Defects in carbon nanosystems

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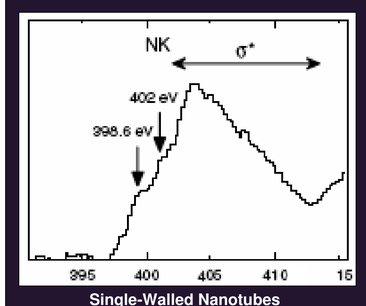
Defects do not just *influence* the behaviour of a material, they often *define* it. Early theoretical nanotube studies focussed on idealised structures, often predicting properties (e.g. Young's Modulus) wildly at odds with experimental results. Only more recently has the crucial role of defects begun to be acknowledged, and latterly, exploited.

This work focuses on the study of atomic scale defects and doping in materials, notably in carbon materials such as graphite, fullerenes and carbon nanotubes. As well as explaining intrinsic point defect structures, this leads to new techniques such as using irradiation as a strengthening mechanism for nanotubes. This builds on earlier graphite studies showing a new range of intrinsic point defects which bridge the gap between atomic layers in graphite. These explain the cause of a major fire at the Windscale nuclear reactor in the 1950s. More recent studies on doping and functionalisation of carbon nanotubes show how nitrogen violates one of the tenets of carbon science (the 'isolated pentagon rule'), resulting in a new family of nitrogen doped fullerene molecules, and how fluorination can lead to chemical superlattices on nanotube surfaces.

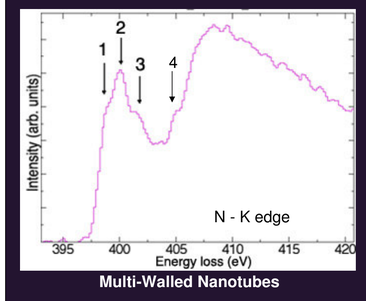
N and P doping of Carbon Nanotubes : nanoelectronics

EELS of nitrogen doped carbon nanotubes shows
- **two N-species in Single-Walled tubes (peaks 1,3)**
- **a further N-species in Multi-Walled tubes (peaks 2,4)**

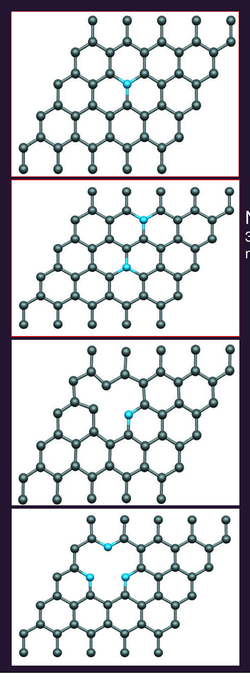
C. Ewels, with O. Stèphan (LPS, U-PSud), M. Glerup (Oslo), A. Loiseau (ONERA)



Single-Walled Nanotubes



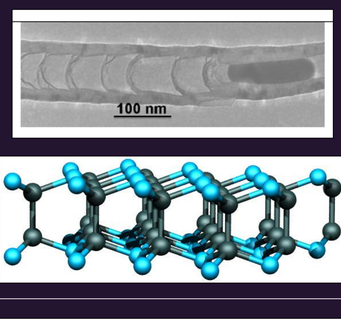
Multi-Walled Nanotubes



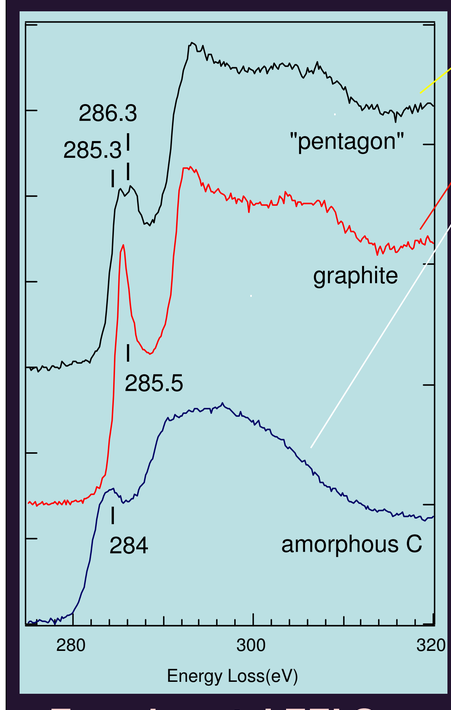
Defect	Formation Energy (eV)	
	Total	per N
Substitutional N	0.42	0.42
N pair at 3rd neighbour	0.67	0.33
N - V	5.52	5.52
N_2 - V	4.27	2.14
N_3 - V	2.53	0.84
Graphite Vacancy	8.15	
Stone Wales defect	5.63	

Defect formation energies in graphite. Graphite, N_2 used as standard states.

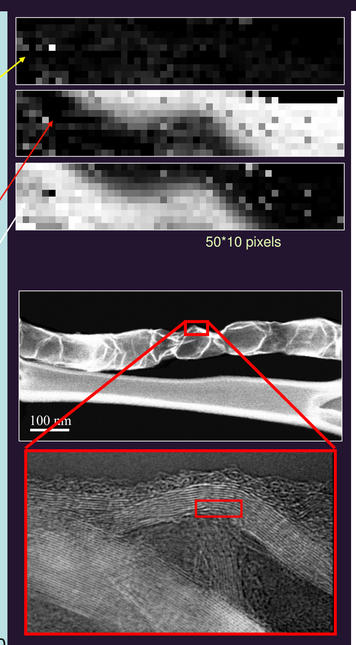
Multi-walled show internal N-rich walls with sp^3-carbon; new CN layered phase?



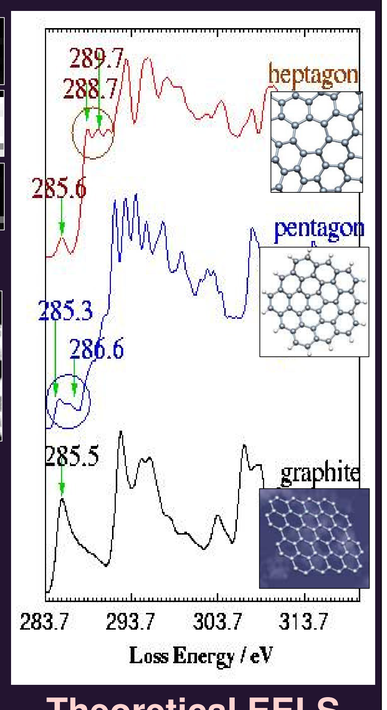
Can we identify individual defects with EELS?



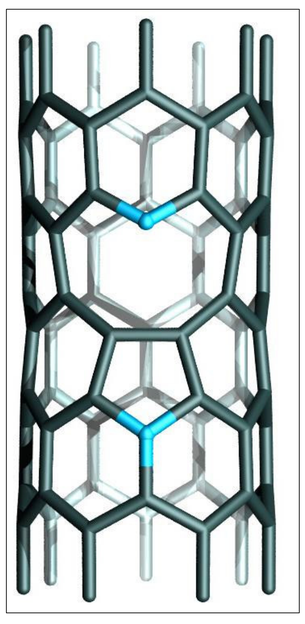
Experimental EELS



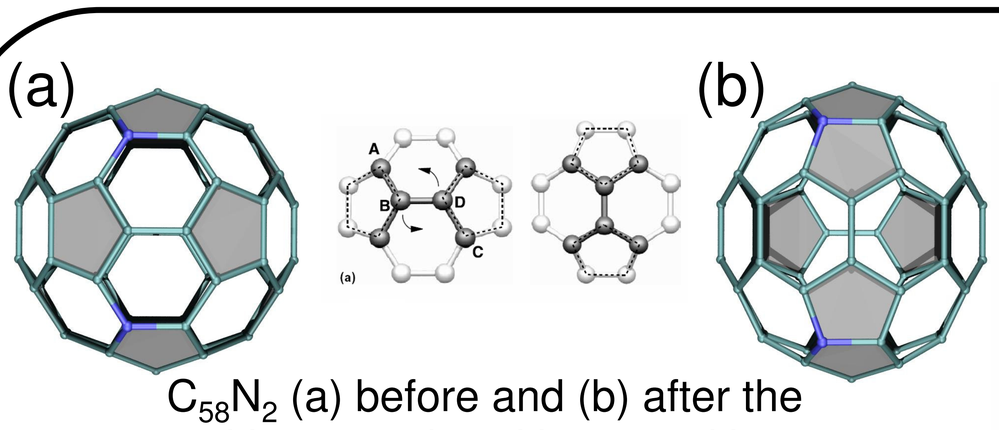
With O. Stèphan (LPS), S. Trasobares (Cadiz), A. El-Barbary, M. Heggie (Sussex)



Theoretical EELS

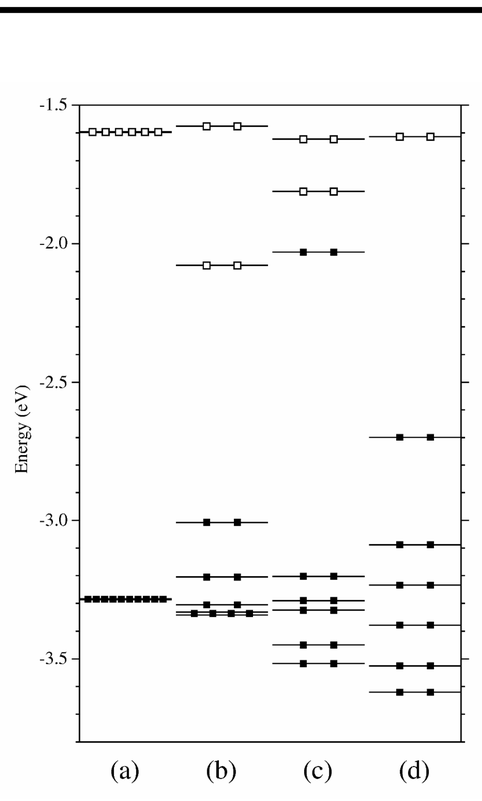


(7,0) carbon nanotube with two nitrogen atoms along the axis (marked in blue), with single vacancy between them.
Vacancy formation energy <2.5eV (normally >5eV).



$C_{58}N_2$ (a) before and (b) after the central hexagon bond is rotated by 90°. The right hand structure contains two pentagon pairs, and is **more stable** by 0.54eV. Nitrogen atoms are marked in blue, pentagons are filled in grey. In classic C_{60} (b) is 1.6eV **less** stable.

Nitrogen stabilises the paired pentagons, and **violates the isolated pentagon rule**



DFT Kohn-Sham eigenvalues (eV) around the HOMO-LUMO gap

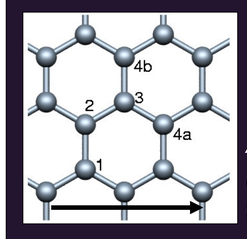
(a) C_{60}
(b) C_{60} with one bond rotation (2 sets of paired pentagons)
(c) As (a) with two substitutional N atoms
(d) As (b) with two substitutional N atoms, one per paired pentagon.

Black (white) squares show filled (empty) states.

- In isolated pentagon case, additional N electron forced to occupy high lying anti-bonding state.
- In paired pentagon case, filled level drops. Pentagon pairs become aromatic.

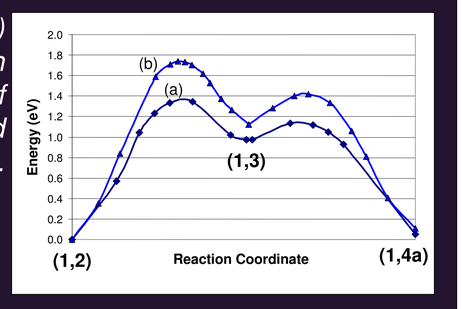
F_2 addition to an (8,8) nanotube

2 F atoms prefer to sit at (1,4a) and (1,2), strongly covalent (see Figure).
(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.



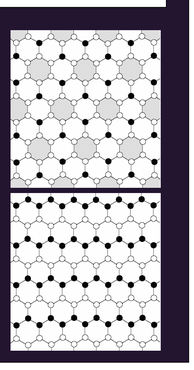
Arrow marks nanotube axis (x,y) indicates 2 F atoms bonded to carbon atoms x and y

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

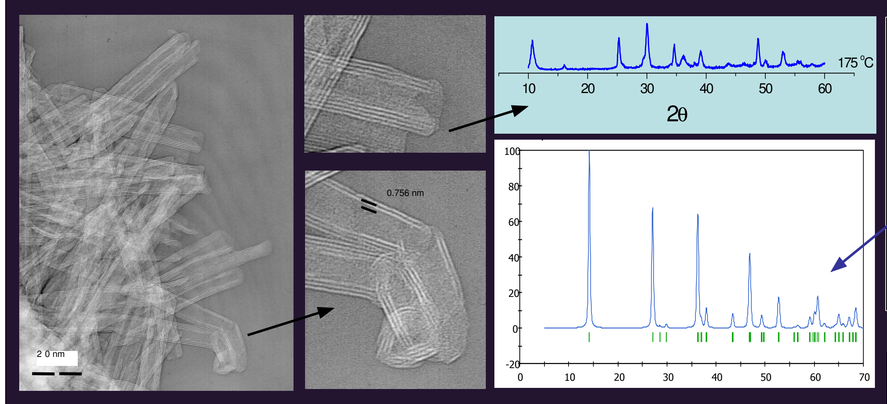


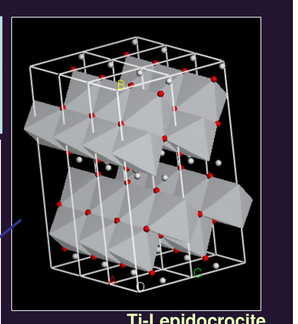
Isolated F migration barrier is low (~0.7eV)
Migration barriers for (1,4) → (1,3) → (1,2) for graphite and nanotube are in range corresponding to a 200-250°C temperature regime.

Fluorination leads to different surface superlattices:
Below 200-250°C restricted migration limits to C_4F coverage
Above 200-250°C, free motion leads to C_2F banded coverage



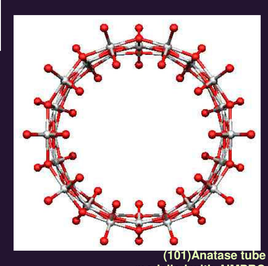
Ti/O nano-scroll structure and surface behaviour



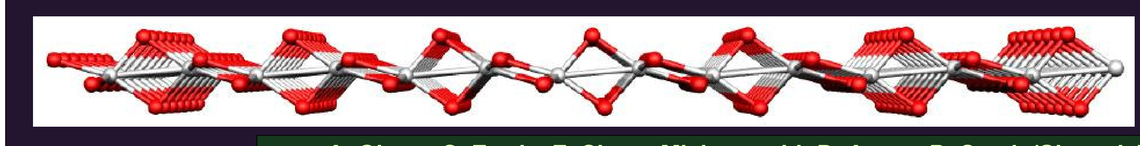


Ti-Lepidocrocite

Scroll structure related to (101) anatase
Modelling possible structures (TiO_2, Ti_3O_7, TiOOH, $H_2Ti_3O_7$, lepidocrocite), comparing with XRD, e-diff, TEM.
DFT modeling of tubes and gas absorption on surfaces.
Material important for photocatalysis, gas sensors, detoxification, H production, etc



(101)Anatase tube modelled with AIMPRO



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