Carbon Nanotubes and NanoBuds – Synthesis, Structure, Functionalisation and Dry Deposition for TCE and TFT Applications

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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. 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 H_2O and CO_2 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 CO_2 and H_2O. 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 C_{42} and C_{60}. Interestingly, evidence of C_{20} 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, based on Raman of individual CNB also observed with HR-TEM and electron diffraction. The main peaks in MALDI-TOF spectrum are attributed to C_{60} ($C_{60}H_2$, $C_{60}H_2O$) and C_{42} ($C_{42}COO$) fullerenes. Accordingly, fullerenes are attached to CNTs via either oxygen (preferable for fullerenes larger than C_{54}) 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 $\mu A/cm^2$ at 1.26 $V/\mu m$. 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. Interestingly, STM of SWCNTs show high crystallinity, with large difficulty of finding defects. HR-TEM studies when heading samples inside TEM up to 500 C will be discussed. We present preliminary results of selective CNB fullerene reaction with amines. Methods for CNB and SWCNT dry deposition at ambient temperature for transparent, flexible field effect transistor (TFT) and conducting electrode applications (TCE) will be discussed. TCEs with sheet resistance below 50 ohm/sq sheet resistance at 80 % transparency for 550 nm photons, as well TFTs with carrier mobilities similar to single crystalline semiconductor polymers have been manufactured.

[1]. A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tománek, and E. I. Kauppinen, (2007) **A Novel Hybrid Nanomaterial.** *Nature Nanotechnology* **2**(3), 156-161**.**
[2]. Nasibulin, A. G., 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**.