UNIVERSIDADE FEDERAL DE ALFENAS

ELECTRONIC PROPERTIES OF DISORDERED FUNCTIONALIZED CARBON NANOTUBES

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SUMARY

- INTRODUCTION
- OBJETIVES
- MATERIALS AND METHODS
- RESULTS
- CONCLUSIONS

INTRODUÇÃO

HOW TO OBTAIN CARBON NAOTUBES (CNTs)?

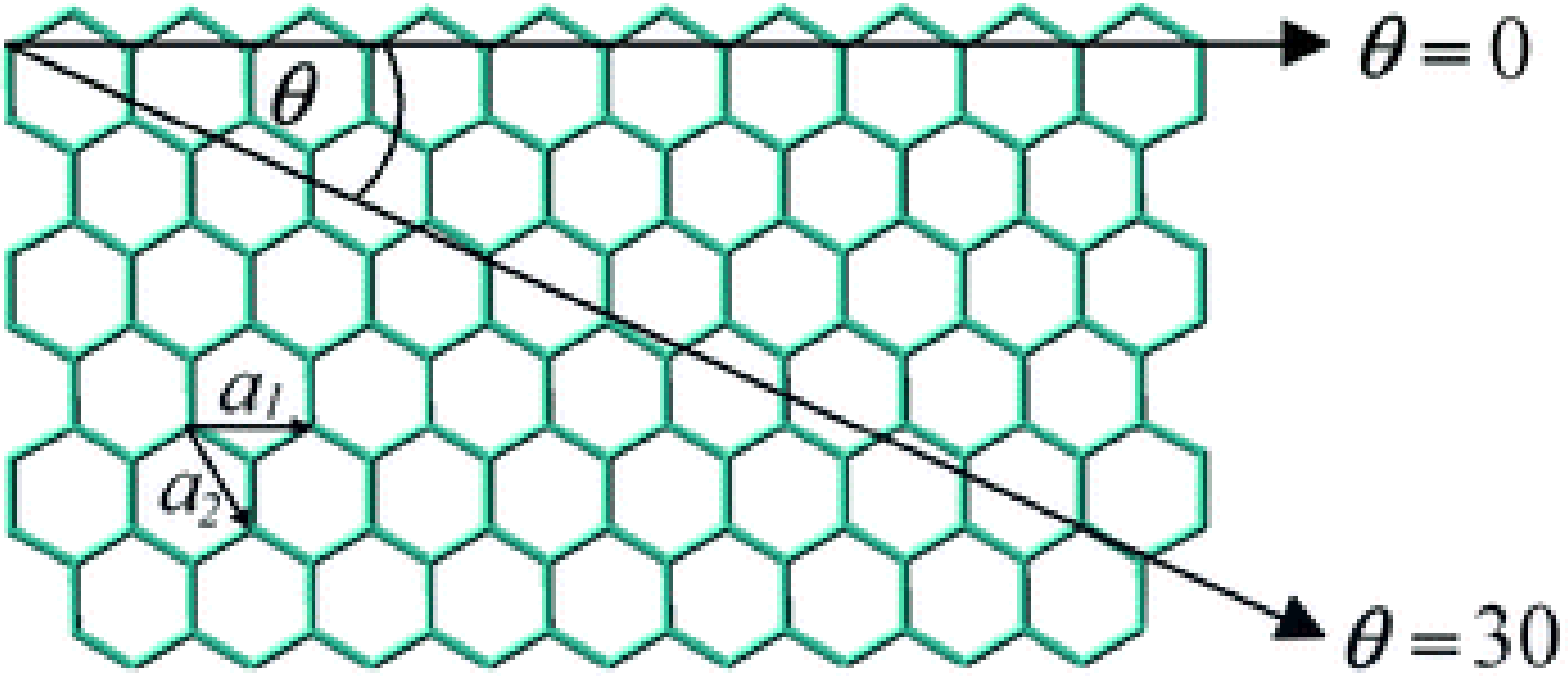


Figure 1 – Diagram of a perfect graphene sheet with the rolling vectors.

SINGLE WALL CARBON NANOTUBES (SWNTs)

- The rolling vectors define the conductive properties of the carbono nanotubes:

n - m = 3q → Metallic

n - m ≠ 3q ou n - m ≠ 0 → Semicondutor

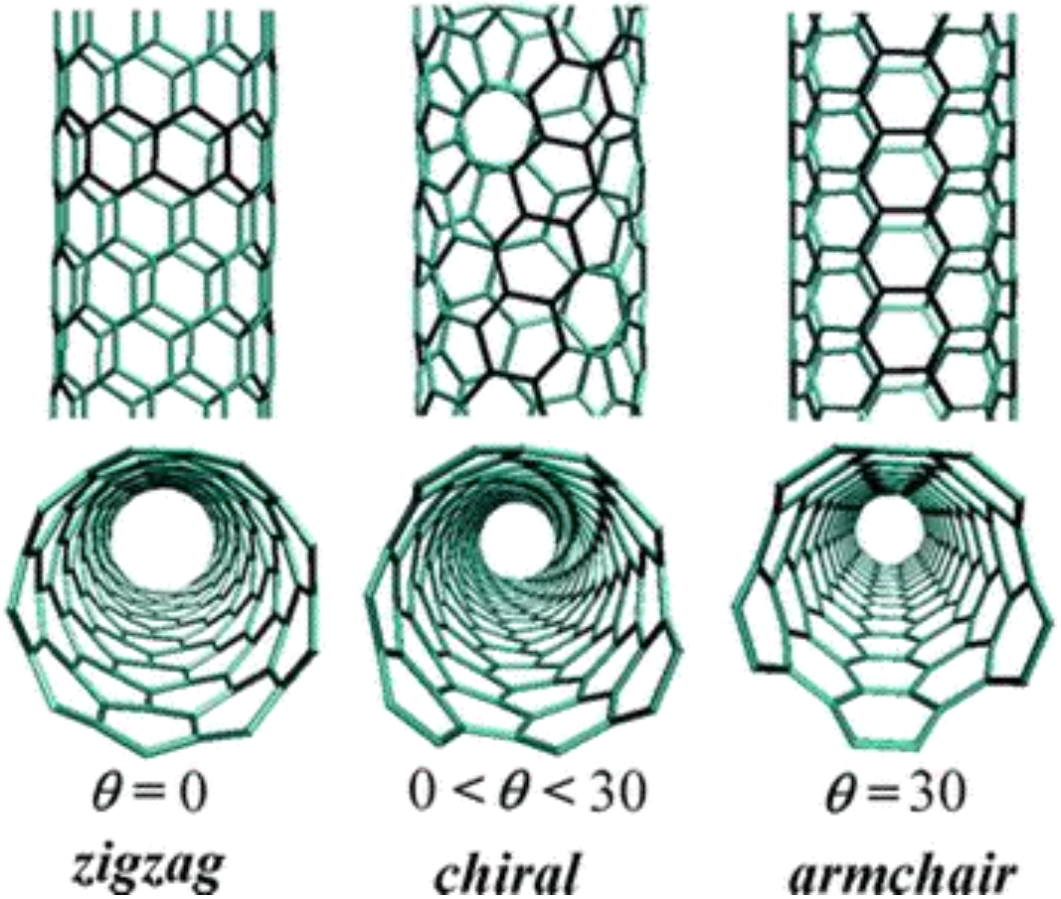


Figure 2 – Single wall carbon nanotubes: zigzag (n;0), chiral (n ≠ m) and armchair (n = m).

MULTIPLE WALLS CARBON NAOTUBE (MWNTs)

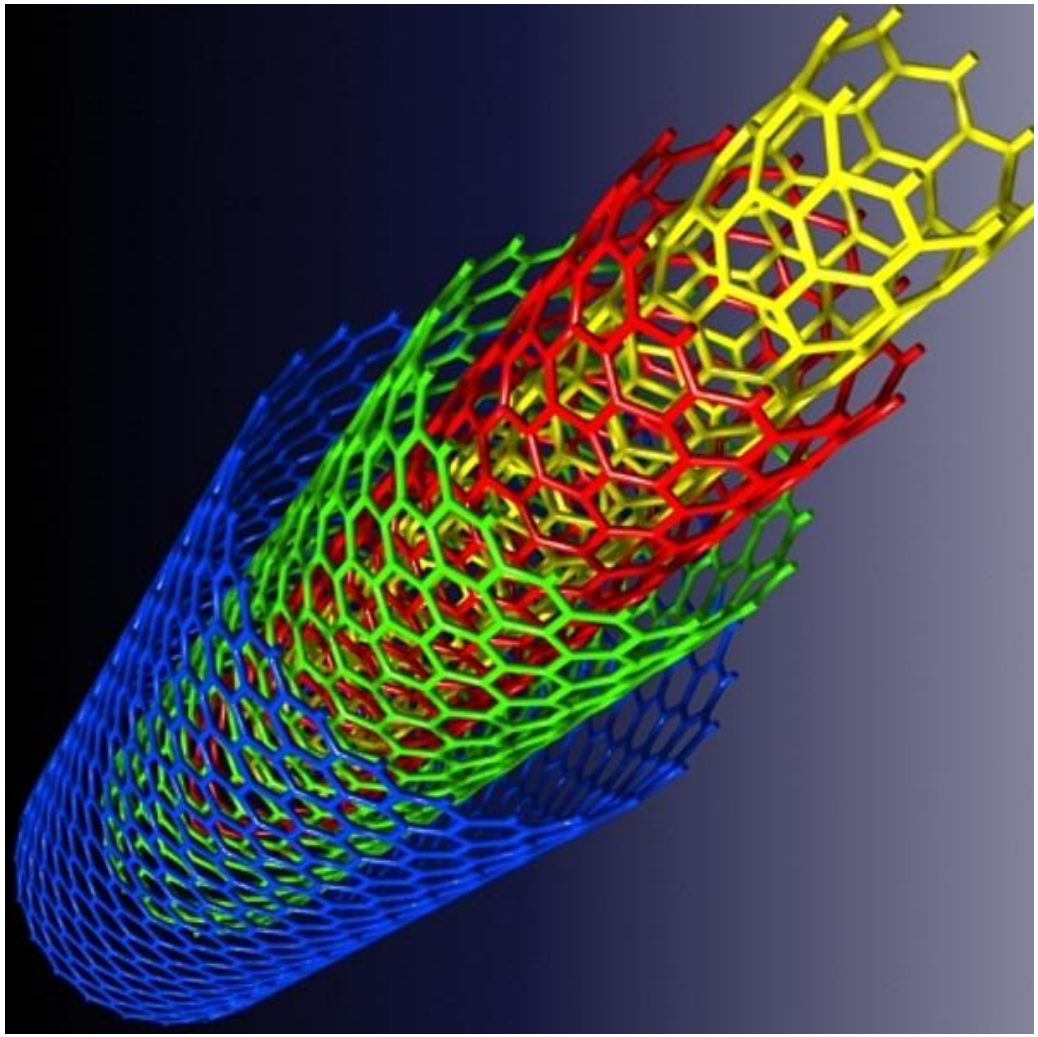
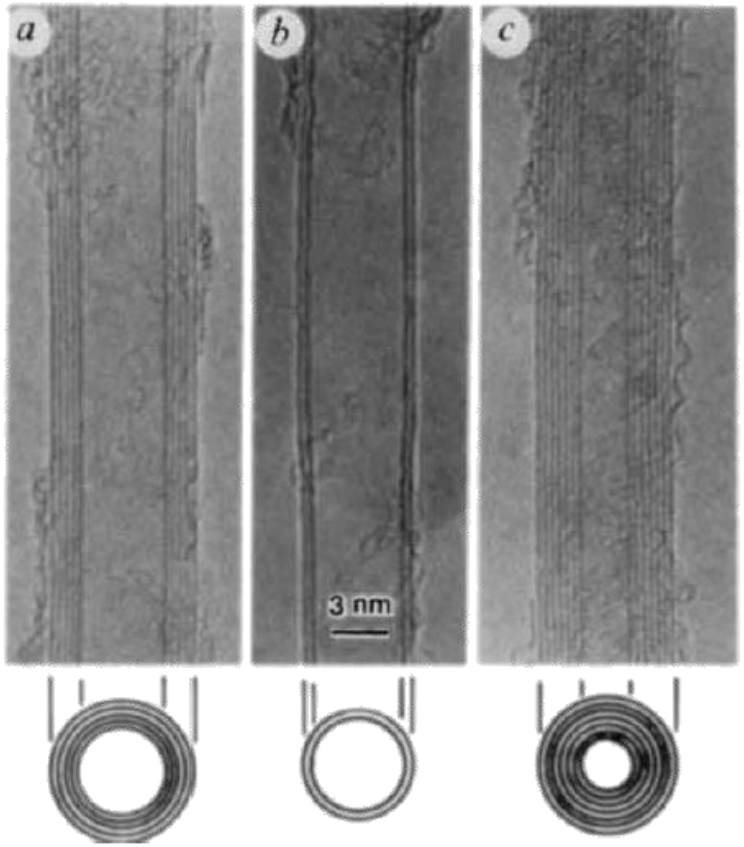


Figure 3 – Multiple wall carbon nanotube.



- Observed for the first time in 1991 by Iijima

- Concentric cylinders with:
  - Separation ~ 0.34 nm.
  - External diameter ~ 4 – 30 nm.
  - Internal diameter ~ 2.2 nm.
  - Length ~ 1 µm.

Figure 4 – Observed multiple wall carbon nanotubes.

IIJIMA, S. Helical microtubules of graphitic carbon. Nature, v. 354, p. 56–58, 1991.

- Single wall carbon nanotubes synthetized in 1993 by Iijima and Bethune

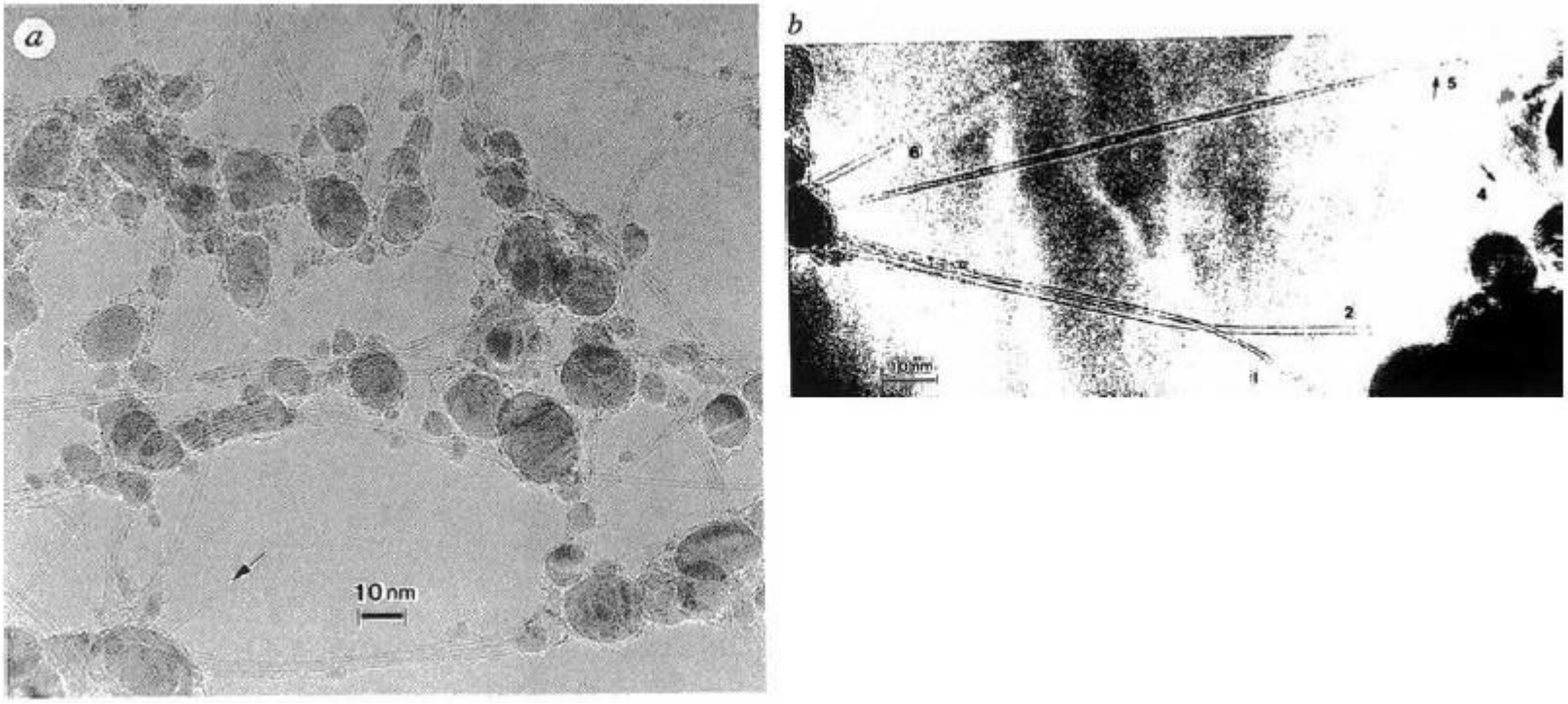


Figure 5 – (a) Electronic micrograph of SWCNTs grown from metallic catalyzers. (b) Electronic micrograph of individual SWCNTs.

IIJIMA, S.; ICHIHASHI, T. Single-shell carbon nanotubes of 1-nm diameter. Nature, v. 363, p. 603–605, 1993.

ELECTRONIC TRANSMISSION IMAGES

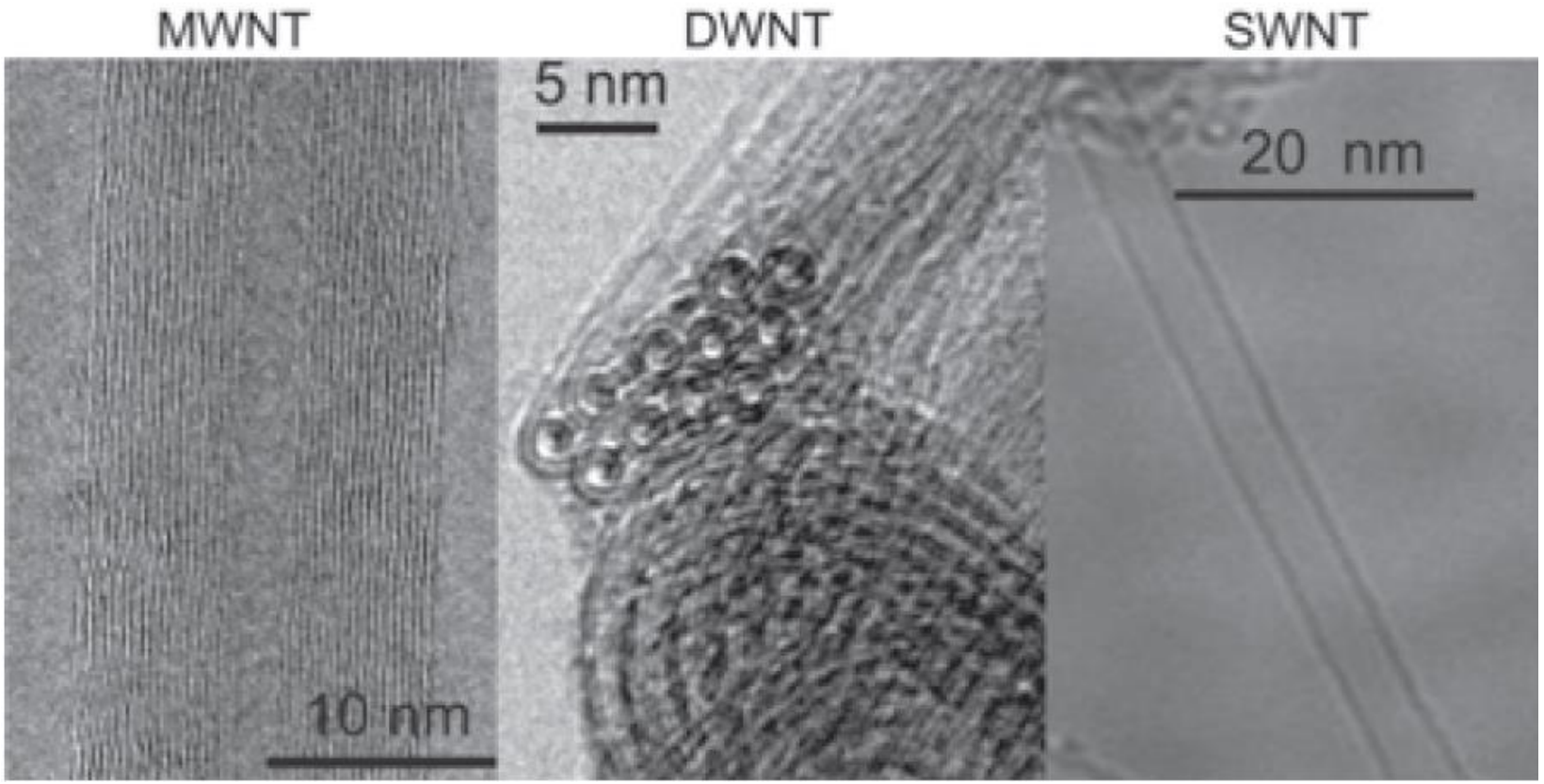
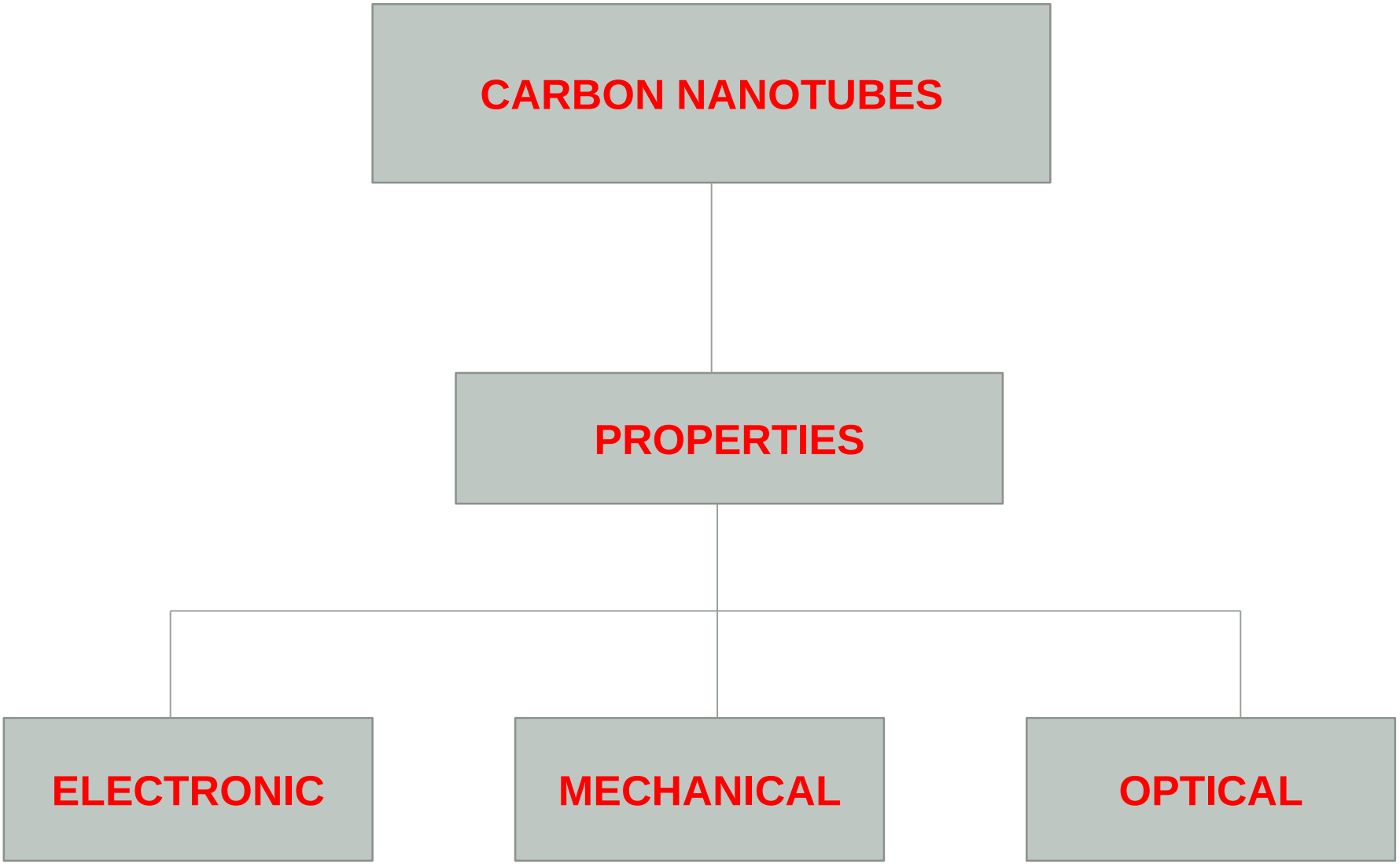
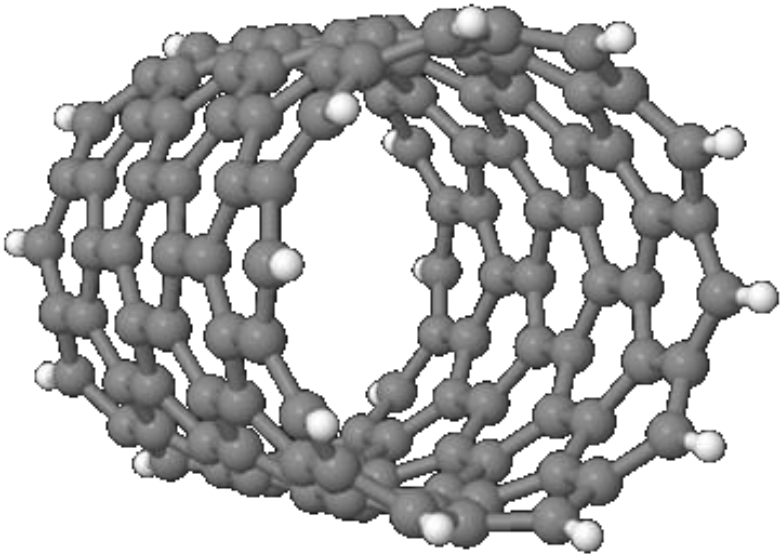


Figure 6 – Electronic transmission images of MWNT, DWNT (double wall nanotubes) and SWNT.

FILHO, A. G. de S.; FAGAN, S. B. Funcionalização de nanotubos de carbono. Quim. Nova, v. 30, p. 1695–1703, 2007.


CARBON NANOTUBES
PROPERTIES
ELECTRONIC
MECHANICAL
OPTICAL

CARBON NANOTUBES



- Used as sensors.
- Chemical sensor ⇨ Respond to local changes in the chemical environment
- Useful respond ⇨ Depends on de magnitude of the environment modifications.
- Should be:
  - ⇨ Sensible ⇨ Selective
- The studied nanotube:
  - ⇨ SWCNT ⇨ Chirality (10,0)

Figure 7 – Single wall carbon nanotube with chirality (10,0).

JANATA, J.; BEZEGH, A. Chemical sensors. Anal. Chem., v. 60, p. 62R–74R, 1988.
JANATA, J. *Chemical sensors*. Anal. Chem., v. 62, p. 33R–44R, 1990.
JANATA, J. Chemical sensors. Anal. Chem., v. 64, p. 196R–219R, 1992.
JANATA, J.; JOSOWICZ, M.; DEVANEY, D. M. Chemical sensors. Anal. Chem., v. 66, p. 207R–228R, 1994.
JANATA, J. et al. Chemical sensors. Anal. Chem., v. 70, p. 179–208, 1998.

OBJETIVES

This present study aimed to carry out a systematic study of the influence of hydroxyl functional groups (OH) and carboxyl (COOH) with different concentrations (5, 10, 15, 20 and 25)% of the atoms in the carbon nanotube surface.

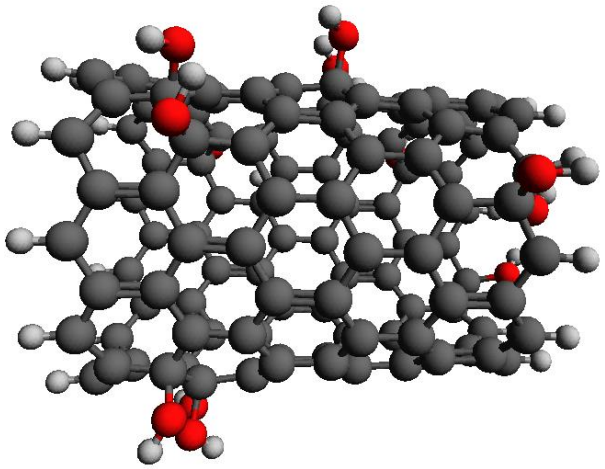
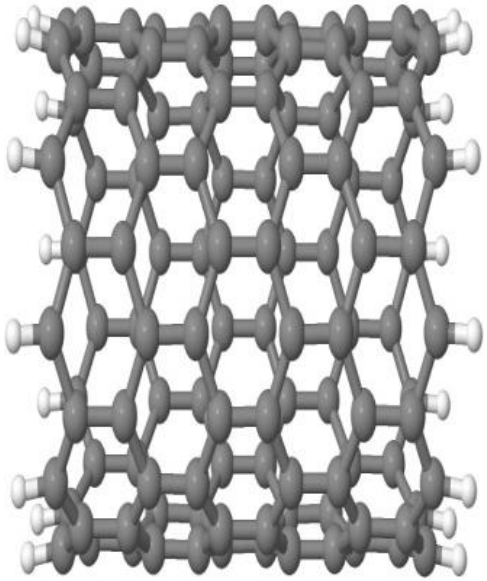


Figure 8 – Carbon nanotube functionalized with 10% of − OH, system CNT−OH.

MATERIALS and METHODS

MATERIALS

SCRIPT



MATERIALS and METHODS

METHODS

GENERATED
10K
STRUCTURES

MOPAC2012®

Jmol

STEWART, J. J. P. Stewart computational chemistry. Colorado Springs, CO, USA, http://OpenMOPAC.net, 2012.
LYAKHOV, A. O. et al. New developments in evolutionary structure prediction algorithm USPEX. Comput. Phys. Commun., v. 184, p. 1172–1182, 2013.
HANSON, R. M. et al. Jmol and the next-generation web-based representation of 3D molecular structure as applied to proteopedia. Isr. J. Chem., v. 53, p. 207–216, 2013.

SEMI-EMPIRICAL

INTERMEDIATE POSITION BETWEEN MOLECULAR MECHANICS AND *AB INITIO*

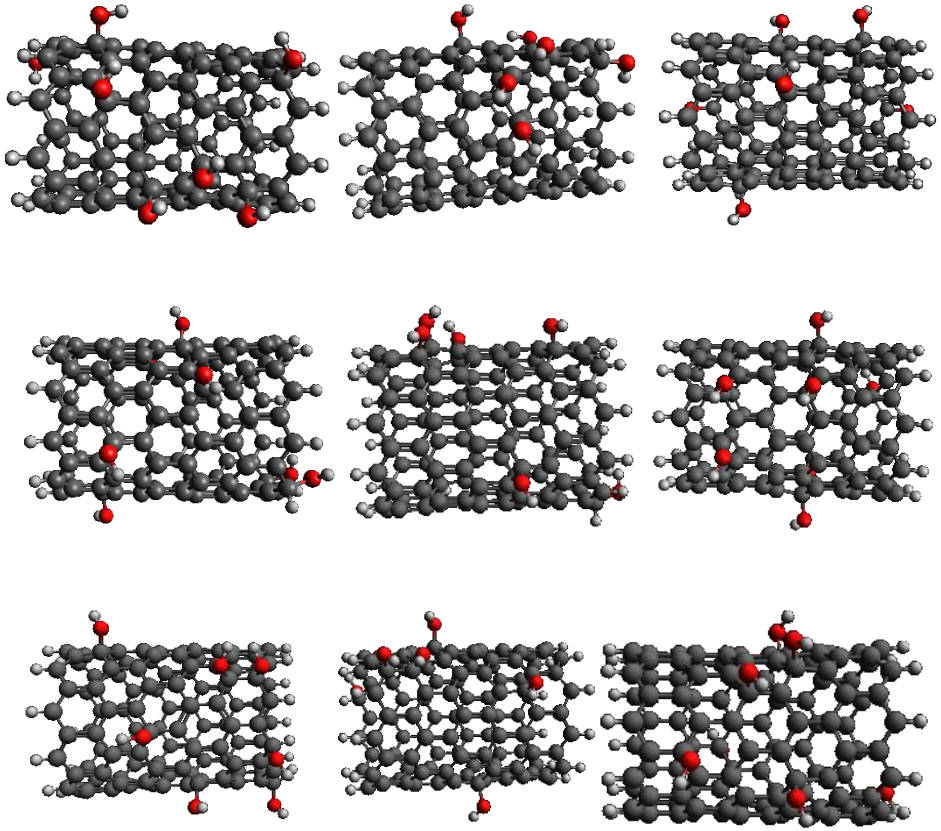
INDICATED → TO UNDERSTAND THE STRUCTURE, PROPERTIES AND ACTIVITY OF MOLECULES.

RELIABLE RESULTS → **LOWER COMPUTATIONAL TIMES**

STEWART, J. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. J. Mol. Modeling, v. 19, p. 1–32, 2013.
STEWART, J. J. P. Stewart computational chemistry. Colorado Springs, CO, USA, http://OpenMOPAC.net, 2012.

RESULTS

ENTROPY



$$S = k_B \ln \Omega$$

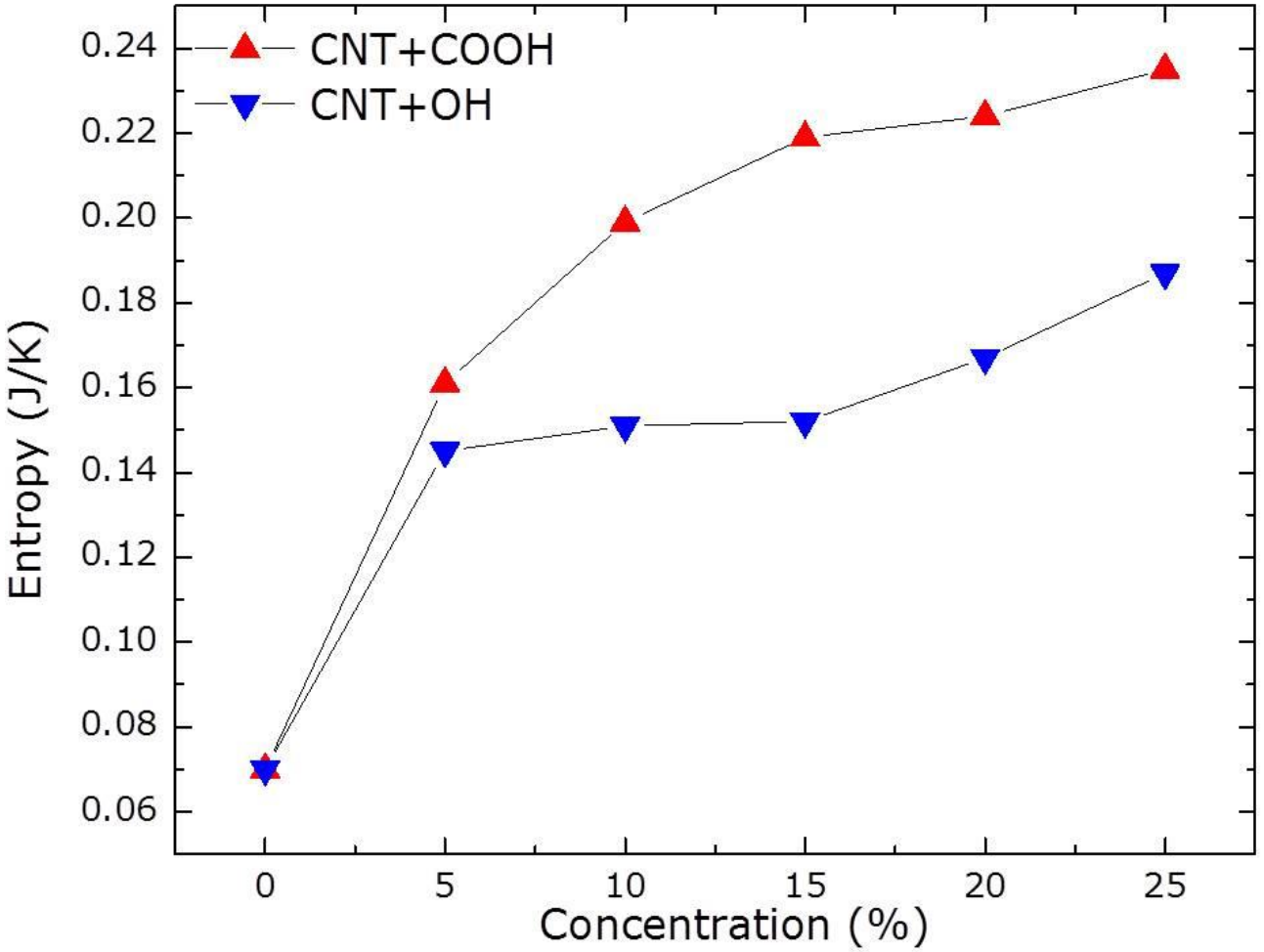
$$S_{str} = -\sum_{A} \frac{N_A}{N} \left\langle \ln\left(1 - F_{A_i A_j}\right) \right\rangle$$

$$F_{A_i B} = \sum_{B_j} \left\{ \frac{\delta\left(R - R_{ij}\right)}{4\pi R_{ij}^2 \left(N_B / V\right) \Delta} \right\} - 1$$

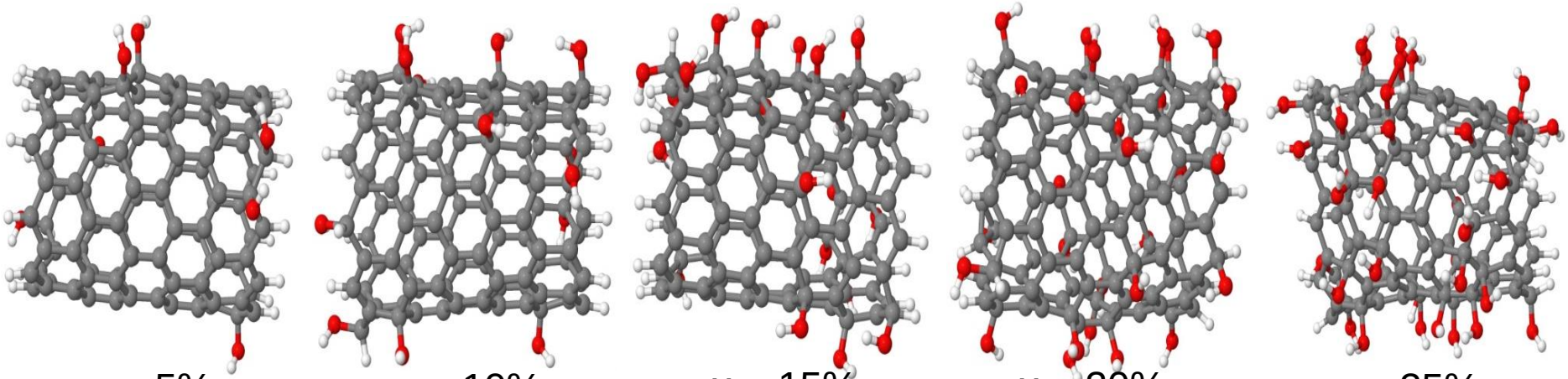
Figure 9 – System CNT-$(OH)_x$ functionalized with 5%.

RESULTS

ENTROPY

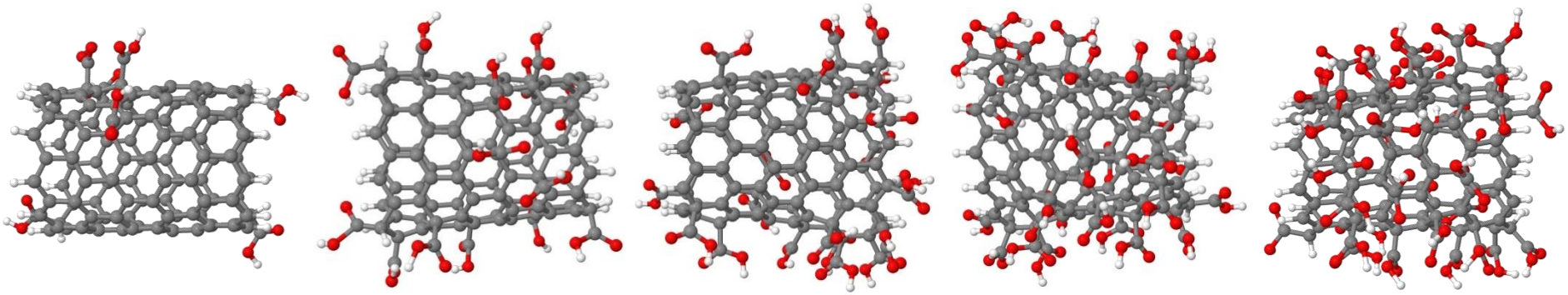


CNT+OH



x = 5% x = 10% x = 15% x = 20% x = 25%

CNT+COOH



x = 5% x = 10% x = 15% x = 20% x = 25%

Figure 10 – System CNT- $(OH)_x$ and CNT-$(COOH)_x$.

MOLECULAR ORBITALS

HOMO - *Highest Occupied Molecular Orbital*

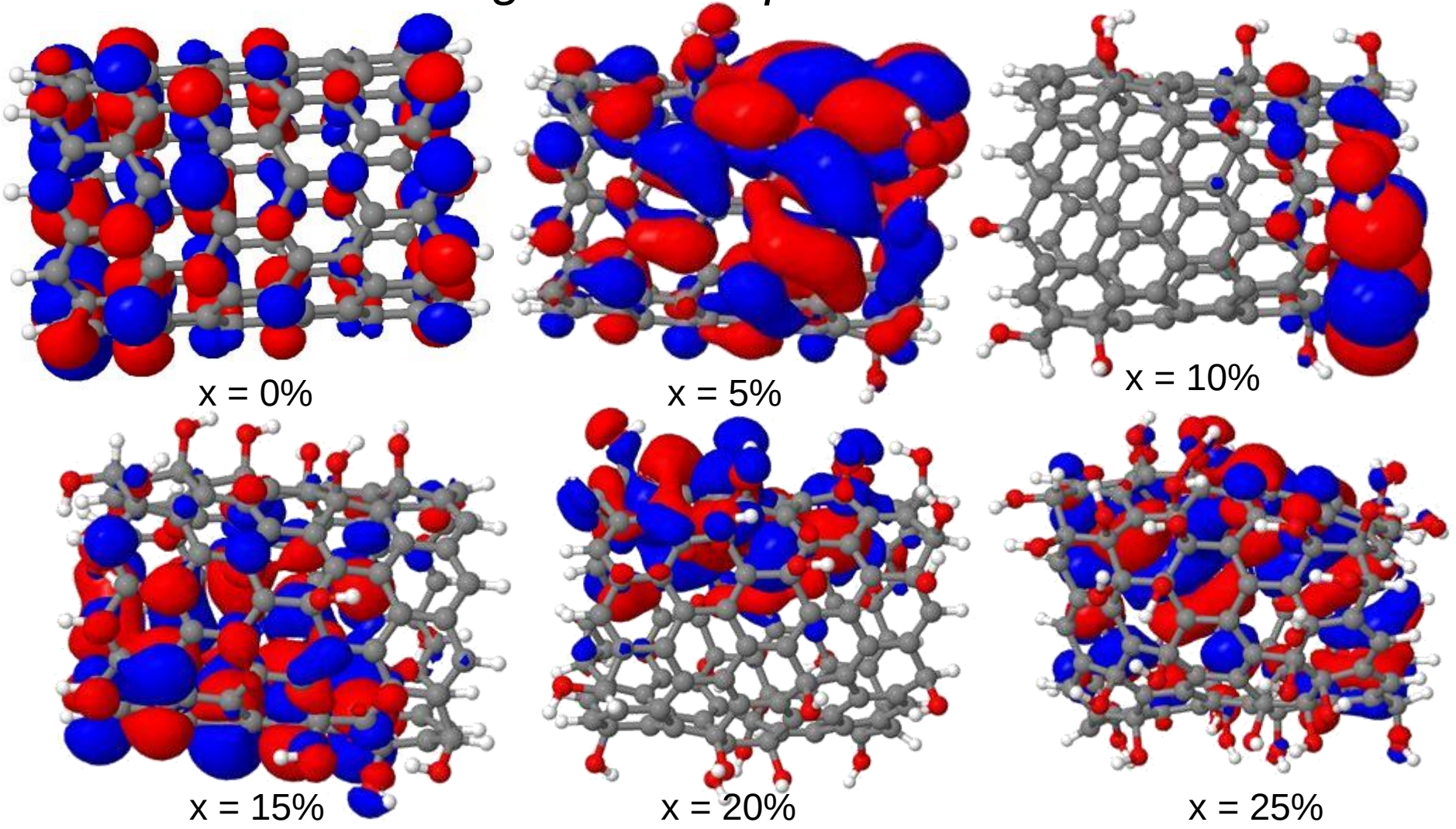
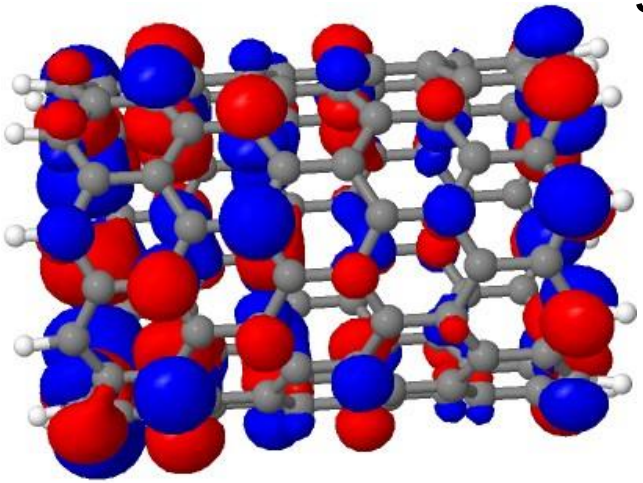


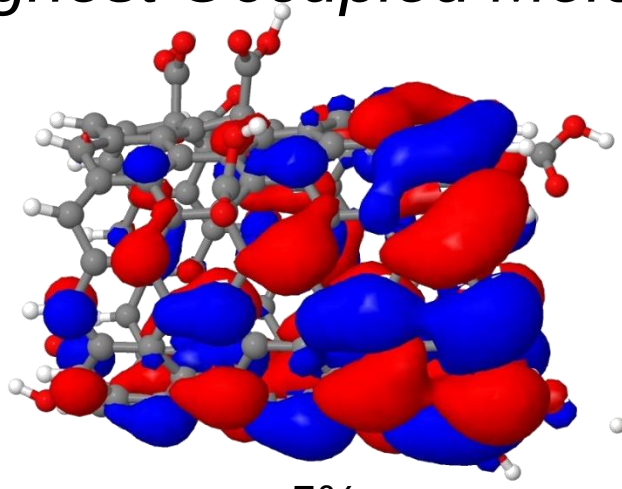
Figure 11 – HOMO of system CNT-$(OH)_x$ (isovalue = 0.01).

MOLECULAR ORBITALS

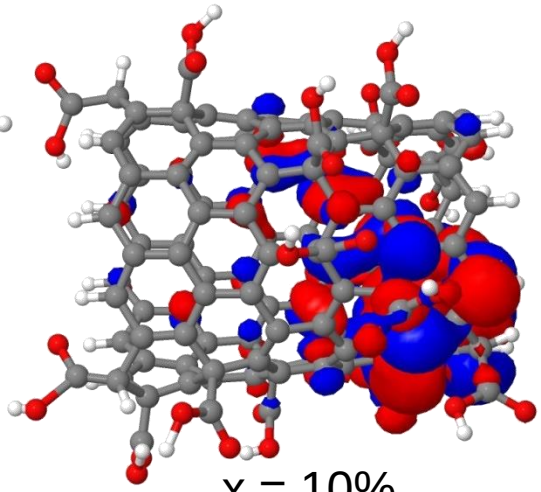
HOMO - *Highest Occupied Molecular Orbital*



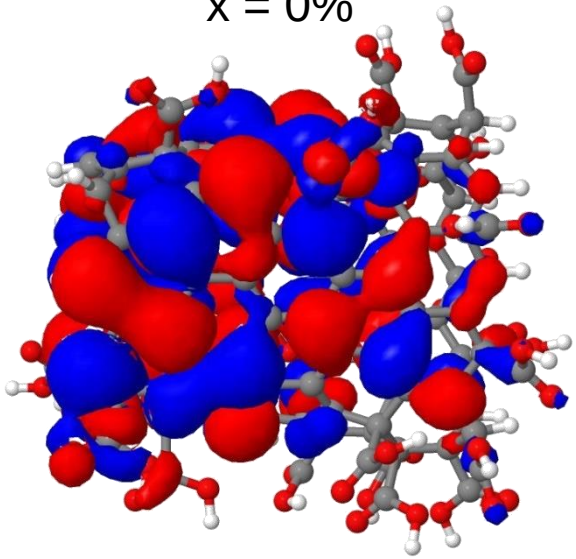
x = 0%



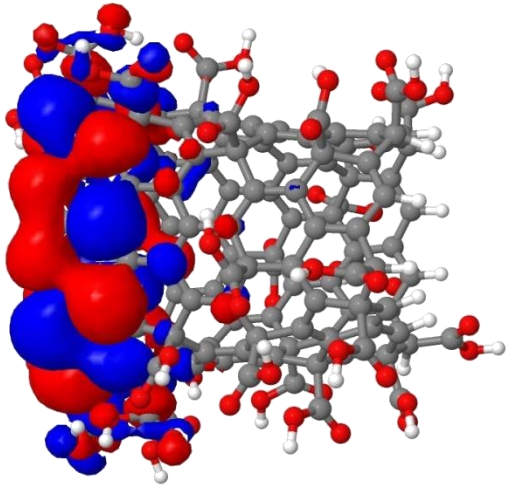
x = 5%



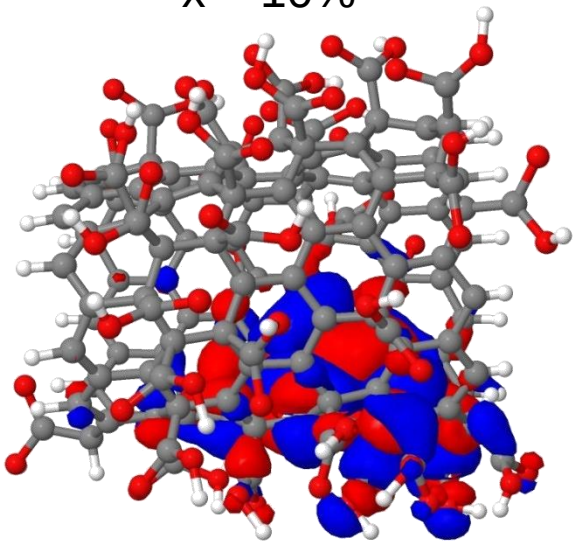
x = 10%



x = 15%



x = 20%



x = 25%

Figure 12 – HOMO of system CNT-$(COOH)_x$ (isovalue = 0.01).

MOLECULAR ORBITALS

LUMO - *Lowest Unoccupied Molecular Orbital*

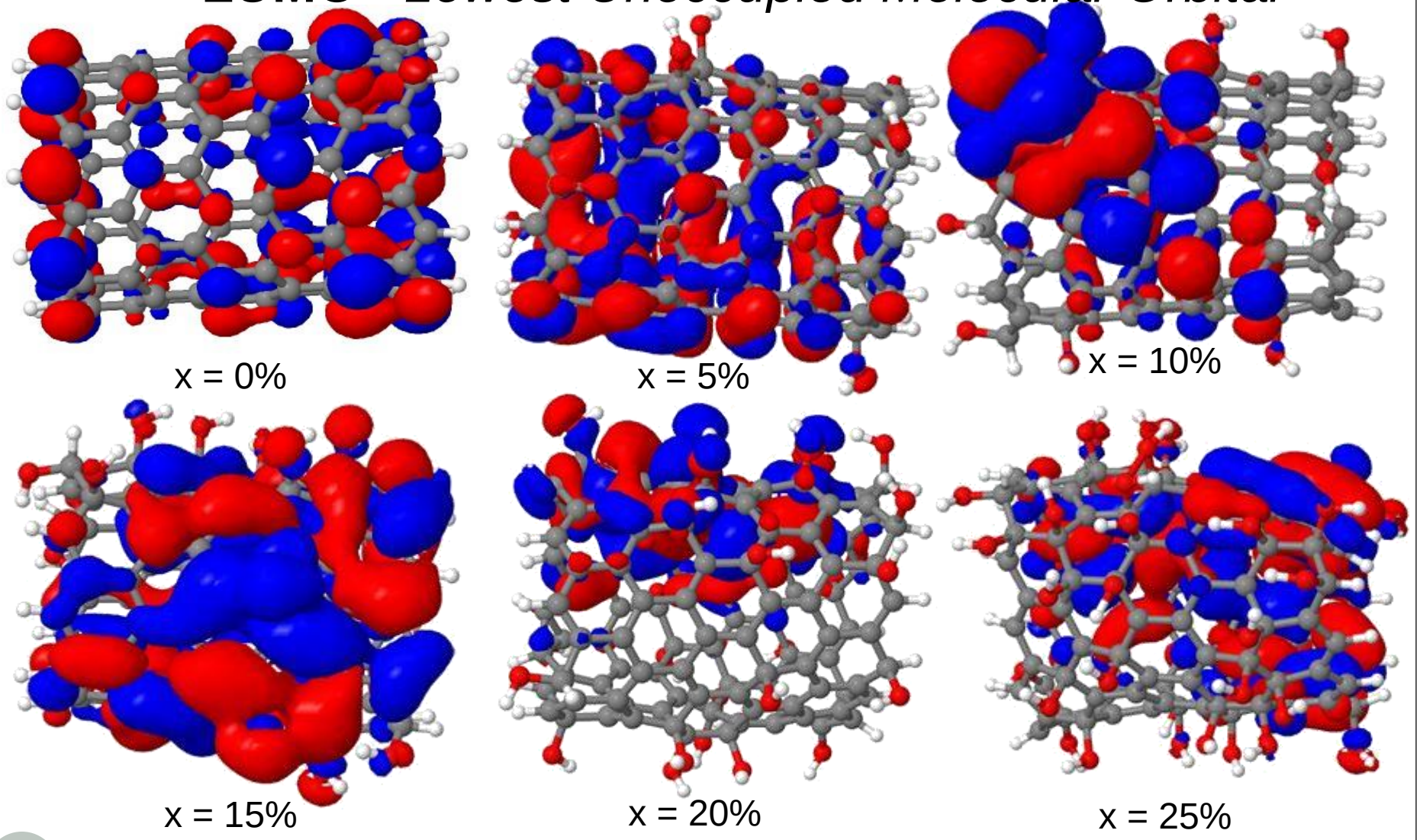
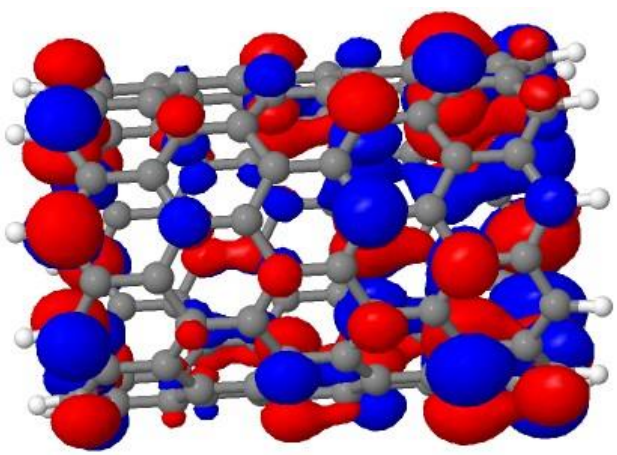


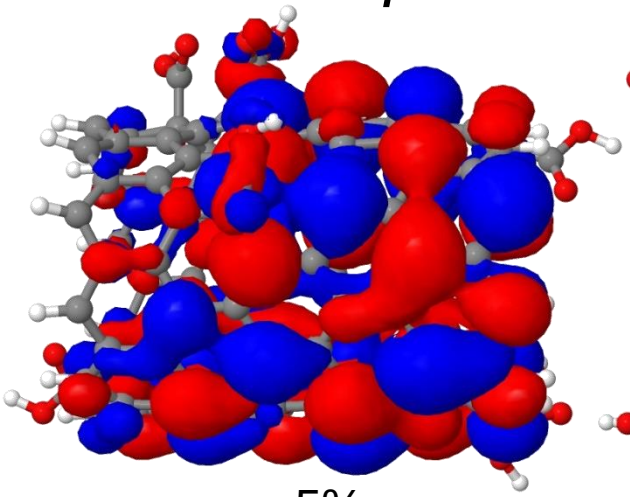
Figure 13 – LUMO of system CNT-$(OH)_x$ (isovalue = 0.01).

MOLECULAR ORBITALS

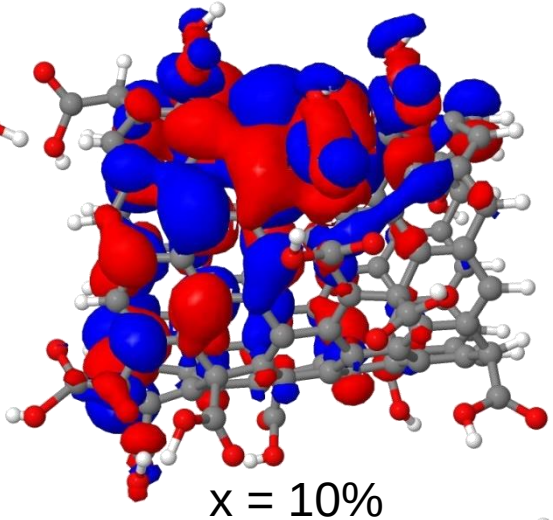
LUMO - *Lowest Unoccupied Molecular Orbital*



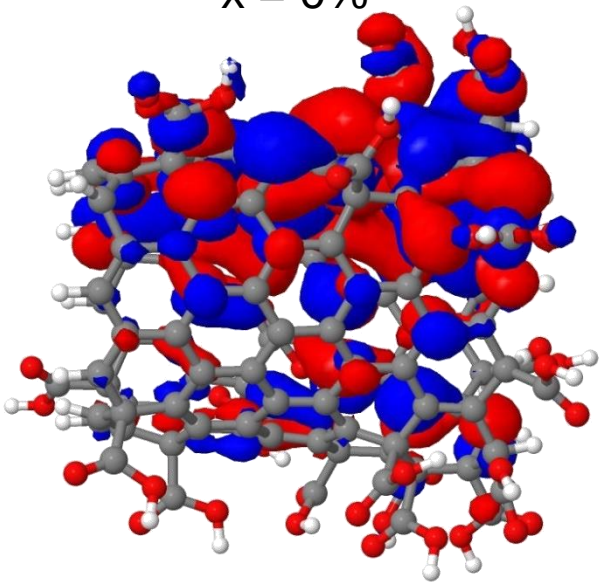
x = 0%



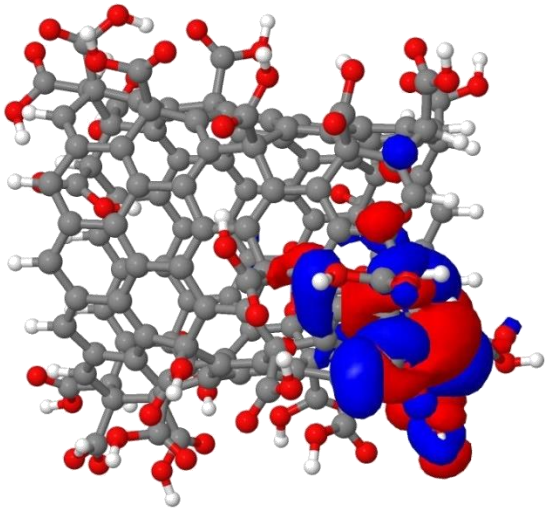
x = 5%



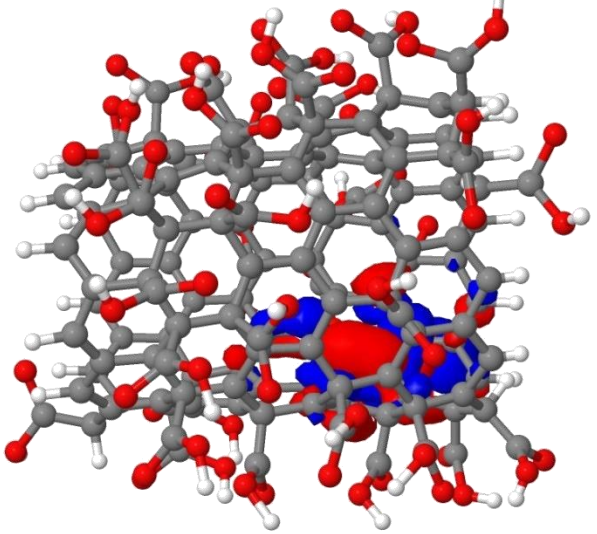
x = 10%



x = 15%



x = 20%



x = 25%

Figure 14 – LUMO of system CNT-$(COOH)_x$ (isovalue = 0.01).

HOMO

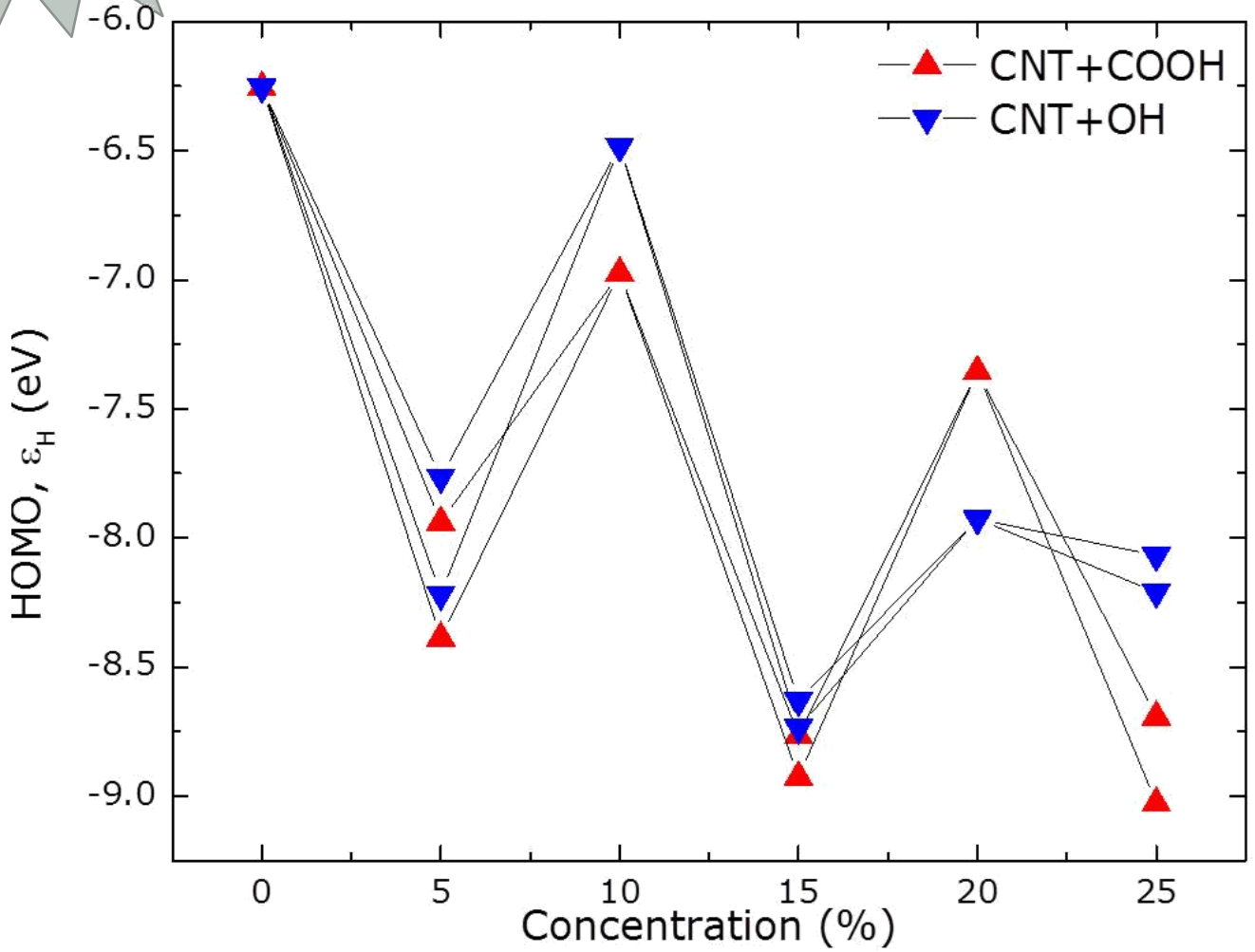


Figure 15 – HOMO energy vs concentration.

LUMO

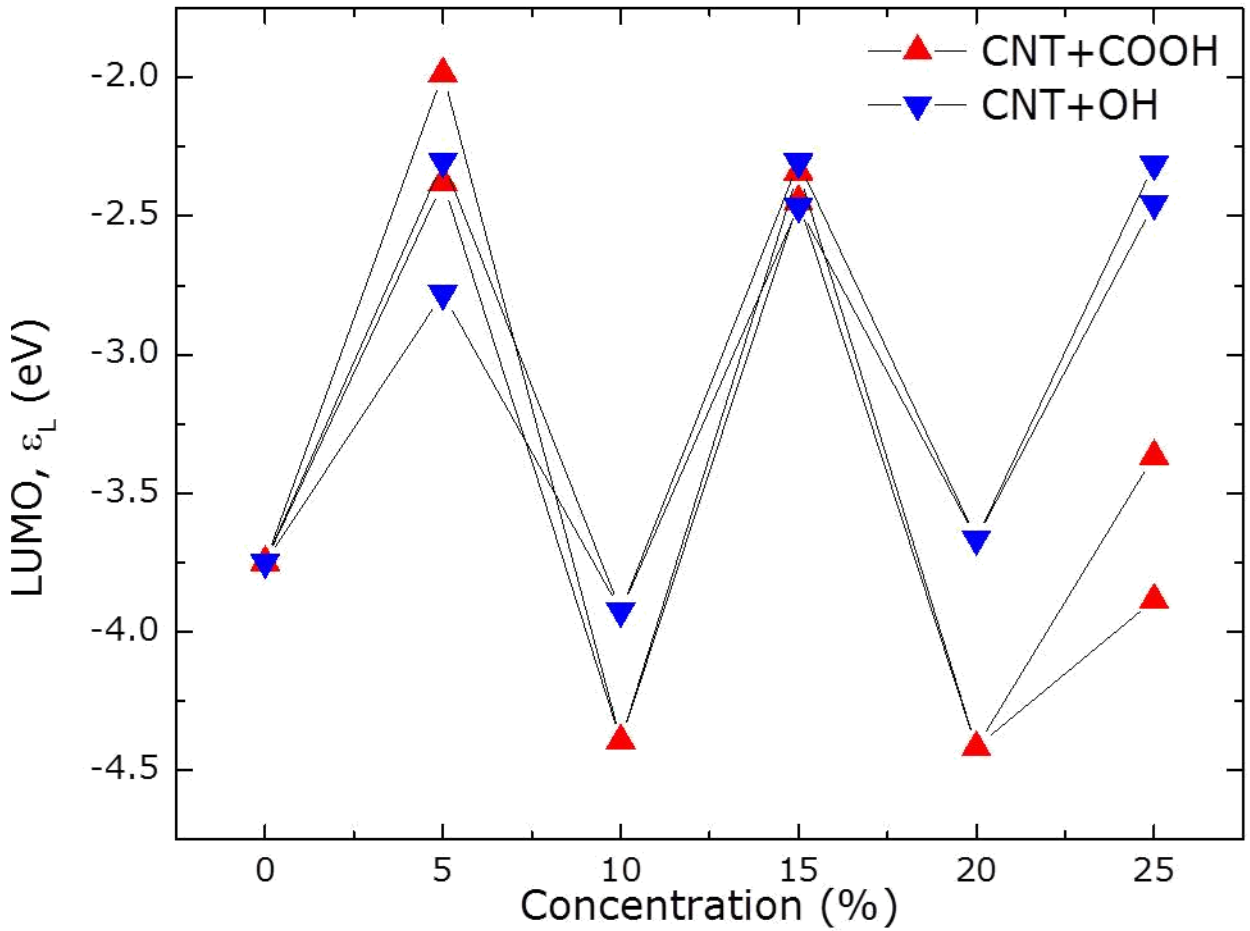


Figure 16 – LUMO energy vs concentration.

GAP

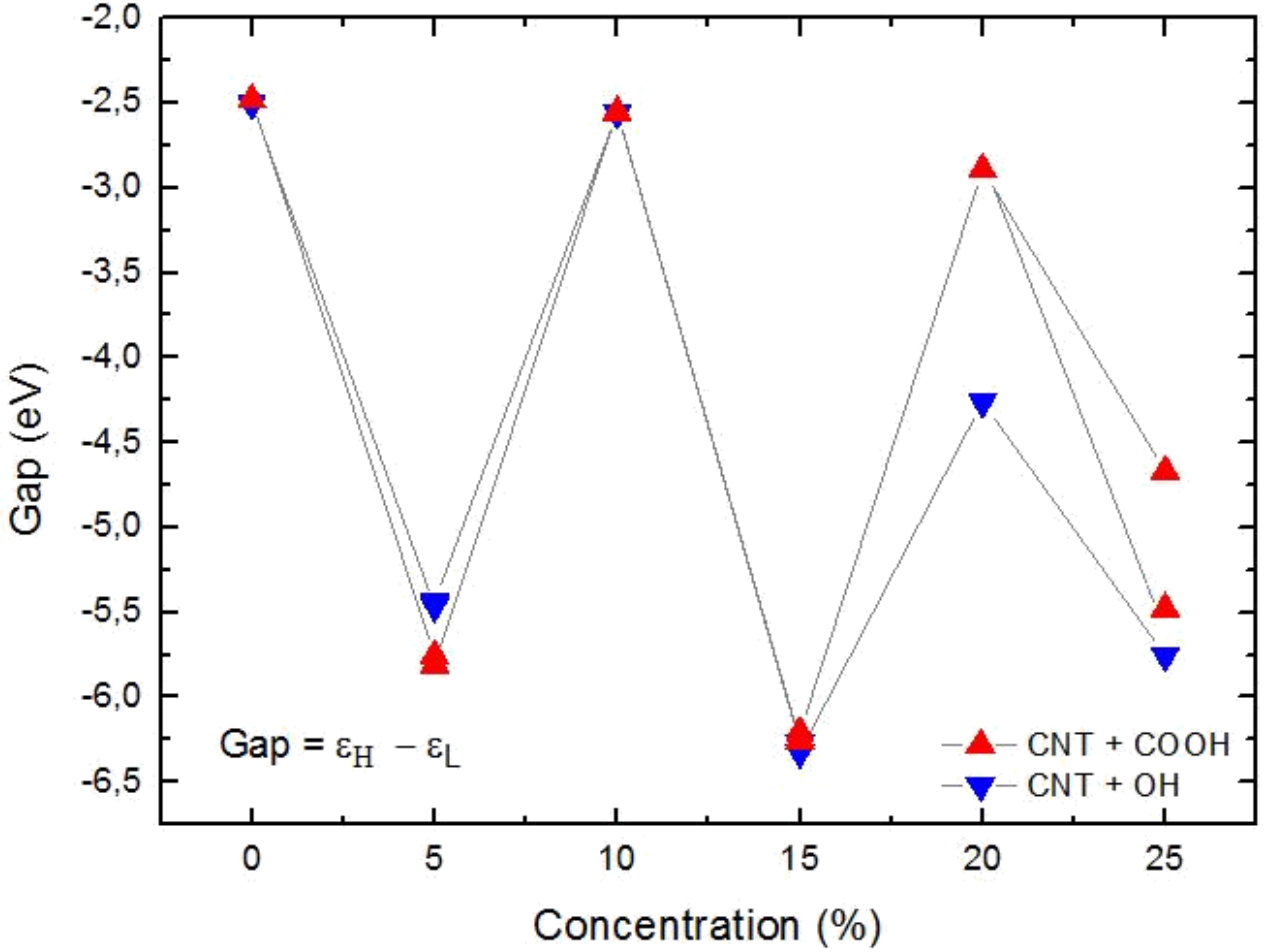


Figure 17 – GAP (HOMO-LUMO) vs concentration.

ELECTRONIC PARAMETERS

Chemical potential (μ)

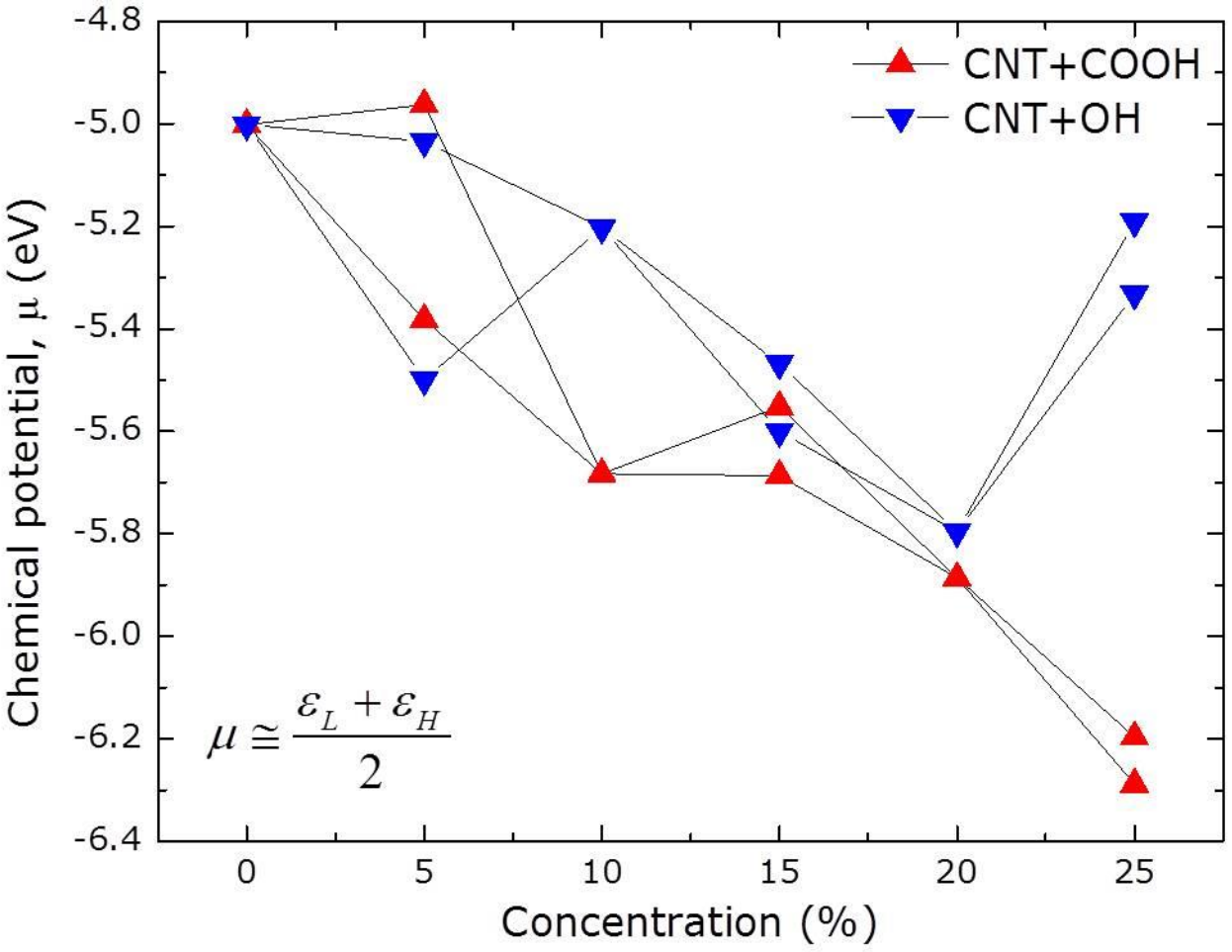
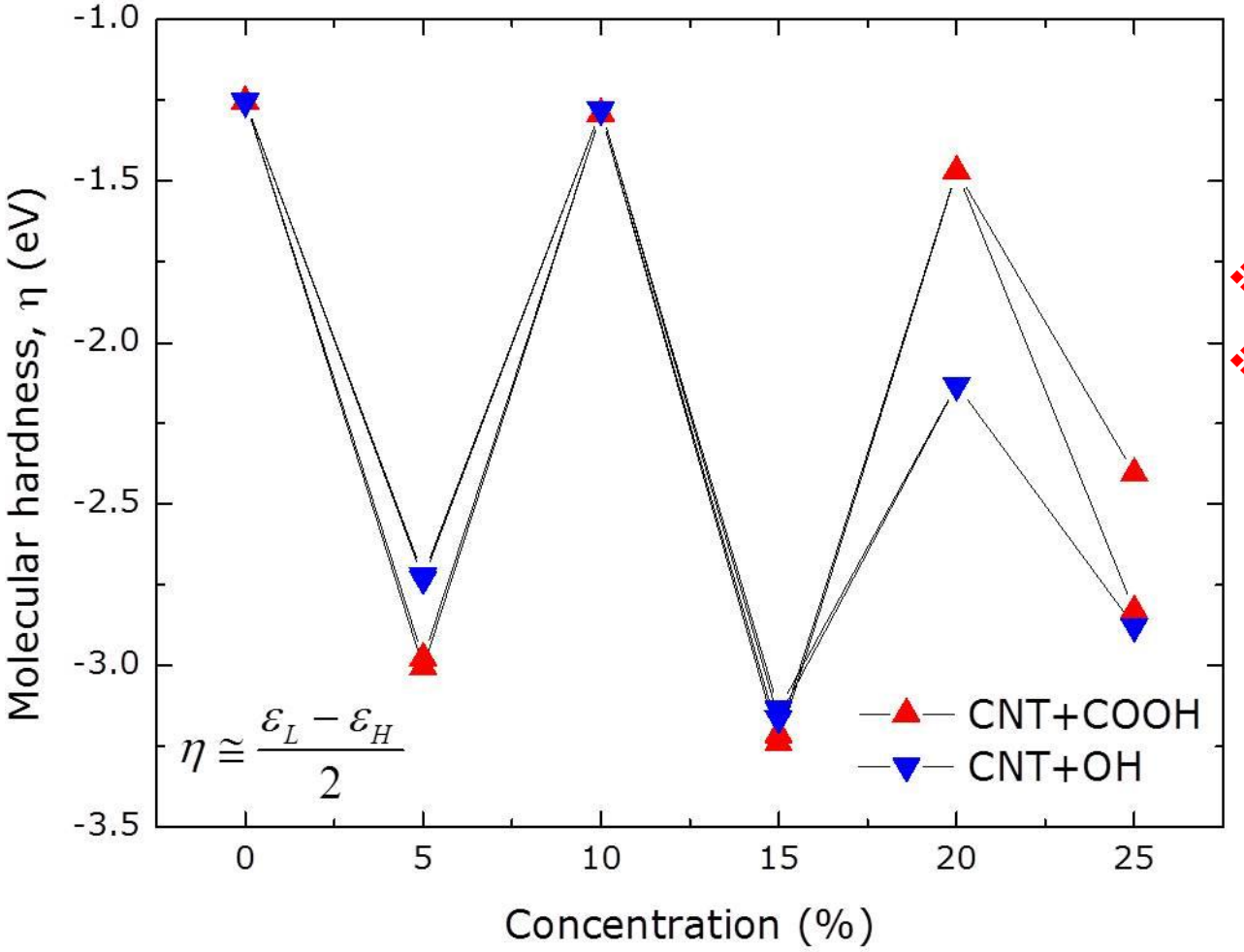


Figure 18 – Chemical potential vs concentration.

PUMACHAGUA, R. et al. Estudio teórico de las propiedades electróicas y estructurales através de la evolución en el ángulo de torsión de CHO-OH, CHS-OH y CHS-SH. *Rev. Soc. Quím. Perú*, v. 75, n. 3, p. 345–352, 2009.

ELECTRONIC PARAMETERS

MOLECULAR HARDNESS (η)



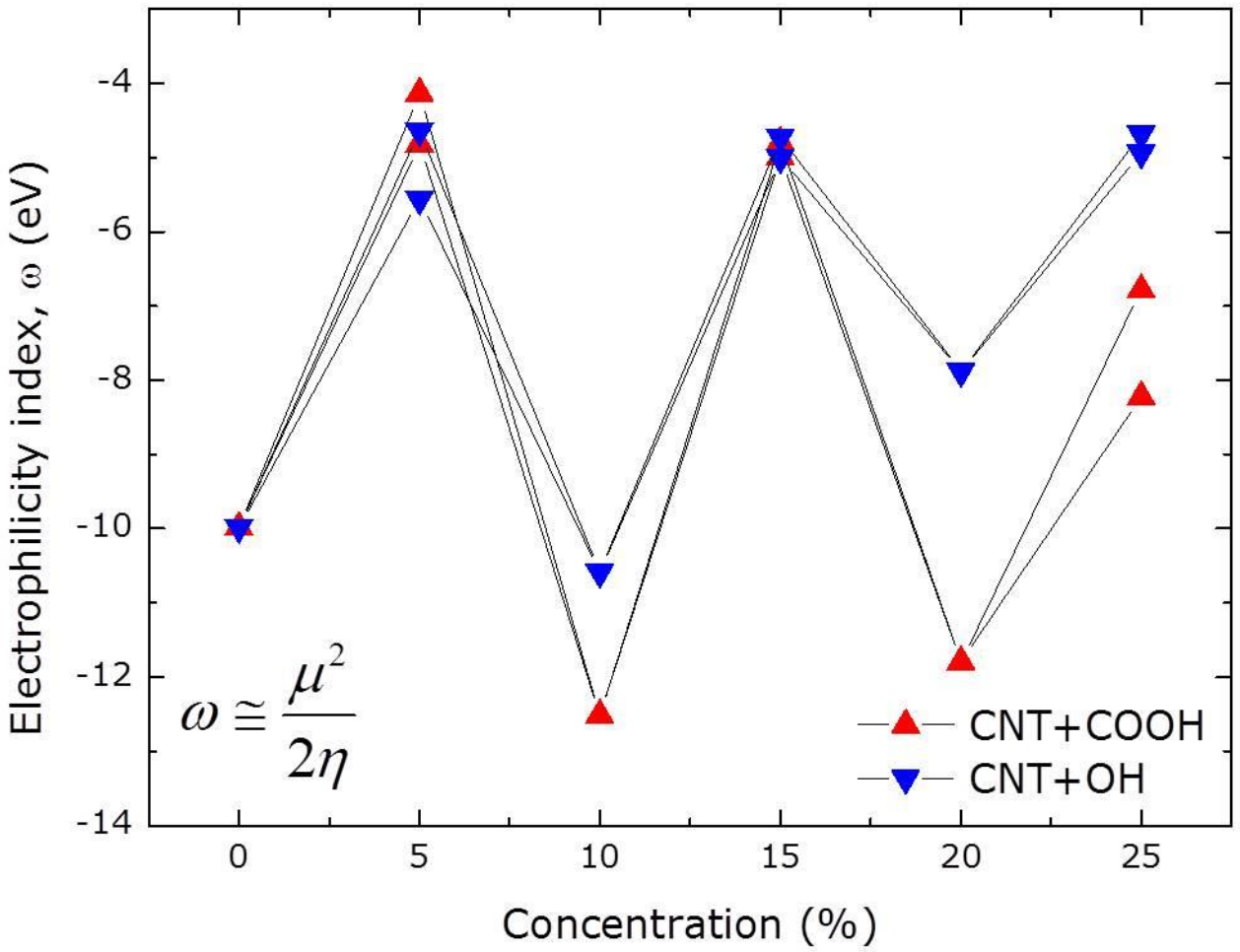
- ↑ Hardness ⇒ ↓ Reativity
- ↓ Hardness ⇒ ↑ Reativity

Figure 19 – Molecular hardness vs concentration.

ARROIO, A.; HONÓRIO, K.M.; SILVA, A. B. F. Propriedades químico-quânticas empregadas em estudos das relações estrutura-atividade. *Quim. Nova*, v. 33, p. 694–699, 2010.
MONCADA, J. L.; MORÁN, G. S. Caracterización de la reactividad intrínseca de los halobencenos en el modelo conceptual de la teoría de funcionales de la densidad (TFD). *Quim. Nova*, v. 31, p. 1255–1258, 2008.

ELECTRONIC PARAMETERS

ELECTROPHILIC INDEX (ω)



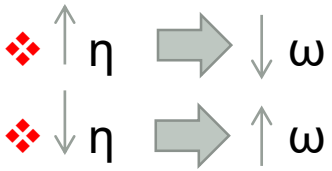
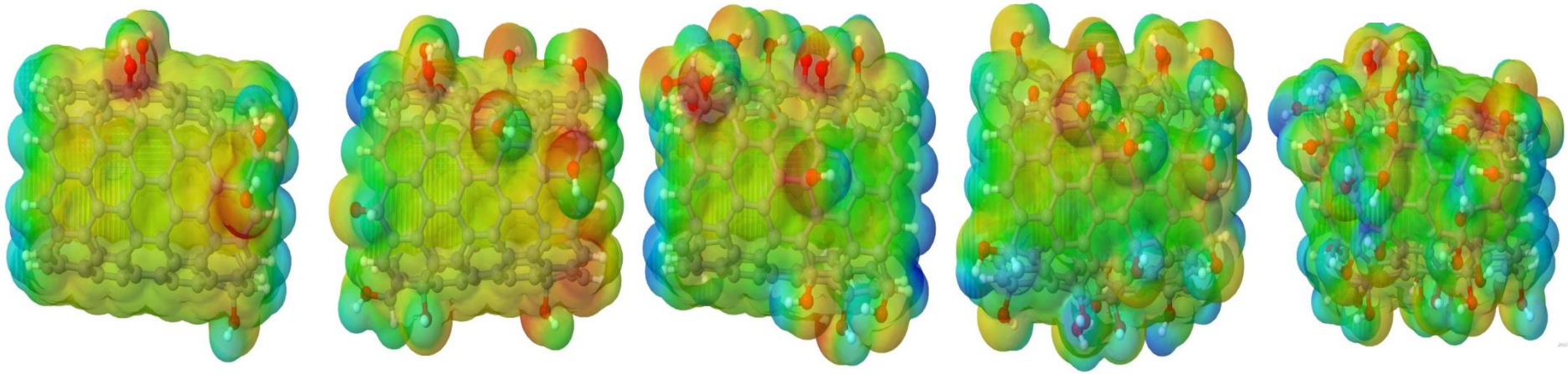


Figure 20 – Electrophilic index vs concentration.

PUMACHAGUA, R. et al. Estudio teórico de las propiedades electrónicas y estructurales a través de la evolución en el ángulo de torsión de CHO-OH, CHS-OH y CHS-SH. *Rev. Soc. Quím. Perú*, v. 75, n. 3, p. 345–352, 2009.

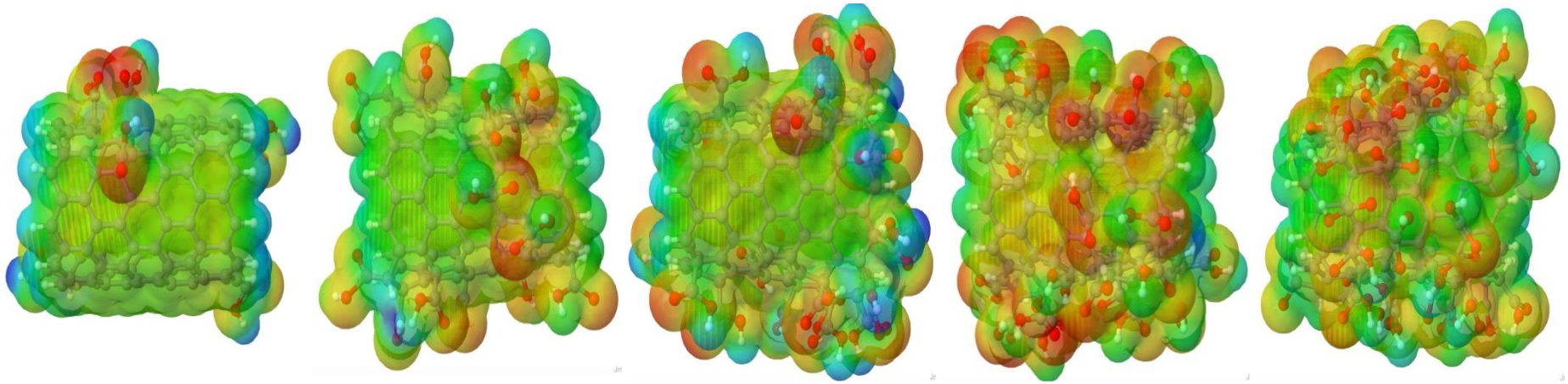
ELECTROSTATIC POTENTIAL

CNT+OH



x = 5% x = 10% x = 15% x = 20% x = 25%

CNT+COOH



x = 5% x = 10% x = 15% x = 20% x = 25%

Figure 21 – Electrostatic potential for systems CNT-$(OH)_x$ and CNT-$(COOH)_x$.

CONCLUSIONS

- Functionalization interval between 0 a 25 %.
- Increase on entropy.
- Optimized structure for each concentration.
- Spin polarization for odd concentrations.
- Functionalized CNTx with 10% more stable. Functionalized with 15% more reactive.
- Electronic parameters for each concentration.
- Oscillatory behavior of electronic parameters.

BIBLIOGRAPHIC

- ARROIO, A.; HONÓRIO, K.M.; SILVA, A. B. F. Propriedades químico-quânticas empregadas em estudos das relações estrutura-atividade. Quim. Nova, v. 33, p. 694–699, 2010.
- BALASUBRAMANIAN, K.; BURGHARD, M. Chemically functionalized carbon nanotubes. Small, v. 1, p. 180–192, 2005.
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