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# Modification of Carbon Nanotubes with Electronegativity Molecules to Control the Adhesion of Low Density Lipoprotein

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## Abstract

Atherosclerosis is a cardiovascular disease that causes accumulation of lipoproteins, which leads to vascular injury and may even cause Acute Myocardial Infarction (AMI). The interaction of vascular endothelium with low - density lipoproteins (LDL) was modified by using two distinct groups of carbon nanotubes (CNTs). The first group was doped with aluminum sulfate ($Al_2(SO_4)_3$) and boric acid ($H_3BO_3$), and the second group was functionalized by chemical route with carboxylic acid (COOH) and glucosamine ($C_6H_{13}NO_5$). The catalysts used to grow the CNTs were Nickel (Ni) 50%, Cobalt (Co) 50% and Cobalt Iron (Fe - Co) 10% - 40%, by sol - gel route. Scanning electron microscopy (SEM), Raman, and contact angle were used to characterize CNTs. The Raman spectra of multi - wall carbon nanotubes showed three bands, which are called D (disorder), G (graphitization) and G' (second harmonic order) which caused by the D band. It is observed that the intensity ratio $I_D$ / $I_G$ increases for functionalized CNTs. CNTs grown from nickel and functionalized by chemical route with glucosamine showed low wettability contact angle for the 2h and 18h oxidized LDL samples. CNTs grown from nickel and doped with aluminum sulfate showed an angle of contact with low wettability for the 2h oxidized LDL sample. An association of the sulphate groups in the density of the load and the cooperativity of the load with arginine and lysine rich peptides of the LDL sample were observed. The CNT catalyzed with (Fe - Co) and doped with boric acid evidenced a low strength of adhesion and greater surface tension for the 18h high degree oxidized LDL; resulting in a repulsion of residues of lysine and arginine of the altered structure of ApoB 100 of the LDL. The obtained CNT structures are presented as a possible devise coating with therapeutic potencial to avoid the progression of atherosclerosis.

**Keywords**: Carbon nanotube; Low - density lipoproteins (LDL); Functionalization; Electronegativity molecules

## Introduction

Cardiovascular diseases are the main cause of death in Western societies, among which atherosclerosis stands out [1,2]. This is a chronic inflammatory process that is characterized by morphological and functional changes in the vascular wall. Resulting in the reduction of the blood flow, associated with a phenomenon of platelet aggregation and thrombosis [3-6], where low density lipoproteins (LDL) are special markers that can be recognized and accepted by endothelium which leads to arterial hardening and occlusion.

Nanotechnology offers new alternatives to find a solution to this disease [7-9]. New biocompatible materials possess nano - metric scales that prevent vascular restenosis, reducing the atheroma [10-12]. CNTs have received enormous attention in biomedical applications such as drug delivery agents, biosensors, bone material scaffolds and even as neuronal growth substrate [13-15]. CNTs can be modified by adding functional groups to enhance their hydrophobicity and improve their compatibility with any target tissue [16-18].

A well - established and efficient method to functionalize the nanotubes is to subject them to prolonged sonication at room temperature, in a mixture of concentrated sulfuric acid and nitric acid. The reaction starts at end caps of the CNTs, due to strong pressure from the hexagon - heptagon pairs, the end caps are quickly removed, leaving open end tubes functionalized with carboxylic acid groups (COOH) [19].

Modification of CNTs doped with molecules of aluminum sulfate ($Al_2(SO_4)_3$), boric acid ($H_3BO_3$), and functionalized by chemical route with carboxylic acid (COOH) and glucosamine ($C_6H_{13}NO_5$) are described in this article. Characterization of the obtained CNT structures was achieved by SEM, Raman, and contact angle analysis.

## Methodology

### Carbon nanotube synthesis

CNTs were synthesized by chemical vapor deposition (CVD). A quartz tube was used to grow CNTs and a furnace equipped with a high precision automated computer temperature controller, which allowed to achieve the desired reaction temperature (700°C). Acetylene was used as the carbon source. The catalysts were nickel (50%), cobalt (50%) and Iron - Cobalt (10% - 40%) for the production of CNTs and the gas mixture was composed of 80 cc/ min nitrogen, 20 cc/ min acetylene and 15 cc/ min hydrogen. The processing sequence included reduction time of 20min, acetylene time of 30min and cooling time of 60 min [20-28].

### CNTs functionalization

**Functionalization by doping:** Doping of the CNTs (Figure 1) was

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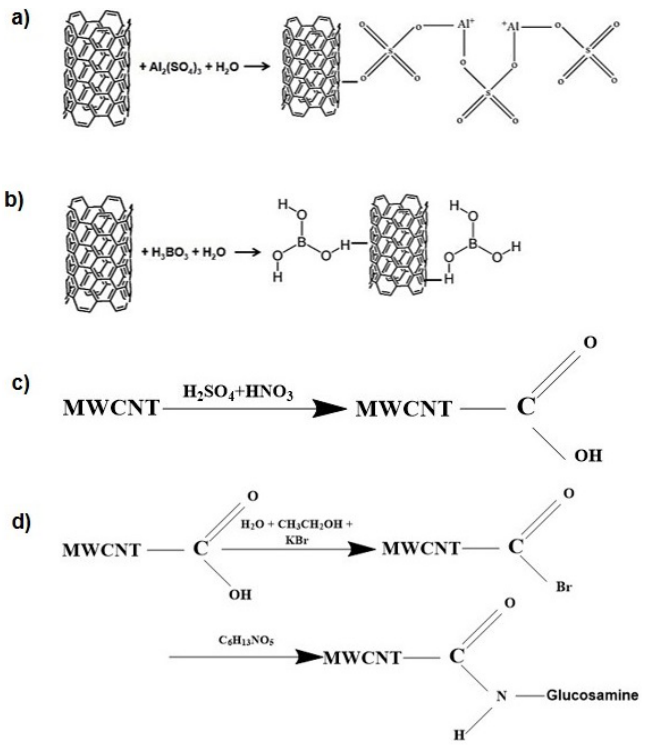


**Figure 1:** MWCNTs doped with a) Aluminum sulfate, b) Boric acid, c) MWCNTs functionalized by chemical route with carboxylic acid, d) MWCNTs functionalized by chemical route with glucosamine [31].

carried out during the synthesis process by using an ultrasonic vaporizer attached to quartz tube of CVD devise. The vaporizer was loaded with a known amount of the precursor. The precursor solution contains the doping electronegativity molecules, either aluminum sulfate (Figure 1a) or boric acid (Figure 1b) both 2% w / v. The vaporized precursor is injected into the reaction zone through pulsated nitrogen gas ($N_2$) carrying a flow of 0.2 L / min.

**Carboxylic acid functionalization (COOH)**: The functionalization of CNT with carboxylic acid is based on the research of Matthew W. Marshall et al. 2006. The functionalization process was achieved by using 1mL of a concentrated solution of $H_2SO_4$ and $HNO_3$ (3:1 v / v) for each 2mg of CNT (Figure 1c). This mixture was sonicated for 20 minutes in a water bath sonicator at a temperature of 20˚C, ice was used to control the water temperature; thus avoiding the breakdown of CNTs and preserving their original lengths. The functionalized CNT were washed with deionized water to remove any excess of acids, until a pH of 5 was reached. The final product was dried in a sealed oven at 60˚C [29].

**Glucosamine functionalization ($C_6H_{13}NO_5$):** Functionalization with glucosamine ($C_6H_{13}NO_5$) in a controlled atmosphere of nitrogen was based on the reports by Leize Zhu et al. [30]. In order to add glucosamine to the CNTs, these must be previously functionalized with carboxylic acid. Initially, 1ml of distilled water, 0.5 ml ethanol was used as solvent followed by 195 µl of a solution of potassium bromide (10 g of KBr in nitric acid at 10%) were mixed per each 75 mg of CNTs (Figure 1d). The described process is known as halogenation and happens so that the diameter and the ion of bromine energy, tends to de - saturate the hydrogen atoms, therefore the hydroxyl group becomes available and is engaged and released; is there then when bromine enters the network.

Subsequently, the sample was placed in a desiccator with controlled atmosphere of nitrogen per 24 h, then the sample was washed 3 times with distilled water and ethanol. After the final wash 134.2 mg of glucosamine was added per each 75 mg of CNT. The sample was washed once again in a desiccator with controlled atmosphere of nitrogen during 72 hrs to avoid product contamination with any grafted polymer or leftover reactive. Once again the sample was washed 3 times with deionized water and left to dry under vacuum [30,31].

## LDL oxidation

Based on the research by Evangelia Chnari [32], three different LDL was tested: unmodified LDL (natural state) and mildly and highly oxidized LDL. LDLs were obtained from porcine plasma with a concentration of 10 µg / mL.

The mildly oxidized LDLs were achieved by incubating 50 µg / ml of LDL with 10 µg of copper sulfate ($Cu_2SO_4$) at 37˚C for 2 hours. Similarly, the highly oxidized LDL was obtained by exposing it to air and increasing the incubation time to 18 hours. In all cases the oxidation was completed with an aqueous solution of 0.01% w / v ethylenediamine tetra - acetic acid (EDTA).

## Characterization

Characterization of the samples was performed in order to know the internal structure, verify the effectiveness of the functionalization and confirm if the functional groups were properly adhered. Methods such as scanning electron microscopy (SEM), Raman spectroscopy, and measurements of contact angle were used.

A scanning electron Microscope JEOL JSM 5300, the beam of electrons was worked with a power of 3 to 5 keV, the electron mode was secondary and retro dispersed a stream of issuance of 75-85 µA and a working distance of 6 mm. The CNT sample was adhere to a microscope sample holder with a carbon double - sided tape. The micro - Raman spectrometer was used with a He - Ne laser (red line) having an approximately energy of 1.92 eV (632.8 nm). Samples were focused with a 50X objective, a grid of 600r / mm was used, the diameter of the irradiated area was 2 µm at room temperature and the integration time was 60 seconds.

Functionalized CNTs were molded into pills to perform analysis of wettability with the natural state and oxidized LDL to establish the contact angle. The measurements were taken at an ambient temperature of 25°C, and results were shown after one second (24 squares). The contact angle was measured using a Dataphysics OCA 15 Number series device, using a syringe with 1ml capacity to apply a drop on the surface of the CNT sample pill.

# Results

## CNT doping with ($Al_2(SO_4)_3$) and ($H_3BO_3$)

**SEM characterization:** The CNTs grown from the nickel (Ni) catalyst and doped with aluminum sulfate (Figure 2a) showed a greater productivity, with tangled growth of structures, and less presence of the catalyzer on the silica deposition base. CNTs grown from the Iron - Cobalt (Fe - Co) catalyst and doped with boric acid (Figure 2c), showed a higher productivity, growth tangled structures, a smaller diameter and less catalyzer presence.

**Raman characterization:** The Raman spectrum of CNTs grown from the nickel catalyst, and doped with aluminum sulfate (Figure 2b), and CNTs grown from the Iron - Cobalt catalyst and doped with

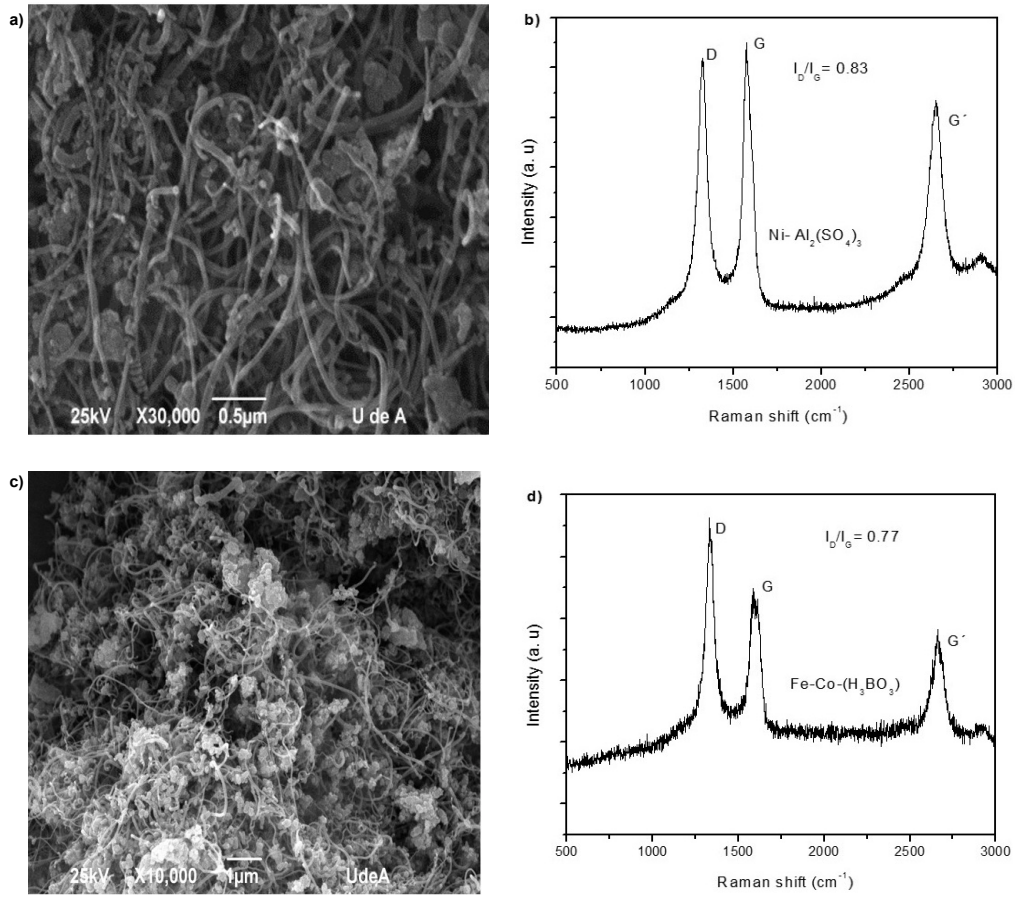


**Figure 2:** SEM micrograph and Raman spectrum of CNTs a) and b) nickel and doped with aluminum sulfate, c) and d) Iron-Cobalt doped with boric acid.

boric acid (Figure 2d), showed the D band approximately at 1350 $cm^{-1}$, indicating defects in the nanotube network and disorder of graphite. The G band can be observed at 1560 $cm^{-1}$ is attributable to graphitic materials; therefore the $I_D$ / $I_G$ index is 0.83, greater than the $I_D$ / $I_G$ for CNTs doped with boric acid which was equivalent 0.77. Such values indicate deposition of aluminum sulfate on CNTs, and the presence of boric acid in smaller quantities. The result obtained by Hoyos shows widening of the bands caused by the amount of material defects, with shifts toward higher frequencies [23].

**Contact angle measurement**: The contact angle measurements performed on the CNT pills doped with $Al_2(SO_4)_3$ (Table 1) and $H_3BO_3$ (Table 2) shows the results of the measurement taken at 9 seconds of exposure to the 0, 2 and 18 hour oxidized LDLs.

Less strength of adhesion and greater surface tension was observed for CNTs - $Al_2(SO_4)_3$, with a contact angle of 179.8° for the two hour oxidized LDL. Material coating properties can be attributed to the CNTs - $Al_2(SO_4)_3$ since it modifies the interaction with the mildly oxidized LDL; avoiding the LDL to reach a complete adherence. Lower bond strength and higher surface tension was observed for CNTs - $H_3BO_3$ when tested with the highly oxidized (18 hours) LDL with a contact angle of 134.6°. CNTs - $H_3BO_3$ it is a material that as a coating modifies the surface of the CNT, retaining the highly oxidized LDL, therefore this material should be considered as a therapeutic option by conducting previous studies of biocompatibility.

## Carboxylic acid (COOH) and Glucosamine ($C_6H_{13}NO_5$) functionalization

**Characterization (SEM):** The CNTs grown from cobalt (Co) catalyst and functionalized by chemical route with carboxylic acid (COOH) (Figure 3a), and CNTs grown on nickel (Ni) and functionalized by chemical route with glucosamine ($C_6H_{13}NO_5$) (Figure 3c) presented a lower productivity, a smaller diameter, silica accumulations, and an increased of nonlinear tangled structures.

**Raman characterization**: Raman spectroscopy of CNTs grown from cobalt and carboxylic acid functionalized (Figure 3b), illustrate that the first band, D band, is at about 1400 $cm^{-1}$, indicating disorder in the graphite layer. An increase of the G band is observed approximately at 1650 $cm^{-1}$ belonging to the first order fundamental vibration, which refers to the tangential elongation. In this case the intensity ratio $I_D$ / $I_G$ is 1.07, indicating the presence of carboxylic acid on the functionalized CNTs. The results are comparable to those obtained by Pradip Kar et al. There was an increment in the ratio of intensity with the increase of functionalized CNT [33].

The Raman spectroscopy results of CNTs grown from nickel catalyst and functionalized by chemical route with glucosamine (Figure 3d), it can be observe that the first D band is at approximately 1350 $cm^{-1}$, indicating graphite defects. The G band, located at approximately 1650 $cm^{-1}$ corresponds to graphitable material. The high ratio $I_D$ / $I_G$ is 1.16 greater than the ratio $I_D$ / $I_G$ 1.07 of carboxylic acid functionalized

| Contact Angle Measurements | | | | | |
|---|---|---|---|---|---|
| a) **Ni–CNT-Al** | | **b) Ni–CNT-Al** | | **c) Ni–CNT-Al** | |
| **Time(s)** | **Angle(°)** | **Time (s)** | **Angle (°)** | **Time(s)** | **Angle (°)** |
| 1 | 30.7 | 1 | 117.1 | 1 | 87.9 |
| 3 | 46.3 | 3 | 179.9 | 3 | 82.6 |
| 6 | 50.3 | 6 | 46.5 | 6 | 64.9 |
| 9 | 46.7 | 9 | 179.8 | 9 | 53.7 |

**Table 1:** CNTs doped with $Al_2(SO_4)_3$ pills to measure contact angle at different times: a) 0 hours, b) 2 hours, c) 18 hours.

| Contact Angle Measurements | | | | | |
|---|---|---|---|---|---|
| a) **Fe–CO-CNT-$H_3BO_3$** | | **b) Fe–CO-CNT-$H_3BO_3$** | | **c) Fe–CO-CNT-$H_3BO_3$** | |
| **Time(s)** | **Angle (°)** | **Time (s)** | **Angle (°)** | **Time (s)** | **Angle (°)** |
| 1 | 35.8 | 1 | 85.2 | 1 | 25.6 |
| 3 | 117.2 | 3 | 84.6 | 3 | 141.7 |
| 6 | 113.6 | 6 | 0 | 6 | 135.5 |
| 9 | 113.2 | 9 | 0 | 9 | 134.6 |

**Table 2:** CNTs doped with $H_3BO_3$ to measure contact angle at different times: a) 0 hours, b) 2 hours, c) 18 hours.

CNTs; the introduction of glucosamine on CNTs is confirmed by band broadening.

**Contact angle measurement**: Contact angle measurements done with CNTs grown from nickel and functionalized with glucosamine are shown in Table 3. CNTs catalyzed with cobalt and functionalized with carboxylic acid Table 4. The results show the measurements taken at 9 seconds of exposure to the LDL at 0,2 and 18 hours of oxidation.

Ni - CNTs - $C_6H_{13}NO_5$ (Table 3) show a low wettability observed with a contact angle after of 115.6° for the 2 hour oxidized LDL, which showed surface modification of functionalized CNTs by high degree of sulfation, increasing the charge density and augmenting LDL binding.

Co - CNTs - COOH (Table 4) presented lower bond strength and higher surface tension at 0 hours with a contact angle of 121.3°. The functionalized CNT with carboxylic acid acts on the native LDL without any structural modification

The aim of this research for future work will be to perform cytotoxic and biocompatibility analysis as well as *in vivo* experimentation in order to assess the dynamic behavior of the functionalized CNT with the lipoproteins LDL**.**

## Conclusions

The presence of aluminum sulfate and boric acid on the CTNs was confirmed by Raman spectroscopy. Evidence of higher productivity of doped CNTs with tangled structure growth and less presence of catalyzer was observed by SEM micrography. Also, for CNT functionalized by chemical route, lower productivity and presence of silica accumulation were observed.

Electronegativity molecules of the CNTs nickel - aluminum, nickel

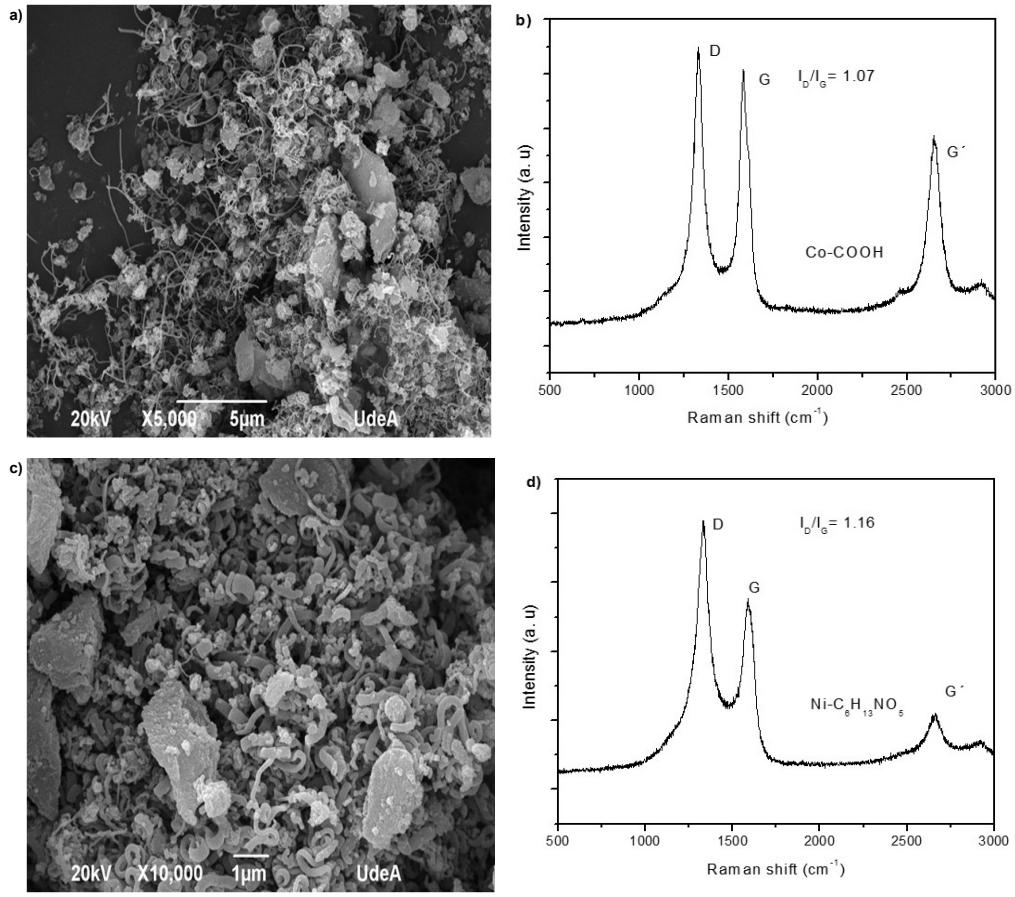


**Figure 3:** SEM micrograph and Raman spectrum of CNTs grown from cobalt and functionalized by chemical route with carboxylic acid a) and b); c) and d) CNTs grown from nickel, functionalized by chemical route with glucosamine.

| Contact Angle Measurements | | | | | |
|---|---|---|---|---|---|
| a) Ni-CNT-$C_6H_{13}NO_5$ | | b) Ni-CNT-$C_6H_{13}NO_5$ | | c) Ni-CNT-$C_6H_{13}NO_5$ | |
| Time (s) | Angle(°) | Time (s) | Angle (°) | Time (s) | Angle (°) |
| 1 | 65.3 | 1 | 110 | 1 | 57.5 |
| 3 | 69.3 | 3 | 111 | 3 | 103.1 |
| 6 | 63.1 | 6 | 118.8 | 6 | 88.5 |
| 9 | 65.5 | 9 | 115.6 | 9 | 96.7 |

**Table 3:** Contact angle measurement pills for CNTs functionalized by chemical route with Ni-CNT-$C_6H_{13}NO_5$ at a) 0 hours, b) 2 hours, c) 18 hours.

| Contact Angle Measurements | | | | | |
|---|---|---|---|---|---|
| a) Co–CNT-COOH | | b) Co–CNT-COOH | | c) Co–CNT-COOH | |
| Time (s) | Angle (°) | Time (s) | Angle (°) | Time (s) | Angle (°) |
| 1 | 91.1 | 1 | 97.5 | 1 | 85.6 |
| 3 | 124.8 | 3 | 92 | 3 | 81.1 |
| 6 | 121.5 | 6 | 98.4 | 6 | 85 |
| 9 | 121.3 | 9 | 101.9 | 9 | 85.1 |

**Table 4:** Contact angle measurement pills for CNTs functionalized by chemical route with Co-CNT-COOH at a) 0 hours, b) 2 hours, c) 18 hours.

- glucosamine, cobalt - carboxylic showed a contact angle with a low wettability to the 2h oxidized LDL. Sulfate and carboxylic groups exhibit an increase in load density and load cooperativity at the union of the rich lysine - arginine peptides of LDL.

The iron - cobalt - $H_3BO_3$ and nickel - glucosamine CNTs are electronegative molecules that showed less strength of adhesion and greater surface tension at 18h oxidized LDL. Interaction of lysine - arginine residues with the altered structure ApoB 100 of LDL was also observed. These electronegative molecules possess therapeutic potential for atherosclerosis treatment in the retention of LDL.

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## References

1. Cassiani CA, Cabrera AG (2009) Síndromes coronarios agudos: epidemiología y diagnóstico. Salud Uninorte 25.
2. Mendis S, Thygesen K, Kuulasmaa K, Giampaoli S, Mähönen M, et al. (2011) World Health Organization definition of myocardial infarction: 2008-09 revision. Int J Epidemiol 40: 139-146.
3. Mendoza Beltrán FC, Isaza Restrepo D, Beltrán Pineda R, Jaramillo Villegas C, Beltrán Bohórquez JR, et al. (2008) Guías Colombianas de Cardiología. Síndrome coronario agudo sin elevación del ST (Angina inestable e infarto agudo del miocardio sin elevación del ST). Rev Colomb Cardiol, 15: 141-232.
4. Carmena R, Duriez P, Fruchart JC (2004) Atherogenic lipoprotein particles in atherosclerosis. Circulation, 109: III - 2.
5. Nakajima K, Nakano T, Tanaka A (2006) The oxidative modification hypothesis of atherosclerosis: the comparison of atherogenic effects on oxidized LDL and remnant lipoproteins in plasma. Clinica Chimica Acta, 367: 36-47.
6. Stocker R, Keaney JF Jr (2004) Role of oxidative modifications in atherosclerosis. Physiol Rev 84: 1381-1478.
7. Albini A, Mussi V, Parodi A, Ventura A, Principi E, et al. (2010) Interactions of single-wall carbon nanotubes with endothelial cells. Nanomedicine 6: 277-288.
8. Psarros C, Lee R, Margaritis M, Antoniades C (2012) Nanomedicine for the prevention, treatment and imaging of atherosclerosis. Maturitas 73: 52-60.
9. Rouhanizadeh M, Tang T, Li C, Hwang J, Zhou C, et al. (2006) Differentiation of oxidized low density lipoproteins by nanosensors. Sensors and Actuators B: Chemical 114: 788 - 798.
10. Ruenraroengsak P, Cook JM, Florence AT (2010) Nanosystem drug targeting: Facing up to complex realities. J Control Release 141: 265-276.
11. Balaguer-Malfagón JR, Pomar-Domingo F, Vilar-Herrero JV, Planas-del Viejo AM, Pérez-Fernández E (2006) Trombosis del stent en la era moderna: incidencia, consecuencias y factores predictores. Revista española de cardiología, 59: 842 - 845.
12. Nebeker JR, Virmani R, Bennett CL, Hoffman JM, Samore MH, et al. (2006) Hypersensitivity cases associated with drug - eluting coronary stents: a review of available cases from the Research on Adverse Drug Events and Reports (RADAR) project. Journal of the American College of Cardiology 47: 175-181.
13. Gangupomu VK, Capaldi FM (2011) Interactions of carbon nanotube with lipid bilayer membranes. Journal of Nanomaterials.
14. Gharib et al. Patent No. US 2012 / 0058170A1. United States. Mar 8, 2012.
15. Lewis DR, Kamisoglu K, York AW, Moghe PV (2011) Polymer-based therapeutics: nanoassemblies and nanoparticles for management of atherosclerosis. Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology 3: 400-420
16. Tian H, Tang Z, Zhuang X, Chen X, Jing X (2012) Biodegradable synthetic polymers: preparation, functionalization and biomedical application. Progress in Polymer Science 37: 237-280.
17. Meng L, Fu C, Lu Q (2009) Advanced technology for functionalization of carbon nanotubes. Progress in Natural Science 19: 801-810.
18. Caves JM, Chaikof EL (2006) The evolving impact of microfabrication and nanotechnology on stent design. J Vasc Surg 44: 1363-1368.
19. Goyanes S, Rubiolo GR, Salazar, Jimeno A, Corcuera MA, et al. (2007) Carboxylation treatment of multiwalled carbon nanotubes monitored by infrared and ultraviolet spectroscopies and scanning probe microscopy. Diamond and related materials 16: 412-417.
20. Iijima S (1991) Helical microtubules of graphitic carbon. nature 354: 56-58.
21. Cornelio JAC, Cuervo PA, Hoyos-Palacio LM, Lara-Romero J, Toro A (2016) "Tribological properties of carbon nanotubes as lubricant additive in oil and water for a wheel–rail system". Journal of Materials Research and Technology 5: 68-76.
22. Mionic M, Alexander DT, Forró L, Magrez A (2008) Influence of the catalyst drying process and catalyst support particle size on the carbon nanotubes produced by CCVD. physica status solidi (b) 245: 1915-1918.
23. Hoyos PLM, García GA, Pérez-R, Gonzalez J, Martinez THV (2014) "Catalytic effect of Fe, Ni, Co and Mo on the CNTs production. IOP Conference series: Material Science and Engineering volumen 59.
24. Pan ZW, Xie SS, Chang BH, Sun LF, Zhou WY, Wang G (1999) Direct growth of aligned open carbon nanotubes by chemical vapor deposition. Chemical Physics Letters 299: 97-102.
25. Li Q, Yan H, Zhang J, Liu Z (2003) 'Pulsed' CVD growth of single - walled carbon nanotubes. Carbon 41: 2876 - 2878.
26. Zhan S, Tian Y, Cui Y, Wu H, Wang Y, et al. (2007) Effect of process conditions on the synthesis of carbon nanotubes by catalytic decomposition of methane. China Particuology 5: 213-219.
27. Porro S, Musso S, Giorcelli M, Chiodoni A, Tagliaferro A (2007) Optimization of a thermal - CVD system for carbon nanotube growth. Physica E: Low - dimensional Systems and Nanostructures 37: 16-20.
28. Musso S, Porro S, Vinante M, Vanzetti L, Ploeger R, et al. (2007) Modification of MWNTs obtained by thermal - CVD. Diamond and related materials 16: 1183-1187.
29. Marshall MW, Popa-Nita S, Shapter JG (2006) Measurement of functionalised carbon nanotube carboxylic acid groups using a simple chemical process. Carbon, 44: 1137-1141.
30. Zhu L, Jin Q, Xu J, Ji J, Shen J (2009) Poly (2-(methacryloyloxy) ethyl phosphorylcholine)-functionalized multi-walled carbon nanotubes: Preparation, characterization, solubility, and effects on blood coagulation. Journal of applied polymer science 113: 351-357.
31. Pompeo Francisco, Resasco E Daniel (2002) "Water solubilization of single - walled carbon nanotubes by Functionalization with Glucosamine". Nano Letters 2: 369 - 373.
32. Chnari E1, Lari HB, Tian L, Uhrich KE, Moghe PV (2005) Nanoscale anionic macromolecules for selective retention of low-density lipoproteins. See comment in PubMed Commons below Biomaterials 26: 3749-3758.
33. Kar P, Choudhury A (2013) Carboxylic acid functionalized multi - walled carbon nanotube doped polyaniline for chloroform sensors. Sensors and Actuators B: Chemical 183: 25-33.