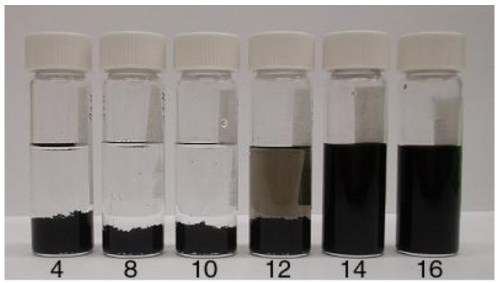
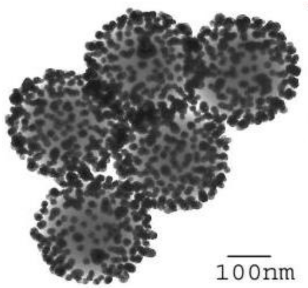
Overview of the Nanomaterials & Toxicology Research at Bristol

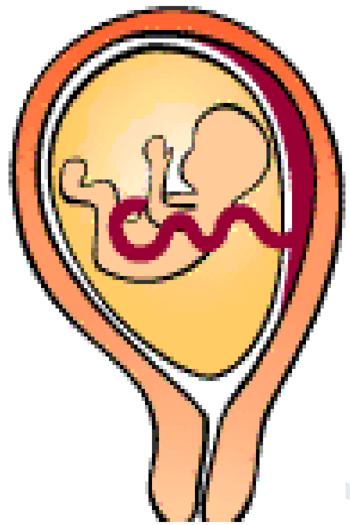
Dr. Sameer S Rahatekar

Lecturer, Aerospace Engineering, University of Bristol



Nanoparticles





Outline

- **Dispersion of Carbon Nanotubes in Aqueous Media using Surfactants and Bio molecules and characterisation of quality of dispersion of carbon nanotubes using UV-vis-NIR**

- **Synthesis and dispersion of graphene using ss-DNA**
  (Dr A Patil, Prof Mann, School of Chemistry, University of Bristol)

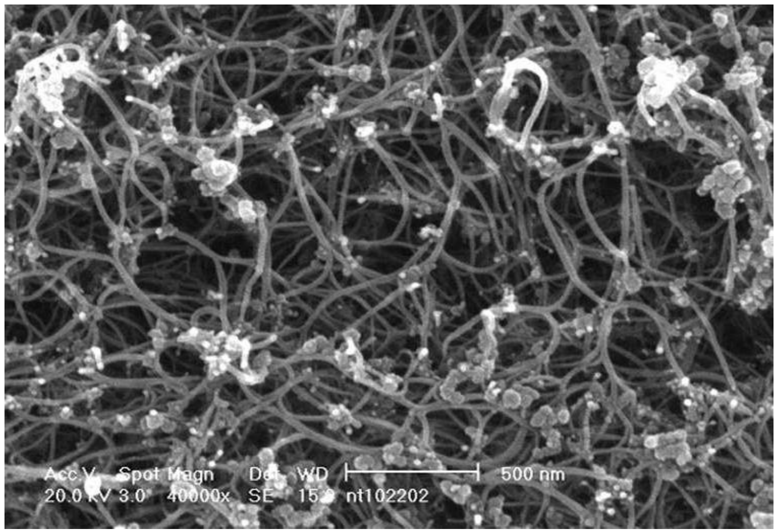
- **In vitro study of exposure of Nanoparticles to Placenta, Proposed in-vitro toxicological study of carbon nanotubes and graphene for placenta**
  (Dr Margaret Saunders, University Hospitals, Bristol)

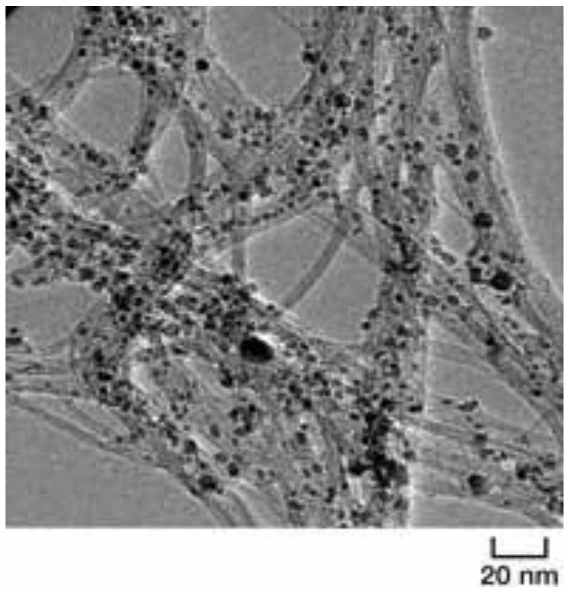
- **Use of chitin/carbon nanotube composites for tissue engineering and best approach to address toxicological issues.**

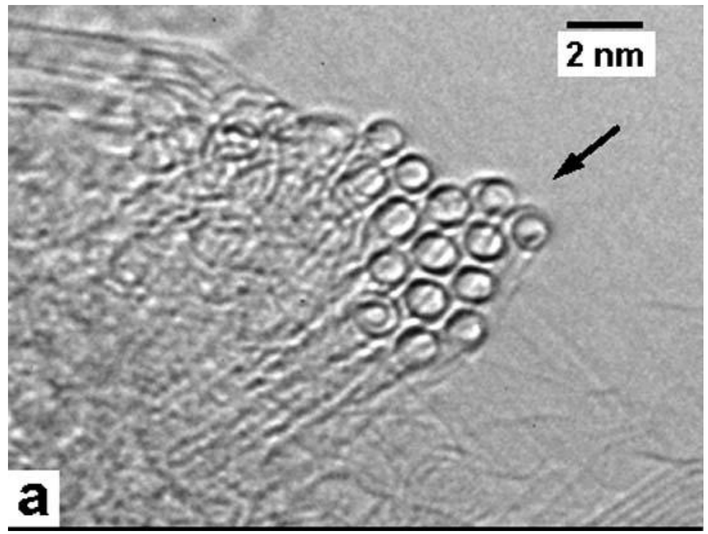
Carbon Nanotubes Synthesis

Chemical Vapor Deposition Synthesis of Single Wall Carbon Nanotubes (SWNTs)

Amorphous carbon, Residual Metal Catalyst Bundles of SWNTs







Carbon Nanotubes Purification and Dispersion

Develop a method for dispersion of carbon nanotube dispersion aqueous medium by removing impurities, and bundled carbon nanotubes

↓ Surfactants + Sonication

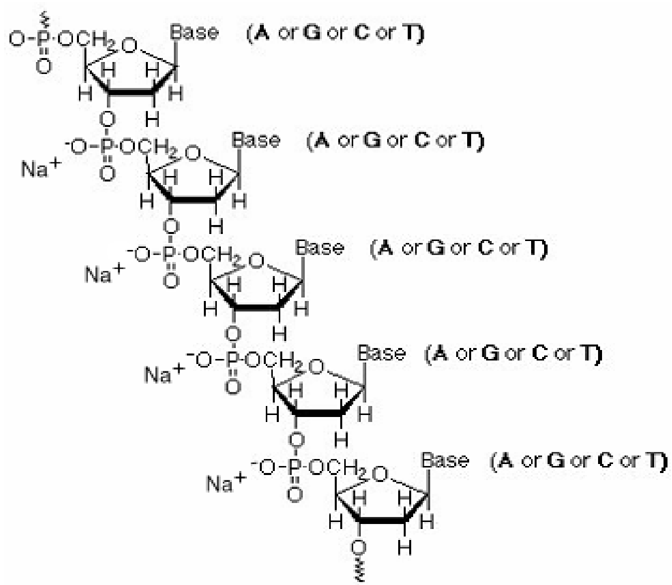
Individually Dispersed SWNTs
(using Range of surfactants such as DNAs, Peptides, Cellulose and bile salts)

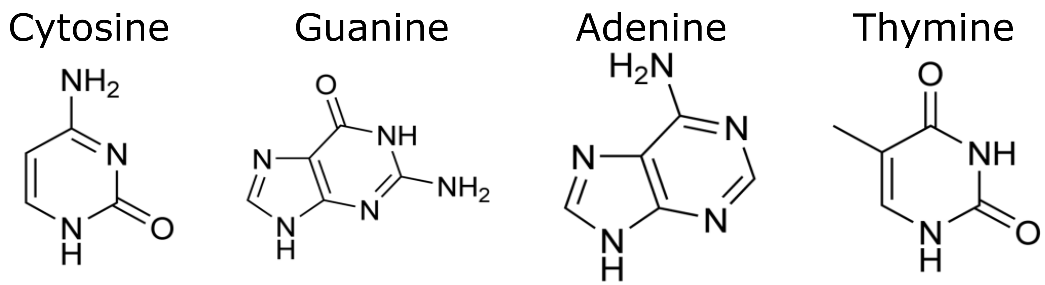
↓

Toxicological Study

Approach – DNA

GT_{15}, T_{30}, A_{30} (Guanine, Thymine, Adenine)



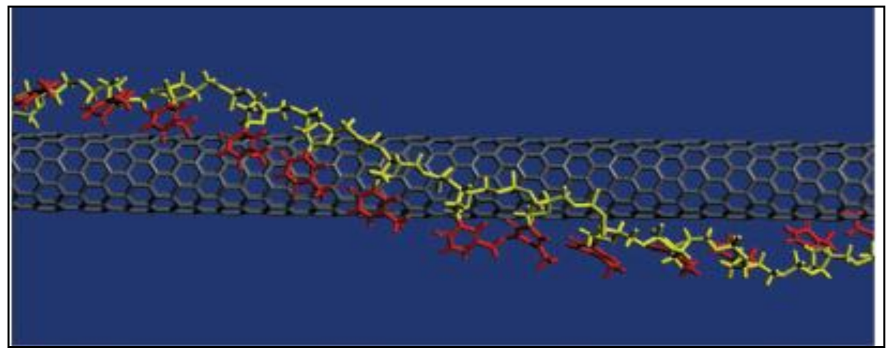


GTGTGTGTGTGTGTGTGTGTGTGTGTGTGT

ACACACACACACACACACACACACACACAC

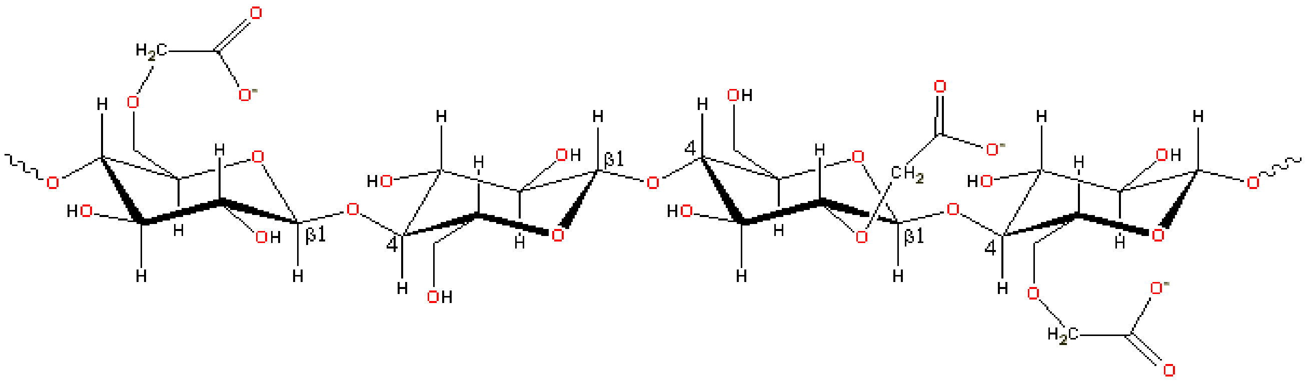
Poly T (T_{30})

Poly A (A_{30})

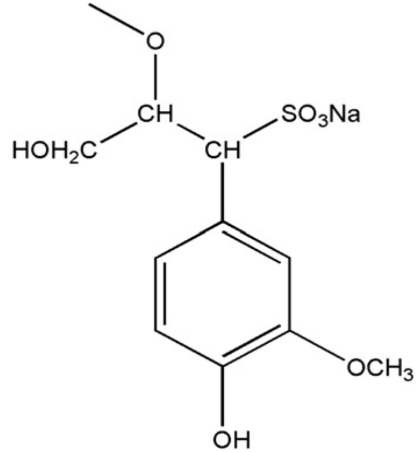


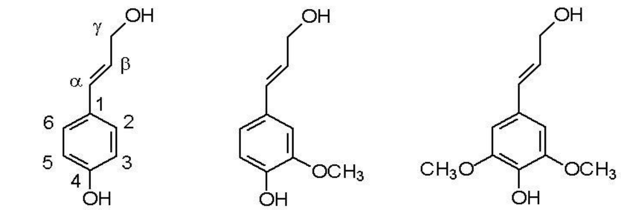
Ming Zheng, *Nature Materials*, 2, *2003*, p. 338

Lignin, Chitosan, Carboxy methyl Cellulose



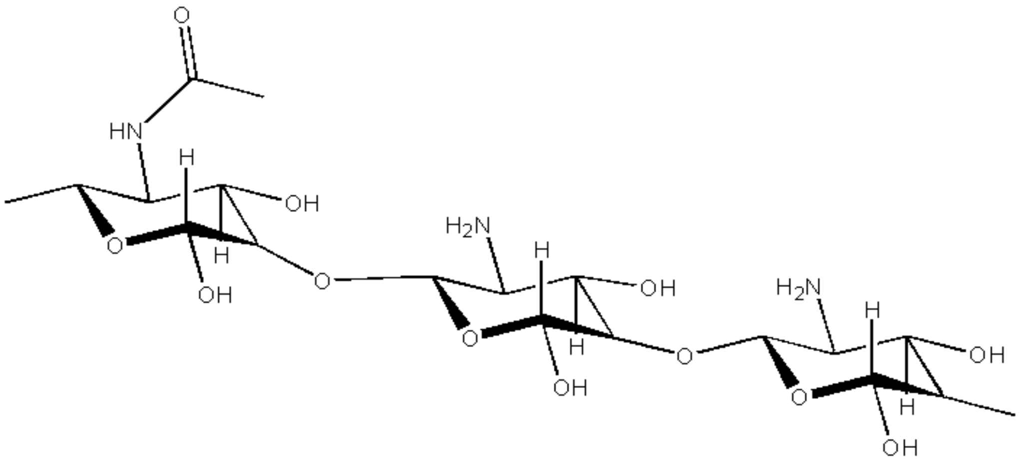
Carboxymethylcellulose[1]





p-coumaryl alcohol Coniferyl alcohol Sinapyl alcohol

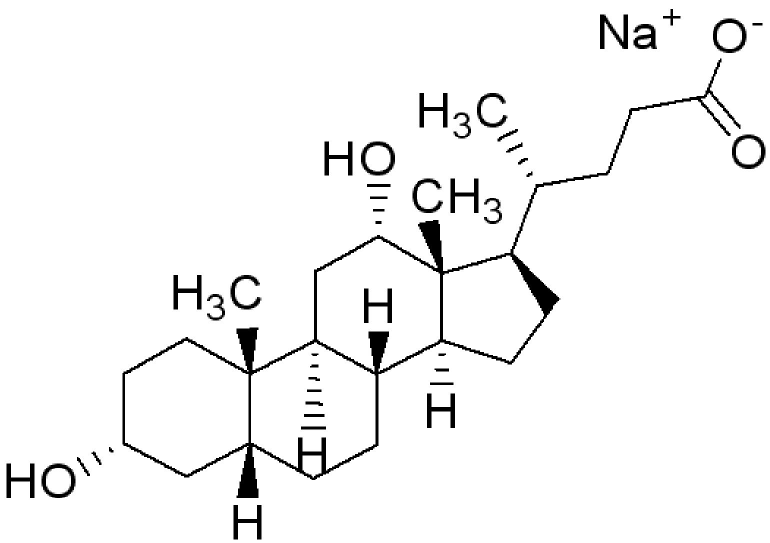
Chemical structures of typical segments of sodium lignosulfonate[3]



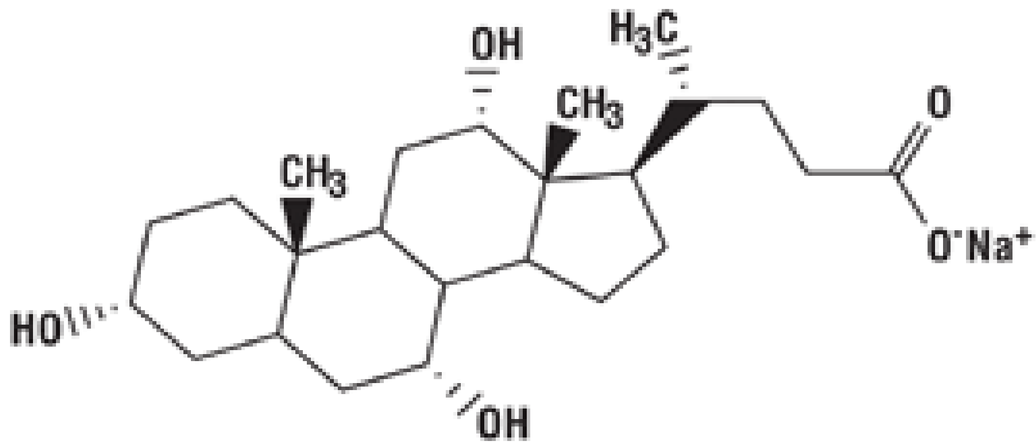
Chitosan[2]

John F. Kadla
University of British Columbia

Bile Salts



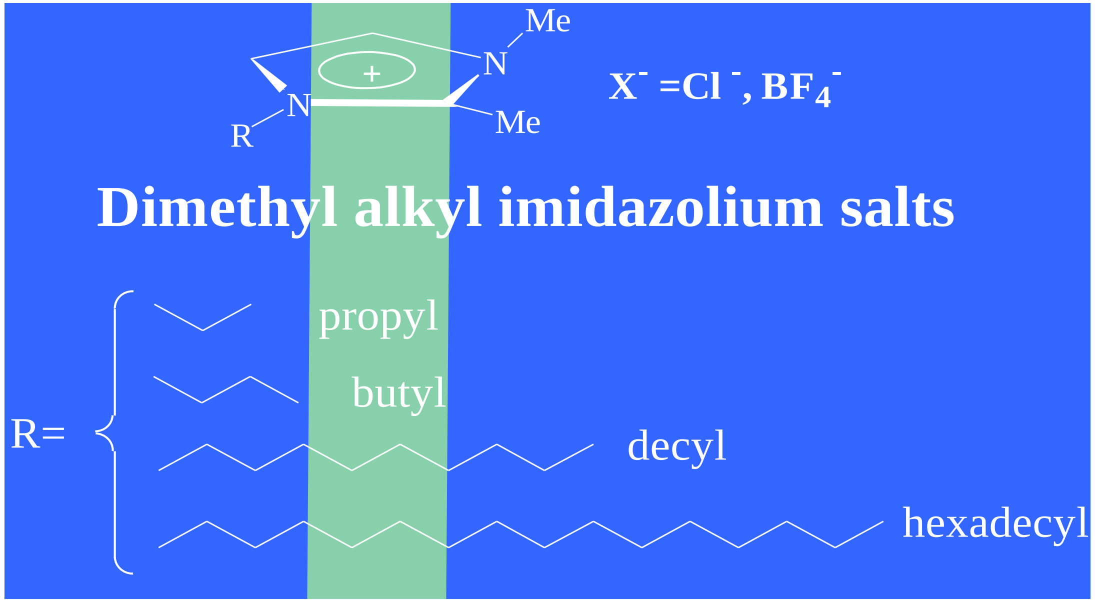
Sodium deoxycholate

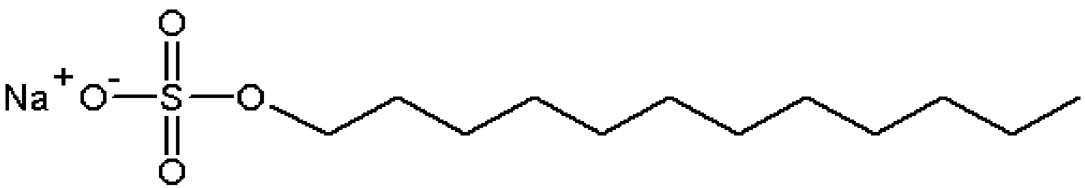


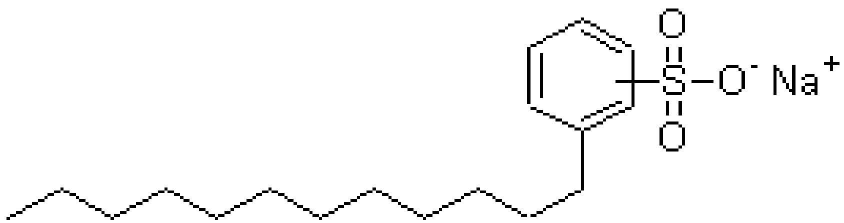
Sodium Cholate

Ishibashi A. and Nakashima N., *Chemistry-A European Journal*, 2004, *12*(29), 7595-7602.

ILs and SDS,SDBS







Sodium dodecyl sulfate[2]

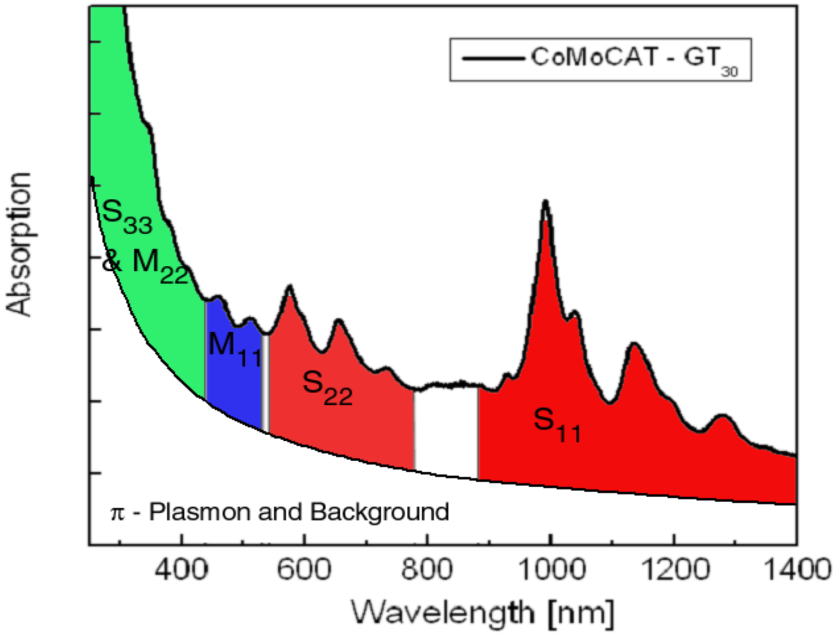
Sodium dodecylbenzene sulfonate [3]

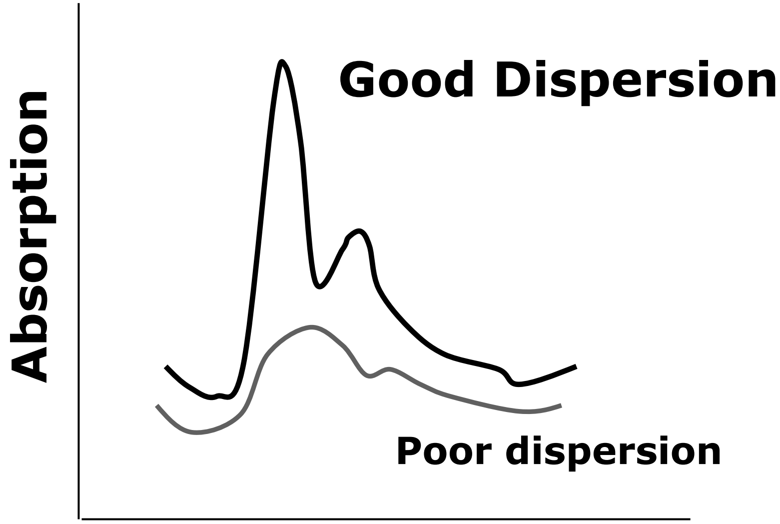
Dispersion of Carbon Nanotubes

Carbon Nanotubes + Surfactant → Sonication, 2hrs → **High speed centrifugation** → Removal of impurities; Removal of large nanotube bundles →

UV-vis NIR Spectroscopy for SWCNT Dispersion

R.B. Weisman et al., *Appl. Phys. A* (2004), 78, 1111





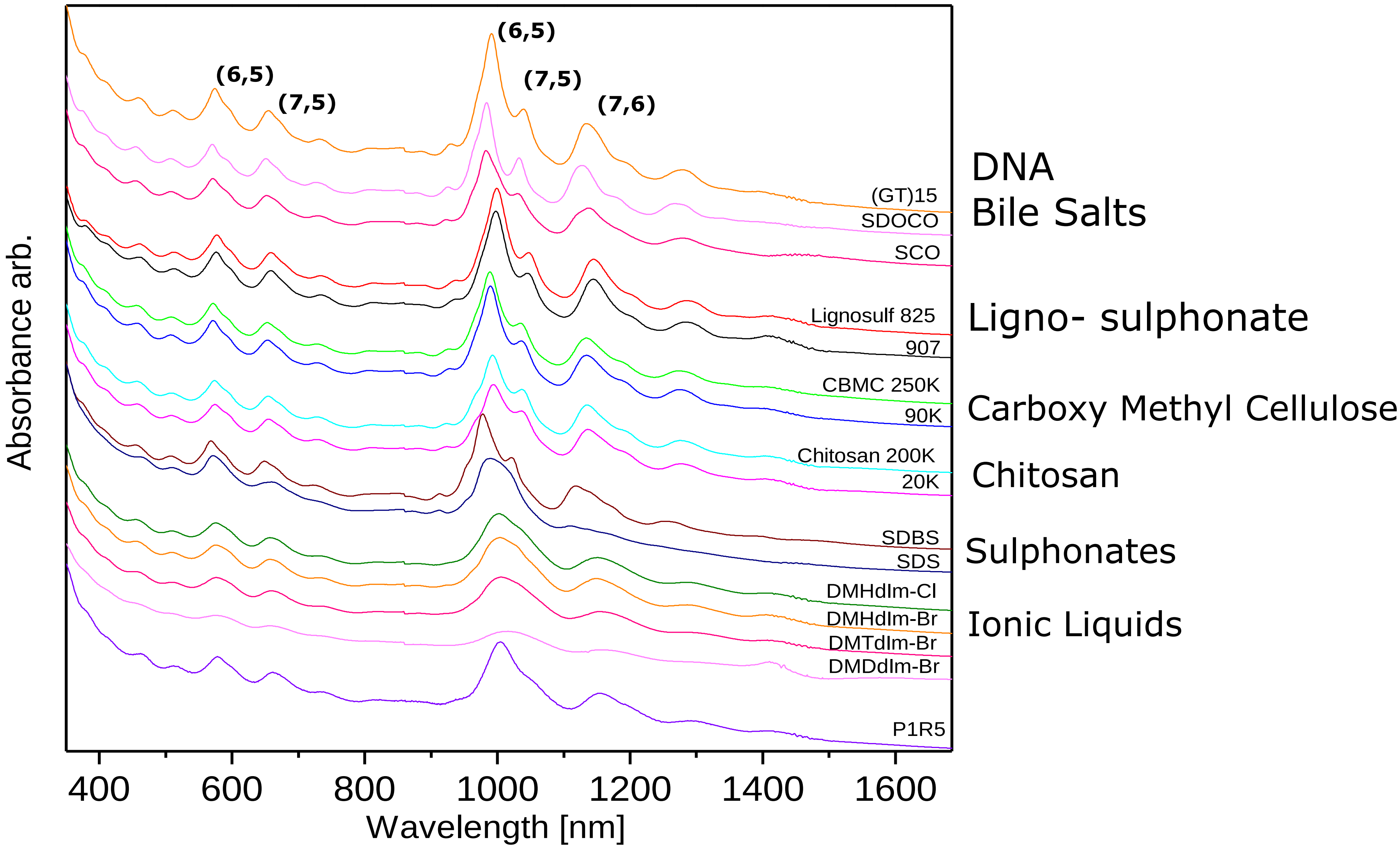
Density of Electronic states for semiconducting SWCNT Showing van Hove transitions

- Quasi one dimensionality of SWCNTs π electrons causes DOS to show van Hove singularities.

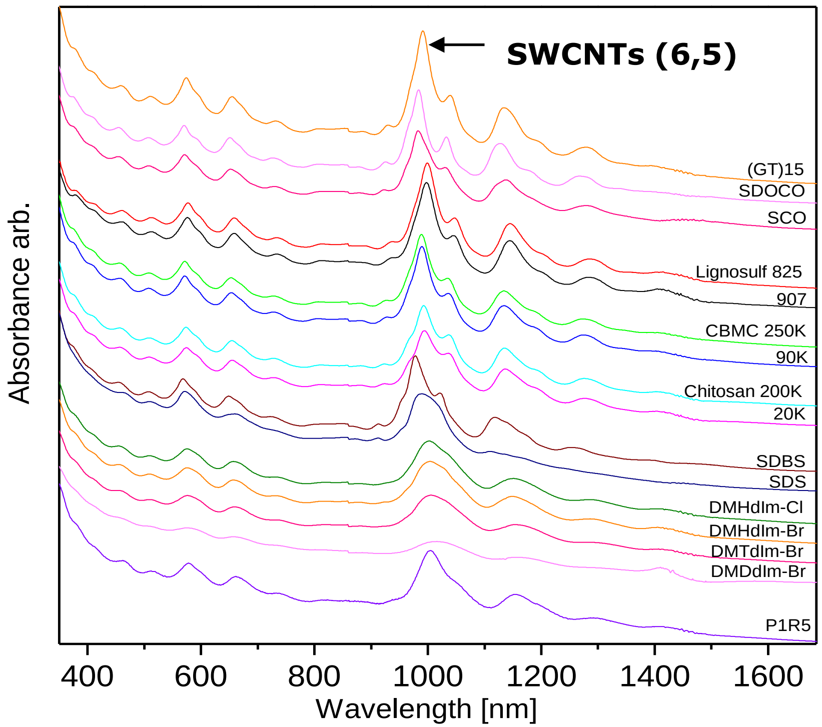
- Therefore the absorption spectra of the SWCNTs is dominated by peaks corresponding to sharp van Hoves transitions

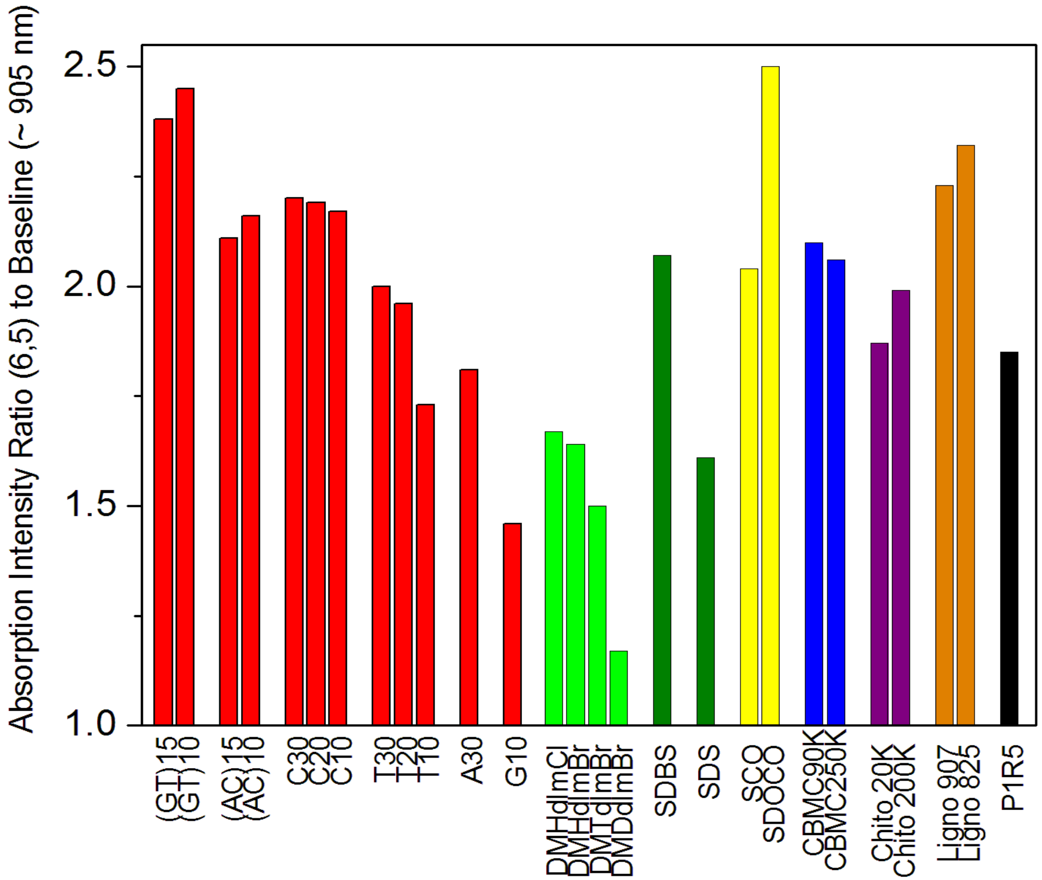
-The first van Hove transition (E11) corresponding to band gap of semiconducting SWCNTs (S11) falls in 800-1600nm range, second van Hove transition fall in 550-800nm. The lowest energy van Hoe transition of metallic tubes appear between 400-600nm

UV-vis NIR Spectroscopy of SWCNT Suspensions



Ability to De-Bundle SWNT



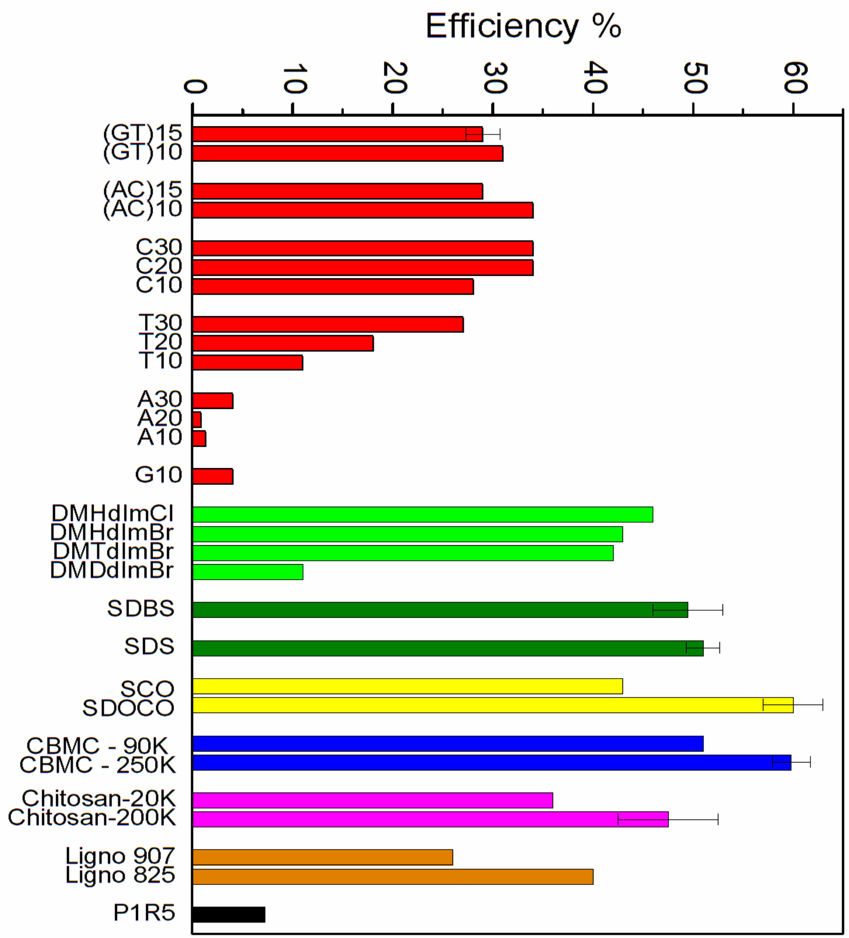


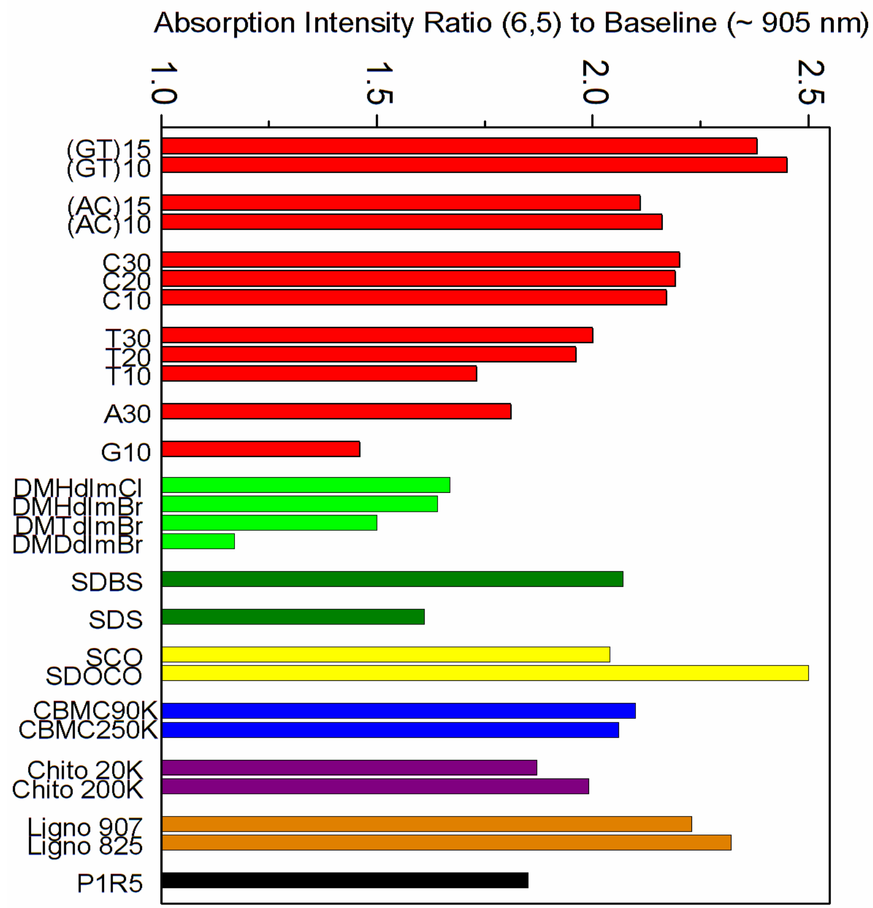
Good UV-vis-NIR absorption peak resolution can be obtained only when SWCNTs are individually dispersed[1,2] (debundled). Hence SWCNTs peak ratio and peak resolution can be used to determine if the larger fraction of SWCNTs are well dispersed (debundled) by a given surfactant/biomolecules.

$$\textbf{Peak Ratio} = \frac{\textbf{Intensity from (6,5) peak}}{\textbf{Intensity of the baseline at 905nm}}$$

1. **O'Connell, *et al*. *Science* 2002, *297*, (5581), 593-596.**
2. **Tan, Y.Q.; Resasco, D.E. *J. Phys. Chem. B*, 2005, *109*, 14454-14460**

Comparison of Efficiency and Ability to Debundle SWCNTs



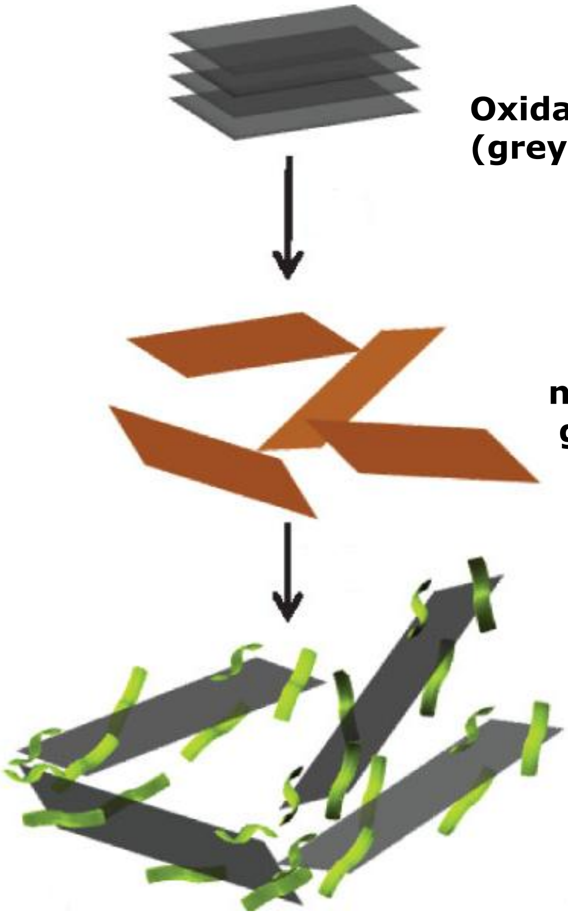


Comparison of Efficiency and Ability to debundle SWCNTs for Different surfactants/Biomolecules

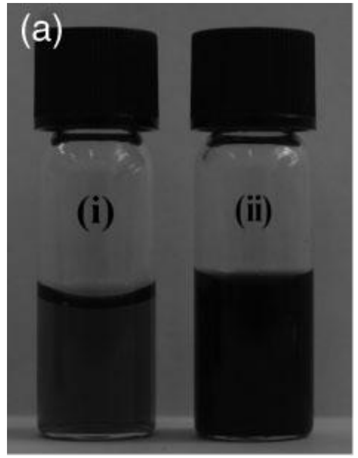
Graphene Synthesis & Dispersion

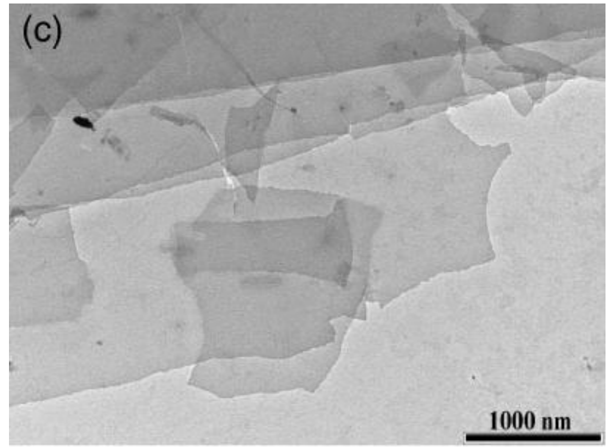
Dr Avinash Patil & Prof Steve Mann

School of Chemistry, University of Bristol

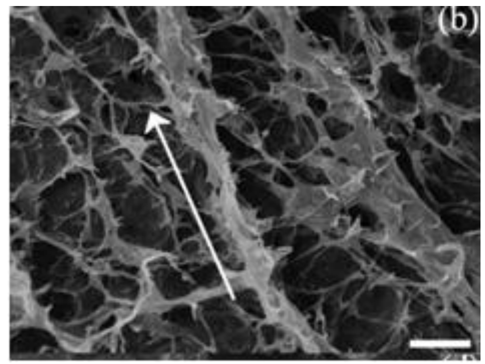


Oxidative treatment of graphite (grey-black) yields delaminated nanometre-thick sheets of graphite oxide (GO) (brown).





Chemical reduction of GO sols with hydrazine in the presence of freshly prepared single-stranded DNA (ssDNA) produces a stable aqueous suspension of ssDNA-functionalised graphene sheets (ssDNA-G).



Patil et al, Advanced Materials, 2009

Vickery et al, Advanced Materials, 2009

Carbon Nanotubes Purification and Dispersion

CVD grown SWNTs

- **Amorphous carbon** → **Removed by surfactant dispersion of SWNTs followed by centrifugation**
- **Residual Metal Catalyst** → **Removed by acid treatment followed by centrifugation**
- **Bundles of SWNTs**

↓ Surfactants + Sonication

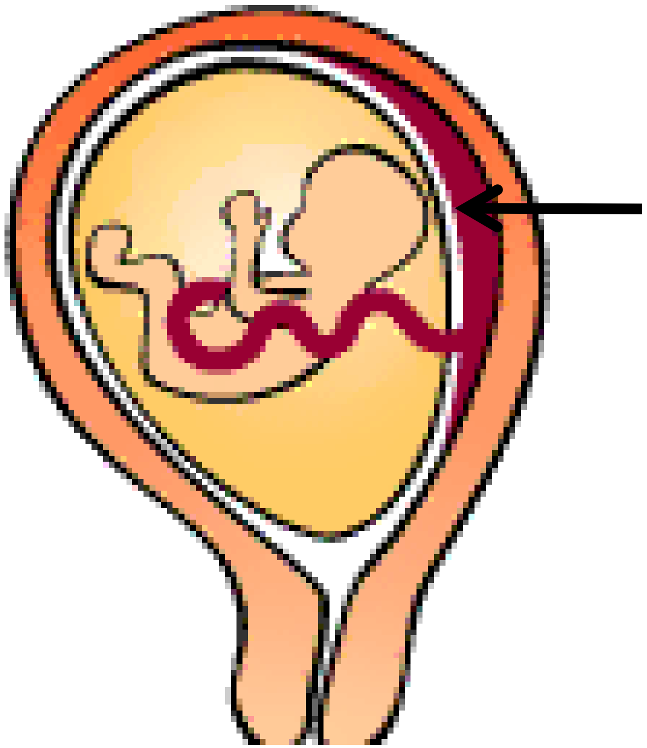
Individually Dispersed SWNTs and Graphene
(using Range of surfactants such as DNAs, Cellulose, Chitisan and bile salts)

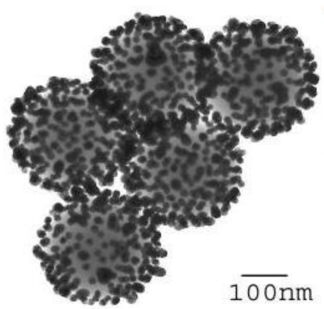
↓

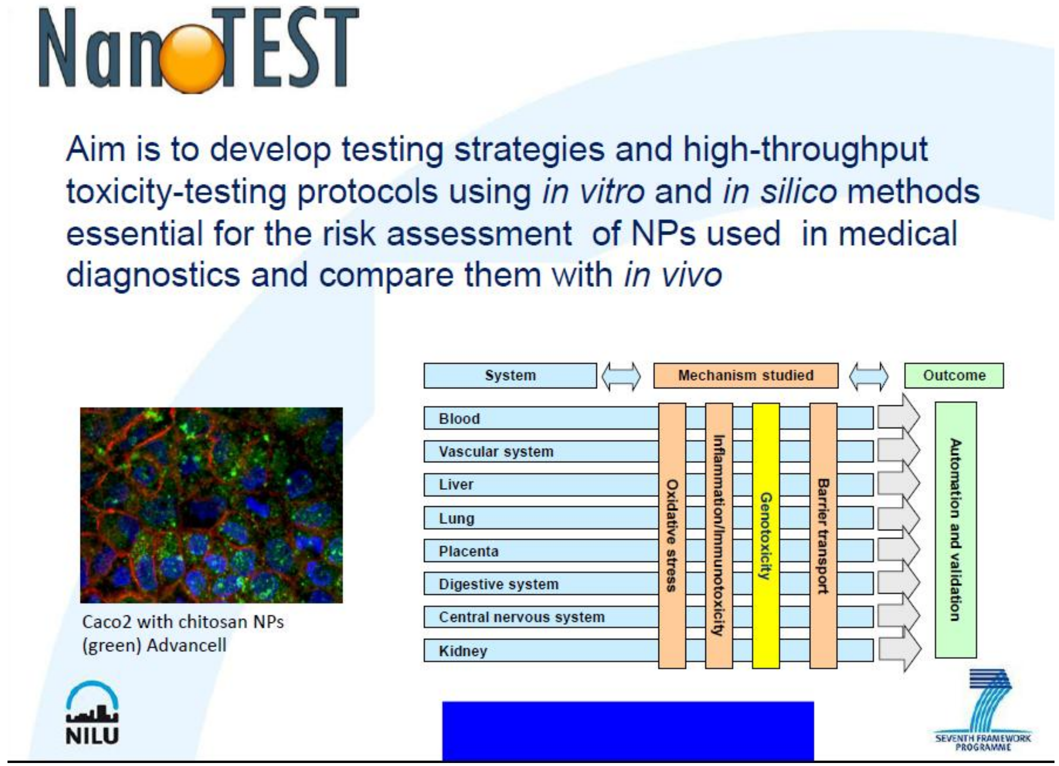
Toxicological Study of Carbon Nanotube Transport Through Placenta
Dr M. Saunders, University Hospitals Bristol

Research Work of Dr Margaret Saunders

- **The developing foetus represents one of the most vulnerable subgroup of human population**
- **Hence it is essential to study the transportation of nanoparticles via placenta**

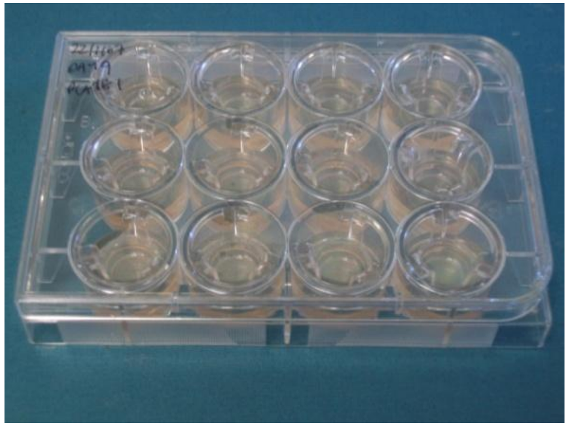


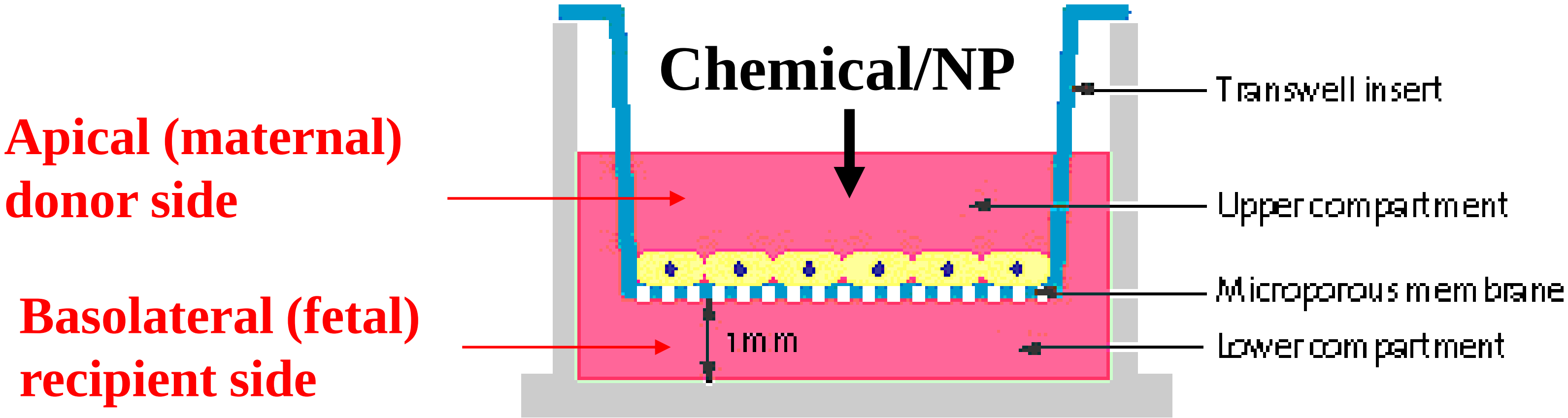




In Vitro Nanoparticles Transportation Study Model

- BeWo human trophoblast cell line
- Resemble normal trophoblasts
- Transwell® inserts
- Permeable membrane (PE, PC)
- 3.0 µm pore size
- Confluent monolayer: functional polarity





Medically Relevant Nanoparticles

- Toxicity, transport, *in vitro* cell culture models: develop HT screening

- Nanoparticles:

  - TiO_2: 15-60 nm (TEM), bimodal 101, 278 nm

  - Fe_3O_4 (coated with oleic acid): 8-10 nm; bimodal 31, 132 nm (DLS), stable ~3 days

  - Fe_3O_4 (uncoated): 8-12 nm (TEM), large agglomerates, 1-50 µm (DLS), < 5 mins

Conclusions

- TiO_2 NP exposure causes cell membrane damage (4h) and dose-dependent DNA damage even at sub-cytotoxic levels

- Fe_3O_4 NP appear safe at clinically relevant levels but coated NP can cross placenta

M.Saunders@bristol.ac.uk

Carbon Nanotube Based Composites for Applications in Tissue Engineering

Collaboration:
Dr Wael Kafienah

Department of Cellular & Molecular Medicine, University of Bristol

Carbon Nanotube substrate for Stem Cell Growth

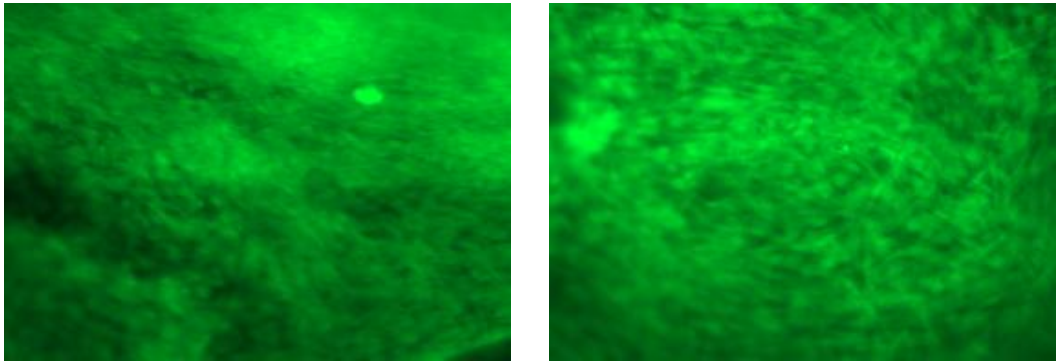
- **Stimulation of neurons via electrical stimulation using implantable electrodes has the potential to treat Parkinson's disease, chemically resistant depression and epilepsy.**

- **Currently, the lifetime of prototype electrodes based on metal or silicon fibre is restricted to 3-6 months. This is due to a mismatch in the elastic/mechanical properties of the electrodes and the surrounding brain tissues, which leads to migration of glial cells to the site of the implant and eventual loss of electrode function.**

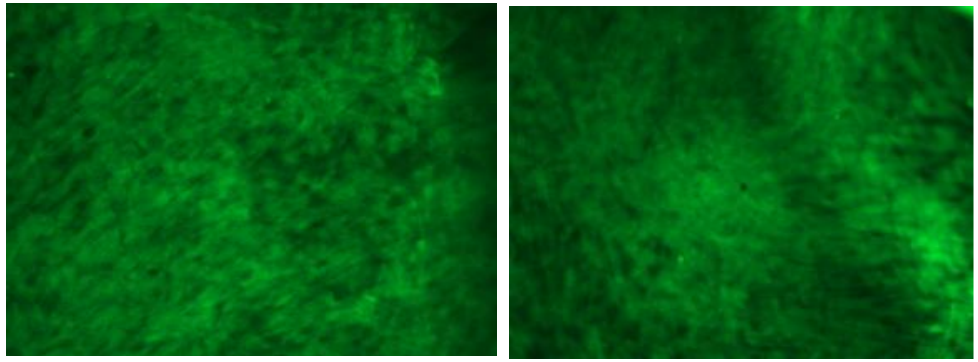
- **To overcome this severe limitation, we propose to use soft, polymer nanotube based electrically conducting substrate for new generation of implantable electrodes. Carbon nanotubes can achieve electrical conductivity in the chitin and silk fibres due to their extremely high aspect ratio and excellent electrical conductivity.**

- **As a part of this study, we will manufacture electrically conducting polymer nanotube composites using ionic liquids as processing solvent and study neuronal development on these fibres.**

Natural Polymer Composites for Stem Cells Scaffolds



Chitin



Chitin+Nanotubes

↓

Electrical Stimulation and alignment of stem cells

What are the types of nanotubes (SWNT, MWNT), length and surface functional groups which can cause minimum damage to the surrounding tissues after polymer matrix degradation?

Future Opportunities

FP7 NMP 2012 Call

NMP.2012.1.3-1
Systematic investigations of the mechanisms and effects of engineered nanomaterial interactions with living systems and the environment

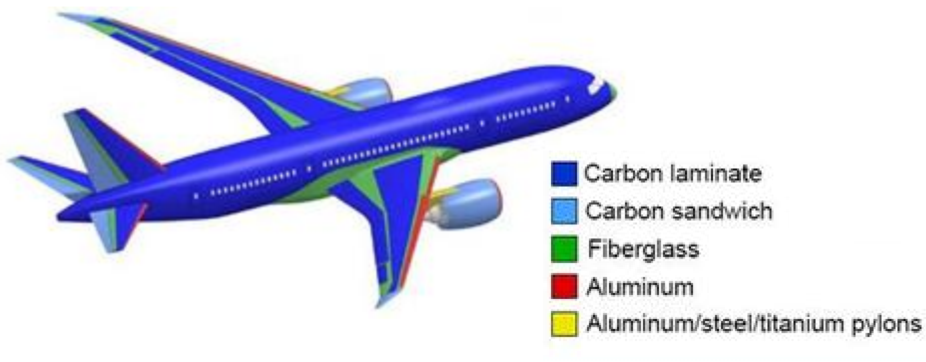
NMP.2012.1.3-2
Modelling toxicity behaviour of engineered nanoparticles

NMP.2012.1.3-3
Regulatory testing of nanomaterials

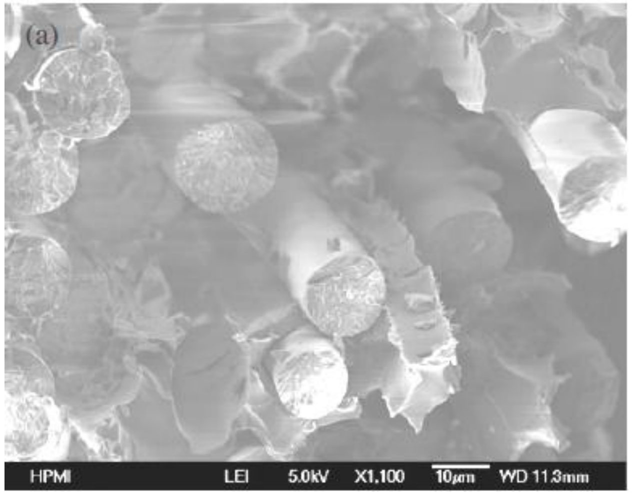
Thanks for you attention

Questions?

Use of CNTs in Aerospace Engineering

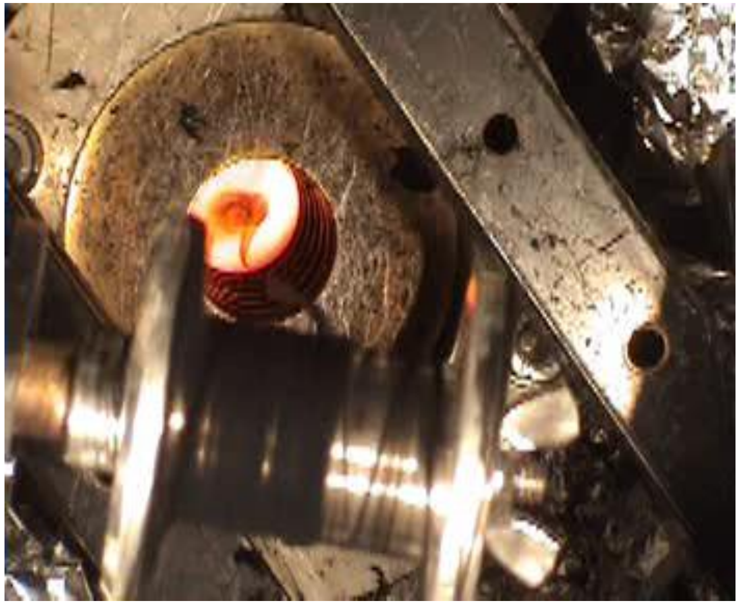


More than 50% by weight of composite materials used in Boeing 787

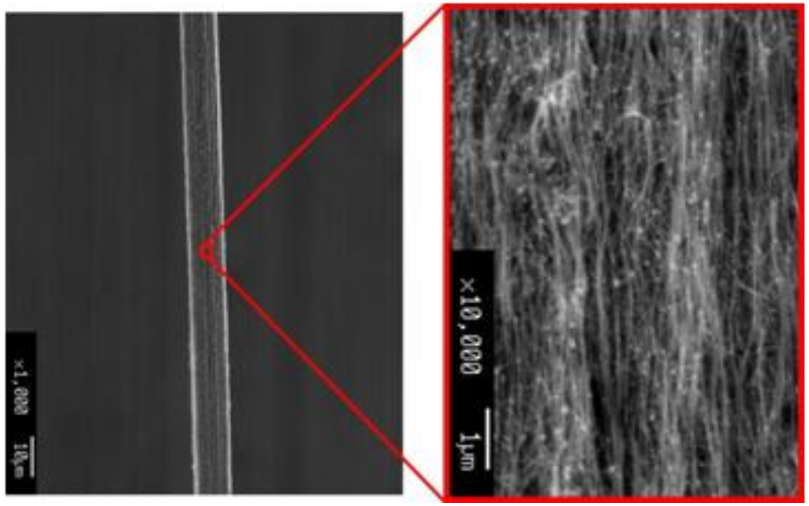


Polymer Fibre Composites

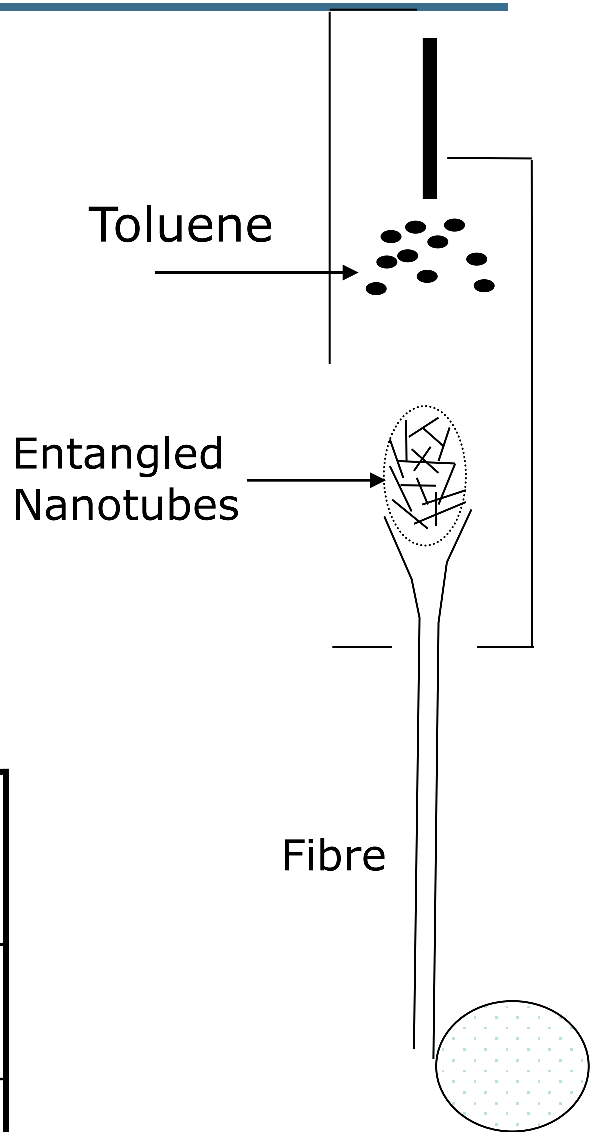
Directly Spun Pure Carbon Nanotube Fibres



Movie 1



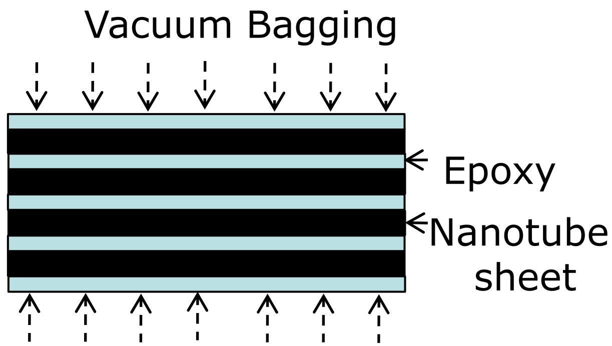
Source: KK Koziol, A H Windle, University of Cambridge



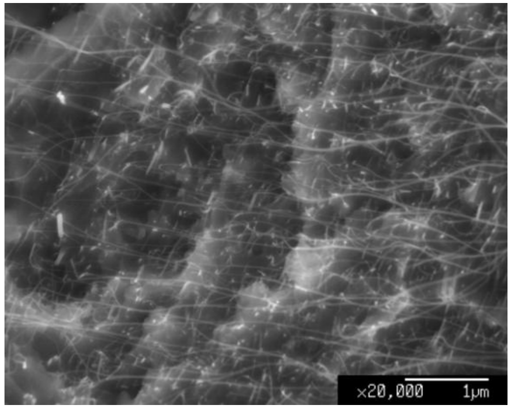
Properties	Tensile strength (GPa)	Thermal Conductivity (W/mk)	Electrical Conductivity (S/m)
Carbon Nanotube Fibre	5 to 9.8	1450	2.5×10^5
Carbon Fibre	3.1 to 6	300	1×10^5

Koziol *et al*, Science, (2008)

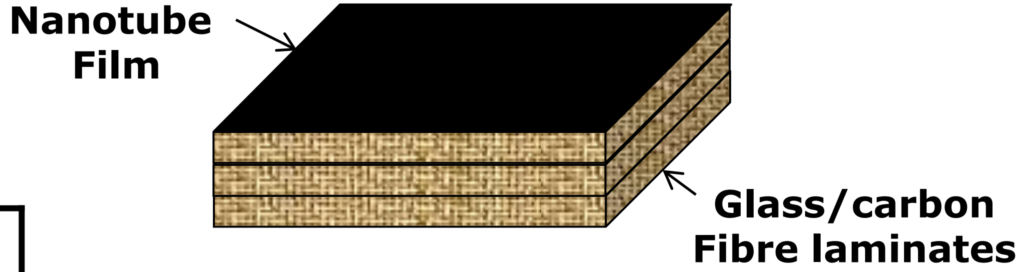
Current Work at ACCIS



Collaboration: K Hazra, K Potter



- Electrical conductivity 4 X10^5 S/m
- Thermal Conductivity 1100 W/m-K



Properties	Electrical Conductivity (alignment direction) (S/m)	Electrical Conductivity (Cross plane direction) (S/m)
Nanotube Film Epoxy Composite	4960	990
Neat Epoxy	2 X 10^{-7}	2 x 10^{-7}

- Inter-lamellar reinforcement
- Improved Inter-lamellar conductivity
- Lightning strike protection
- Electrical Actuation & Energy Storage
- Morphing wing aircraft component

Carbon nanotubes Based Multi-Scale Composites

Carbon nanotube reinforced multi-scale composites allows this 54-foot boat

- **Weigh only 8,000 pounds**
- **Carry up to 15,000 pounds of payload more than 2,500 miles.**
- **Compared to other existing USVs, the Piranha USV has triple the payload capacity and ten times the range.**

Recycling of Composites

Mechanical Recycling by Grinding

Ground composites powder which can be reused for moderate strength requirement applications

Energy Recovery by Incineration

→

- Energy recovery due to burning of polymer resin
- Recovery of carbon fibre for reuse

Protocol for Safe handling of Carbon Nanotube during Recycling?