NANOTUBI DI CARBONIO.
SINTESI, APPLICAZIONI, OPPORTUNITÀ
Milano, 16.05.2013 - POLIMI

POLITECNICO DI MILANO

Potenzialità e Complessità delle Applicazioni di CNT

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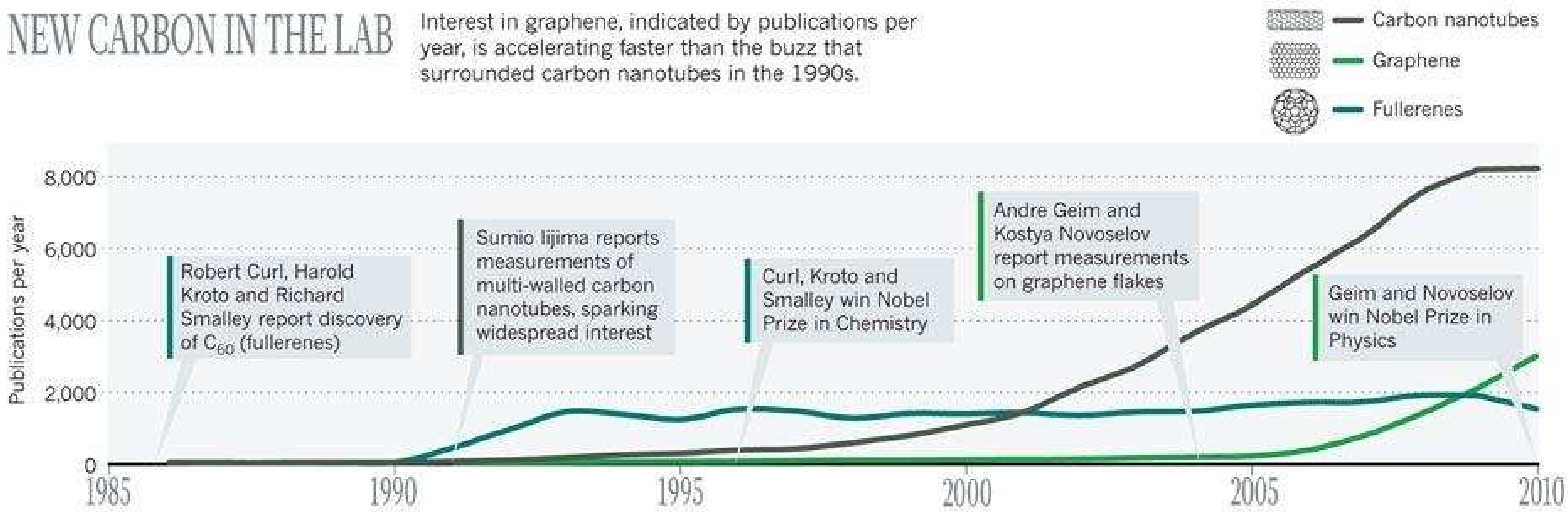
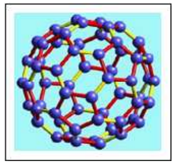
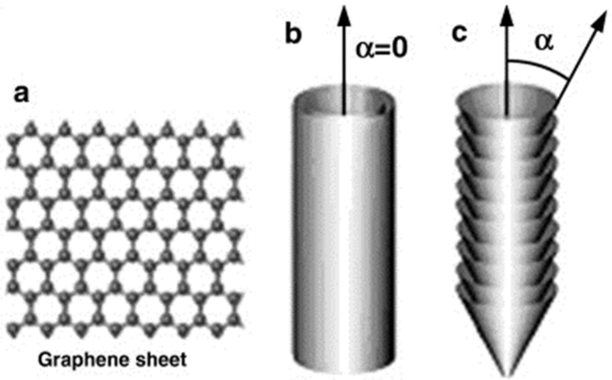
New Carbon Materials



Richard Van Noorden, Nature, 469, 14-16 (2011)



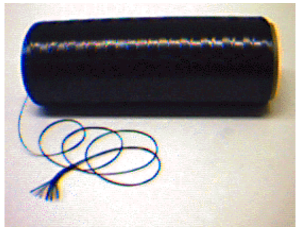
fullerene



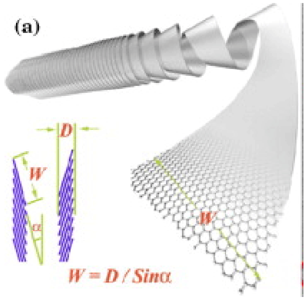
Graphene sheet

Multi-walled nanotube

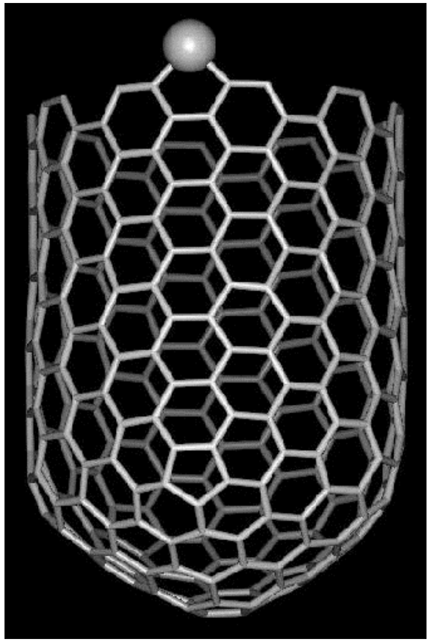
Nanofiber cup stacked



Carbon fibers



Carbon Nanotubes

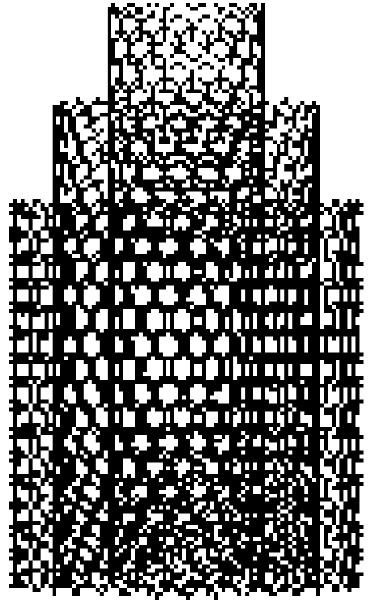


A few nanometers

Single-walled carbon nanotubes (SWNT)

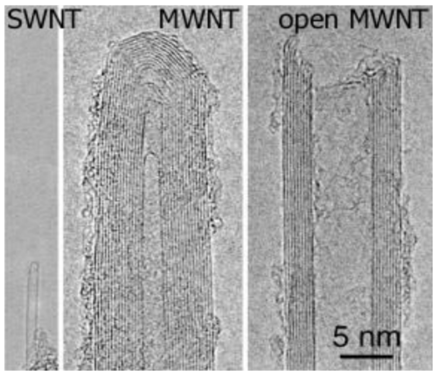
- Tensile strength 150 GPa
- Young's modulus 1 TPa
- Electrical resistivity 10^{-4} ohm·cm
- Maximum current density 10^{13} A·cm^{-2}
- Thermal conductivity > 3000 W·K^{-1}·m^{-1}
- Field emission properties
- Expansion and contraction upon charge injection (~1%)
- Semi-conducting nanotubes
- High specific surface (> 1000 m^2·g^{-1})
- Photo-electrical properties
- Anisotropic material

…



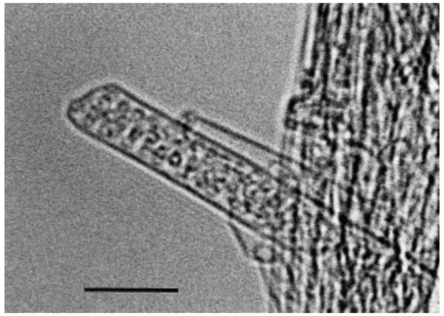
A few tens of nanometers

Multi-walled carbon nanotubes (MWNT)



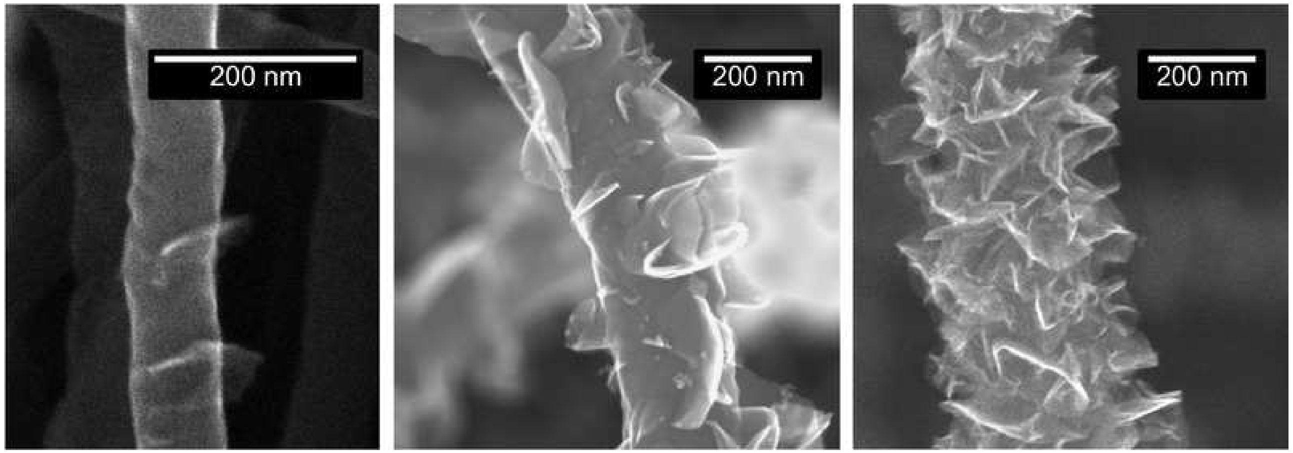
Decoration of CNT by Organized Carbon Atoms

Fullerene peapods: chains of C60 inside single-wall carbon nanotubes



Carbon *NanoBud*

Graphenated carbon nanotubes by microwave plasma enhanced CVD

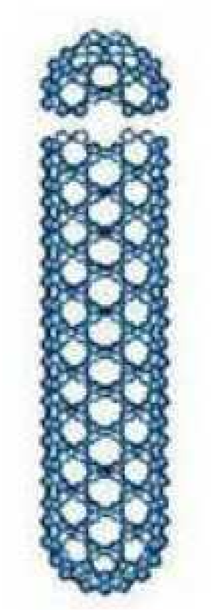


CNT: MacroMolecules or Materials?

Molecule:
- Number of atoms
- Type of atoms
- Type of bonds
- Geometry and shape
- Electronic structure
- Quantum effects
- Macromolecule distribution

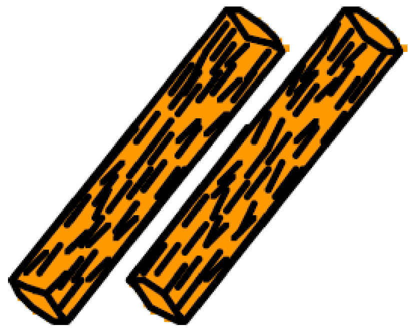
Material:
- Particle size distribution
- Particle number and concentration
- Aggregation/agglomeration
- Self assembly/recognition (adsorption and insertion)
- Filler surface interaction with medium
- Mean physical properties (conduc. (T, e^-), charge, etc.)

The Stake

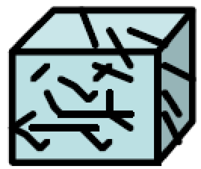


Nanotubes
properties

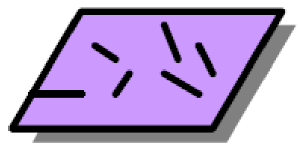
Transfer nanoscale properties to macroscopic materials



Fiber



Bulk materials



Coatings

Fields of Application of CNT

CNT in Polymeric materials

- *Multifunctional composite fillers*
- *Mechanical (strength) improvement*
- *Electrical conductive/antistatic composites*
- *Thermal conductive composites*
- *Fire retardancy*
- *Oxidation stable composites*
- *UV/visible stable composites*

Polymeric Coating

- *Conductive transparent films (pol.)*
- *Improve toughness, hardness, abrasion resistance films*

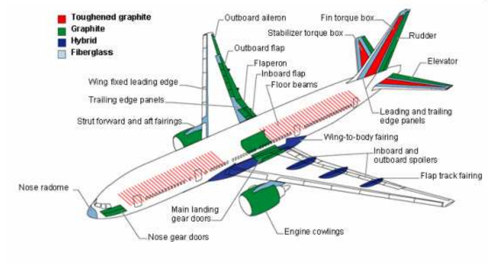


FIGURE 1-3 Production primary and secondary structure for the Boeing 777, an example of 1990s commercial application of composites.

CNT in Biomedicine

- *Biosensing*
- *Tissue Engineering*
- *Drug Delivery*

CNT in Electrochemical systems

- *Litium battery*
- *Fuel cells*
- *Electric double-layer capacitor*
- *Sensors*

Textile applications

- *Shielding textiles (decontaminating, superhydrophobic, fire retardant, adhesive, anti staining)*
- *Vital functions monitoring (sensors)*
- *EM waves shielding textiles*

Potential Applications

Targeted Segments

Electrical conductivity

Conductive Polymers/Composites

- Automotive Fuel System
  - Fuel lines
  - Filter Housing
- Packaging or Electronics
  - Blister Tapes
  - Water Boxes
- IBCs Drums for Ex-Zones
- EMI Protection (housing)
  - Mobile phones
  - Sat-Nav System
  - Control Panels

Dispersions

- Coating / Ink
  - RFID Antenna

- Electronic painting
  - Exterior Car Part
- Galvanizable Polymers
- Polymer Fibers

Mechanical strength

Reinforced Composites

- Sports Goods
- Aircraft Parts
- Windcraft Blades
- High-End Automotive Parts

Adhesives

Elastomers

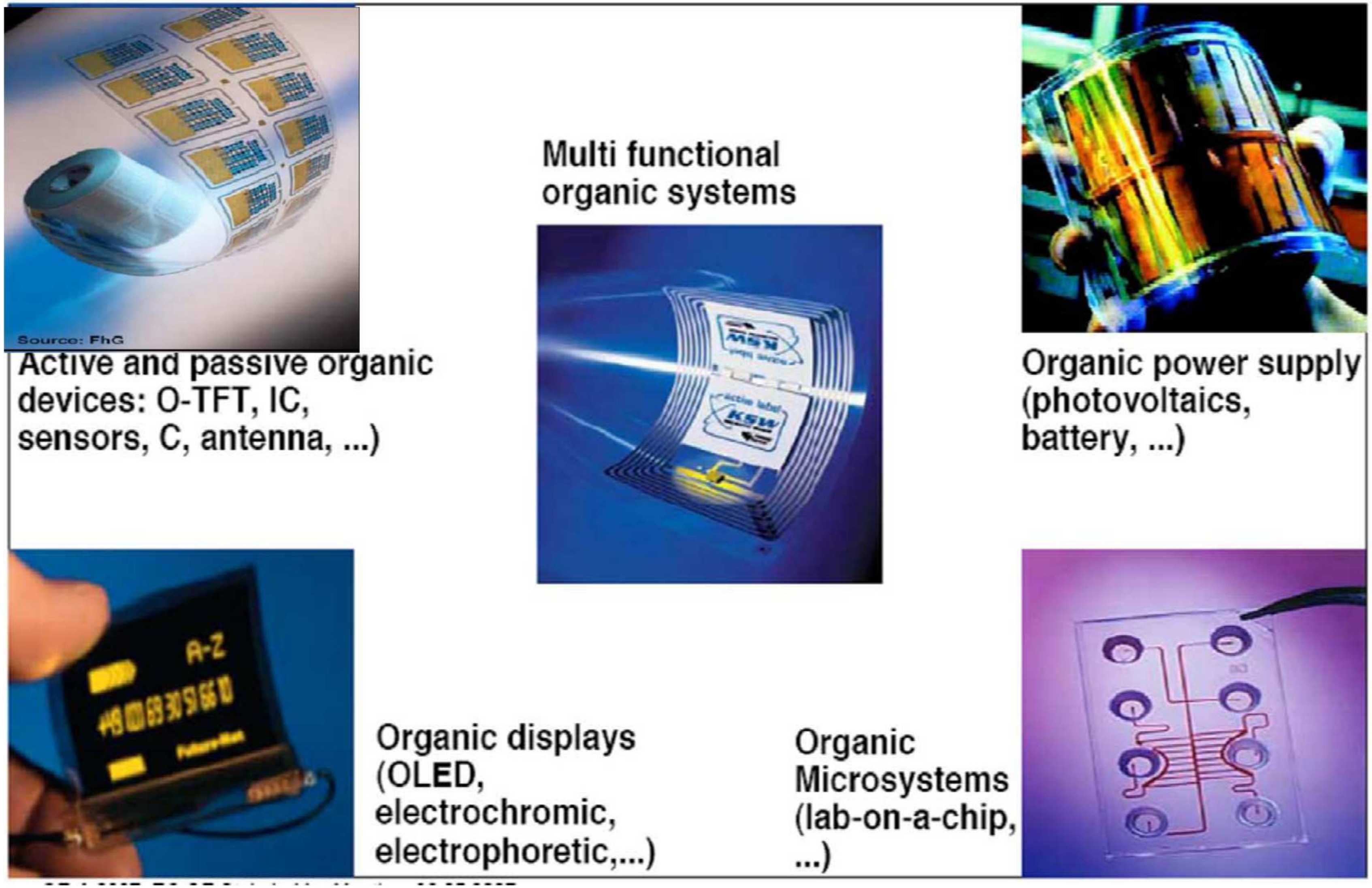
Thermal conductivity

BU Coatings, Adhesives, Sealants

Antistatic

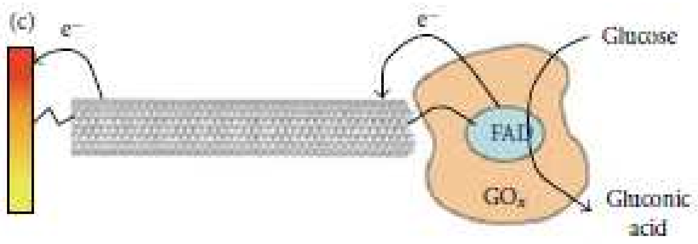
Source: Bayer

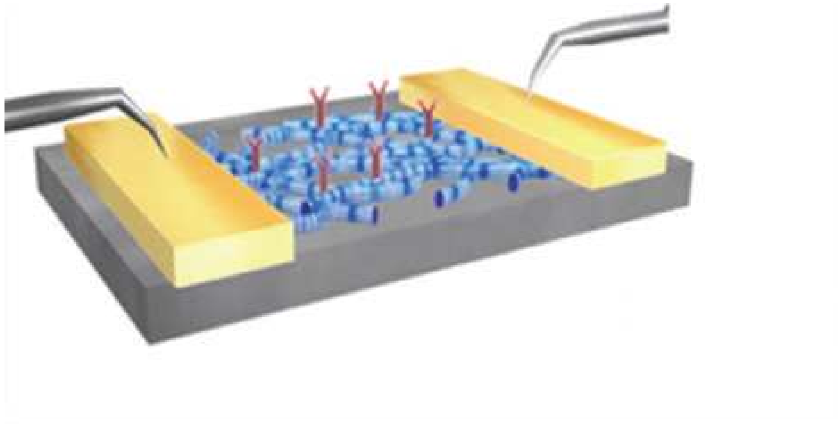
Flexible Organic Electronics: A Key Technology for CNT



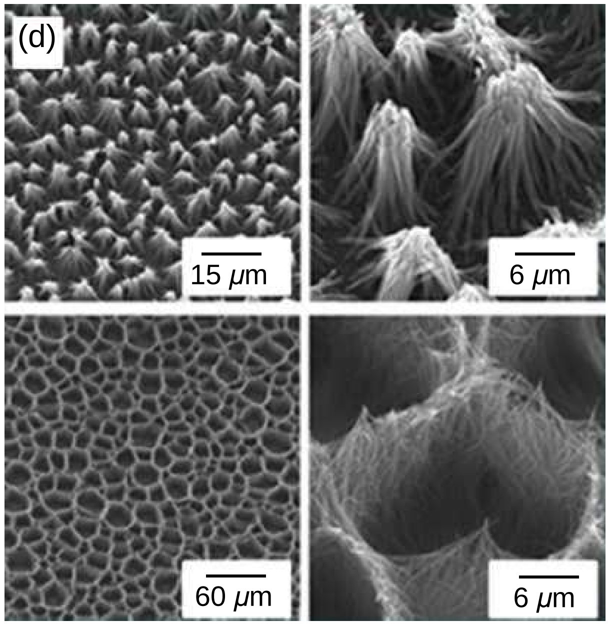
CNT Application in Biomedicine

Biological sensors

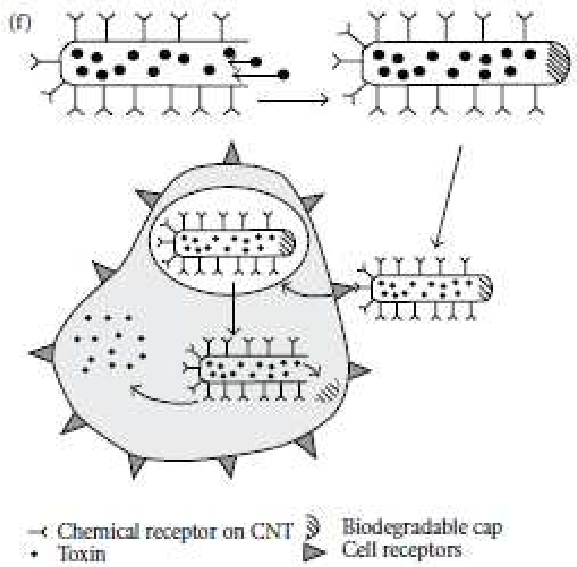




Scaffolds for Tissue Engineering



Drug delivery

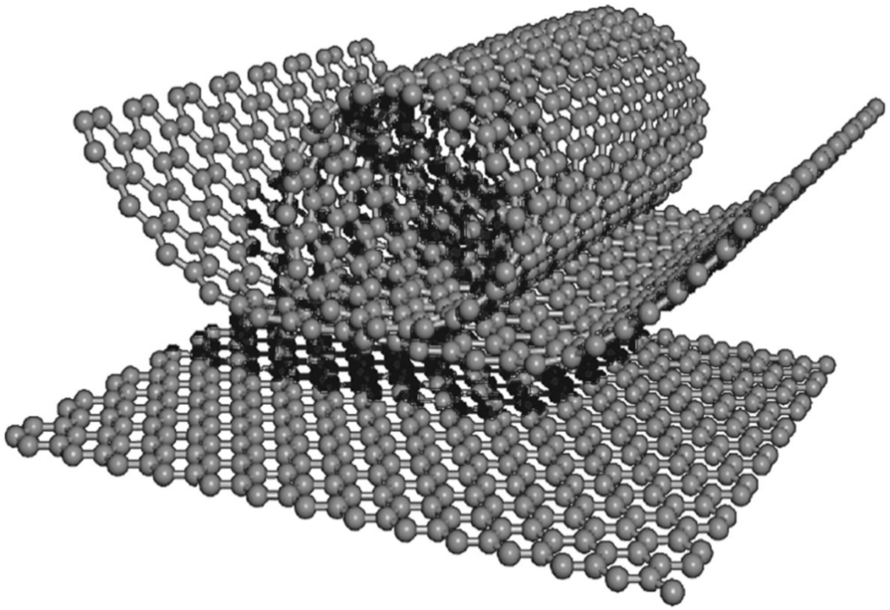


CNT – Material Variability

CNT are **complex materials characterized by different structure, topology, size, and presence of impurities and defects**. The synthetic method used dictates CNT properties such as the distribution of diameters and lengths, degree of entanglement, defects, chirality, and crystallinity, as well as the overall quality of the product. They must be considered as inorganic defective 2D materials.

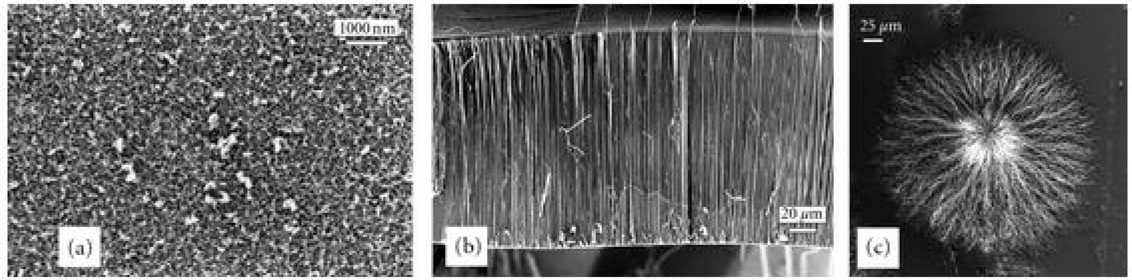
Key factors in CNT

- Nanostructure*
- Particles concentration*
- Particle size/distribution*
- Particle number
- Aggregation/agglomeration*
- Surface absorbability*
- Surface areas*
- Surface charge*
- Self-assembly*
- Quantum effects
- Tube ends
- Metal/molecule encapsulation

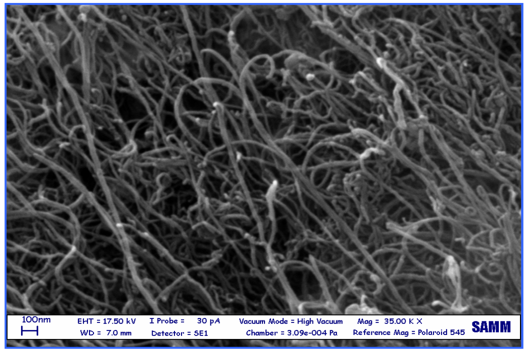


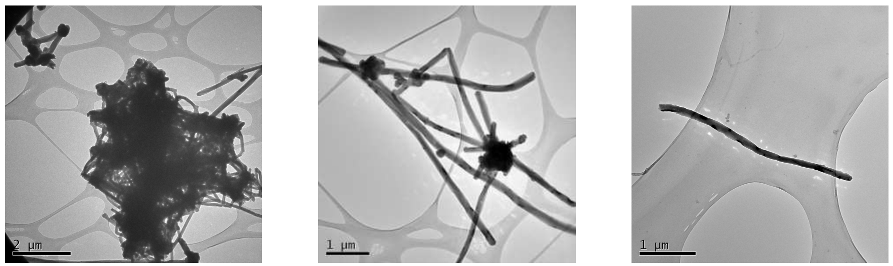
Orientation/order of CNTs

Various orientations of CNTs grown using chemical vapor deposition on Si substrates: (a) entangled, randomly orientated CNTs; (b) vertically aligned CNTs; (c) dense “dandelion-like” CNT structure grown using plasma-enhanced chemical vapor deposition on an etched, catalyst-free Si substrate.[1]



Degree of self assembling MWCNT (d) bundle, (e) local bundle, (f) exfoliated.[2]



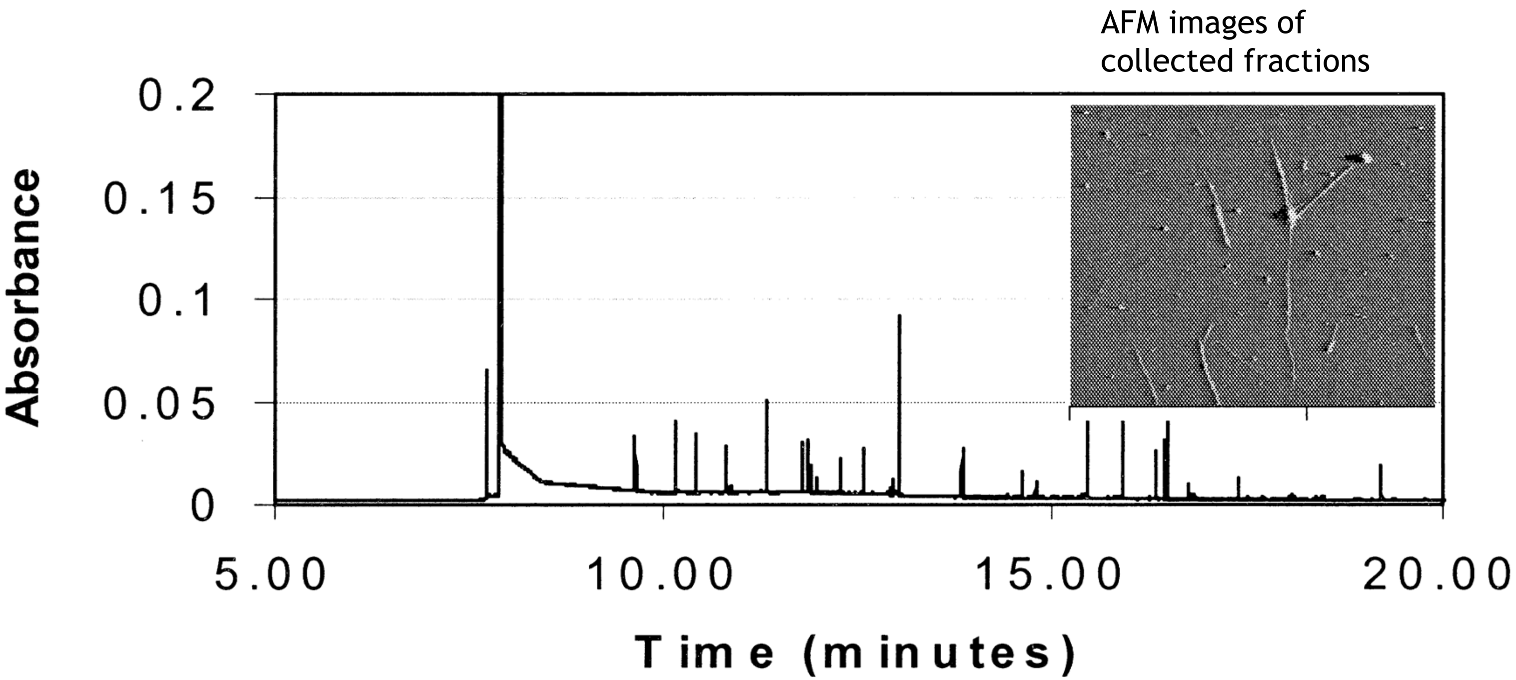


(d) (e) (f)

[1] S. Kumar, I. Levchenko, K. Ostrikov, and J. A. McLaughlin,*Carbon*, vol. 50, no. 1, pp. 325–329, 2012.

[2] Mazzocchia, Citterio Tito, Nanotechnè, Pau congress 2012

Distribution/Purification of Single-Walled Carbon Nanotubes by Capillary Electrophoresis (CE)



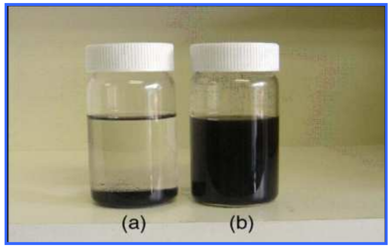
Stephen K. Doorn et al. J. Am. Chem. Soc. 2002, 124 (12), pp 3169–3174

CNT Dispersion Technology

FEATURES:

- CNT bundles exfoliation
- CNT properties retained
- Homogeneous/stable suspensions
- Low viscosity
- Highly concentrated formulations
- Ready to use

pH=4 pH=9.5



Ar-COOH functionalized MWCNT vs. pH (H_2O)

Chitosan wrapped MWCNT at pH 7

PROPERTIES:

- **Electrical conductivity**
- **Impact resistance & stiffness**
- **Strength**
- **Thermal conductivity**

- Electronics-grade purity
- Surfactant-free formulation
- Benign solvent system

Controlled manipulation

- **Spray**
- **Screen printing of CNT composite paste**
- **Ink jet**
- **Electrophoretic deposition**
- **Self alignment**

Covalent vs. Noncovalent Functionalization

*	Covalent	Noncovalent
Solubility	Organic and Aqueous Solubility	Organic and Aqueous Solubility (Reversible)
Binding Int.	Reversible under Harsh Cond.	Reversible with Varying Solvent Cond.
Hybridization	sp^3	sp^2
Conjugation	Decreased	Unaffected
Electronic Prop.	Altered	Unaffected

(1) Covalent surface modifications

a) Acid purification/oxidation
b) Oxigenated group derivatization
c) Heteroatoms insertion and derivatization
d) Cycloaddition
e) Isotope substitution

(2) Noncovalent surface modification

α) π–π stacking
b) electrostatic interactions
c) hydrogen bonding
d) van der Waal's forces

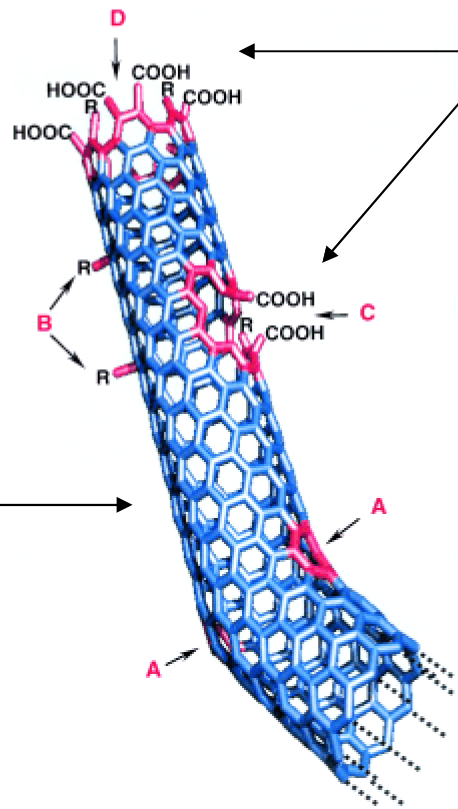
(b–d: Polymer wrapping)

*Chen, R. J. et al. *J. Am. Chem. Soc.* **2001**, *123*, 3838-3839. Dai, H. *Acc. Chem. Res.* **2002**, *35*, 1035-1044.
(1) H. C. Wu et al., *J. Mater. Chem.*, **2010**, *20*, 1. (2)

Chemical Functionalization of CNT: General Approaches

Substitution reactions:

- Free Radical
- Cationic
- Nitrene/carbene
- Cycloaddition

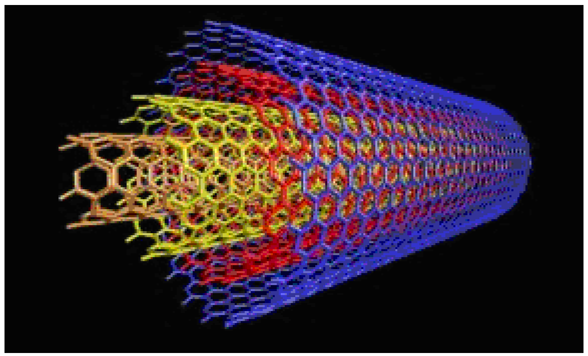


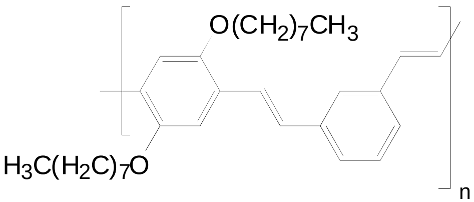
Condensation reactions:

- Esterification
- Amidation

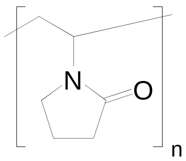
Oxidation reactions:

- O_2 / O_3
- Metal oxidants

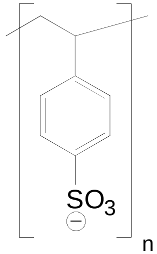




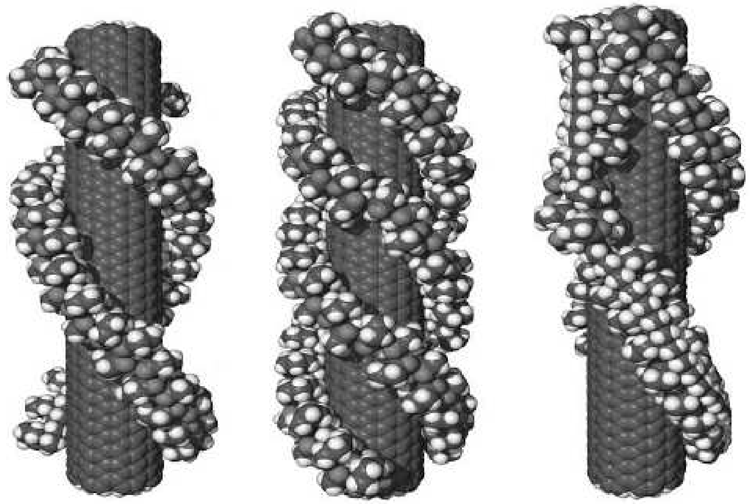
PmPV-*co*-DOctOPV



PVP



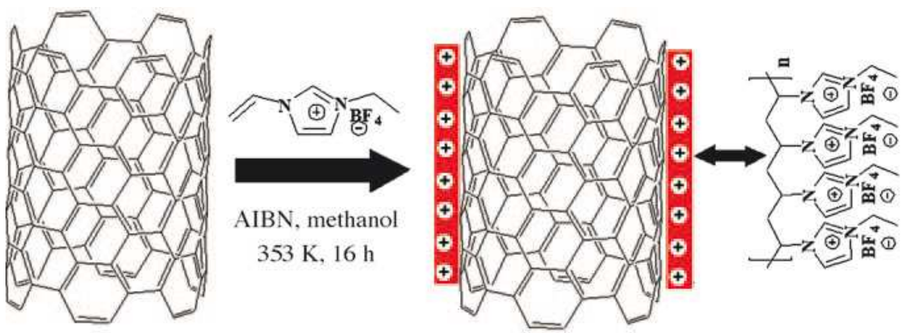
PSS



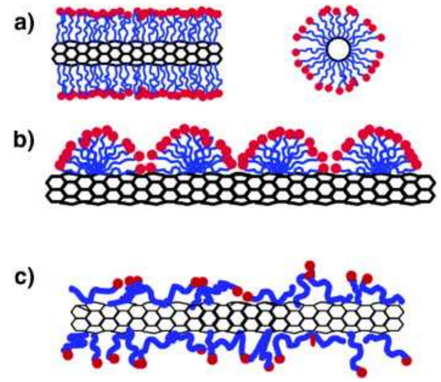
Double Helix   Triple Helix   "Switchback"

Pristine Nanotubes (Insoluble Precipitate) + Free Polymer $\underset{\text{THF}}{\overset{\text{Water}}{\rightleftarrows}}$ Polymer-Wrapped Nanotubes (Soluble)

Ionic liquids

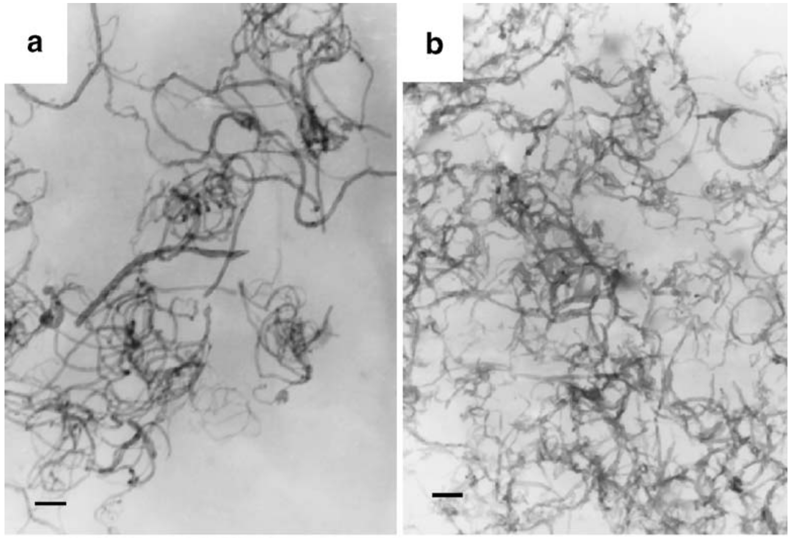


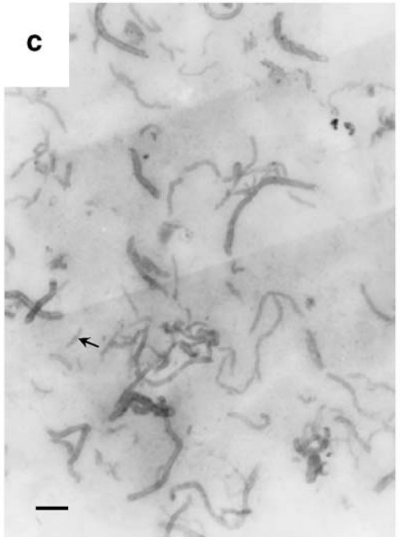
Surfactants



Dalton, A. B. et al. *J. Phys. Chem. B.* **2000**, *104*, 10012-10016.
O'Connell, M. J. et al. *Chem. Phys. Lett.* **2001**, *342*, 265-271.

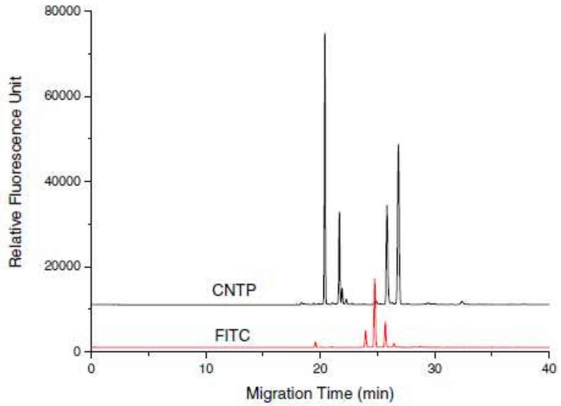
Carboxy-derivatization and further amidation/CNTP fluorescent labeling

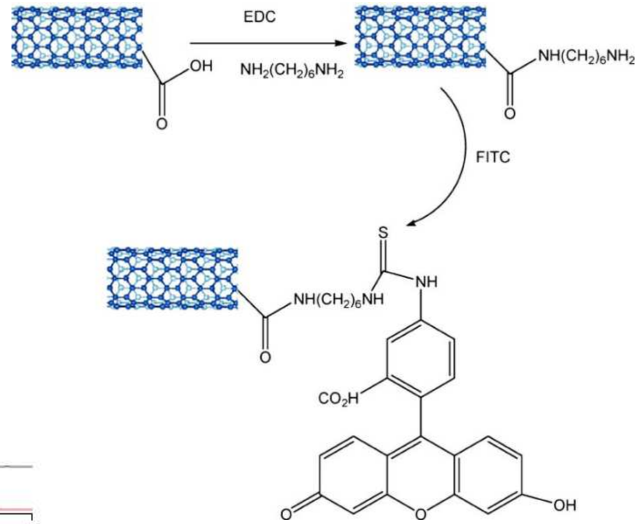




TEM images of multiwalled CNT before (a) and after (b) oxidation (COOH), and of fluorescently labeled CNTP (c). The scale bar corresponds to 200 nm. The arrow in (c) indicates a short oxidized multiwalled carbon nanotube

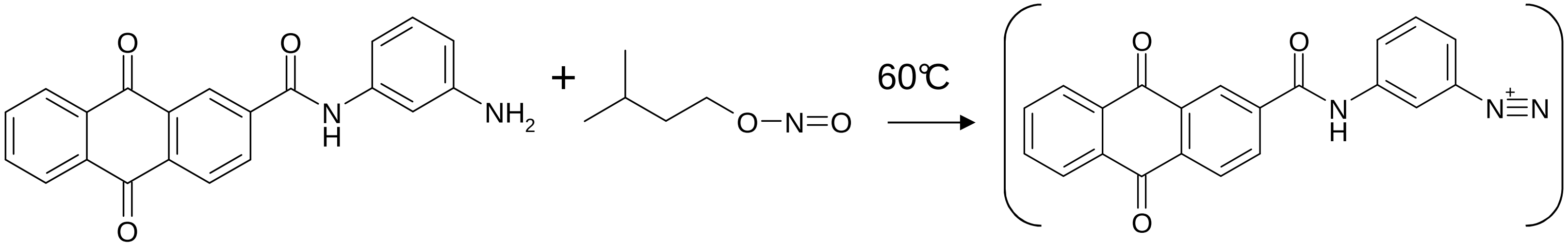
Electrophoretic separation

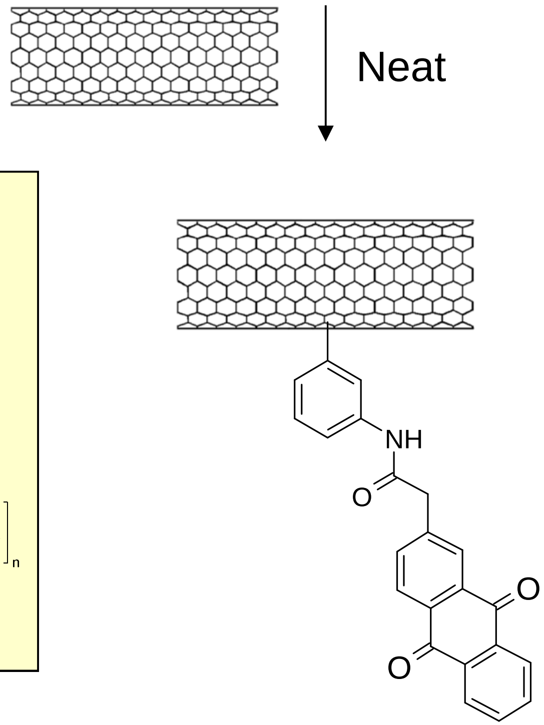




H. Xiao et al. Anal Bioanal Chem (2007) 387: 119–126

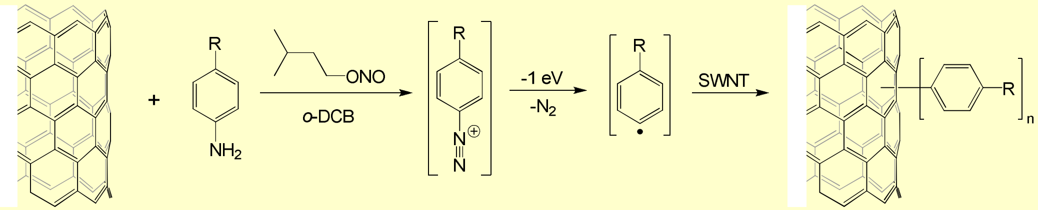
Functionalization of MWCNT via Arenediazonium Salts Decomposition





Aril radical functionalyzation

$ArNH_2$ + i-AmONO → Ar• → Ar-CNT

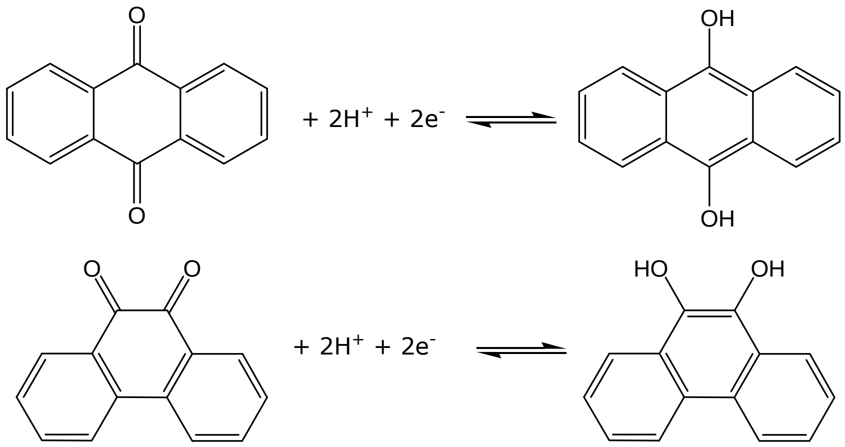


N. Karousisa, H. Ali-Boucetta, K. Kostarelosb, N. Tagmatarchis
Materials Science and Engineering B 152 (2008) 8–11 and ref. therein

What IP Teaches

Anthraquinone
AQ
(ASM*)

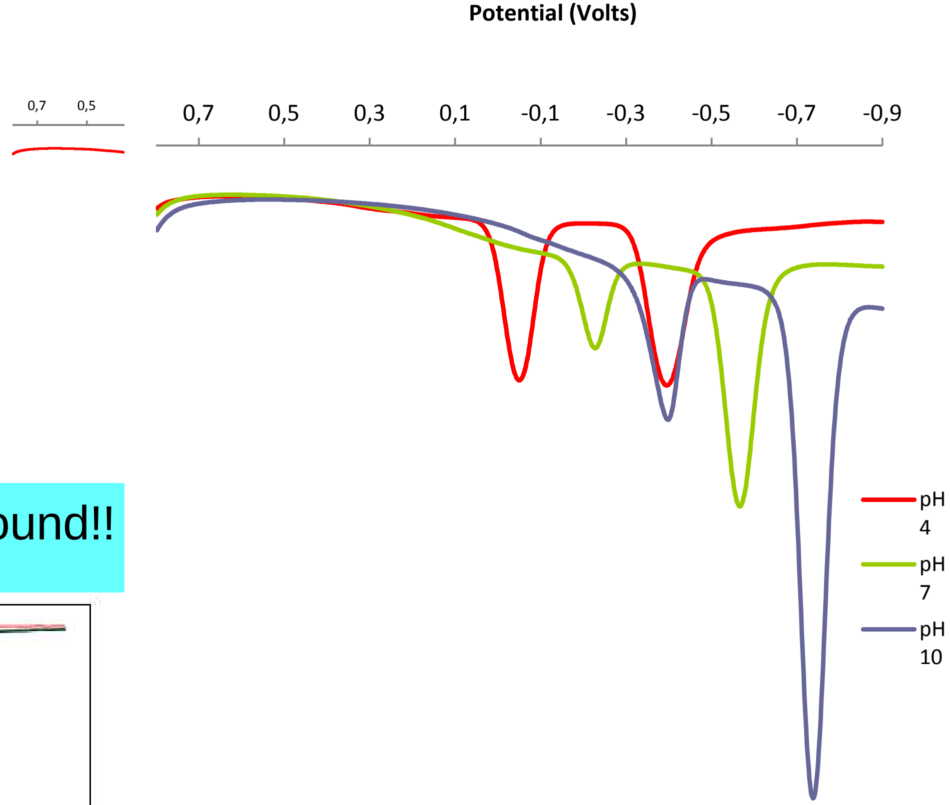
Phenanthrenequinone
PAQ
(ASM)



- The voltage at which the reaction occurs is proportional to pH
- Square Wave Voltammetry shows current spikes as reactions occur
- Therefore- this is a direct measurement of pH- Unlike old probes
- Sensor is internally referenced via an AIM**

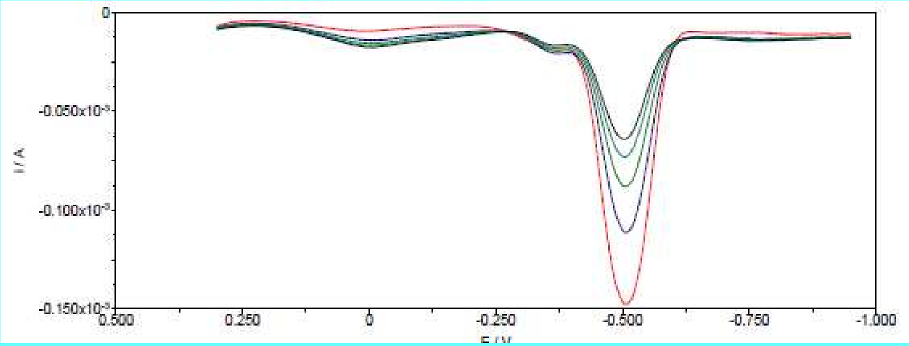
Nanotubes pH sensor

pH Sensing (

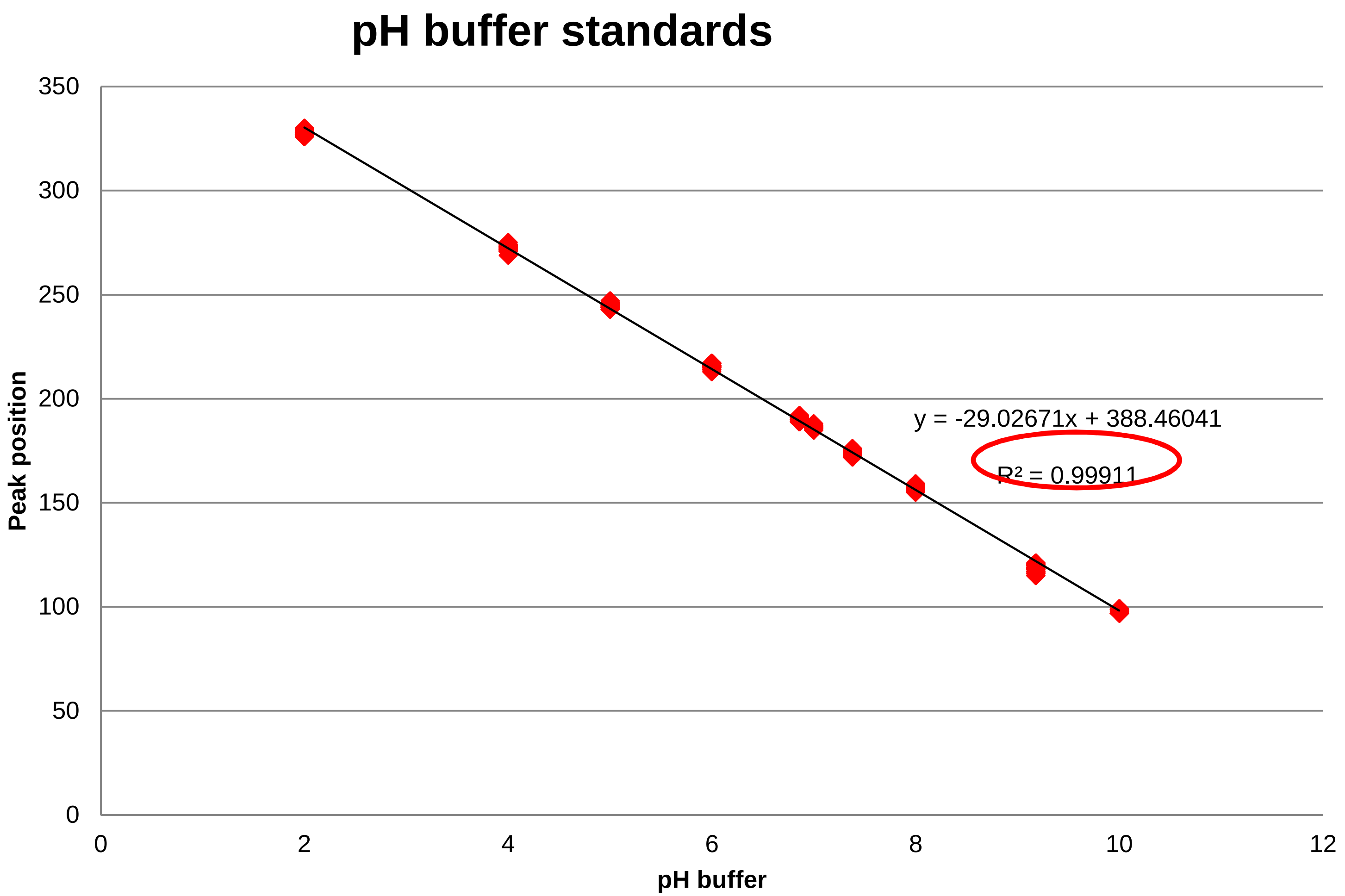


Having 2 ASMs
increases accuracy
and precision

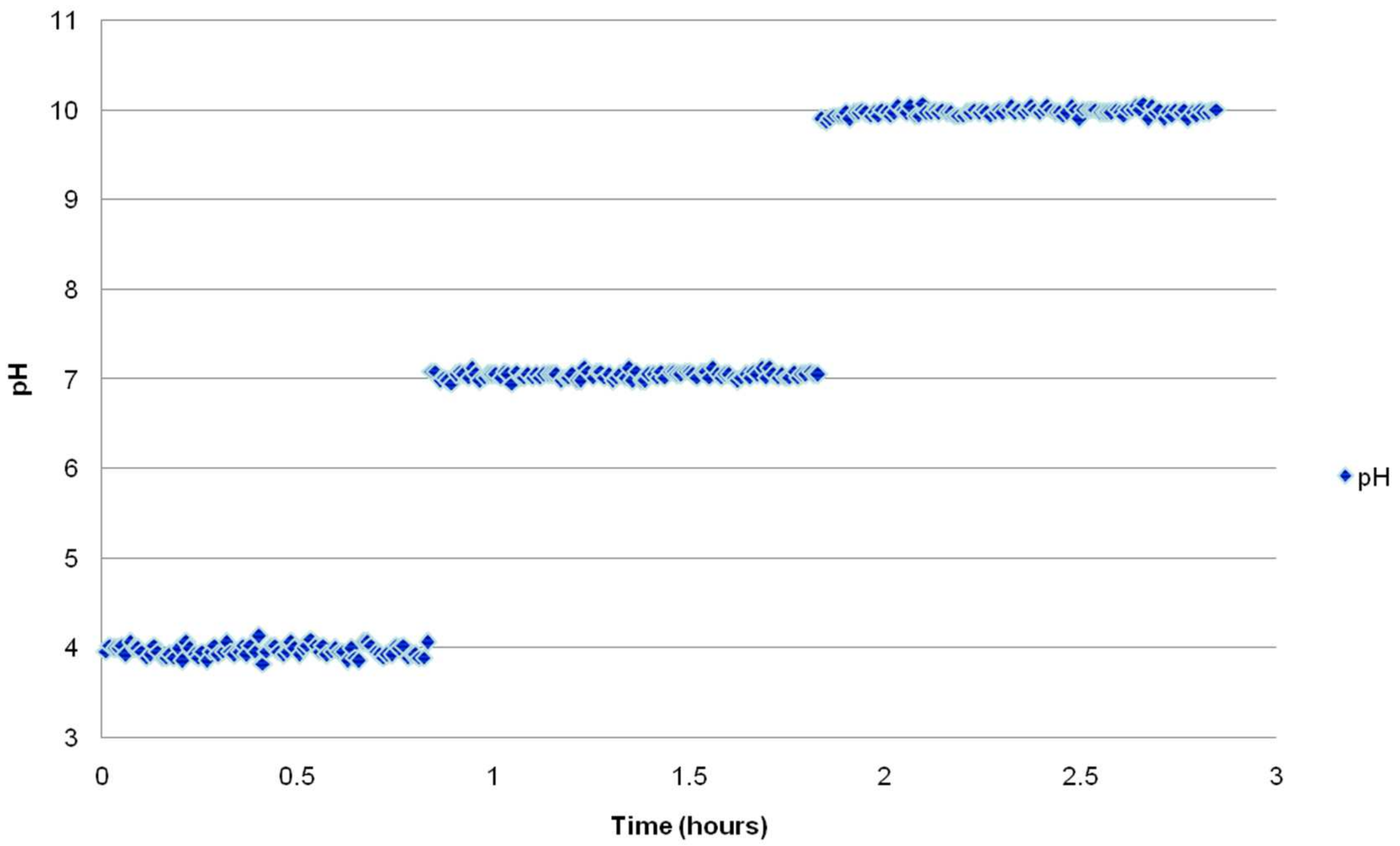
Adsorbed material non covalently bound!!



Beta-1: Linearity & pH Range



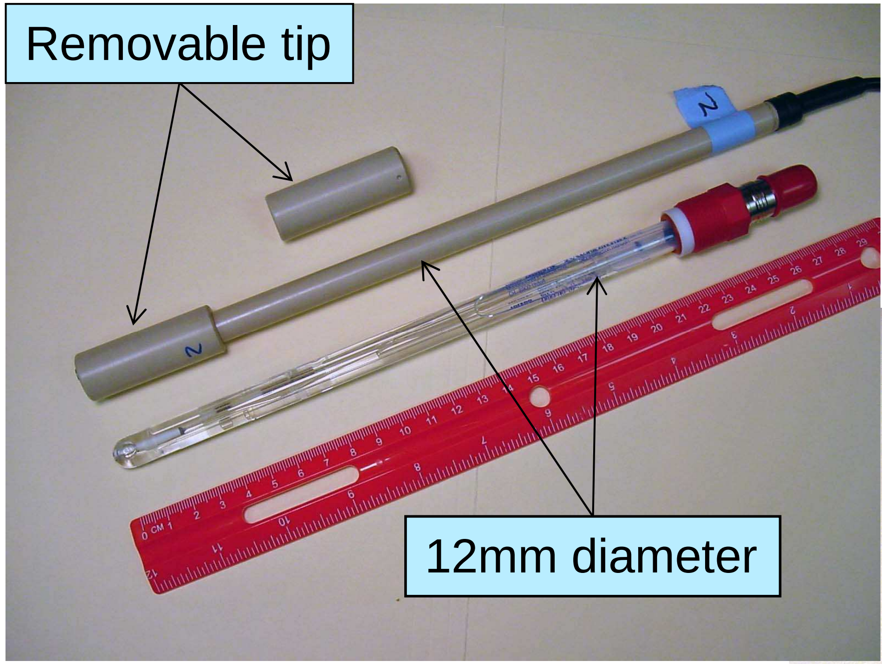
Beta-1: Sensor Stability- pH vs. Time

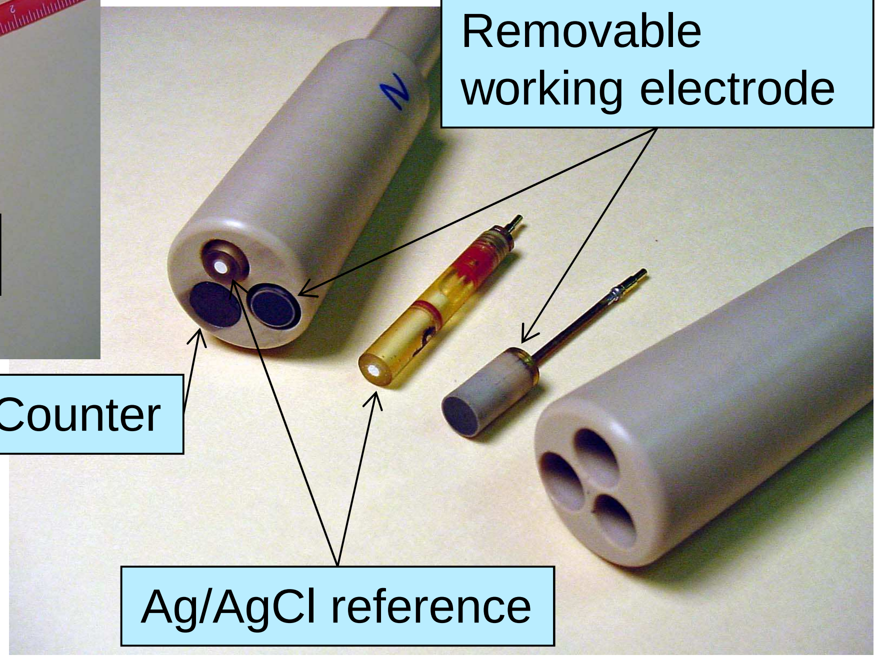


Alpha-1 Sensor Preparation

- AQ-MWCNT* + PAQ-MWCNT + AIM + graphite + epoxy Mix to form carbon paste
- Carbon paste is packed and cured
- Sensor surface is then polished to a smooth finish

Sensor pH Measurements





Problems in Analytical Methods for CNT Functionalization Detection

Method	Sample	Information	Limitations
TGA	solid	functionalization ratio	no evidence for covalent funct., not spec.
XPS	solid	elements, funct. Ratio	no evidence of covalent funct., not spec., quantication complicated
Raman	solid	sp^3 indicated by D mode	not specific, quantica-tion not reliable
Infrared	solid (ATR-IR) or solution	Subst. groups	no direct evidence for covalent funct., quantif. not possible
UV/visible	solution	Sidewall funct.	not specific or quanti-tative, need highly dis-persed sample

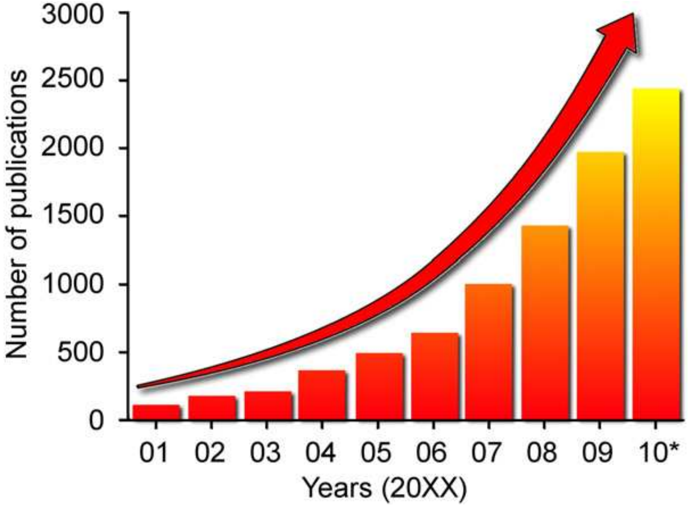
L. Zeng, A. R. Barron
http://cnx.org/content/m22299/1.4/

CNT Analytical Methods

Method	Sample	Information	Limitations
Solution NMR	solution	substituents	no evidence of covalent functionalization, high solubility of sample
Solid state NMR	solid	substituents, sp^3 quant. at high fun.	high functionalization needed, long time for signal acquisition
AFM	solid on substrate	topography	only a small portion of sample characterized, no chemical identity
TEM	solid on substrate	image of distri-bution dispersion	only a small portion of sample characterized, no chemical identity
STM	solid on substrate	distribution	no chemical identity conductive sample only

CNT Safety

In 2010-12, the National Institute for Occupational Safety and Health presented guidelines for occupational exposure and indicated the safety level that did not result in tumorigenesis.1 NIOSH is recommending an exposure limit of 7 $\mu g \cdot m^{-3}$ elemental carbon as an 8-h time-weighted average respirable mass airborne concentration.
The toxicity is again until investigation.[2,3,4]



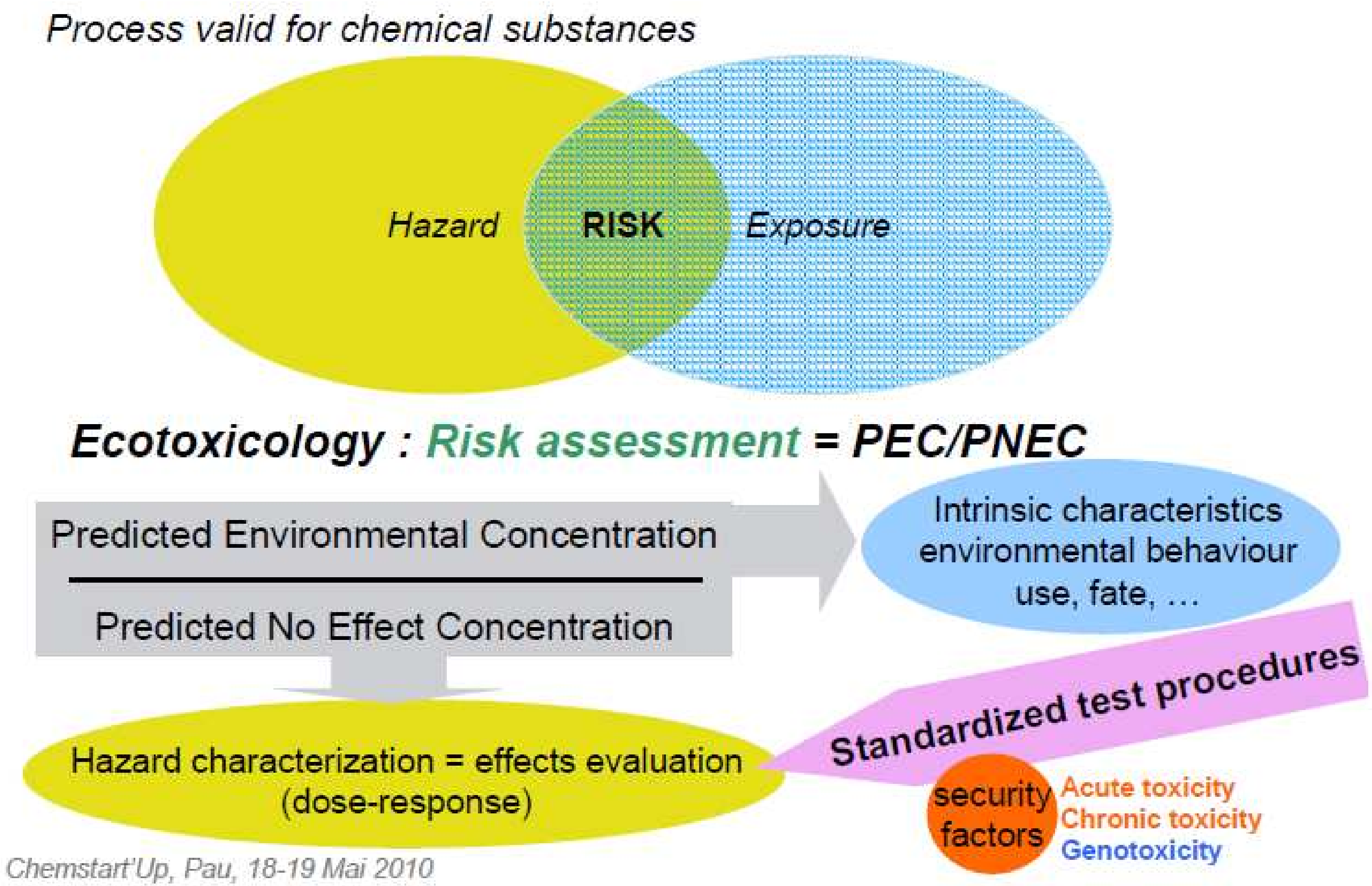
[1]Bulletin NCI, 2010, http://www.cdc.gov/niosh/docket/review/docket161a/pdfs/carbonNanotubeCIB_PublicReviewOfDraft.pdf.

[2]H. Haniu, Y. Matsuda, K. Takeuchi, Y. A. Kim, T. Hayashi, and M. Endo, "Proteomics-based safety evaluation of multi-walled carbon nanotubes," *Toxicology and Applied Pharmacology*, vol. 242, no. 3, pp. 256–262, 2010.

[3]H. Haniu, N. Saito, Y. Matsuda, et al., "Effect of dispersants of multi-walled carbon nanotubes on cellular uptake and biological responses," International Journal of Nanomedicine, vol. 6, pp. 3295–3307, 2011. ibid. 3487-3497.

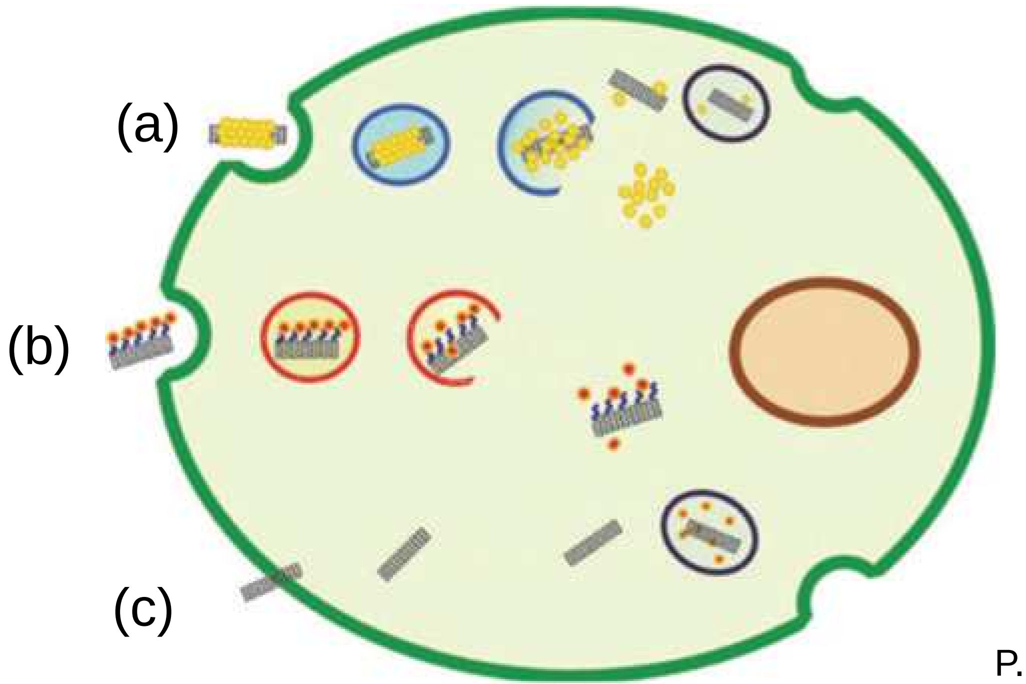
[4]T. Tsukahara and H. Haniu, "Cellular cytotoxic response induced by highly purified multi-wall carbon nanotube in human lung cells," *Molecular and Cellular Biochemistry*, vol. 352, no. 1-2, pp. 57–63, 2011.

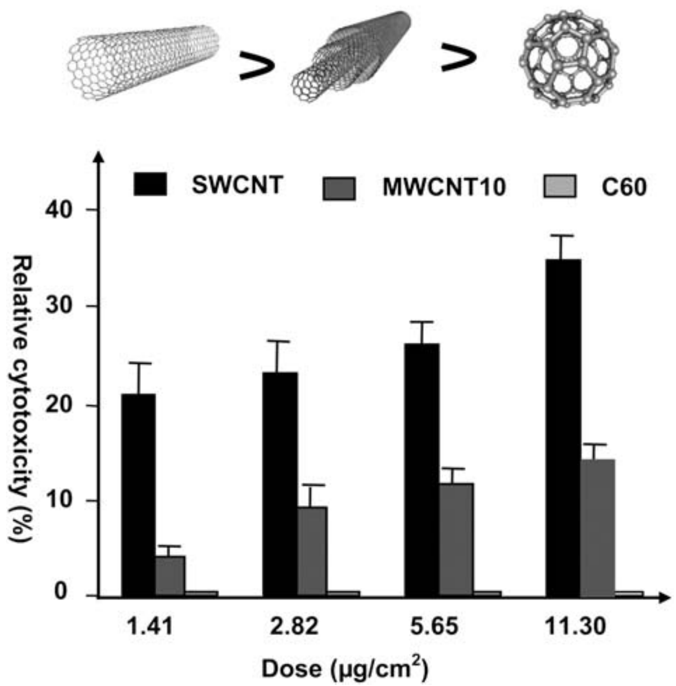
Ecotoxycological Risk Assessment



In Cell Fate

The cellular uptake pathways, subcellular localization and intracellular trafficking of differently functionalized CNTs. (a) Supermolecularly functionalized CNT via endocytosis, (b) covalently functionalized CNT bound with drugs via endocytosis, and (c) individual or specifically functionalized CNT via direct penetration





P. Ghafari, et al., Nature Nanotechnology, vol. 3, no. 6, pp. 347–351, 2008.

Summary

At present, catalytic MWCNTs and CNFs appear as the optimum choice, given that such materials can be most readily obtained in large quantities with a good to high purity.

But … (some issues can/must be improved)

- These materials are intrinsically defective and wavy, both of which are expected to be highly detrimental to the mechanical performance
- Safe use must be identified and proved – toxicity can be reduced by polar group insertion or wrapping with biocompatible polymers
- Their synthesis must be improved. Somehow nanotubes with a crystalline quality closer to arc-grown nanotubes need to be obtained at a cost similar, or indeed below, current CVD-grown product.
- Analytical issues must be targeted - homogeneity control in CNT functionalization must be addressed
- The interactions of polymers with highly curved surfaces at the molecular scale, are still largely unknown.