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Effects of Oxidation and Chlorination Steps of HiPco Single-walled Carbon Nanotubes Revealed by XPS, TGA-MS and HR-TEM Studies

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One strategy to covalently functionalize single-walled carbon nanotubes (SWCNTs) is to oxidize the side-walls by an acidic treatment step to create COOH carboxylic functions and then convert these functions to COCl groups by reacting with SOCl2. The acid chloride functions can subsequently be reacted with many different grafting groups and offer great flexibility in terms of chemistry on tubes. However, the control of the functionalization process, i.e. the control of the number of covalent defects and the efficiency of the overall grafting process without destroying the intrinsic electronic and mechanical properties of CNTs, requires estimating the number of defects created at each step. In the present work, different oxidative conditions have been used to create SWCNTs with different kinds and densities of oxidized functions. A HiPco sample from NanoIntegris (SuperpureTM grade, highly purified sample), was used as one of the best starting materials commercially available on the market. The use of such a clean sample, with less than 2% of metallic impurities and less than 5% of carbonaceous impurities, is absolutely essential in order to obtain reliable results for quantitative analysis. This allowed us to quantify the number of created defects by spectroscopic, thermal and microscopic techniques, especially X-Ray photoelectron spectroscopy (XPS), thermogravimetric analysis coupled with mass spectrometry (TGA-MS) and high-resolution transmission electron microscopy (HR-TEM) associated with energy-dispersive X-ray spectroscopy (EDS). After the chlorination step with SOCl2, these techniques quantified the number of chlorine atoms grafted on the CNT side-walls. Finally, a grafting reaction with ferrocene derivatives and other electro-active groups was also successfully done on these samples. These functionalized CNTs were deposited on a glassy carbon electrode and cyclic voltammetry was used to evaluate the electrochemical activity of this modified electrode toward electron shuttle of biological interest such as nicotinamide adenine dinucleotide (NADH). The combination of techniques used in this study enabled estimating the level of functionalization at each step of the process, which gives a strong rationale for the optimization of such CNT treatment.