SP12 Ultracentrifugal sorting of empty and water-filled carbon nanotubes: in situ 2D fluorescence-excitation and Raman spectroscopy

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Since the pioneering work of Arnold *et al.* [1], density gradient ultracentrifugation (DGU) has emerged as an extremely versatile technique for the sorting of carbon nanotubes (CNTs) by diameter/chirality, electronic type (metal/semiconductor), length and even enantiomers, even though the mechanisms are not yet fully understood. For example, counter-intuitively it is found, in nearly all DGU studies, that increasing diameters possess increasing densities. We have recently shown that this is due to the presence of water-filled CNTs.[2] The intact (and therefore empty) CNTs can be isolated from the filled ones and follow the intuitive sorting order, moreover allowing an enhanced structure sorting by DGU.[2] Also the specific surfactant choice can have a significant effect on the diameter sorting.

In this paper we present 2D wavelength-dependent fluorescence-excitation and Raman spectra measured directly after DGU, in situ, as a function of height, in the centrifuge tube. As such, very detailed information on the chirality-density relation is obtained, allowing for studying and optimizing the DGU sorting process. We will in particular discuss the different sorting for two commonly used surfactants, sodium cholate and sodium deoxycholate, [3] which only differ by one hydroxyl group but result in very different diameter-density dependencies.

[1] M S Arnold *et al.,* Nature Nano 1 (2006) 60
[2] S Cambré *et al.,* Angew Chem Int Ed 50 (2011) 2764
[3] W Wenseleers *et al.,* Adv Funct Mater 14 (2004) 1105

SP13 Resonant Raman spectroscopy of nitrogen-doped single-walled carbon nanotubes (N-SWNT)

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Vertically aligned nitrogen-doped single-walled carbon nanotubes (N-SWNT) were investigated via resonant Raman spectroscopy. In order to have a basis for comparison, two samples were used in the experiments: one grown with pure ethanol (SWNT) and another one grown with a mixture of ethanol/acetonitrile as feedstock (N-SWNT) [1]. Different laser energies in the ultraviolet, infrared and visible ranges (from 1.53 to 3.8 eV), were used to excite the sample and investigate its resonant behaviour. In order to create a map of the transition energy versus the radial breathing mode frequency, tuneable lasers were employed and a Raman spectrum was acquired every 2nm.

The effects of the incorporation of nitrogen on the electronic and phonon structures were studied. Despite the low amount of nitrogen incorporated (0.2%), shifts in the optical transitions of the nanotubes were detected, showing modifications in the electronic properties upon doping. Additionally, the D and G' bands dispersive behaviour was studied.

[1] T. Thurakitseree, C. Kramberger, P. Zhao, S. Aikawa, S. Harish, S. Chiashi, E. Einarsson, S. Maruyama, Carbon 50 (2012) 2635-2640