HRTEM and EELS Analysis of Functionalized Carbon Nanotubes

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Introduction:

To reveal answers to challenging questions of nanotube science, we tested two powerful electron microscopy techniques as tool to describe and visualize structure of chemically functionalized carbon nanotubes. We aim to sub-nm resolution in EELS, which seem to be critical in discovering potential chemical reactivity of different locations of individual CNT. We selected three different systems representing the chemically modified CNT.

Conclusion:

To our knowledge we show for the first time ever the EELS imaging of few isolated metal atoms inside endohedral metallofulerene peapods.

We also achieved detection of very low amount (less 1%) of sulfur (S) and proven covalent bonding onto surface MWCNT.

The last of interesting systems is fluorinated C_{60} peapods, where we show homogeneous fluorination across whole surface.

Thiolated MWCNT

Experimental:

Sample: Raw Arc grown MWCNT were first oxidized in acid reflux and then thiolated (P4S10) to attach sulfur containing groups on surface.

Possible reaction are:

MWCNT-OH + P4S10 → MWCNT-SH

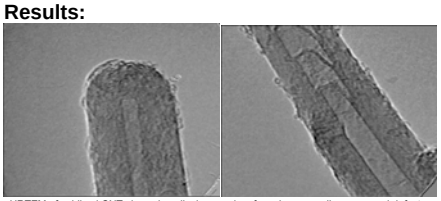
MWCNT-COOH + P4S10 → MWCNT-CSOH

MWCNT-SH + MWCNT-CSOH → MWCNT-CSSH

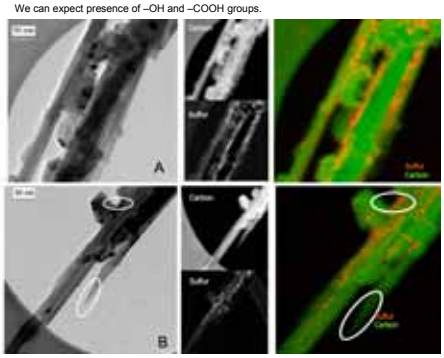
HRTEM: Philips CM200 with LaB_6 filament, operated at 200 kV

EELS/EFTEM: Zeiss 912 Ω energy filter, operated at 120 kV, employing a three-window technique. Sulfur (165 eV) and Carbon (284 eV) edges were used with an energy window of 20 eV.

Results:



HRTEM of oxidized CNT shows heavily damaged surface, layers peeling away and defects. We can expect presence of –OH and –COOH groups.



Elemental mapping confirms presence of Sulphur in concentration of 0.6% and clarifies it's location to outermost surface layer of MWCNTs. We confirmed creation of new covalent bonds (C-S) by Raman Spectroscopy.

$Dy_3N@C_{80}@SWCNT$

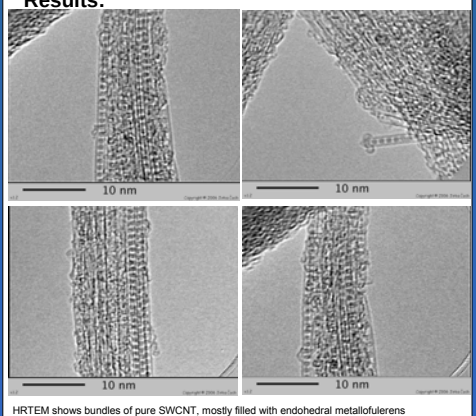
Experimental:

Sample: Endohedral metallofullerene peapods, namely Dy3N@C80@SWCNT

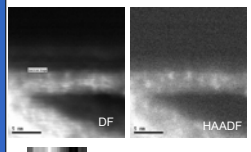
HRTEM: on Philips CM200 with LaB6 filament, operated at 120 kV (to reduce beam damage)

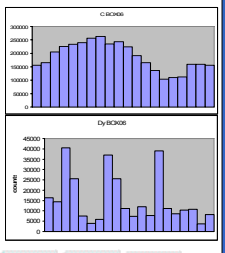
EELS/HAADF: is on VG501 STEM at 100 kV

Results:



HRTEM shows bundles of pure SWCNT, mostly filled with endohedral metallofulerens





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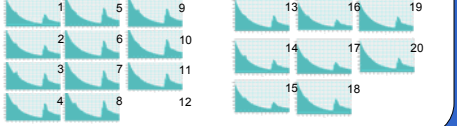
We took 20 point EELS linescan with very short integration time due to beam damage and confirmed presence of Dy. From position of maxima of integrated peaks, corresponding to Dy concentration can be shown that we image individual metallofulerenes.



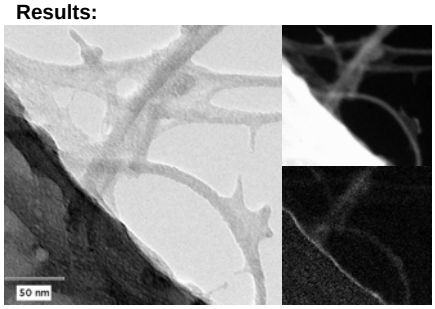
Fluorinated Peapods

Experimental:

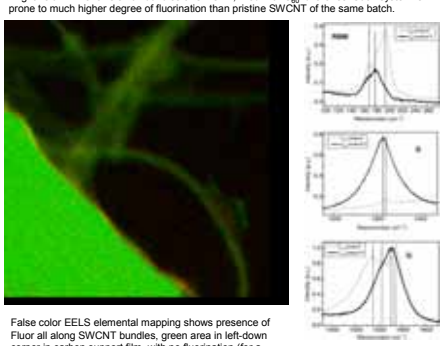
Sample: Laser Ablation SWCNT were allowed to form peapods with C_{60} at 500°C, then fluorinated by XeF_2 at low temperature, resulting in 18 % F (corresponding to C_4F)

EELS/EFTEM: Zeiss 912 Ω energy filter, 120 kV,

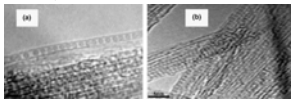
Results:



Bright field TEM shows small bundles of SWCNT, filled with C_{60} fullerenes. Such system is prone to much higher degree of fluorination than pristine SWCNT of the same batch.



False color EELS elemental mapping shows presence of Fluor all along SWCNT bundles, green area in left-down corner in carbon support film, with no fluorination (for a reference)



Bright field HRTEM shows structure of C_{60} peapods before (a) and after (b) fluorination. Structure is preserved even at high degree of fluorination.

Raman spectra of the fluorinated C_{60} peapods in the region of RBM, D and G mode. The gray line represents the spectra of the pristine peapods

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http://www.JirkaCech.com/E-MRS-2006.pdf