Fluorination of carbon nanotubes

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Fluorination of carbon nanotubes is the gateway to chemical functionalisation, providing an ideal "test system" for investigating site activity and addition patterns. Fluorination enables nanoparticle solubility in a variety of polar solvents, easy separation and purification, and alters mechanical and electrochemical response. Nanotube fluorination pyrolytically "cuts" nanotubes, generating short tube segments, and fluorine can be substituted with more complex addends, opening the way to complex chemical functionalisation of fullerenes and nanotubes.

We present results of *ab initio* studies of fluorination of carbon nanotubes. Our intention is to understand the different types of bonding observed in nanotube fluorination, and compare with CF_4 plasma treatment of CVD nanotube samples.

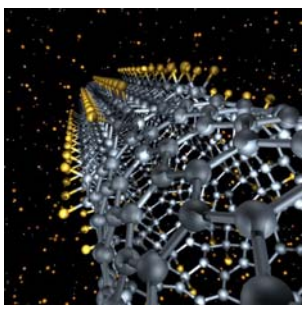
Tube walls not very reactive (excluding defect sites)
React with dry F_2 gas, followed by substitution reactions if required
Fluorination behaviour different at different temperatures
Highest coverage C_2F, compared to CF in graphite
Lower coverage, STM shows bands,
abrupt circumferential edges

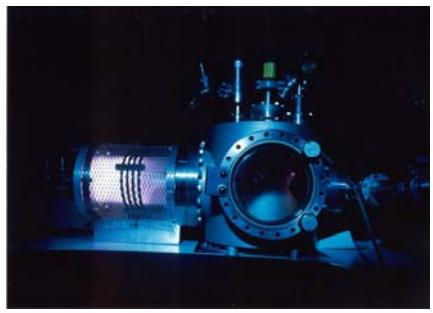
Changing Temperature Regimes:

0 - 200°C	"Semi-ionic" bonding, lower F coverage. Characteristic FTIR peaks: 1105/1600cm^{-1}.
200 - 250°C	Switch to "covalent" bonding. *Bands* observed. FTIR: 1200(1210) /1070cm^{-1}. Increasing sample resistance.
250 – 300°C	Coverage increases to maximum C_2F, still "covalent bonding".
300+ °C	Tubes break down, notably in TEM where small planes, folded layered fragments, etc form. Exact temperature depends on nanotube sample (300-400).

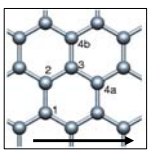
K.F. Kelly et al., Chem. Phys Lett., 313 (1999) 445.

Fluorine banding on carbon nanotube observed via STM





Low Coverage – F_2 addition to an (8,8) nanotube

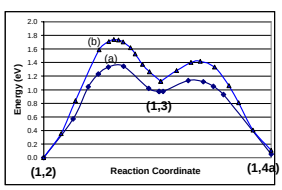


The notation (n,m) throughout the poster indicates two fluorine atoms sited above carbon atoms n and m on the diagram above. The arrow shows the axis of the (8,8) nanotube.

DFT Calculations for large nanotube sections.

Preferred (1,4a) and (1,2) addition of F_2 pair, strongly covalent.
(1,3) is much less stable (comparable to isolated F binding).
Little distortion of tube – isolated F and F_2 source of semi-ionic XPS F signal.

Migration barriers (eV) for fluorine pair migration on the surface of (a) graphite and (b) an (8,8) carbon nanotube.



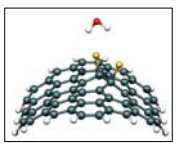
Isolated F migration barrier is low (~0.7eV)
Migration barriers for (1,4) → (1,3) → (1,2) for graphite and armchair are in range corresponding to a 200-250°C temperature regime.

Suggests:

Below 200-250°C: Surface addition of F, or (1,2) or (1,4) F_2.
Two F can rapidly migrate to form a (1,4) F_2 pair.
(1,2) F_2 cannot rearrange on surface due to high migration barrier through the (1,3) arrangement.
(1,4) F_2 cannot move to close-packed (1,2) for same reason.
Maximum coverage at (1,4) spacing is 25%, consistent with experiment.
Above 200-250°C: F can migrate through the (1,3) configuration, allowing rearrangement into axial lines, giving maximum 50% C_2F coverage.

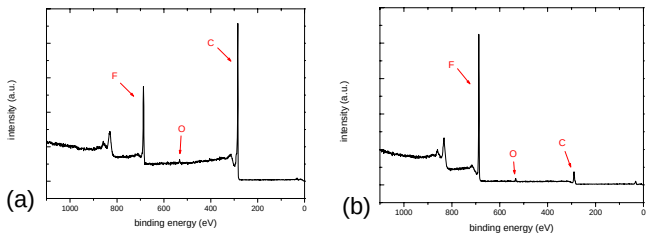
Role of solvents in promoting F surface rearrangement

Preliminary test cluster calculations show:
Weak binding H_2O to armchair F_2 (1,2) = 0.2eV
⇒ Tubes water soluble
Lowers migration barrier (1,2) → (1,3) by 0.4eV
⇒ H_2O catalyses F rearrangement on nanotubes
Consistent with $C_{60}F_{36}$, which rearranges at RT.

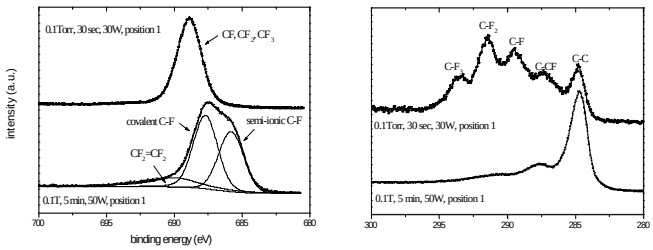


CF_4 plasma treatment of CVD nanotubes

- Inductive RF plasma chamber, CF_4 gas
- Plasma conditions : treatment time, power, pressure, position in the chamber
- XPS studies using an SSX-100 spectrometer, 0.9eV resolution.
- Non-purified CVD nanotubes (Nanocyl)
- Up to 2gr of CNT can be functionalized in a single plasma treatment with the magnetic stirring method



XPS for CNTs treated by CF_4 plasma under different conditions :
(a) 0.1Torr, 5min, 50W, giving F(18%), O(1%), C(81%)
(b) 0.1Torr, 30sec, 30W, giving F(66%), O(1%), C(33%)



F1s and C1s spectra of CNTs treated by CF_4 plasma under different conditions (detailed above).

- After plasma, XPS reveals C, O and F at the nanotube surface.
- Plasma conditions give significantly different surface F/C ratios.
- Oxygen impurity concentrations remain consistently low.
- Short plasma treatment reveals range of CF_n type peaks, longer treatment gives more 'stable' fluorinated tube signal.