Carbon NanoBud (CNB^{TM}) – A Novel Nanomaterial: Synthesis, Structure, Thin Film Field Emission and Transport Properties

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We present synthesis, structure and field emission properties of a novel hybrid carbon nanomaterial, NanoBuds^{TM}, combining fullerenes and single-walled carbon nanotubes (CNTs) . NanoBuds consist of fullerenes attached to the *outside* surface of CNTs, i.e. nanotubes are functionalized with fullerenes (1). Two floating catalyst methods for their selective synthesis have been developed, using pre-made iron catalyst particles by a hot wire based PVD method or grown *in situ* via ferrocene vapour decomposition in the presence of CO and trace amounts of H_2O and CO_2. TEM images show spherical structures i.e. fullerenes at the surface of the tube. Their spherical nature was confirmed by tilting samples within a HR-TEM. Statistical size measurements 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. Raman spectra show a pronounced G-band at 1600 cm^{-1} associated with CNTs, and only a weak D-band at 1320-1350 cm^{-1}. 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. EELS observations with TEM also showed the existence of oxygen. Scanning tunneling microscopy (STM) and spectroscopy (STS) measurements of samples deposited on Au(111) substrate confirmed the covalent nature of fullerene bonding to the tube. 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. In-situ deposited i.e. non-purified planar NanoBud mats showed stable cold electron field emission with a current density of 189 $\mu A/cm^2$ at 1.26 V/µm. The threshold voltage was about 0.6 V/µm, compared to over 2 V/µm for similarly produced planar nanotube mats. In addition, we present novel method for direct integration of CNBs (and SWCNTs) into flexible thin film electronics structures, like transparent thin films to replace ITO. The electrical conductivity of as-produced thin CNB as well as SWCNT mats as the fundction of film transparency will be presented.

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**.

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