NON-COVALENT FUNCTIONALIZATION OF SINGLE-WALL CARBON NANOTUBES TO IMPROVE WATER-SOLUBILITY

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Single-wall carbon nanotubes (SWNTs) are well-ordered all-carbon graphitic nanomaterials with a one-dimensional cylinder structure. They are of high surface area, high mechanical strength but ultra-light weight, unique electronic properties and excellent chemical and thermal stability, which makes them potential building blocks in nanoscale bioapplications. The focus of current research has been in the development of biosensor materials based on carbon nanotubes, as there is experimental evidence that biomolecules (proteins, carbohydrates and nucleic acids) can be immobilized either on the surface or in the hollow cavity of nanotubes.

The major technical obstacle in the research of nanotube bioconjugates has been the intrinsic insolubility of SWNTs in aqueous media and the difficulties in exfoliating SWNT bundles into isolated tubes. By non-covalent modification it is possible to introduce functional groups on SWNT surfaces without disrupting the hexagonal sp^2 carbon network. The most important factors when evaluating the water-solubility of modified nanotubes are the extent of functionalization, water-solubility of adsorbed species and the strength of interactions between adsorbates and nanotubes. Recently, different polyaromatic molecules have been shown to adsorb on SWNT sidewalls through $\pi - \pi$ interactions [1-4].

We have studied the capability of several ionic pyrene and naphthalene derivatives to adsorb on SWNTs and to improve their water-solubility (fig.1). SWNTs used in this work have been synthesized by the HiPco process and purified with a thermal oxidation – acid extraction cycle. The modification procedure involves ultrasonication to disperse nanotubes and dialysis to remove unattached adsorbate molecules. The solubility of modified SWNTs is in the range 0.1 – 0.3 g/L, and the solutions are usually stable for several months (fig.2).

Modified SWNTs have been characterized with UV-Vis-NIR, Resonance Raman and XPS spectroscopy. The number of sp^3 defects on tube walls has not been found to increase upon functionalization, which shows that interactions are non-covalent in nature. An adsorption mechanism based on charge-transfer from adsorbates to SWNTs is postulated based on the observed upshifts in the C 1s core level spectra.

The ionic charge densities on modified SWNTs have been calculated from atomic concentrations determined by XPS and found to be almost independent from the size of adsorbate (0.07 – 0.11 ionic charges per one aromatic ring on SWNT surface). Based on this observation, we suggest that the attachment of ionic functionalities on SWNTs is primarily limited by electrostatic repulsion between adjacent charges and not by the molecular size of adsorbed species. Hence, in order to achieve maximal improvement in water-solubility, adsorbates should be small in size but still capable of sufficiently strong interaction with nanotubes to ensure stability.

References:

[1] R. J. Chen, Y. Zhang, D. Wang, H. Dai, J. Am. Chem. Soc., **123** (2001) 3838.
[2] N. Nakashima, Y. Tomonari, H. Murakami, Chem. Lett., **31** (2002) 638.
[3] H. Xin, A. T. Woolley, J. Am. Chem. Soc., **125** (2003) 8710.
[4] J. Zhang, J.-K. Lee, Y. Wu, R. W. Murray, Nano Lett., **3** (2003) 403.

Figures:

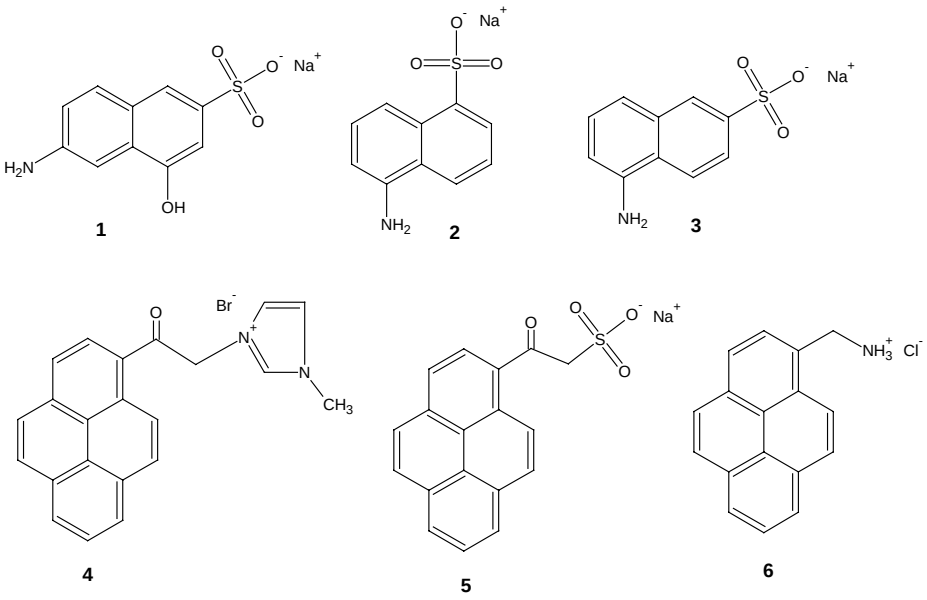

Figure 1. Structures of the polyaromatic adsorbates **1** – **6** used in this work.

Figure 2. From left: Aqueous solutions of SWNT-**4**, SWNT-**3**, SWNT-**5** and SWNT-**1**, prepared 1 – 6 weeks before imaging.