants*. *Inter. J. of Thermophysics* 2005; 26: 647.
47. Gracia-Espino E, López-Urías F, Terrones H, Terrones M. *Doping (10, 0)-Semiconductor Nanotubes with Nitrogen and Vacancy Defects*. *Mater. Express* 2011; 1: 127-135.
48. Pereiro M, Baldomir D. *Structure and static response of small silver clusters to an external electric field*, *Phys. Rev. A* 2007; 75: 033202.