

Ultra-Short Carbon Nanotubes as Novel Biotracers

R. Faes¹, L. Cognet², C. Jaillet-Bartholome¹, B. Lounis², L. Oudjedi² and P. Poulin¹

¹ Centre de Recherche Paul Pascal CNRS UPR 8641, France

² Laboratoire Photonique Numérique et Nanoscience, Université de Bordeaux, France
faes@crpp-bordeaux.cnrs.fr

Abstract

Ideal optical tracers for bioimaging should be nanosized, biocompatible and visualizable in nearIR wavelengths that can penetrate within biological tissues. Conventional fluorescent molecular labels are not active in the nearIR spectrum. Carbon nanotubes exhibit suitable optical properties and also strongly absorb nearIR irradiation. They can therefore be visualized via photothermal effects [1] in addition to photoluminescence. Unfortunately available nanotubes are generally too long (length>100nm) for bioimaging applications. In this context, ultra-short carbon nanotubes (CNTs) would offer a unique opportunity to become a novel type of highly efficient biolabels. We develop in this work ultra-short CNTs and their biofunctionalization, for a use as nearIR nanolabels. We target in particular the achievement of nanotubes shorter than 100 nm that can be visualized by photothermal spectroscopy [1] or photoluminescence. Ultrashort nanotubes are prepared by strong sonication treatments known to be efficient at cutting CNTs [2], chemical treatments [3] and sorted by length using Density Gradient Ultracentrifugation (DGU) [4].

The UV-vis-NIR absorption spectra of several fractions are shown in Fig. 1. The absorption peaks in 900-1300 nm range are due to the lowest E_{11} subband transitions. Multiple peaks corresponding to various semiconducting SWNTs are present in the sample. Both first and second subband absorption peaks show blue shifts as the average nanotube length is reduced. The shift is monotonic: shorter fractions show stronger blue shift. We can attribute the observed length-dependent spectra blue shifts of SWCNTs to finite length effects, that are due to quantum confinement along the SWCNT length [5].

The spectral shifts ΔE_{11} can be calculated using the following expression :

$$E = \frac{hc}{\lambda} \text{ thus } \Delta E(\text{eV}) = \frac{1240}{\lambda_2} - \frac{1240}{\lambda_1}$$

where ΔE is the spectral shift in electron-volts, and λ_2 and λ_1 are the wavelengths associated CNTs of a given chirality. We found high spectral shifts for the upper fractions of the vial after DGU process as shown in Fig. 2. This can be correlated to the theoretical estimation of the length :

$$\Delta E = \frac{(\hbar^2 \times k_{z1}^2)}{2m^*} = \frac{\hbar^2}{2m^*} \times \frac{\pi^2}{L^2}$$

with \hbar the reduced Planck constant, m^* the mass of the exciton, k_{z1} the quantization of wave vector along the length of the tube and L the length of the tube.

This theoretical estimation is confirmed by qualitative tapping mode AFM images of different fractions (Fig. 3). The shortened SWCNTs are identified as less than 15 nm for the fraction F, whereas their original length was approximately 1-2 μm . The CNTs showed an average length of 45 nm for the fraction F, whereas the average length for the fraction N was 812 nm.

Different approaches are used to functionalize ultra-short CNTs : on one hand the covalent functionalization for photothermic spectroscopy, and on the other hand the non-covalent functionalization, with molecules such as pyrene butyric succinimide, for the preservation of the luminescence properties.

Finally, biological tests will be performed by the "Laboratoire de la Synapse" at Bordeaux to image the plasticity of synapsis of glutamate receptors.

References

- [1] Berciaud S., Cognet. L., Poulin P., Weisman B., Lounis B., Nano Letters, **7** (2007) 1203-1207.
- [2] Lucas A., Zakri C., Maugey M., Pasquali M., Van der Schoot P., Poulin P., The Journal of Physical Chemistry C, **113** (2009) 20599-20605.
- [3] Price B. K., Lomeda J.R., and Tour J.M., Chemistry of Materials, **21** (2009) 3917-3923.

[4] Sun X., Zaric S., Daranciang D., Welsher K., Lu Y., Li X. and Dai H., The Journal of the American Chemical Society, 130 (2008) 6551-6555.

[5] Wu, J.; Duan, W. H.; Gu, B. L.; Yu, J. Z.; Kawazoe, Y. Appl. Phys. Lett., 77 (2000) 2554–2556.

Figures

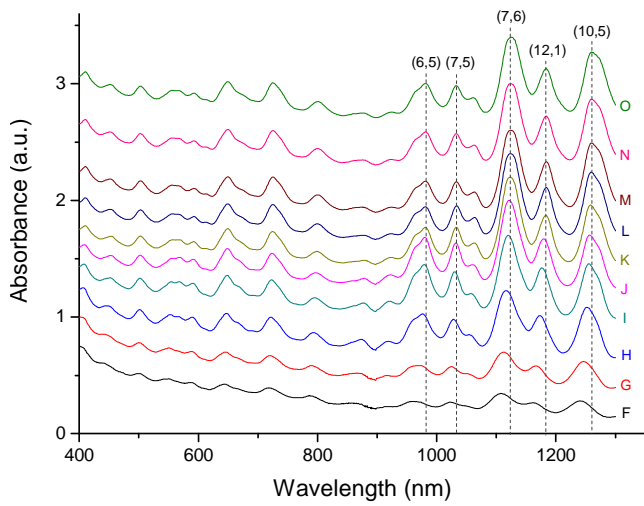


Fig. 1 UV-Vis-IR measurements of different fractions of CNTs sorted by DGU. The CNT length is increasing from the bottom (F) to the top (O).

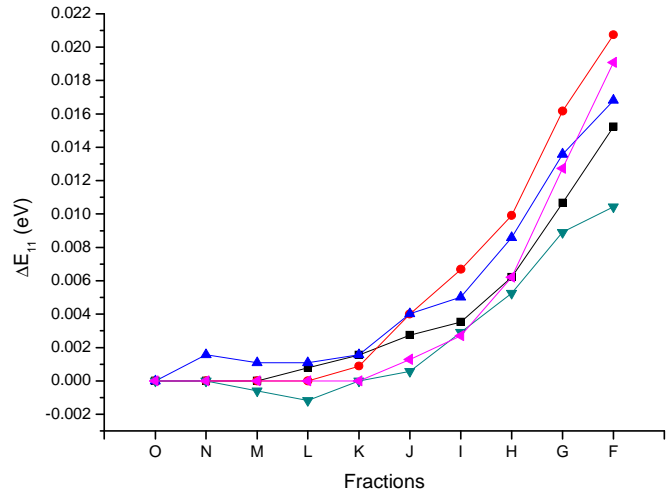


Fig. 2 Spectral shifts ΔE_{11} for the upper fractions, calculated from the different CNTs chiralities ((10,5) in black, (12,1) in red, (7,6) in blue, (7,5) in Green and (6,5) in pink).

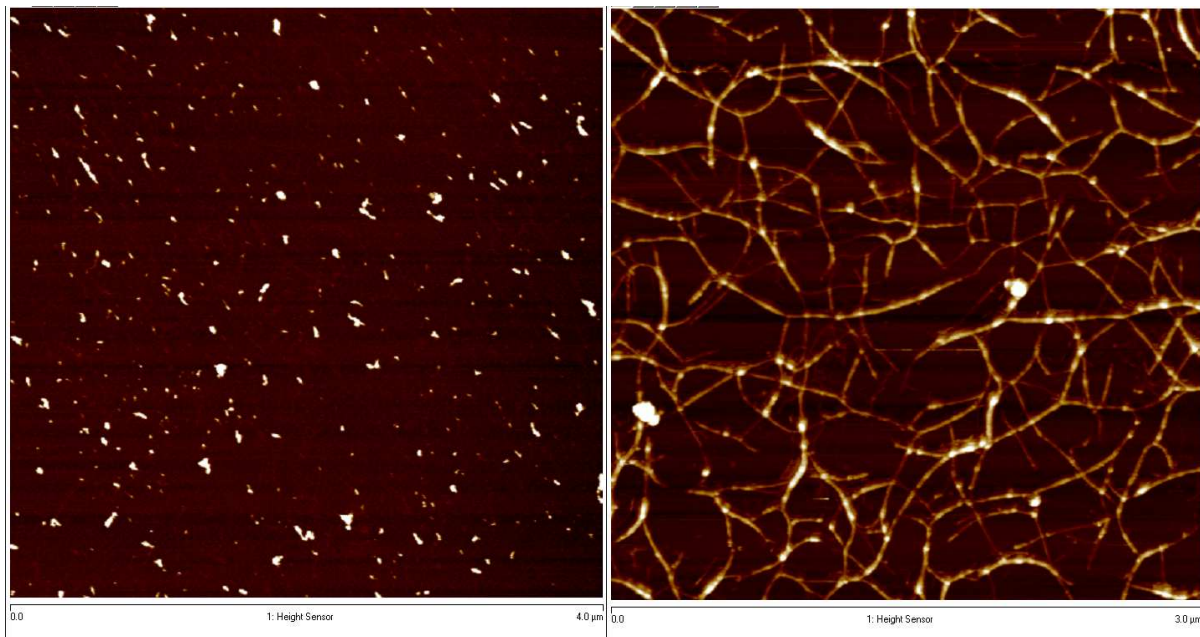


Fig. 3 AFM image of spin-coated CNTs fraction F (left) and fraction N (right) onto mica substrate.