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NOVEL HYBRID CARBON NANOMATERIAL: FULLERENE-FUNCTIONALISED CARBON NANOTUBES

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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 (FIG. 1). 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} (FIG. 2). 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 at 1400 cm^{-1} and 1370 cm^{-1} are likely associated with fullerenes even though they are considerably shifted compared to the 1469 cm^{-1} peak of the $A_g(2)$ pentagonal mode and 1427 cm^{-1} peak of the first-order Raman $H_g(2)$ mode of pure C_{60}. 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 (FIG. 3) 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 A/cm^2 at 1.26 V/m.

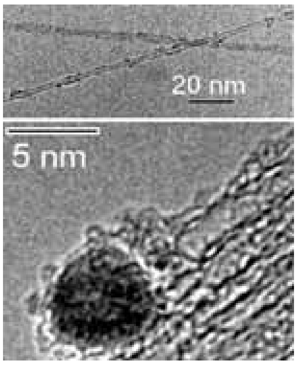

FIG. 1. A HREM image showing fullerenes on the surface of the CNTs.

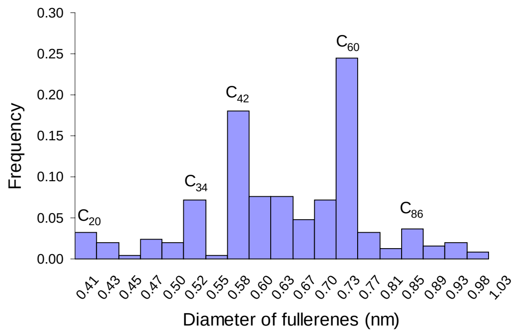

FIG. 2. Statistical size distributions of fullerenes showing the majority of fullerenes consisting of C_{42} and C_{60}.

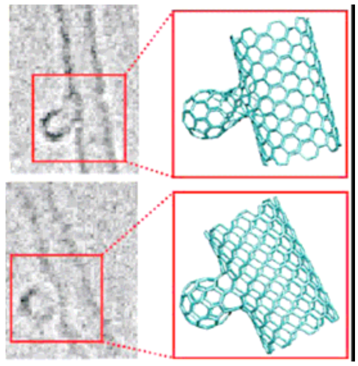

FIG. 3. An atomistic computer simu-lation model by COMP and ALSIM illustr-ating the covalent bonds at the nanotube-fullerene.