Nanobud - Novel Carbon Nanomaterial: Coating Nanotubes with Fullerenes

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Both fullerenes and single-walled carbon nanotubes (CNTs) are of great interest since they exhibit unique and useful chemical and physical properties. We have discovered a novel hybrid nanomaterial combining these structures, i.e. consisting of fullerenes covalently attached to the outside surface of CNTs, called fullerene-functionalised CNTs [1] . Two one-step, continuous methods for their selective synthesis have been developed: using pre-made iron catalyst particles by a hot wire generator method and particles grown in situ via ferrocene vapour decomposition in the presence of CO and trace amounts of H2O and CO2 etching agents. Fullerenes are formed on the surfaces of aerosol iron particles together with CNTs during carbon monoxide catalytic disproportionation under the influence of trace concentrations of CO2 and H2O. TEM images at low magnifications originally suggested that most synthesised nanotubes have an "amorphous coating". However, careful investigations revealed that much of the coating is, in fact, composed of fullerenes. Their spherical nature has been confirmed by tilting samples within a HR-TEM. Statistical size measurements of fullerenes performed on the basis of HR-TEM images revealed that the majority of fullerenes consists of C42 and C60. Interestingly, evidence of C20 fullerenes, the smallest possible dodecahedra is found. For an independent characterization of the structures in question, we performed Ultraviolet-visible (UV-vis), Raman, and Fourier Transform Infrared (FT-IR) spectroscopic and Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectrometric measurements. Raman spectra show a pronounced G-band at 1600 cm-1 associated with CNTs, and a weak D-band at 1320-1350 cm-1. In addition, characteristic features associated with fullerenes were observed. The main peaks in MALDI-TOF spectrum are attributed to C60 (C60H2, C60H2O) and C42 (C42COO) fullerenes. Accordingly, fullerenes are attached to CNTs via either oxygen (preferable for fullerenes larger than C54) or carboxylic (for smaller fullerenes) bridges, which was confirmed by FT-IR measurements. Atomistic density-functional-theory based calculations showed that systems composed of fullerenes and nanotubes with single vacancies covalently functionalized through ester groups can indeed exist, although being metastable with respect to forming a perfect tube and oxidized fullerenes. Calculations indicate that in addition to oxygen-based bridges, some fullerenes might be directly covalently bonded to CNTs or even make hybrid structures. This novel material showed very high cold electron field emission efficiency with a current density of 189 μA/cm2 at the electric field strength as low as 1.26 V/μm. STM experiments were carried out to map local DOS showing fullerene to modify locally the bands, and to verify the strong fullerene bonding to SWCNT. We present mechanistic investigations on both SWCNT as well as CNB formation mechanisms [2]. Methods for both CNB and SWCNT dry deposition at ambient temperature to manufacture transparent thin film field effect transistor (TFT) with high carrier mobility and transparent, flexible thin film conductor (TFC) with sheet resistance comparable to high temperature deposited ITO will be discussed. The control of parent nanotube diameter distributions with floating catalyst reactor operation conditions will be discussed, based on optical absorption characterization of thin film samples. Combined Raman and TEM studies of an individual nanobud will be presented [3].

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[2]. A.G. Nasibulin, A. S. Anisimov, P. V. Pikhitsa, H. Jiang, D. P. Brown, M. Choi, and E. I. Kauppinen, Investigations of NanoBud formation. Chemical Physics Letters, 446 (2007) 109–114.

[3]. Y. Tian, D. Chassaing, A.G. Nasibulin, P. Ayala, H. Jiang, A. S. Anisimov, E. I. Kauppinen (2008) Combined Raman Spectroscopy and Transmission Electron Microscopy Studies of a NanoBud Structure. J. American Chemical Society. 130, 7188–7189.