BIO Web of Conferences **129**, 22035 (2024) https://doi.org/10.1051/bioconf/202412922035
EMC 2024

Functionalization of Single-Walled Carbon Nanotubes Analyzed by Spatially-Resolved EELS

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Background incl. aims

Surface functionalization of 1D and 2D nanomaterials is a perfect way for controlling their properties [1-5]. Very detailed structural and chemical composition analyses, at the atomic scale, of such surface modifications are required in order to determine their impact on the electronic/optoelectronic properties. Transmission electron microscopy (TEM) and in particular, spatially-resolved electron energy loss spectroscopy (SR-EELS) developed in an aberration-corrected TEM, is the most powerful technique to get this information. Indeed, having access to a close to 1 angstrom electron probe, the atomic configuration and concentration of the different species of these functionalized nanomaterials can be obtained [1-5]. In this contribution, we report an in-depth study of the atomic configuration of covalent and non-covalent functionalized (pi-stacked and endohedral) single-walled (SW) C-NTs via SR-EELS [5].

Methods

These studies have been developed via spatially-resolved EELS performed using a liquid-nitrogen holder (−170 °C) and Thermo Fisher Scientific Titan Low-Base microscope, working at 80 kV. This microscope is equipped with a Cs probe corrector, a monochromator and an ultra-bright XFEG electron source. The HRTEM studies have been carried out in a Thermo Fisher Scientific Titan Cubed microscope (equipped with a Cs image corrector), under the same cryogenic conditions (−170 °C) and at 80kV.

Results

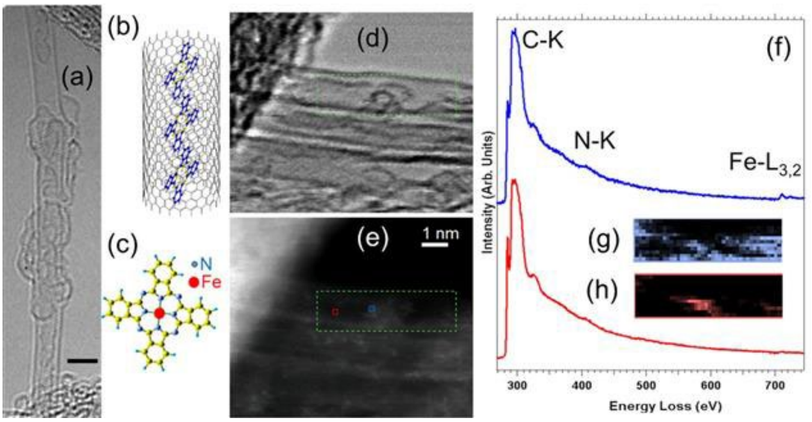
We have investigated different systems of functionalized NTs (covalent and non-covalent (endohedral and pi-stacked)), for getting local information about these different hybrid configurations, studying the chemical environment and bonding of the NTs and the organic moieties [2-5]. Figure 1 illustrates some of these results, in particular the case of endohedral functionalization: iron-phthalocyanine (Fe-Pc) moieties in single-walled nanotubes [5]. Figure 1 (a) corresponds to a HRTEM image of one of these individual filled single-walled C-NTs. Figure 1 (b) displays an atomic-sketch, showing the supramolecular order of the Fe-Pc within a SWNT and Fig. 1 (c) shows an atomic-sketch of one of these Fe-Pc molecules (a Fe atom is surrounded by 4 pyrrolic-like subunits). As it is well known, these NTs tend to be organized in bundles. Figures 1 (d) and (e), which correspond to of STEM (BF and HAADF) micrographs, show one these bundles of SW-CNTs. A 24x12 EELS spectrum-image (SPIM) has been recorded in the green marked area on one of these NT. (f) EEL spectra extracted from the squared regions marked in Fig. 1(e). They correspond to four EEL spectra each of them. C-K, N-K and Fe-L_2,3 edges are clearly seen. From these spectra, nitrogen and iron elemental maps can be obtained, see Fig. 1 (g) and (h). These studies reveal the supramolecular organization of the organic moieties (in this present case showed in this figure, iron-phthalocyanines) used for the functionalization of the NTs [5].

Conclusion
In summary, these works provide very rich information about these hybrid and complex nanomaterials, opening fascinating perspectives for optoelectronic applications of such nano-systems. All these aspects will be discussed in this contribution.

Graphic - Figure: (a) HRTEM micrograph of a SW-CNT filled with iron-phthalocyanine (Fe-Pc) moieties. (b) Atomic-sketch showing the supramolecular order of these Fe-Pc entities within a SW-NT. (c) Atomic-sketch of a Fe-Pc (a Fe atom is surrounded by 4 pyrrolic-like subunits. (d)-(e) BF- and HAADF-STEM images of a bundle of filled SWNT. A SPIM-EELS has been recorded in the green marked area. (f) EEL spectra extracted from the squared regions marked in Fig. 1(e). They correspond to 4 EEL spectra each of them. C-K, N-K and Fe-L2,3 edges are clearly seen. (g)-(h) N and Fe elemental maps. [5]

Funding:
Research supported by the Spanish MICIU (PID2019-104739GB-100/AEI/10.13039/501100011033), the Government of Aragon (DGA) through the project E13_23R and the MICIU with funding from European Union NextGenerationEU (PRTR-C17.I1) promoted by the Government of Aragon.

Graphic:



Keywords:

Functionalization, Nanotubes, Cryo-TEM, STEM-EELS, HR(S)TEM

Reference:

[1] R. Canton-Vitoria, T. Scharl, A. Stergiou, A. Cadranel, R. Arenal, D.M. Guldi, N. Tagmatarchis, Angewandte Chemie Int. 3976-3981 (2020).
[2] A. Setaro, M. Adeli, M. Glaeske, D. Przyrembel, T. Bisswanger, G. Gordeev, M. Weinelt, R. Arenal, R. Haag, S. Reich, Nature Comm. 8, 14281 (2017).
[3] F. Ernst, Z. Gao, R. Arenal, T. Heek, A. Setaro, R. Fernandez-Pacheco, R. Haag, L. Cognet, S. Reich, J. Phys. Chem. C 121, 18887–18891 (2017).
[4] L. Alvarez, et al., J. Phys. Chem. C 119, 5203–5210 (2015).
[5] R. Arenal, L. Alvarez, J.-L. Bantignies, Submitted.