

Study of covalent grafting of Fluorescein Isothiocyanate on double-walled carbon nanotubes

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Abstract

Over the past decades the popularity of Carbon nanotubes (CNTs) rose drastically and made them the subject of an intense research effort. Nowadays, new applications for CNTs are found each year, leading to foresee an increase of their production and their use for new nanomaterials. Therefore, it became not only legitimate but also necessary to study their toxicity and environmental impact.

The use of those CNTs always requires their dispersion which is generally obtained through their functionalization. In the case of covalent grafting, the question of the competition between real grafting and simple adsorption (also likely to happen) is very relevant and has never been really investigated in a rigorous way. This question is however a central one in many current debates, and especially in the field of nanotoxicology and biomedical applications [1a-l] of CNTs, where their functionalization by fluorophores is used to track the latter inside cells. The visualization of the fluorescence is then naturally associated to that of the CNTs. However, fundamental questions are raised as there is no simple evidence that a fluorescent molecule simply adsorbed onto a CNT will indefinitely stay there once inside a cell. In order to answer those questions we chose to deeply investigate the covalent grafting of the Fluorescein Isothiocyanate (FITC, fluorophore commonly used for toxicity studies) onto Double-walled carbon nanotubes (DWCNTs) [2]. The aim of the work presented here is to fully understand the mechanisms involved behind the three steps of the functionalization process (1- Carboxylation of the DWCNTs, 2- Grafting of 1,4-diaminobutane as a linker, 3- Grafting of FITC) [3][4], by using different experimental techniques such as Transmission Electronic Microscopy, Raman spectroscopy, X-ray Photo-electron Spectroscopy and Neutron Vibrational spectroscopy. The preliminary results obtained with XPS and Neutron spectroscopy already seem to indicate that both covalent and non-covalent grafting happen while the functionalization process. In addition to the combination of those techniques, DFT calculations are performed, expecting deriving quantitative information and distinguish between simple adsorption and covalent grafting for a given molecule.

References

- [1a] C. Salvador-Morales, E. Flahaut, et al., *Molecular Immunology*, 43, (3), (2006), 193 ; [1b] E. Flahaut, et al., *Carbon*, 44, (6), (2006), 1093; [1c] J. Cheng, E. Flahaut, S. H. Cheng, *Environmental Toxicology and Chemistry*, 26, (4), (2007), 708 ; [1d] F. Mouchet, P. Landois, E. Flahaut et al., *Nanotoxicology*, 1, (2), (2007), 149 ; [1e] F. Mouchet, et al., *Aquatic Toxicology*, 87, (2), (2008), 127 ; [1f] F. Mouchet, et al., *Nanomedicine*, 5, (6), (2010), 963; [1g] K. W. Kwok, et al., *Nanomedicine*, 5, (6), (2010), 951 ; [1h] D. Crouzier, et al., *Toxicology*, 272, (1-3), (2010), 39; [1i] V. Neves, et al., *Adv. Funct. Mater.*, 20, (19), (2010), 3272 ; [1j] V. Sanz, et al., *Carbon*, 49, (15), (2011), 5348 ; [1k] E. Meunier, et al., *Nanomedicine*, 8, (6), (2012), 987 (DOI:10.1016/j.nano.2011.11.004); [1l] V. Neves, et al., *Nano Research*, 5
- [2] E. Flahaut et al., *Chem. Commun.*, (2003), 1442-1443
- [3] T. Bortolamiol et al. Double-walled carbon nanotubes: Quantitative purification assessment, balance between purification and degradation and solution filling as an evidence of opening. *Carbon* 78, 79–90 (2014).
- [4] T. Bortolamiol. Nanotubes de carbone biparois : fonctionnalisation et détection in vitro. (Université Paul Sabatier).