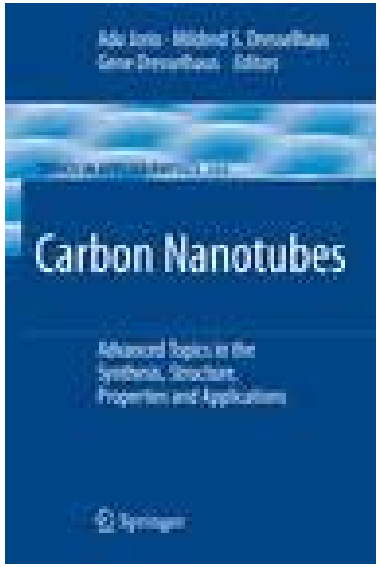
# Outline

Jean Christophe Charlier
Ado Jorio
E. Flauhaut
Jing Kong
Mario Hofmann
**Mildred S. Dresselhaus**

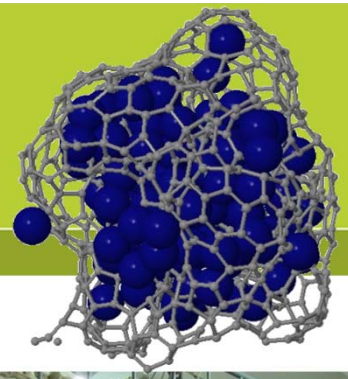
- **What we learned at NT08; Achievements and Trends**
- **Reports from satellite meetings**
- **Challenges & Future Work**



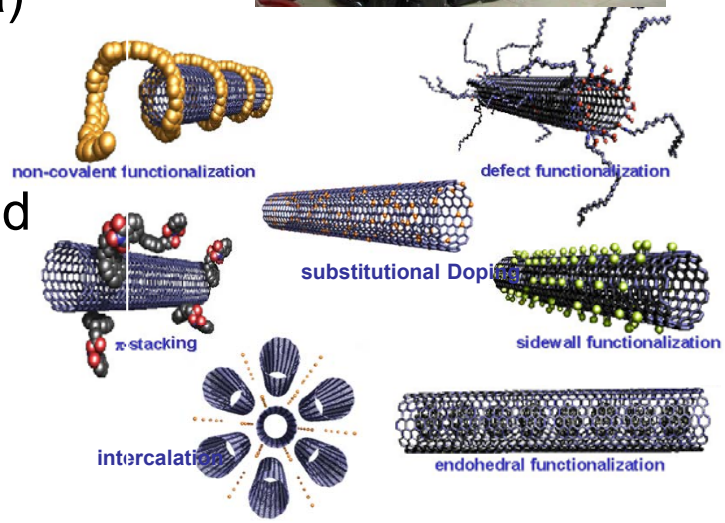

"*Advanced Topics in the Synthesis, Structure, Properties and Applications of Carbon Nanotubes*",

by A. Jorio, M.S. Dresselhaus & G. Dresselhaus

# Synthesis I

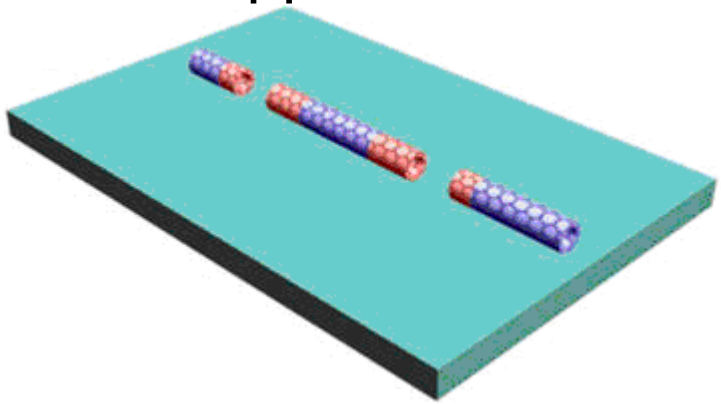


- Progress with understanding mechanism
  - Role of clusters  and carbon chains in early nucleation stage
  - Catalyst size, shape, composition
  - Possible special role for sulfur??
  - Fiber growth and control
  - Large scale synthesis of SWNTs
- Separation methods
  - Metallic/semiconducting SWNTs (Kataura)
  - (n,m) separation by density-gradient ultra centirufgation method (DGU) (Hersam)
  - improved understanding of surfactants and solvation process



# Synthesis II

- What are people working on?
  - Strongly dominated by CVD (95/96 posters)
  - Growth is more closely connected to application
  - Highlight: SWNT cloning
  - More emphasis on
    - Functionalization
    - Doping
    - Graphene

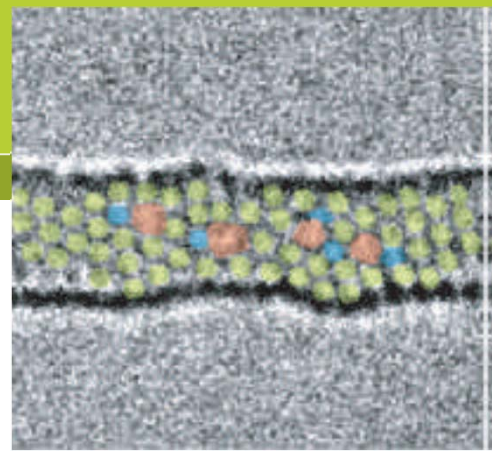


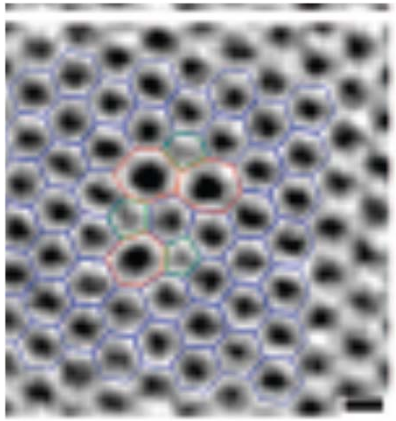
- Increasing interest in DWNTs but still many more papers on SWNTs
- Increasing interest and more papers on networks (Martel)

# Characterization

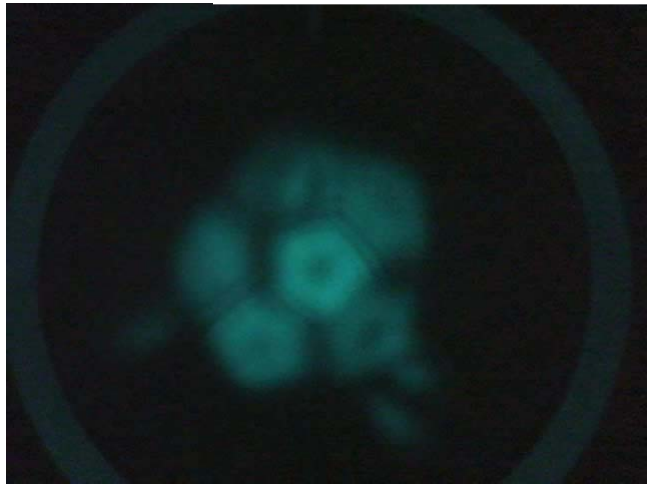
- Major advance in HRTEM - Aberration corrected optics and monochromatic electron beams now available; low voltages becoming more common for imaging carbon e.g. 80 keV.
  - Defects (individual atoms, molecules & vacancies, and distinguishing between different kinds of defects)
  - New Technique to determine accurately chirality (n,m) by Electron Diffraction (no calibration required and gives tilt angle also)
  - In-situ growth experiments have been performed using Environmental and Standard Microscopes (revealing both carbon surface diffusion and bulk diffusion)
  - More in-situ experiments are being performed
- Field emission microscopy reveals
  - adsorption kinetics on the pentagonal face of a MWNT
  - Growth dynamics of a nanotube

Iijima

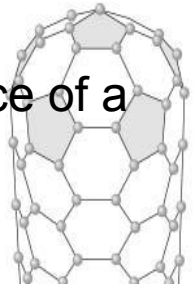




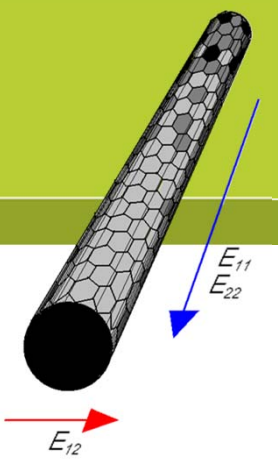
Zettl



Koichi. Hata

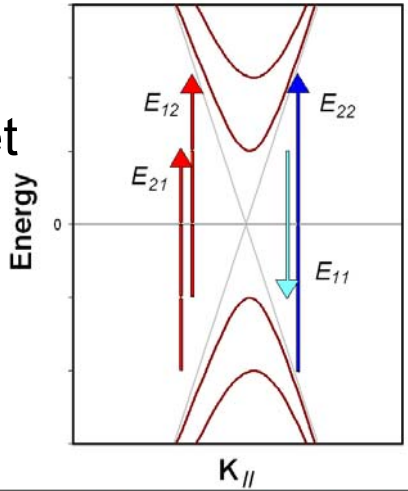


# Photophysics



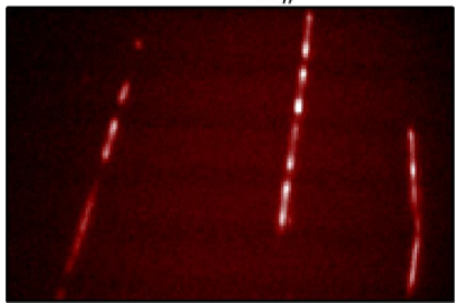

## Exciton Phenomena

- Fine structure observed at individual SWNT level for higher lying exciton states of $E_{11}$ band (Lefebvre)
- Photoluminescence yields ~10% seen by several groups
- $E_{12}$ and $E_{21}$ transitions observed by cross-polarized PL and Raman, yielding generally consistent results
- Brightening of excitons observed thermally, lowest singlet dark state at ~10 meV below bright state
- Clarification of $E_{33}$ and $E_{44}$ transitions relative to $E_{11}$ and $E_{22}$ (Doorn)
- Joint experiments (TEM+Raman, Transport+Raman, Strain + Raman, etc)



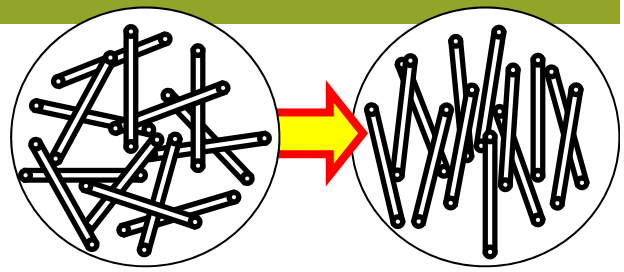

## Raman

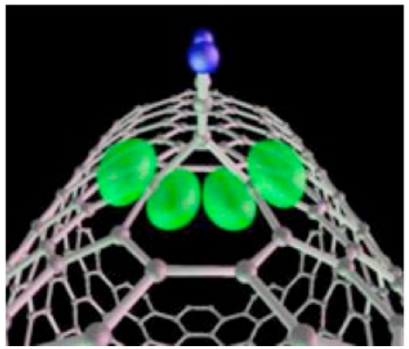
- Progress with G band for metallic SWNTs
  - G band lineshape
  - Dependence on Fermi level, $E_{Laser}$, chirality
  - Out-of-equillibrium of G- excitations (Cronin)
  - Comparison of Kohn anomaly for SWNTs and graphene

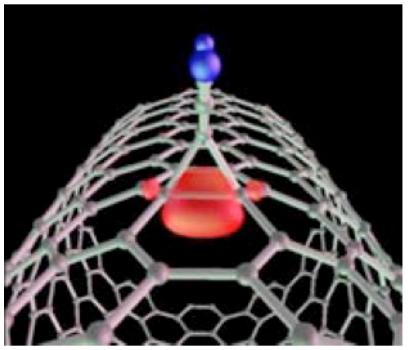


# Chemistry of Nanotubes

- Increased emphasis has been given to theoretical calculations which guide experimental implementation of functionalization strategies
  - Cyclo-addition makes it possible to add groups which enhance functionalization without affecting electrical and thermal conductivity (Marzari)
  - Application of knowledge gained from polymers is applied to large scale assembly of fibers from nanotubes (Pasquali)



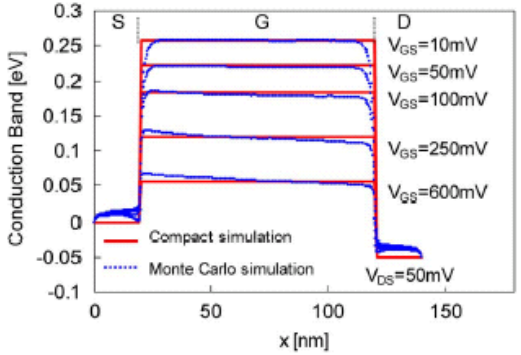




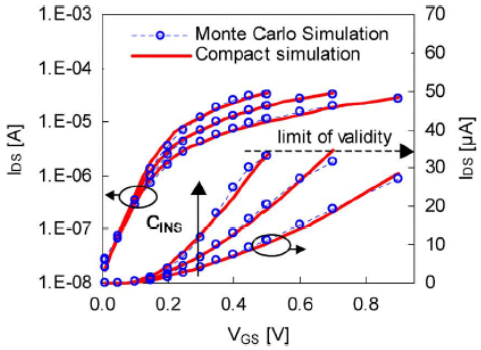
# Transport in Nanotubes

- Many experimental papers on FETs for CNTs and graphene
- Much greater interest in networks

**Quantum transport in CNTFET within a multiscale simulation framework**




**Semi-classical Monte Carlo and Compact modelling are accurate enough for ideal ohmicCNT-FETs.**




**Dr. Philippe Dolffus, Paris, France.**

**Electronic properties of CNT bundles and interconnects**

**Dr. Yu Zhukovskii, Riga, Latvia**

**Electronic transport in CNTs : from Luttinger Liquids to correlated superconductivity**

**Dr. S. Bellucci, Frascati, Italy**

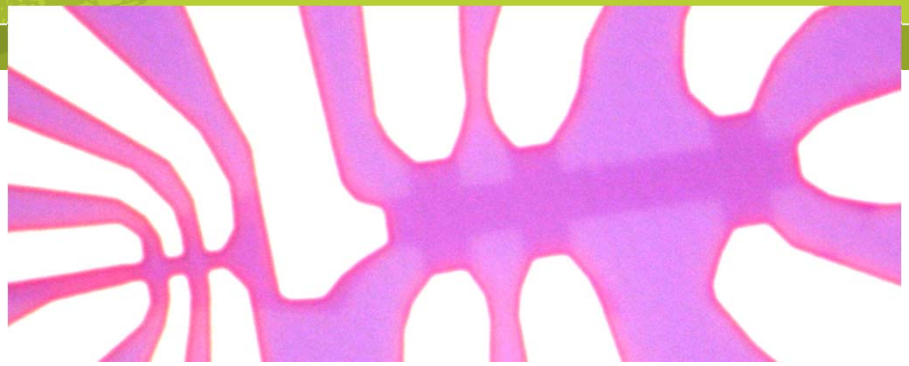
**Semiconductor CNT quantum dot : interacting electron states**

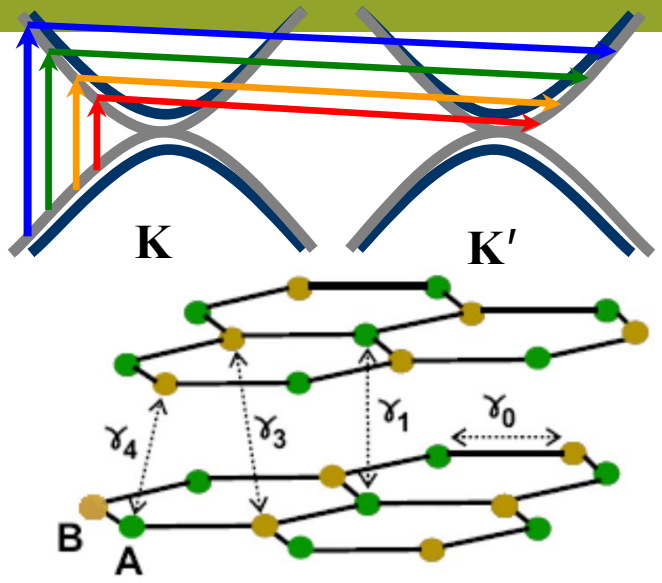
**Dr. M. Roy, Leicester, UK**

**Non-equilibrium MD : flow through NT**

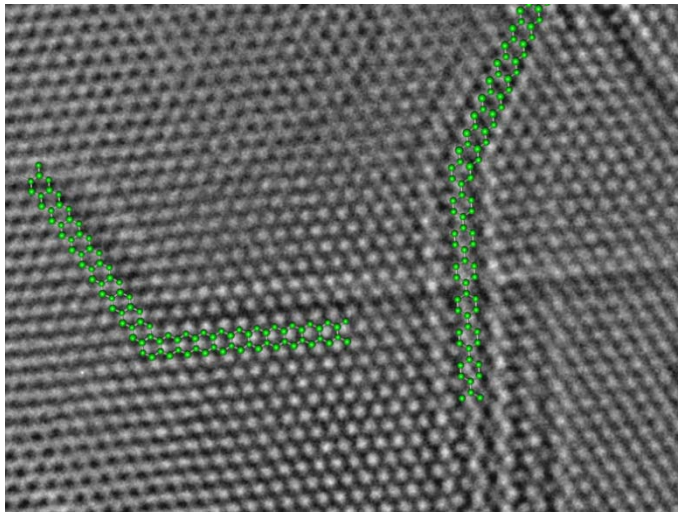
**Dr. J. Cannon, Surrey, UK**

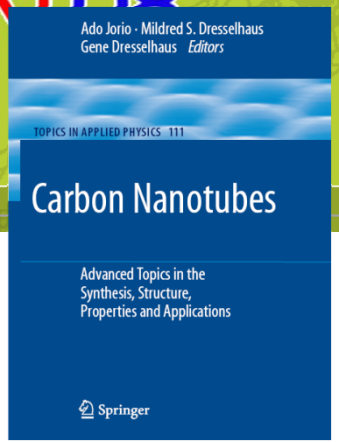
# Graphene






- Hot topic now expanding rapidly, first in theory and now also in experiment
- New techniques for synthesis under development
- Prediction of superconductivity on the edge state
- Many similarities are observed between NTs and graphene stimulating movement between the fields, for example, G' band studies in bilayer graphene allows evaluation of the electronic bonding energy coefficients (Pimenta)
- Graphene edges play a key role in nanoribbon properties. And they need to be further investigated, both by experiment and theory
- New theoretical prediction of a spin polarized state may lead to new research frontiers



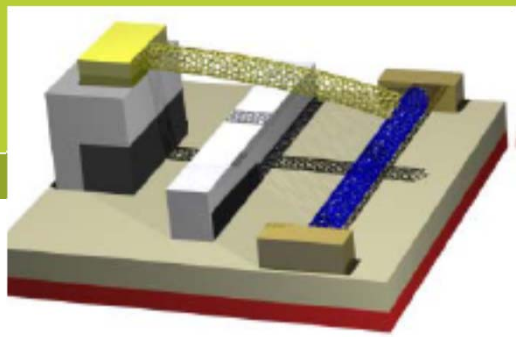



# Applications roadmap for Carbon Nanotubes

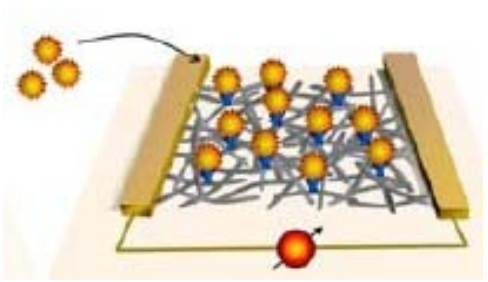
*by M. Endo, M. S. Strano, P. M. Ajayan*

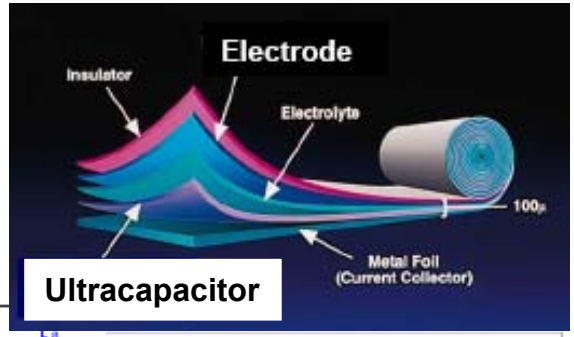
| | **Large Volume Applications** | **Limited Volume Applications (Mostly based on Engineered Nanotube Structures)** |
|---|---|---|
| **Present** | - Battery Electrode Additives (MWNT)<br>- Composites (sporting goods; MWNT)<br>- Composites (ESD* applications; MWNT)<br>*ESD – Electrical Shielding Device | - Scanning Probe Tips (MWNT)<br>- Specialized Medical Appliances (catheters) (MWNT) |
| **Near Term (less than ten years)** | - Battery and Super-capacitor Electrodes<br>- Multifunctional Composites (3D, damping)<br>- Fuel Cell Electrodes (catalyst support)<br>- Transparent Conducting Films<br>- Field Emission Displays / Lighting<br>- CNT based Inks for Printing | - Single Tip Electron Guns<br>- Multi-Tip Array X-ray Sources<br>- Probe Array Test Systems<br>- CNT Brush Contacts<br>- CNT Sensor Devices<br>- Electro-mechanical Memory Device<br>- Thermal Management Systems |
| **Long Term (beyond ten years)** | - Power Transmission Cables<br>- Structural Composites (aerospace and automobile etc.)<br>- CNT in Photovoltaic Devices | - Nano-electronics (FET,Interconnects)<br>- Flexible Electronics<br>- CNT based bio-sensors<br>- CNT Filtration/Separation Membranes<br>- Drug-delivery Systems |

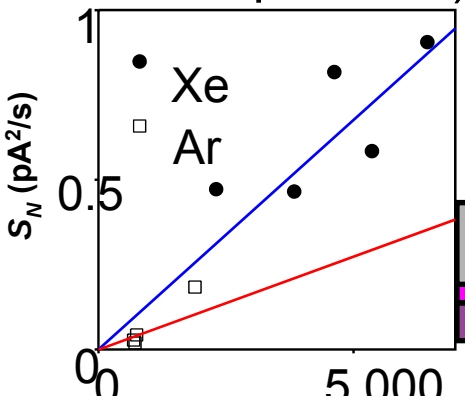
# Applications

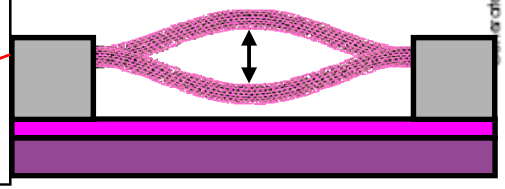


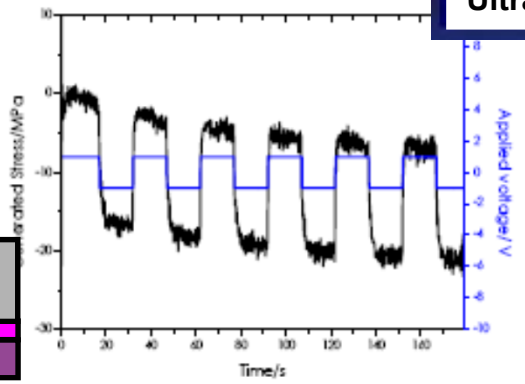
- Increasing interest in applications, especially for nanotube transistors and transparent electrodes
- Chemical and biosensors from individual and multiple nanotubes
- Nanotubes as reinforcements
  - For polymers/ceramics
  - As electrode material
- Biological applications: sensors, drug delivery agents, muscle actuators, tissue growth scaffold
- Mass detection at single atom resolution is possible with NEMS sensors (even at room temperature)



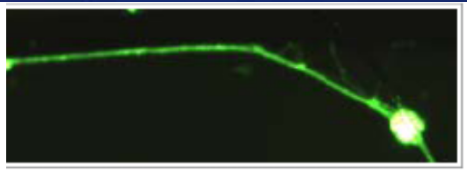


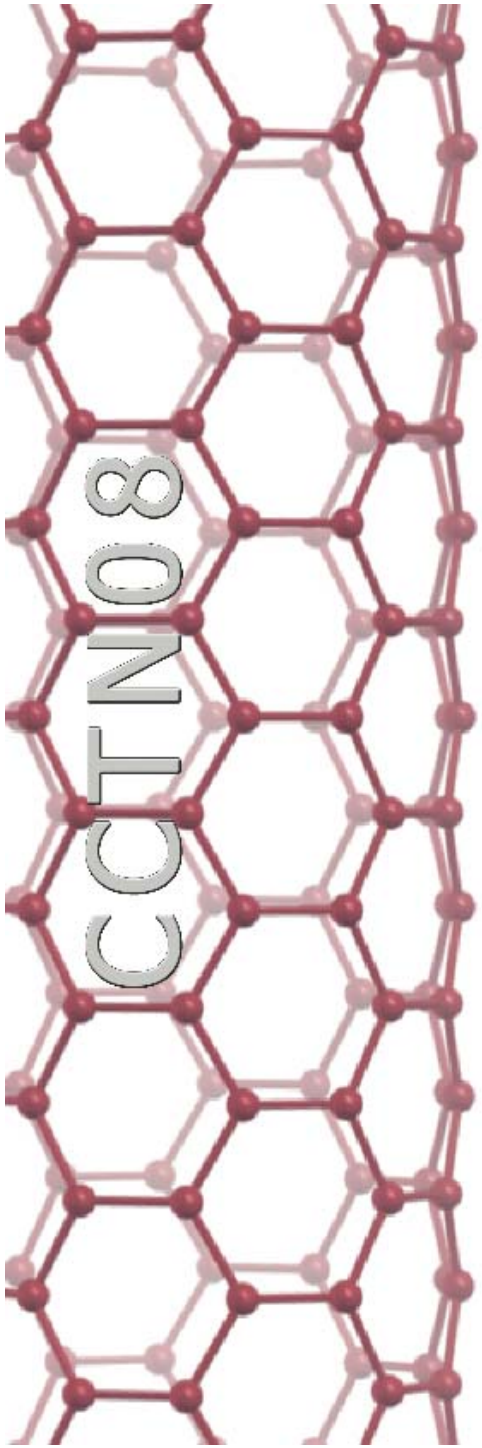






Artificial muscle



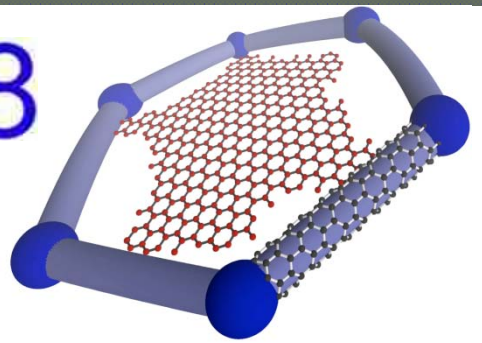
Scaffold for Neuron growth




# Computational Challenges and Tools for Nanotubes

CCTN08

NT08



# SUMMARY !

*Organizers:*

**Stephan Roche**
INAC/CEA - France

**Jean-Christophe Charlier**
University of Louvain - Belgium

**Hisashi Nakamura**
RIST - Japan

**David Tomanek**
Michigan State University - USA

June 28, 2008
Le Corum, Montpellier, France

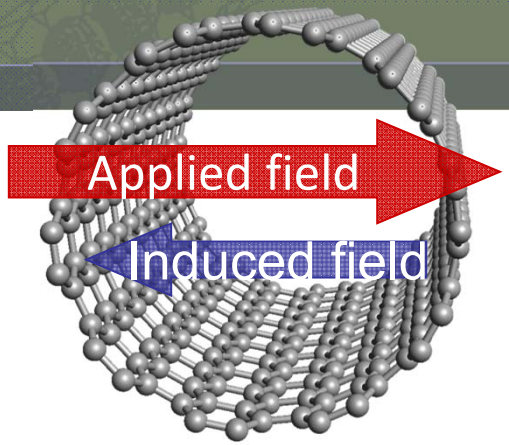
Sponsors

RIST

GDR-I Nano-I

# Optical and mechanical properties of nanotube structures

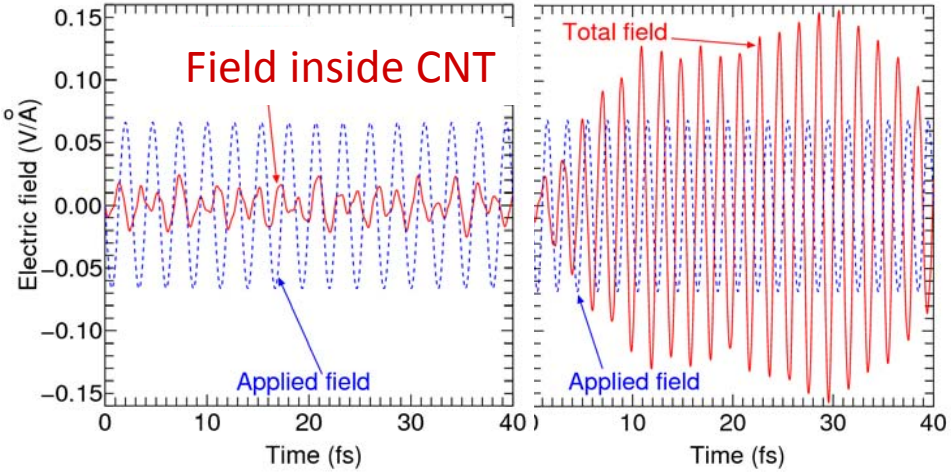
## Mechanical properties of Nanotubes




**Modulation of Optical field inside carbon NTs with cross-polarization direction**

Off resonance

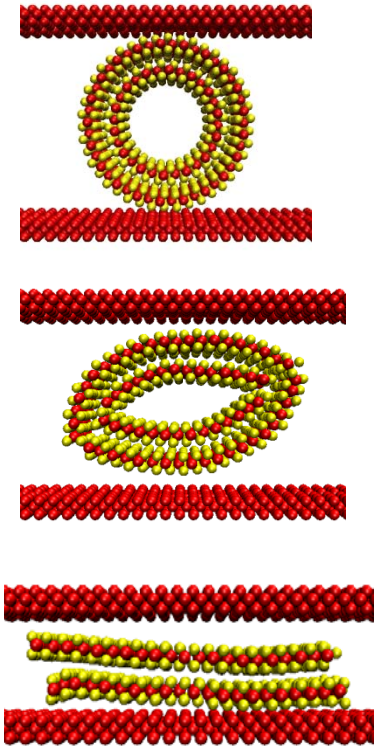
Near resonance




**Field enhancement even inside CNT!**

**Dr. Yoshiyuki Miyamoto, NEC Japan.**

C, but also $MoS_2$ :

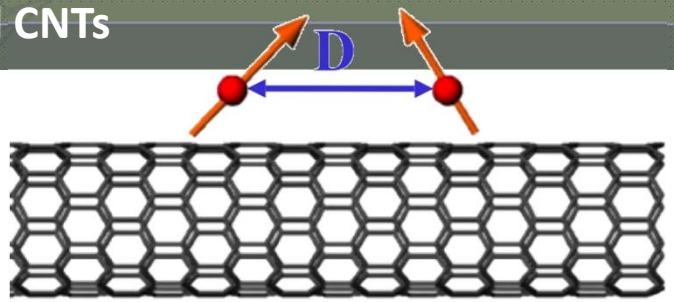


The extreme squeezing of MoS2-NTs could explain excellent lubrication properties of $MoS_2$ based nanoparticles.

**Prof. Gotthard Seifert, Dresden, Germany.**

# Chemical reactivity and functionalization of CNTs

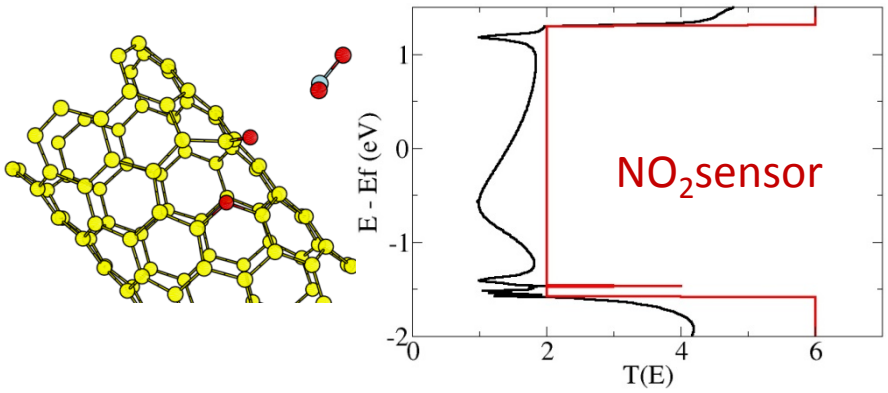
## Long-range interaction in magnetically doped CNTs




**How are the magnetic moments coupled ?**
**How does the couplig decay with D ?**

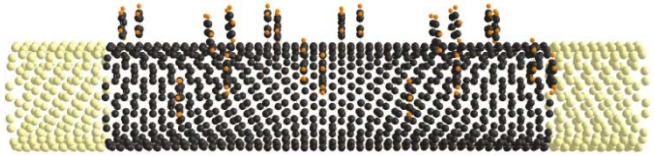
**Dr. M.S. Ferreira, Dublin, Ireland**

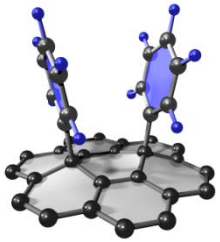
## Gas-sensors based on defective CNTs

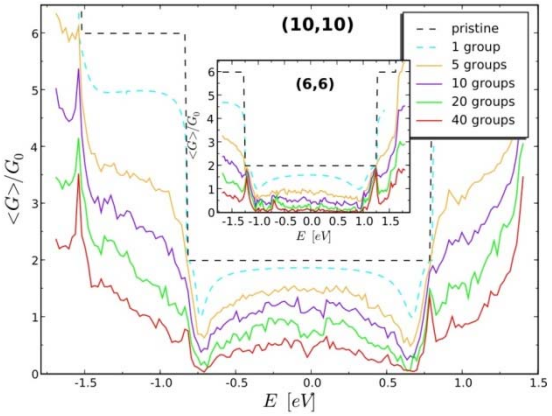


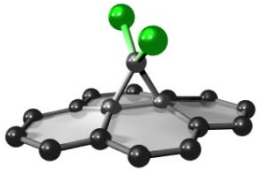

**Dr. Z. Zanolli, Louvain, Belgium**

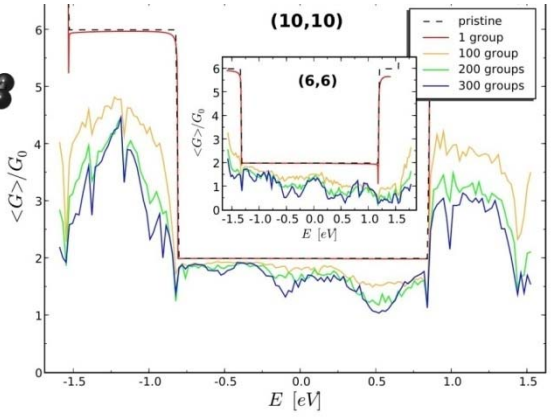
## Electronic transport in CNTs grafted With phenyl and carbene molecules







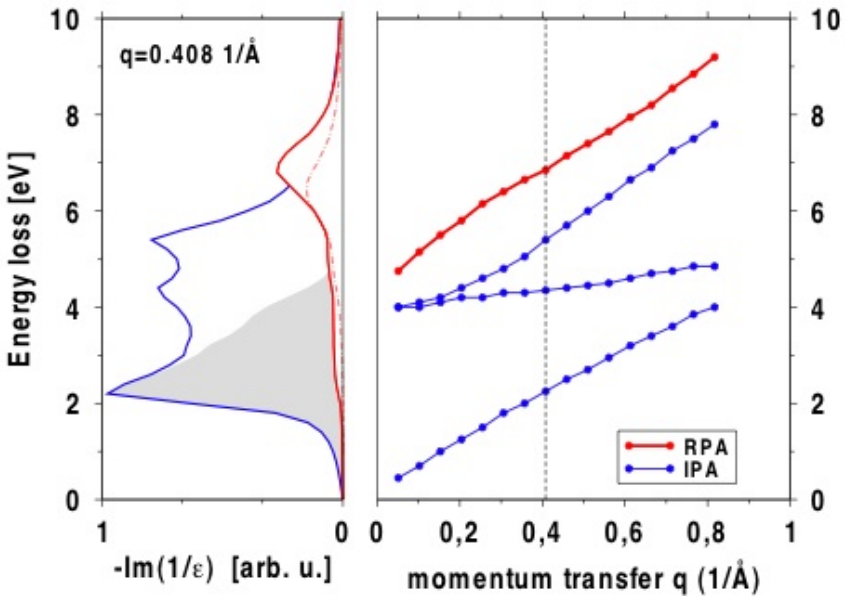






**Alejandro Lopez-Bezanilla, Grenoble, France**

# Graphene structure and properties

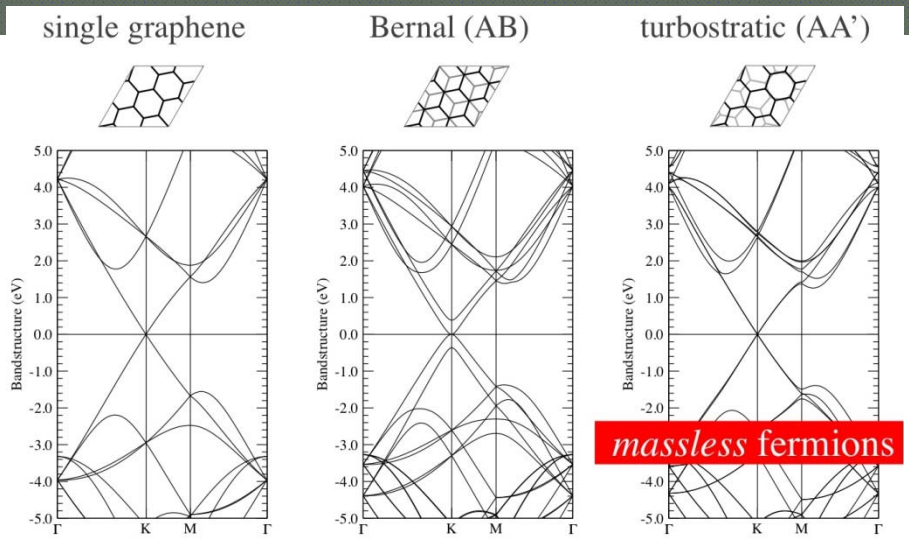
## Ab initio electronic excitations in carbon nanotubes and graphene




**The study of graphene (single- and bi-layers) allows to reproduce the linear plasmon along the tube axis for isolated tubes with large diameter and bundles.**

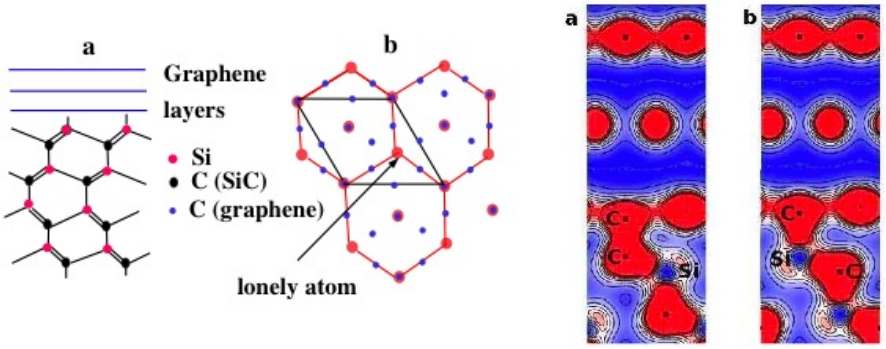
**Dr. C. Giorgetti, Palaiseau, France**

## Few layer graphite : electronic properties




**Dr. L. Henrard, Namur, Belgium**

## Electronic structure of epitaxial graphene



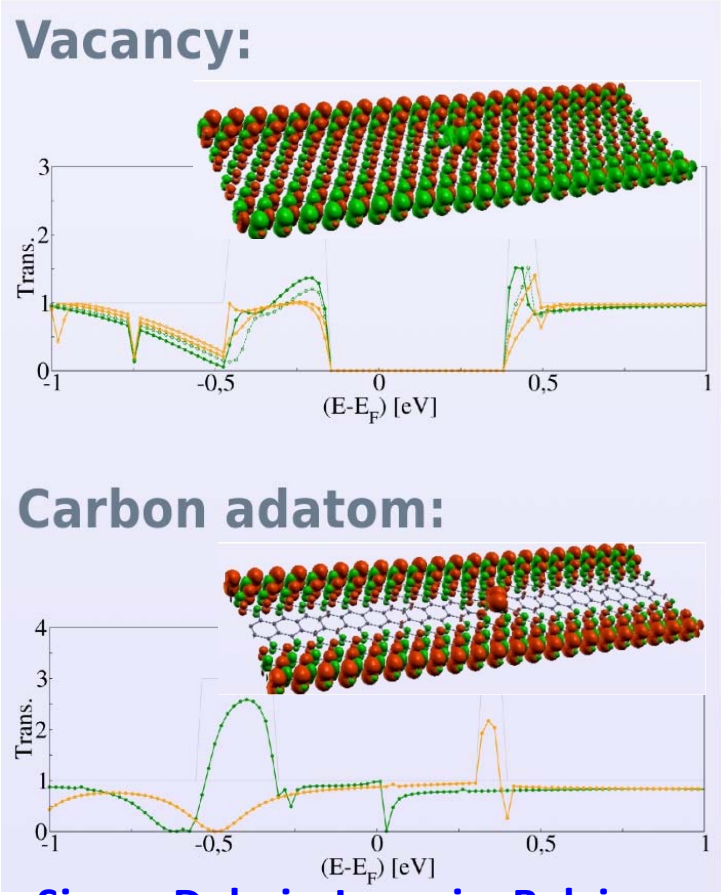

**François Varchon, Grenoble, France**

# Graphene nanoribbons: structure and properties

## Optoelectronic properties of carbon nanotubes and nanorribbons

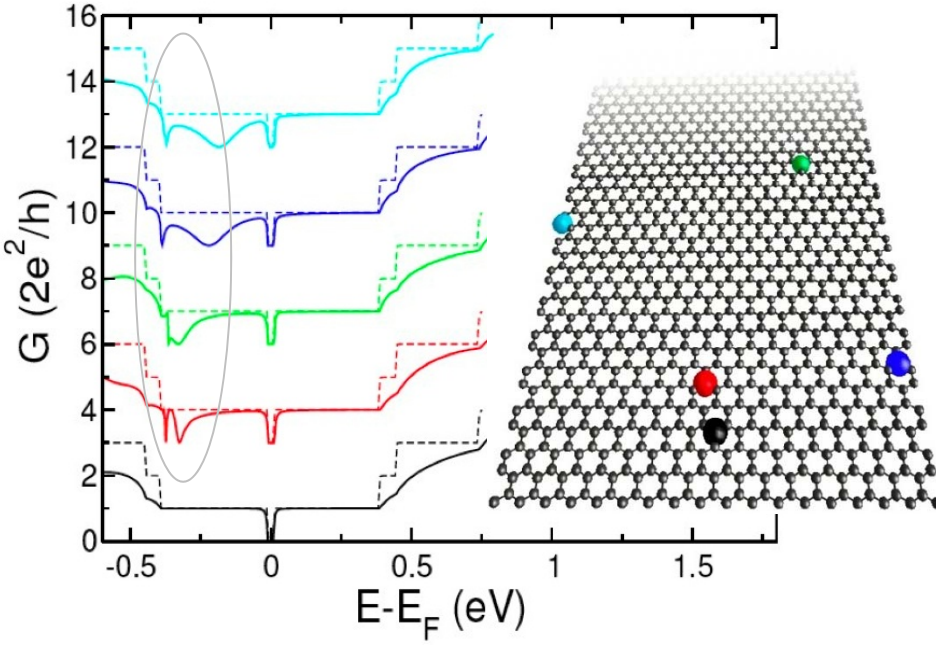
Dr. A Ruini, Modena, Italy

## Spin-transport in defected graphene ribbons




Simon Dubois, Louvain, Belgium

## Electronic transport properties of chemically doped nanoribbons




Dr. B Biel, Grenoble, France

## Magnetic behavior of substitutional transition metal dopants in graphene

Dr. A. Ayuela, San Sebastian, Spain

## Electronic wave guides and superlattices in graphene

Dr. L. Chernozatonskii, Russia

# Summary from Metrology Satellite (MSIN08)

Ado Jorio
Annick Loiseau
June 28, 2008
followed (MSIN07) in Brazil

# Metrology for Post synthesis processing

- Recently there were major advances in separation of heterogeneous samples
  - Chirality
  - Length
  - Handedness
  - Electronic properties: Metal vs Semicoducting
- Mass production process (10 ton/year) for SWNTs is promised for 2010

**All require standards for characterization**

# Characterization/Metrology

What's in your sample?

- Several techniques such as spectroscopy, electron diffraction and others have to be harmonized to give a common picture of a sample

- Standard reference materials will contribute to the harmonization process

# Suggestions for metrology on carbon nanotubes

- To deliver such a standard reference material the following exploratory steps are needed
  - Test whether exploratory reference material is valuable. This test is being attempted by NIST in 2009. Help from research groups is needed.
  - Determination of which properties should be investigated
  - Whole suite of reference materials will be needed for different properties and analysis techniques
- Standard should be specific to application
  - Demand from the application side has to determine priority
  - Which applications are ready to be tested against standards?

Metrology satellite for NT09 is strongly requested,
Ado Jorio will do follow up

# 1st Carbon Nanotube, Biology, Medicine and Toxicology Satellite Symposium

- **6 invited speakers**
- **10 contributed talks**
- **30 posters**
- **80 – 100 participants**

**4 Main topics:**

- IMAGING
- MEDICINE
- TOXICITY
- ECO-TOXICITY (Environmental Impact)

E. Flahaut, CIRIMAT, France and K. Kostarelos, University of London, UK)

## IMAGING:

- CNT can be imaged in real time both in vitro and in vivo by NIR fluorescence (*)
- X-Ray fluorescence (**)
- TEM is often used in vitro, almost only in the case of large MWNT (***)

## MEDICAL APPLICATIONS SOON AVAILABLE?

***CNTs can be targeted to tumour tissue via appropriate functionalisation***

- Cancer treatment (hyperthermia, (targeted) drug delivery)

***CNTs can enter the cytoplasm and/or nucleus***

- ***a new form of drug delivery system***
- Therapeutics (drug delivery) and gene therapy

***CNTs can be used as scaffolds for cell growth***

- Tissue engineering and biocompatibility

(*) NIR detectors not commercially available
(**) Low availability – need for a metal inside the CNT for detection
(***) Lots of structures present in cells unfortunately look like *few-walled* CNT

## TOXICITY:

**Interaction between nanotubes and cells s*trongly depends on:***

- Synthesis route (residual catalysts, purity)
- Length, diameter, stiffness
- Functionalization
- Agglomeration state, biopersistence (excretion)

***Main exposure route: inhalation***

- Similarities between CNTs and asbestos? lack of realistic exposure scenario…

## ECOTOXICITY (Environmental Impact)

***CNT worldwide production of a few hundred of tons per year***

***CNT are used or will be used soon in more and more commercial products (sport equipments, cars, paints and coatings, medical applications etc.)***

There are only a very limited number of toxicity studies on CNT, but they usually show some toxicity from 10 mg/L, a rather unrealistically large dosage for the environment.

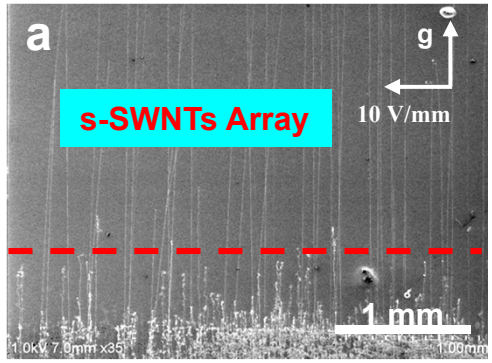
# Conclusions

- Exposure of cells to low concentrations (< 1 mg/L) usually do not cause much harm to cells (under proper experimental conditions)
- Promising applications in the field of medicine
- "Are CNT toxic?" the result is dependent on surface chemistry and morphology. Eventually the toxicity standards and standard operating conditions need to be established: such as protocols to protect researchers, production workers and the environment
- Thorough characterisation of the CNT samples is mandatory for correct analysis of data
- Principle of precaution: as in the case of any chemical!
  Wear gloves, a lab coat and an appropriate dust mask (FFP3)

**Need for an update next year at NT'09!**

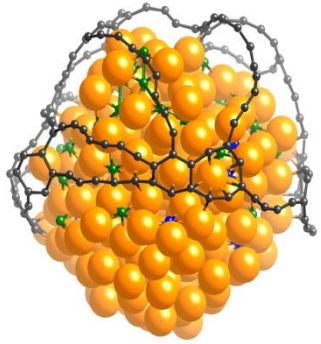
# Challenges and future work

- **Synthesis**
  - Remains the main focus
  - Control of processing for reproducibility regarding structure and properties
  - Control of (n,m) during synthesis, cloning etc
  - Control of the number of graphene layers and sample sizes
  - Control of ribbon synthesis
  - Standards are needed for sample specification



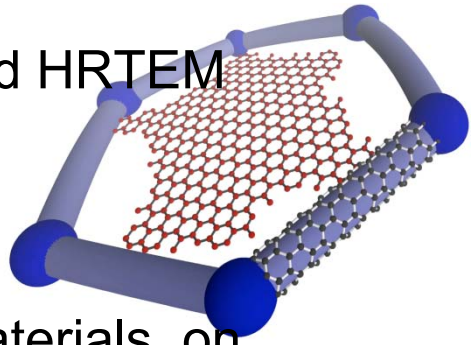

- **Functionalization and chemistry**
  - Multi-technique characterization
  - More joint theory/experiment projects

- **Characterization**
  - New techniques such as aberration corrected HRTEM for studying growth, cloning and defects
  - Joint experiments (HRTEM + Raman etc)
  - More near field optics, time resolved studies



# Challenges and future work, cont'd

- **Photophysics**
  - Further clarification of diameter characterization of $\omega_{RBM} = A/d_t + B$
  - Elucidation of triplet state
  - Comparative studies with nanotube, graphene, intercalation compounds
  - Need simultaneous multi-technique studies (HRTEM + Raman, etc)
  - More on new techniques---e.g. aberration-corrected HRTEM
- **Other topics**
  - Spintronics in nanotubes and graphene
  - More on thermal properties
  - More on non-carbon nanotubes, on single layer materials, on ribbons
  - New physical phenomena (SERS for bio)
  - Coupling metrology to science and practical applications
  - Coupling metrology to toxicology in nano-carbon applications



# Future NTxx Conferences

- NT09 in Beijing, China
- NT10 in Montreal, Canada?
- NT11 in Cambridge, UK?