Potentialité des NANOFORMES de CARBONE Pour les applications composites

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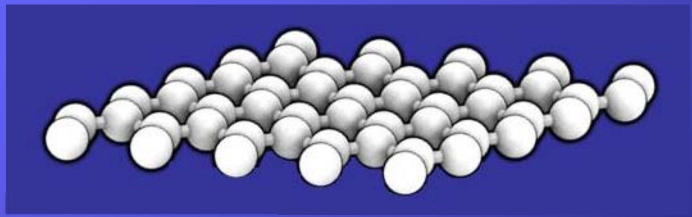
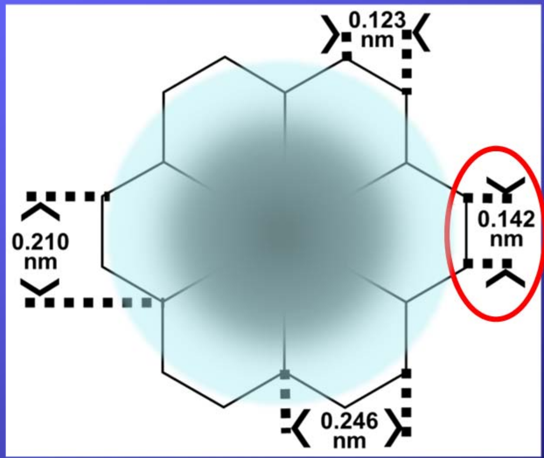
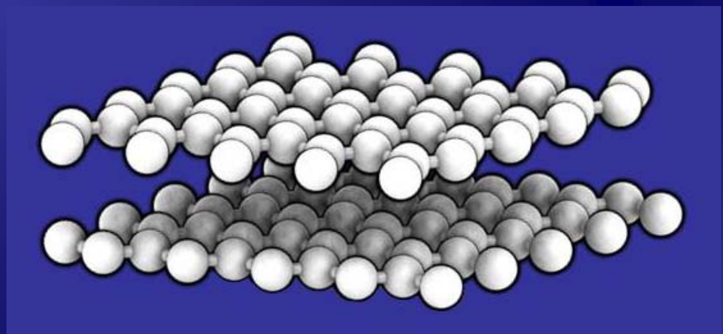


GRAPHENE



C-C : very short (= strong) σ bond (524 kJ/mole)

Each C atom has an unpaired π electron → cloud of delocalised π electrons

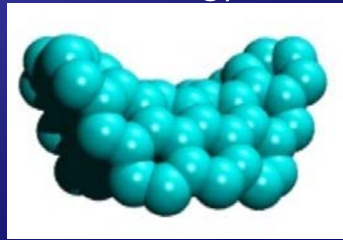


Cohesion maintained by sharing both π electron clouds
→ weak (van der Waals) bond
→ (7 kJ/mole)

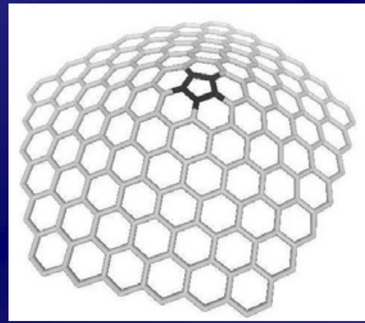
- High in-plane mechanical strength and modulus
- High in-plane conductivity (electrical, thermal)
- Low transverse mechanical and transport properties

DEFECTS in GRAPHENE

7-ring)



5-ring)



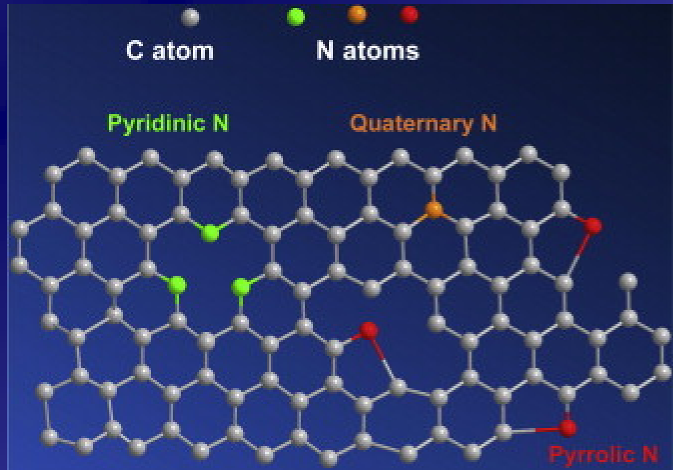
single graphene

- heterocycles
- vacancies
- heteroatoms

in-plane

- *sp*^{3} carbons
- heteroatoms
- chemical groups

edges

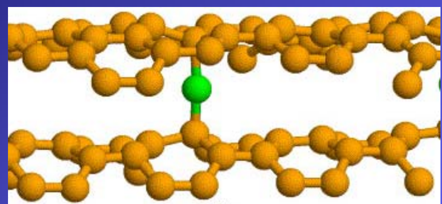


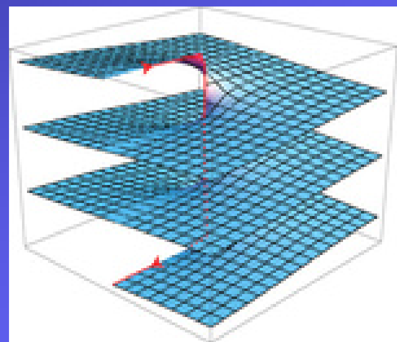
multiple graphenes

- screw dislocation
- Interstitial atoms
- …

out-of-plane

- → Nanotexture





GRAPHENE-BASED NANOCARBONS

- Fullerenes
- Nanohorns
- Carbon blacks

3 nanoD

- Nanotubes :
  - SWCNT (n,m)
  - MWCNT concentric, herringbone, bamboo
  - Meta-CNT doped, filled, functionalised, substituted coated/decorated,

  2 nanoD

- Nanofibres :
  - MWCNF concentric, herringbone, platelet
  - Meta-CNF doped (intercalated), functionalised, coated/decorated, substituted

  2 nanoD

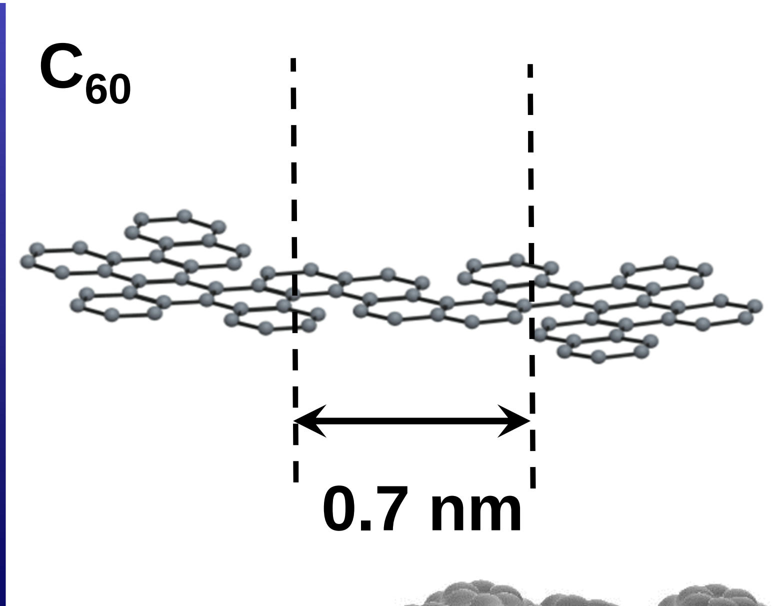
- Graphene/s (planar):
  - flakes, nanoplatelets
  - nanoribbons
  - discs/cones
  - nanowalls

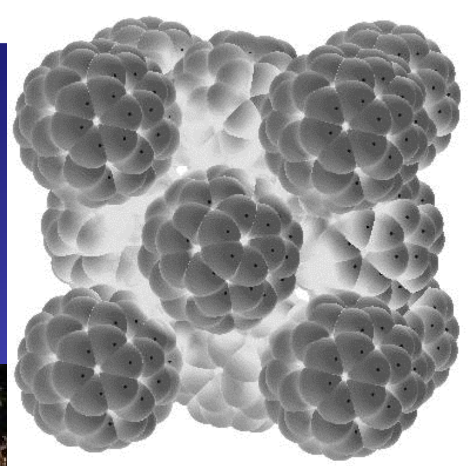
  1-2 nanoD

FULLERENES

Discovered: 1985 (Kroto, Curl, Smalley)

.C_{60}: Black solid, cubic/hexagonal structure (fullerite)
.Density (fullerite): 1.65 g.cm^{-3}
.Sublimation at 400-500°C
.Soluble in organic solvents (toluene)
.Electron acceptor/donor
.Bulk conductivity: 0.001 S/m
.Modulus (of the individual molecule) : ~900 GPa





Weak cohesion (van der Waals)

Synthesis method:
electric arc (sublimation of graphite electrode, no catalyst)

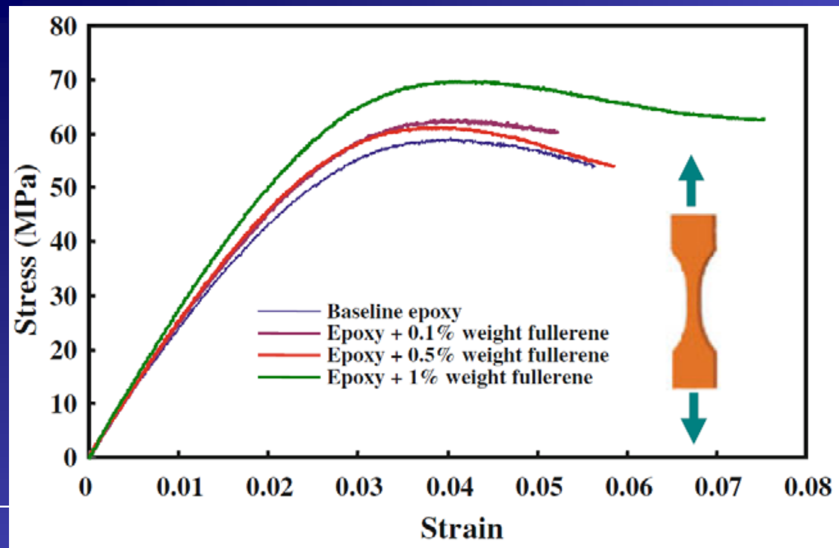
Capacity production: ton scale

Average market price (C_{60}):
10 000-100 000 US $/kg
(Aldricht, Solarischem, SES Research, Mascot, Yurui Chemical, etc.)

Higher fullerenes : scarce, more expensive

Potential/real use in composite systems: Filler

- Cosmetics
  (trap for free-radicals, anti-oxidant)
- Anti-corrosion paints and coatings
- Organic solar cells
  Dennler et al, AdvMater21(2009)1323
- Low-friction coatings
- Hard coatings



Rafiee et al, J Nanopart Res (2010)

Advantages:

- High purity (molecule, chemistry)
- High dispersibility (soluble)
- Low nanofiller loading
- Functionalisability → large compatibility
- Biocompatibility

Drawbacks:

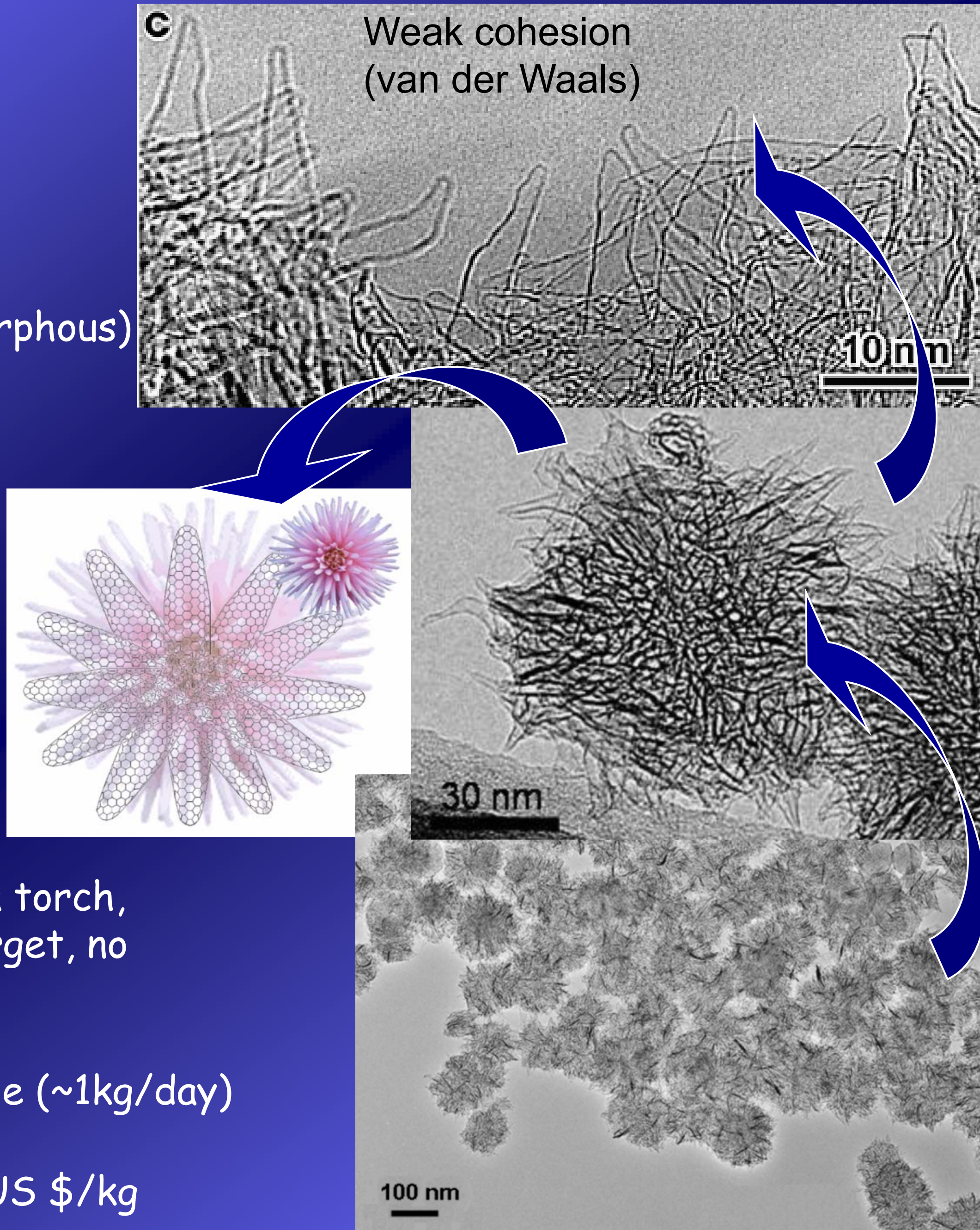
- Cost
- Aspect ratio
- Low inter-fullerene cohesion

NANOHORNS

Discovered: 1994 (Harris)
Rediscovered: 1998 (Iijima et al)

.Black solid, powder, no structure (amorphous)
.Density: 1.1 g/cm^3
.Not soluble, unless they are doped
.Specific surface area: 250-300 m^2/g, expendable to ~1500 m^2/g upon mild oxidation
.Conductivity: 0.0001 S/m (in resorcinol formaldehyde aerogels)

Ideal (poetic!) model



Synthesis method:
electric arc, laser pulverisation, plasma torch, (sublimation of graphite electrode/target, no catalyst)

Capacity production: 100 kg scale (~1kg/day)

Average market price: ~400 000 US $/kg
(Carbonium, Phosphorex, NEC…)

Iijima et al, Chem Phys Lett 309(1999)165

Potential use in composite systems: Filler

- Coatings (antistatic, hydrophobic…)

Advantages:

- High conductivity
- High surface area
- Functionalisability → large compatibility
  → tunable reactivity

Resulting bulk conductivity of filling resorcinol-formaldehyde aerogel mesopores: 0.0001 S/m

Tao et al, Langmuir 23(2007)9155

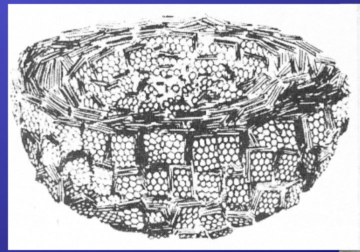
Drawbacks:

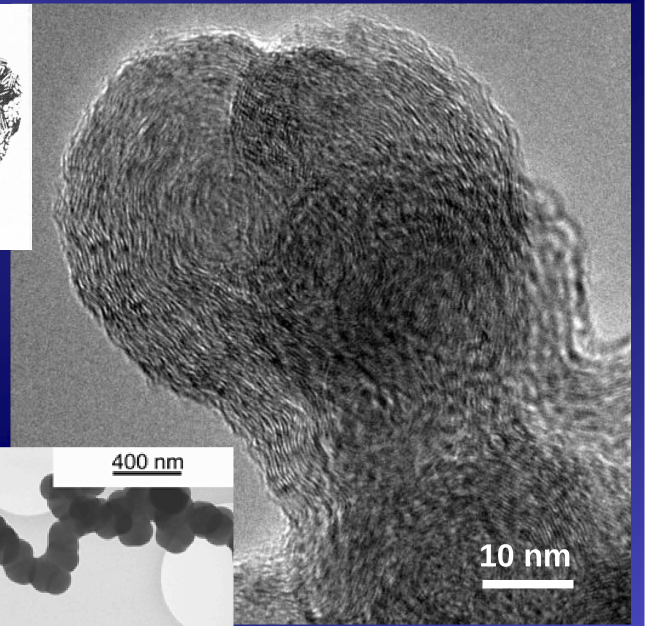
- Cost
- Low aspect ratio
- Low (van der Waals) inter-nanohorn cohesion
- Dispersibility?

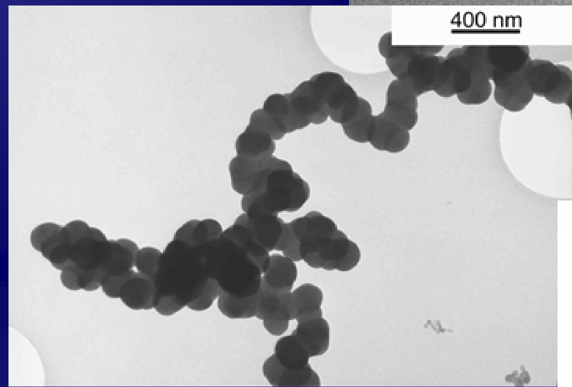
Carbon blacks

Since XIXth Century

.Graphene-based, polyaromatic, turbostratic
→ NOT amorphous (and ≠ from soot)
.Tunable nanotexture and surface reactivity
.Tunable morphology:
from isolated spheres to ramified chains to grape-like aggregates
.Tunable properties:
Surface area: 5-350 m^2/g
Conductivity: 5-20 S/m







Synthesis method:
incomplete combustion of gaseous (→ ('thermal blacks', 'acetylene blacks') or vaporised (→ 'furnace blacks') hydrocarbons → homogeneous nucleation in gas phase

Capacity production: ~8-10 million tons/year

Average market price: 6-15 US $/kg

Real use in composite systems: Filler

- Reinforcement, hardener *(~75%: rubber → tires)*
- Conducting component (antistatic plastics)
- Pigments *(inks, paints, toners, plastics, food, cosmetics)*
- Protective coatings (wave absorbent, UV)

Advantages:

- tunability
- cost
- Functionalisability → large compatibility
- More favourable aspect ratio (vs fullerene, nanohorn)

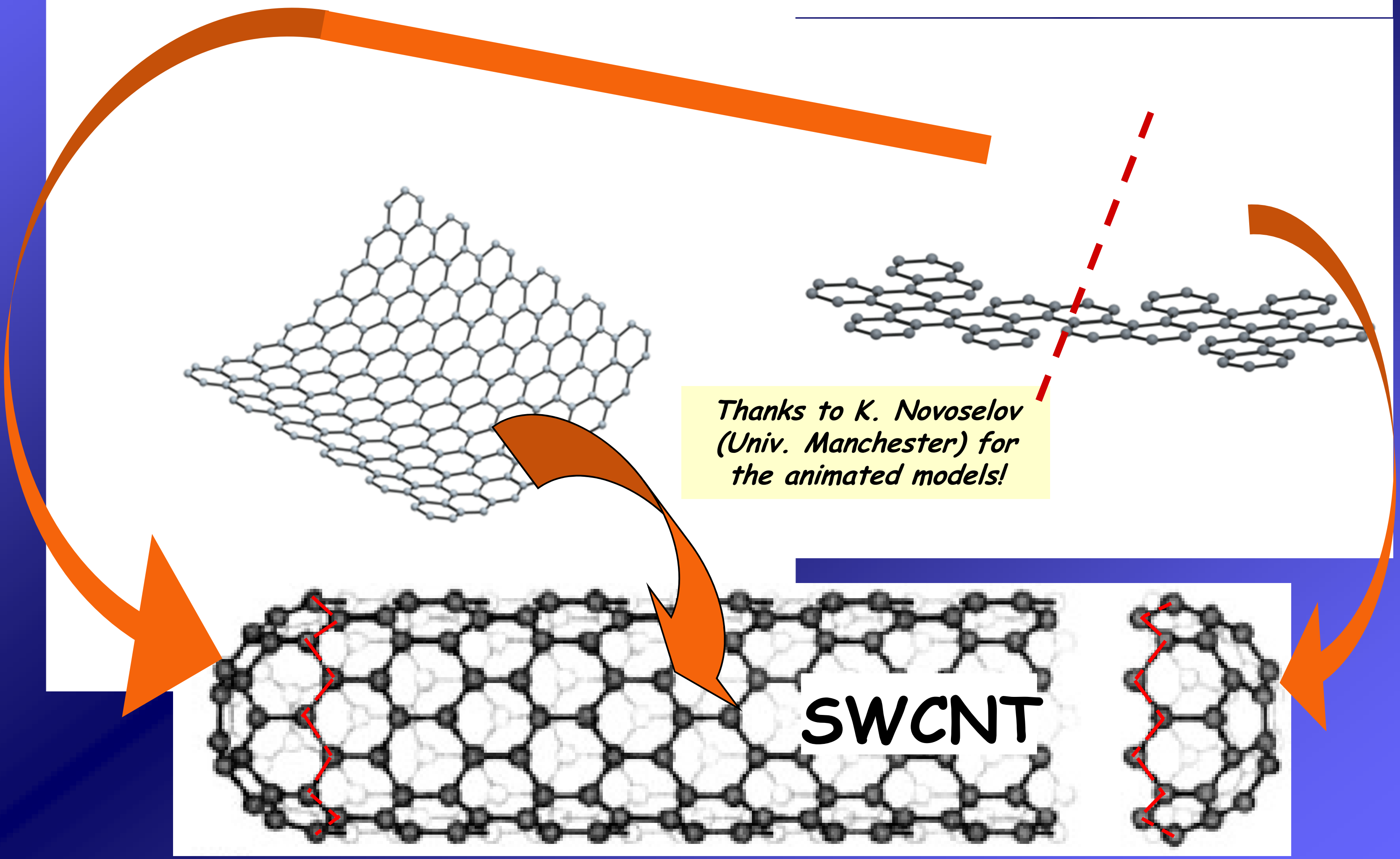
Drawbacks:

- Performance (mechanical, transport) will never be extreme

Single-Wall Carbon Nanotubes

Discovered: 1993 (Bethune et al; Iijima et al)

1 wrapped graphene … + …1 half-fullerene at both ends



Structure
(molecular)

$$\vec{OA} = \vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

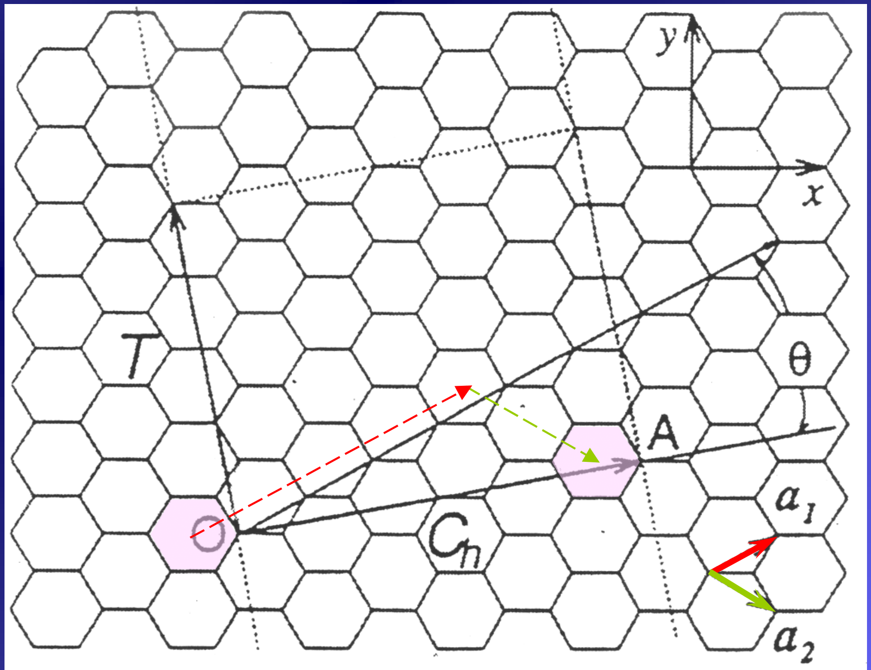
$$\vec{a}_1 = \frac{a\sqrt{3}}{2}\vec{x} + \frac{a}{2}\vec{y} \quad \textit{and} \quad \vec{a}_2 = \frac{a\sqrt{3}}{2}\vec{x} - \frac{a}{2}\vec{y} \qquad \textit{where} \quad a = 2.46\ \text{Å}$$

$$d = \frac{\left|\vec{C}_h\right|}{\pi} = \frac{a_{cc}\sqrt{3\left(n^2 + m^2 + nm\right)}}{\pi}$$

$$\textit{where} \quad \underset{\text{(graphite)}}{1.41\ \text{Å}} \leq a_{c=c} \leq \underset{(C_{60})}{1.44\ \text{Å}}$$

$$\cos\theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$$

Single graphene



(4,2)

(n,m)

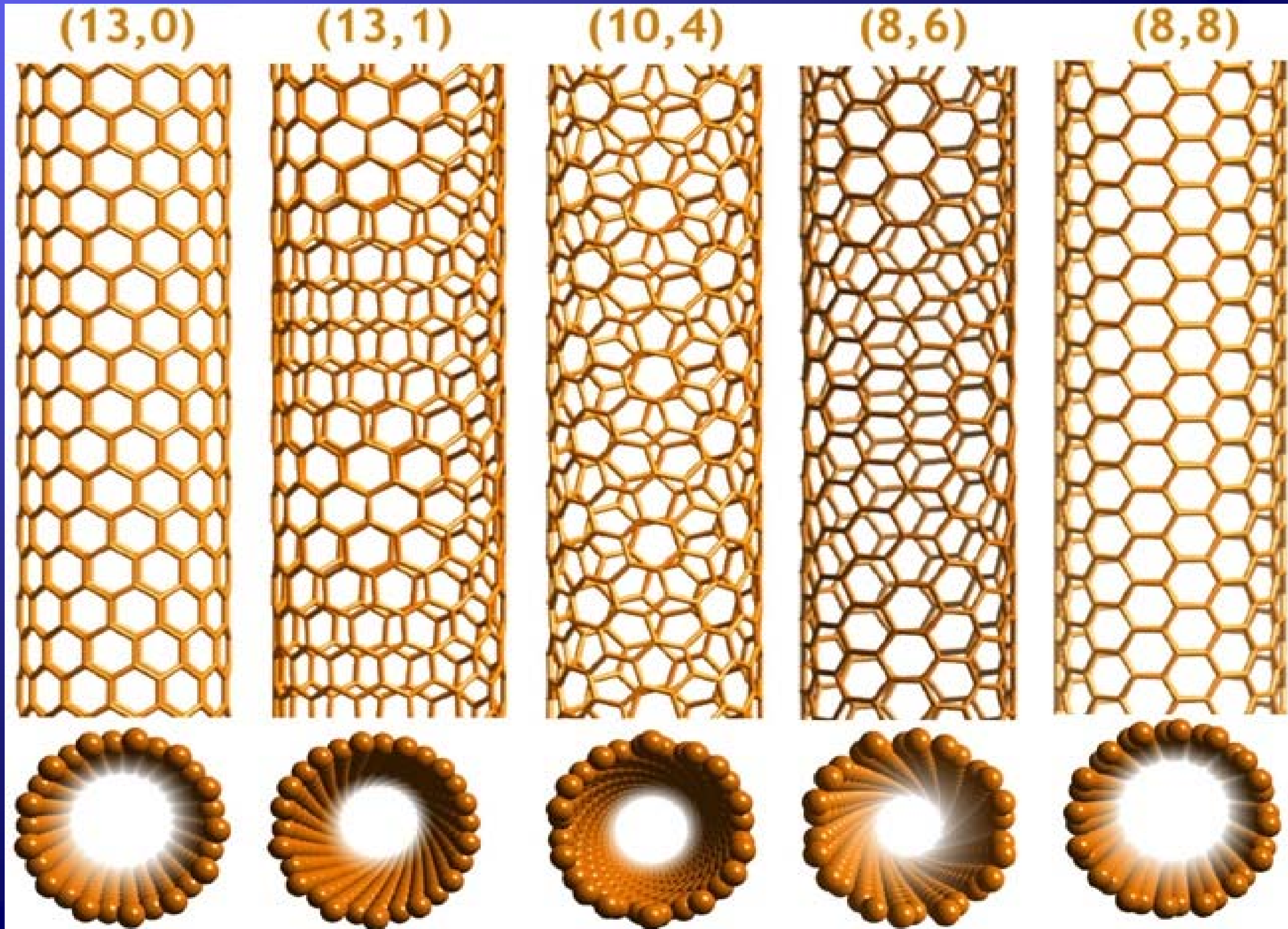
$m \leq n$

$\theta < 30°$

Hamada et al, PRL92

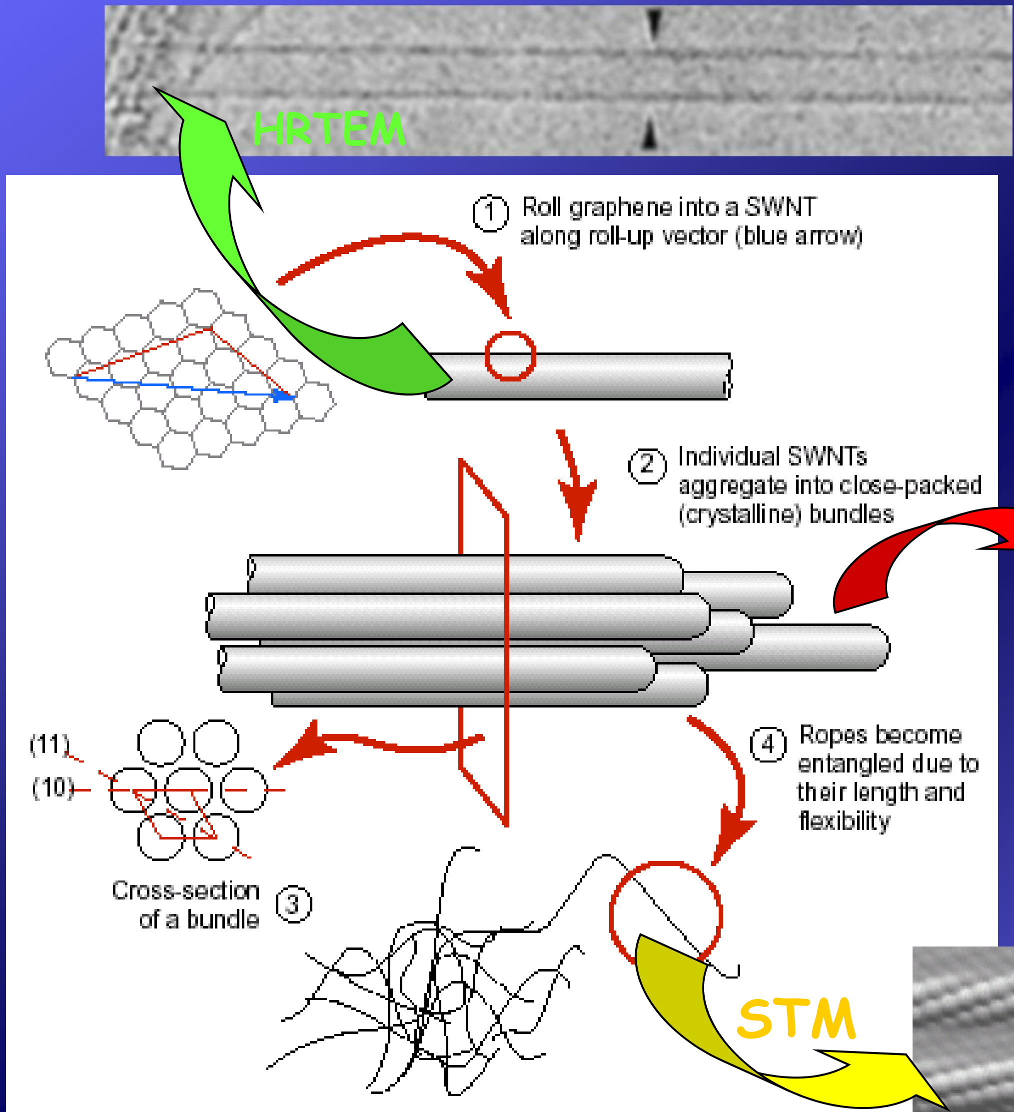
Structure
(molecular)

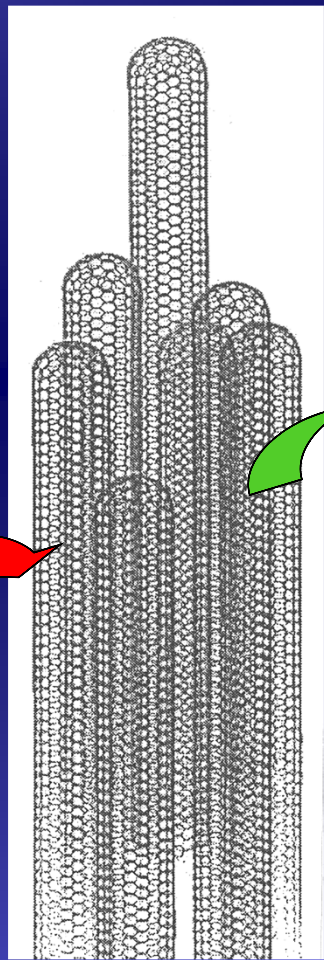
zig-zag *armchair*



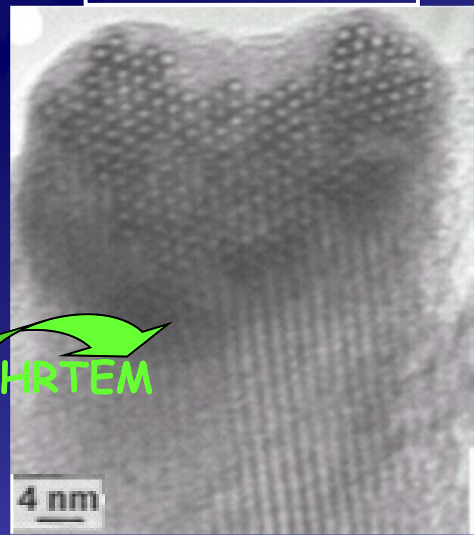
Macromolecule / Nano-Object

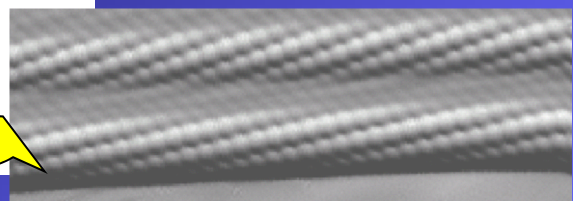
Texture / morphology





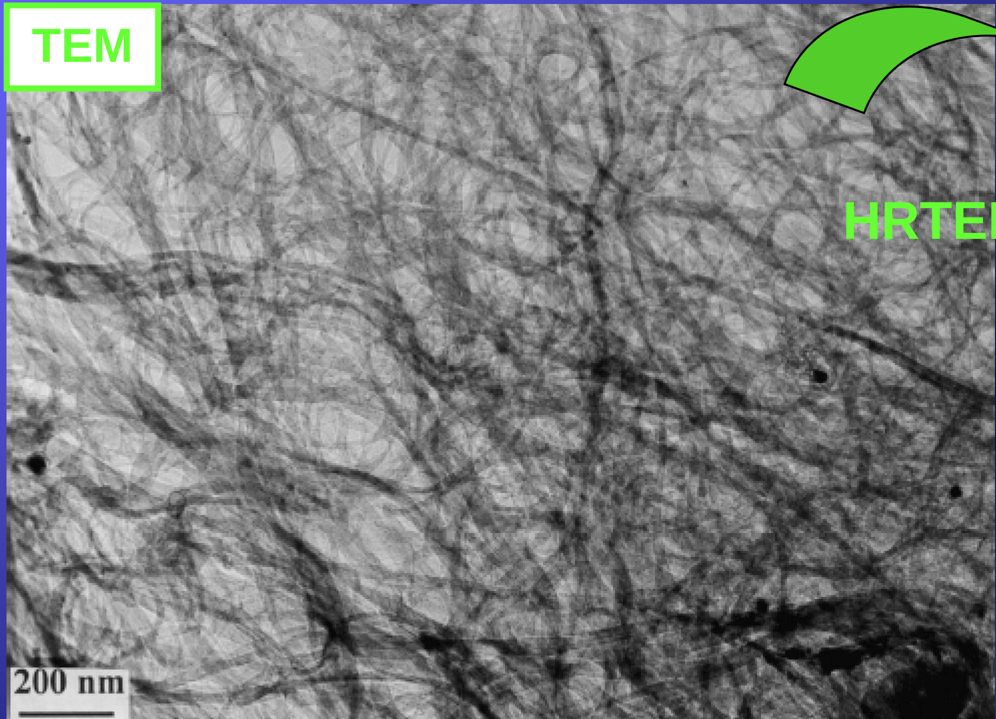
Cross-section





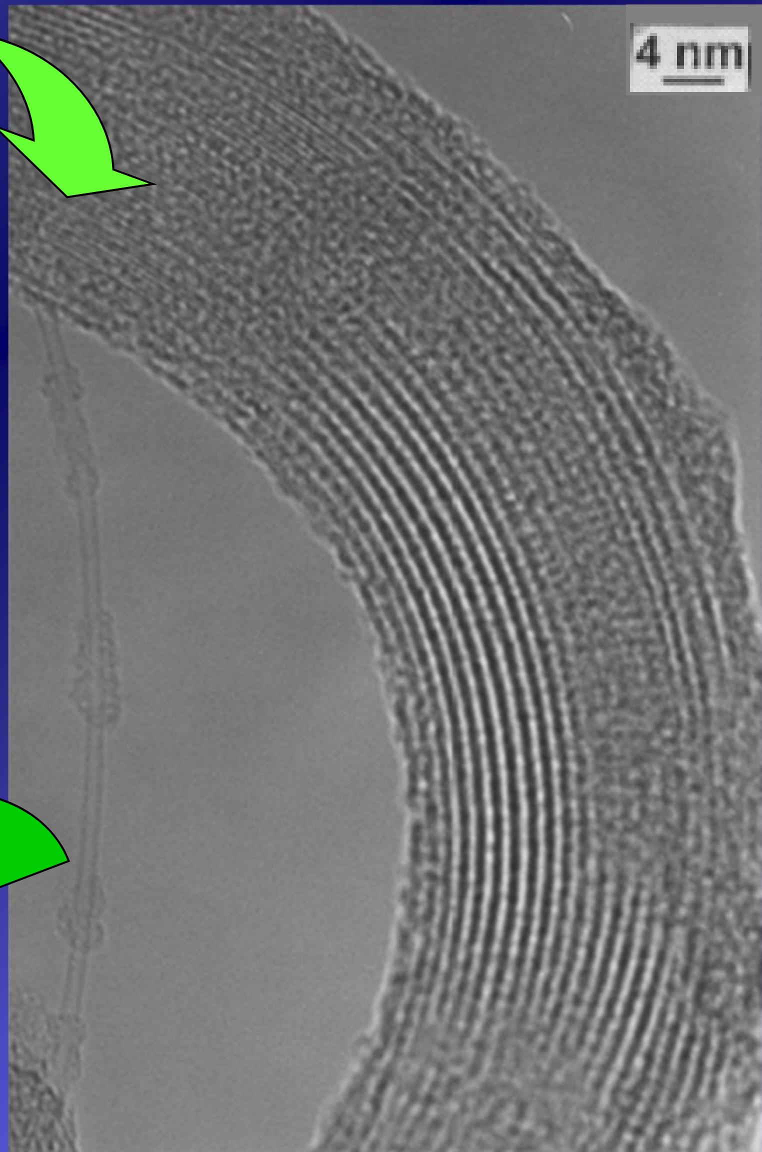
Weak interactions (van der Waals) between SWCNTs

Morphology, texture

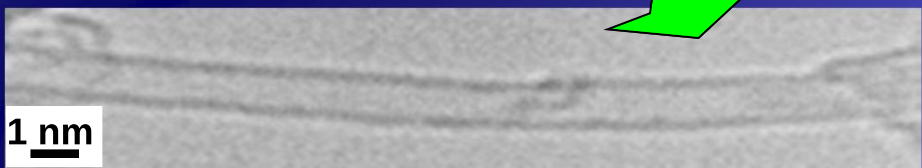


Raw SWNTs from PLV

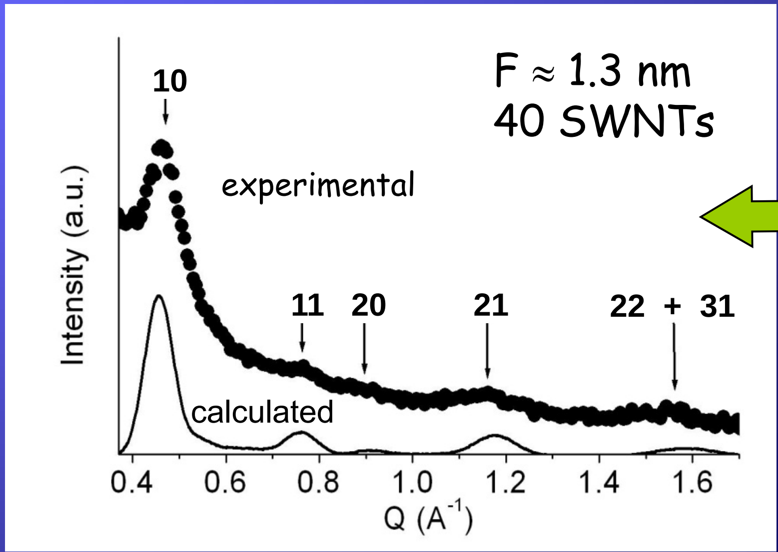
HRTEM

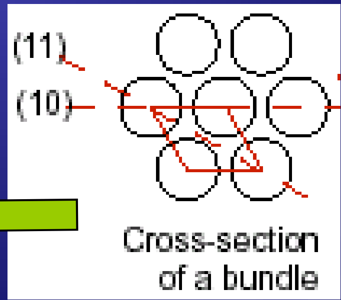


HRTEM



Structure
(crystallographic)





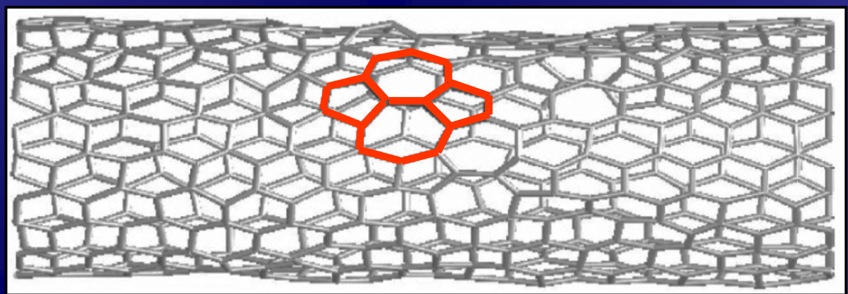
2D hexagonal lattice

armchair

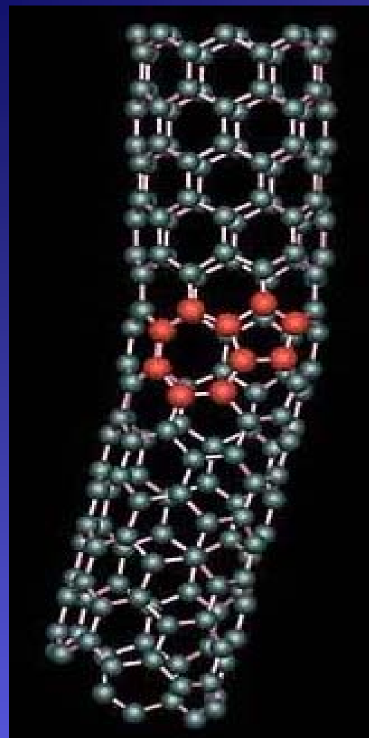
zig-zag

Defects: Hetero-cycles

Also: vacancies (minor occurrence)



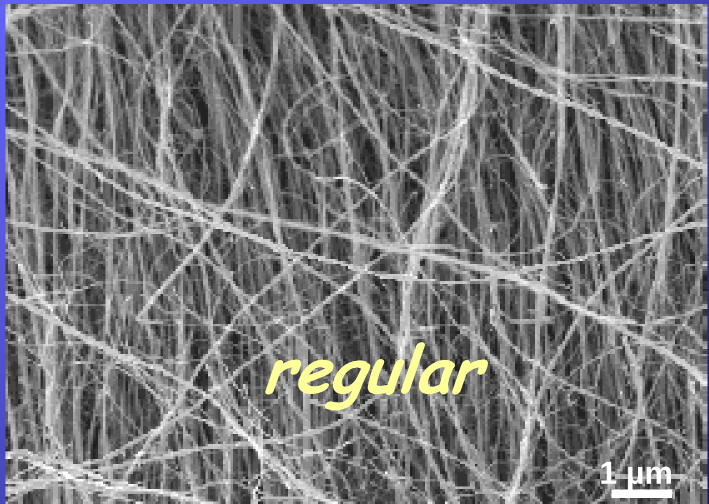
Dienes ("Stone-Wales") defect

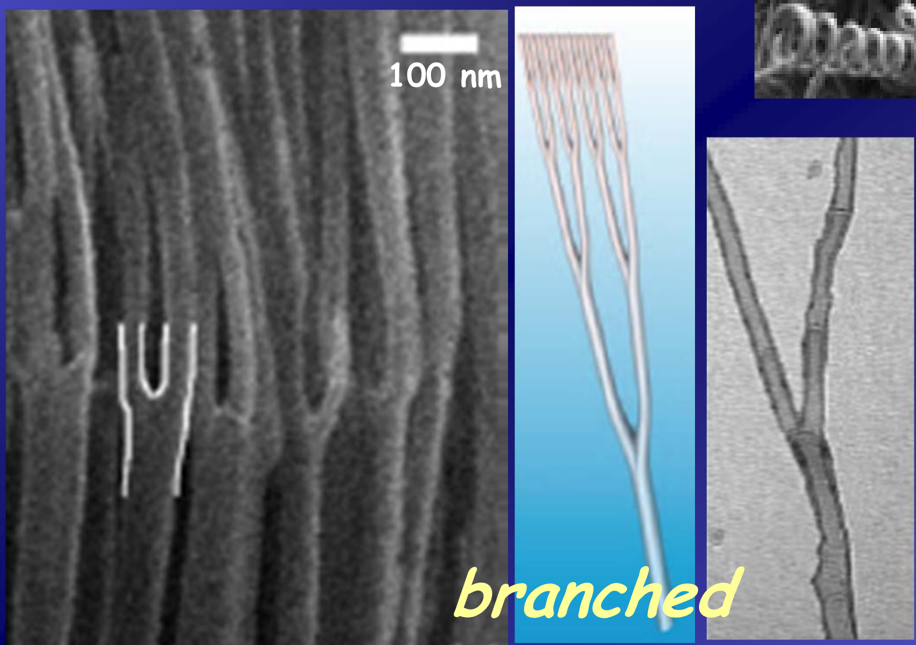


Multi-wall carbon nanotubes

Discovered: 1952 (Radushkevich & Lukyanovich)
Rediscovered: 1991 (Iijima)

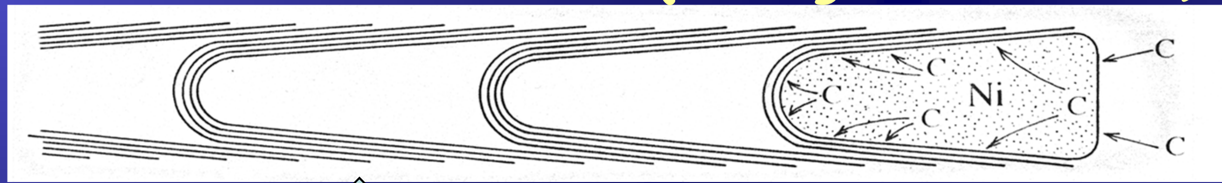
Morphology

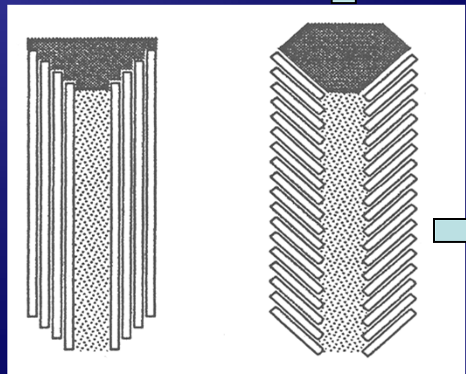




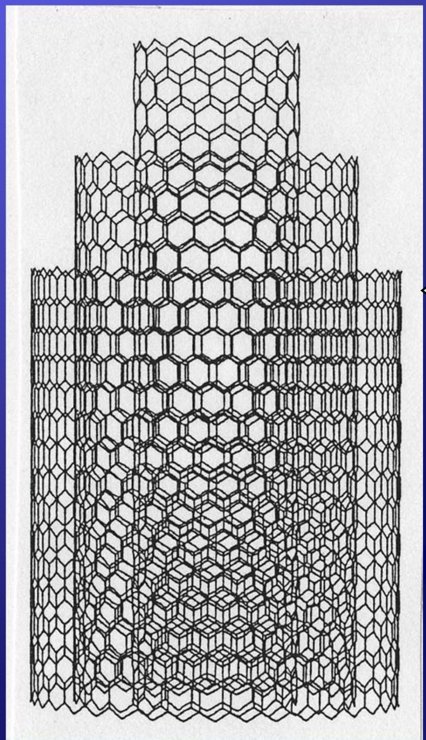
Texture

hb-MWCNTs (herringbone – bamboo)



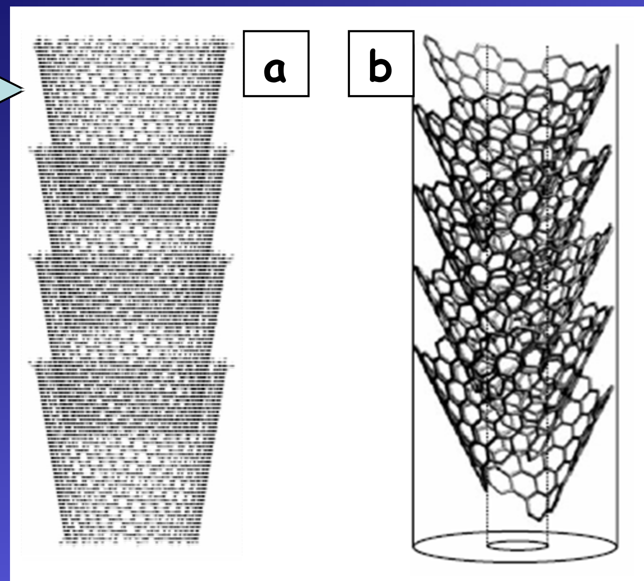


Depending on catalyst and P, T conditions



c-MWCNTs
concentric

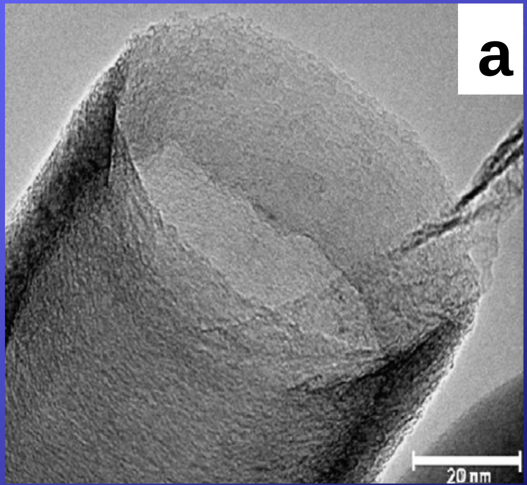
h-MWCNTs (herringbone)

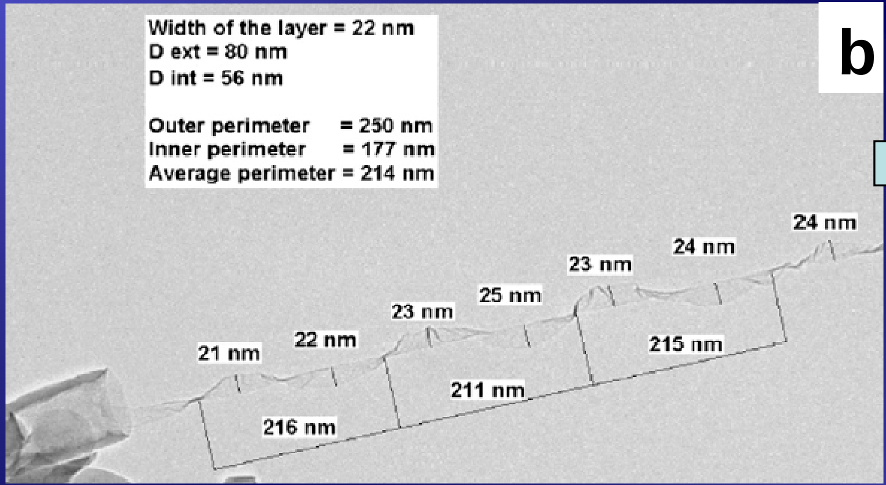


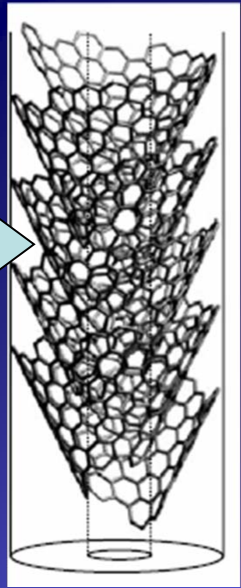
"Cup-stack" or "helical"

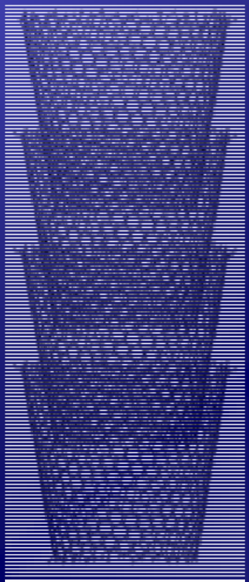
Texture

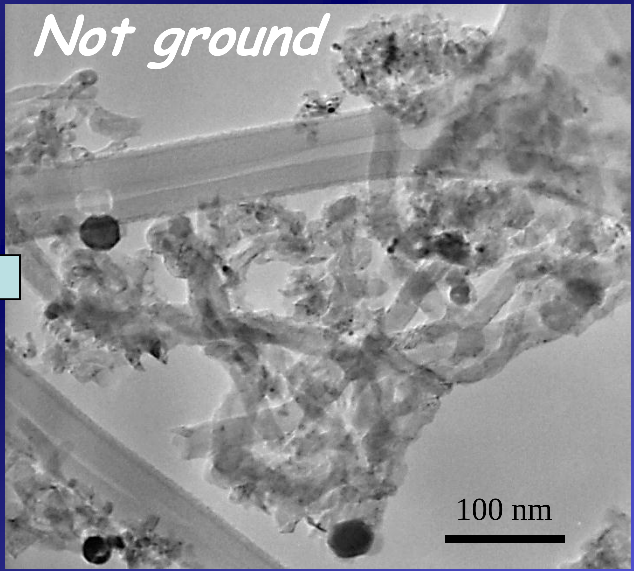
h-MWCNTs (helical)

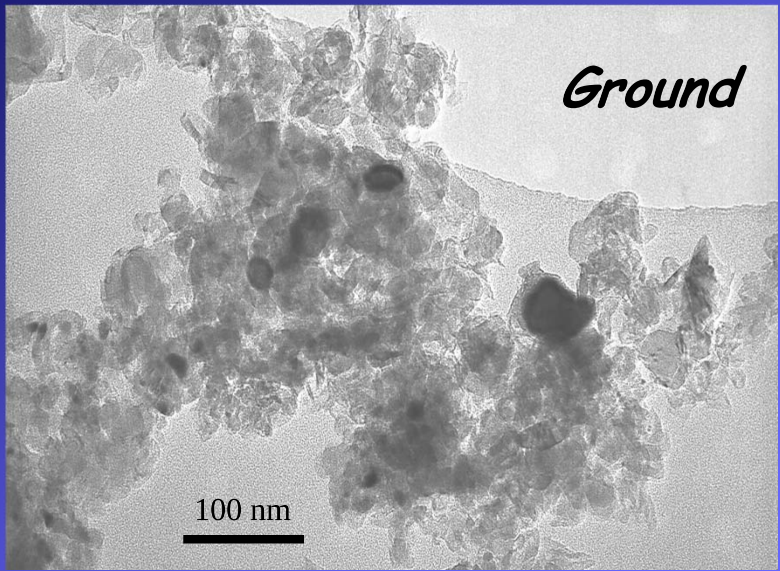






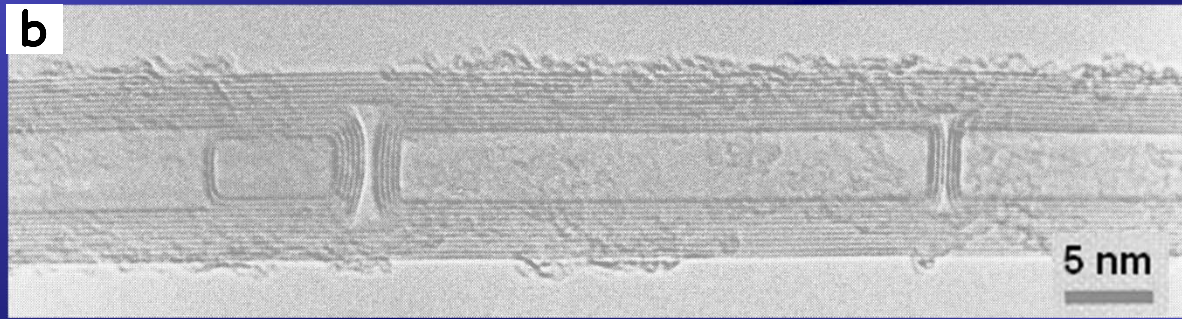




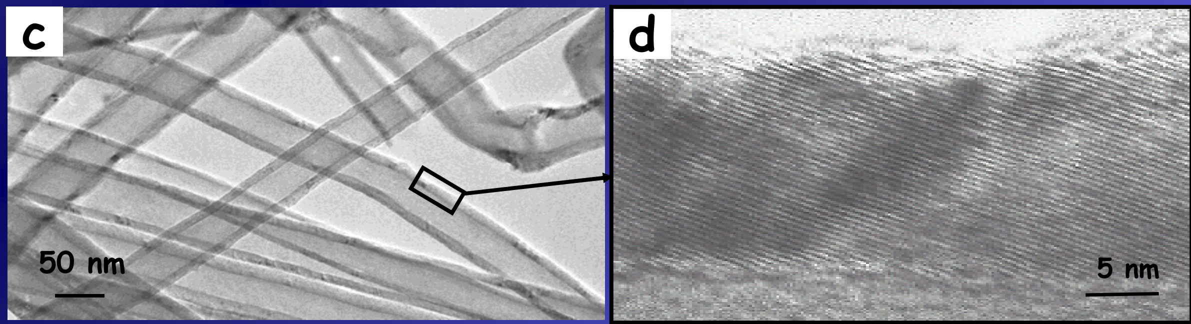


Texture

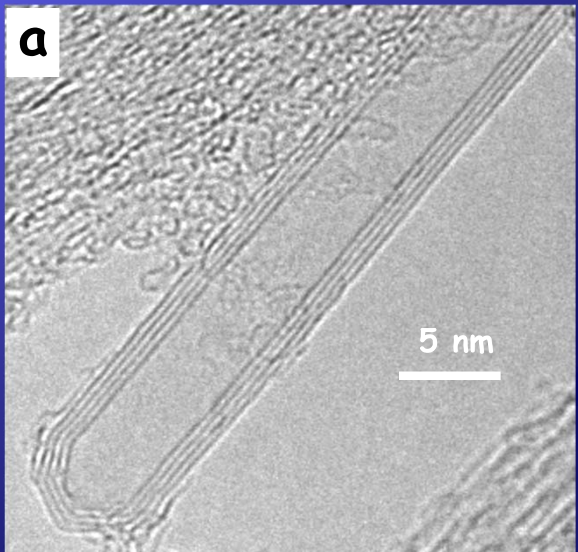
cb-MWNTs *(concentric-bamboo)*



h-MWNTs *(herringbone)*



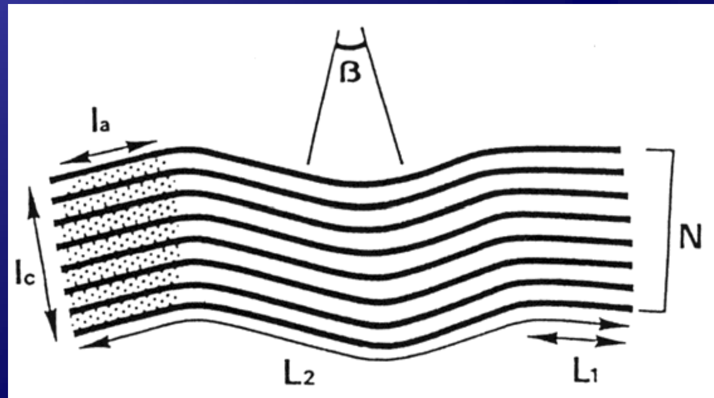
hb-MWNTs *(herringbone – bamboo)*



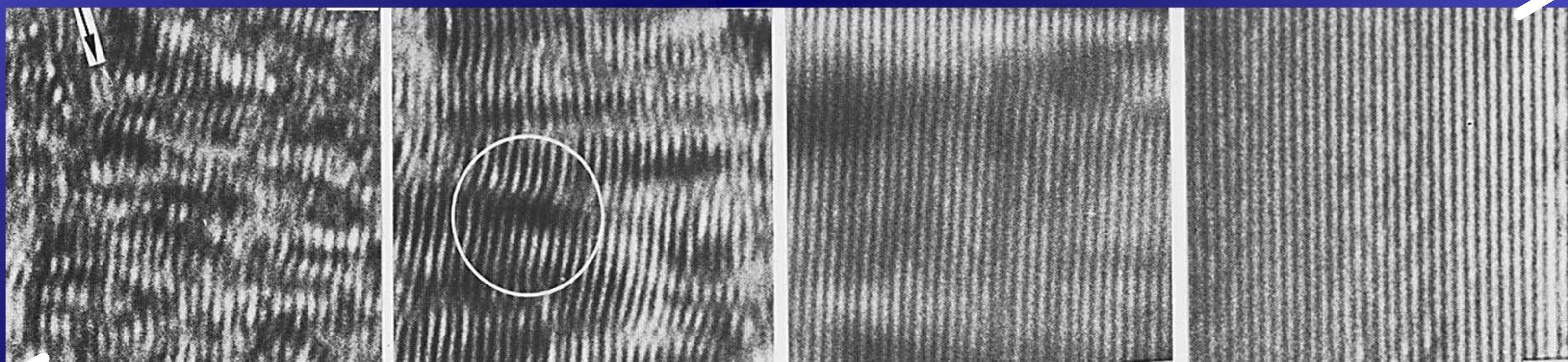
c-MWNTs
(concentric)

Nanotexture

L_1 Average length of the stiff fringes
L_2 Average length of the continuous (yet distorted) fringes
N Average number of fringes within the coherent graphene stacks
β Average misorientation angle



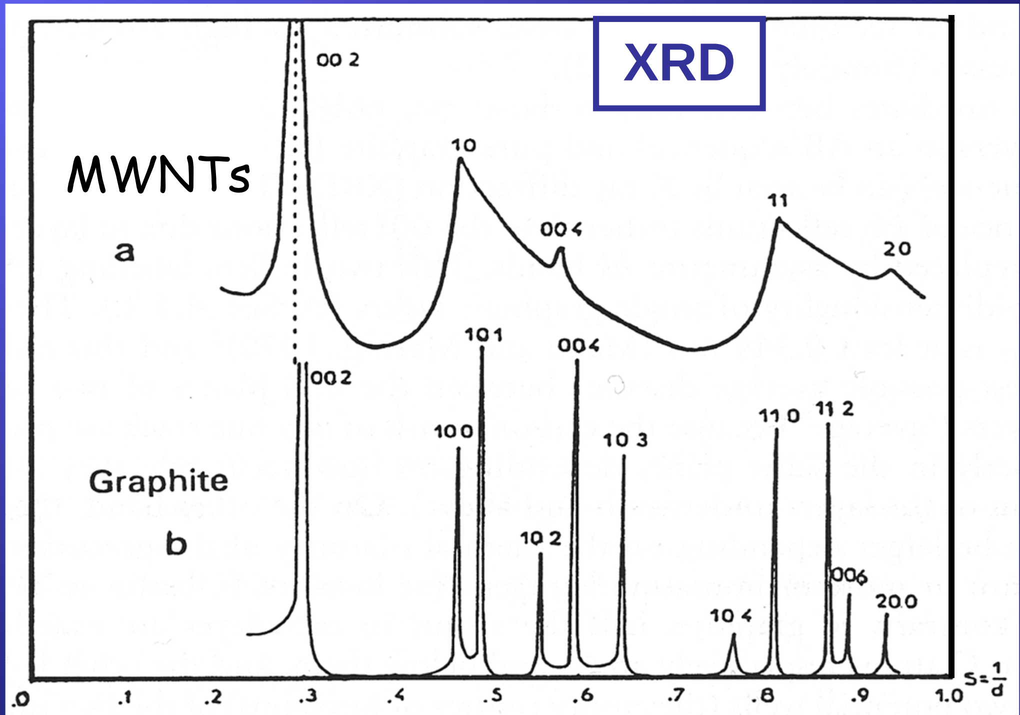
Thermal treatment



Oxidation, irradiation

All kinds of defects: vacancies, heterocycles, disclinations, heteroatoms, *sp*^{3} carbons, surface groups, …

Structure



1D hexagonal lattices with periodic stacking

→ Turbostratic structure

Graphite: Periodic stacking of 1D hexagonal lattices with orientational relationship (ABAB…) → 3D hexagonal

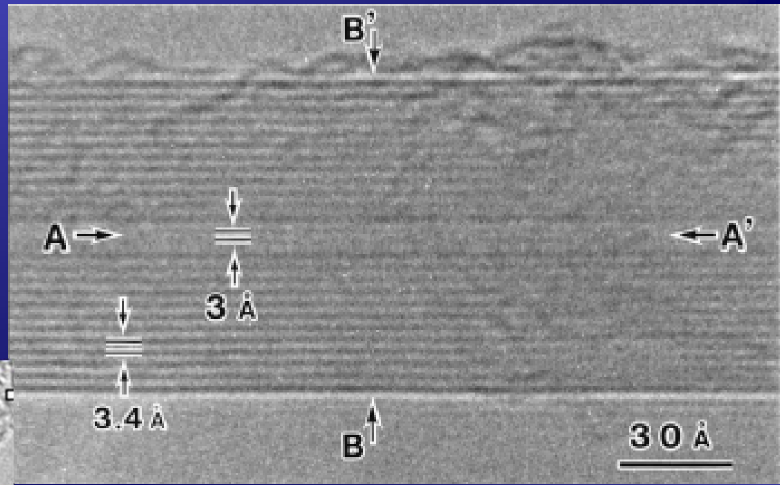
Threshold of radius of curvature for commensurability ~0.5 μm

Graphitisation/commensurability possible via thermal treatment upon facetisation

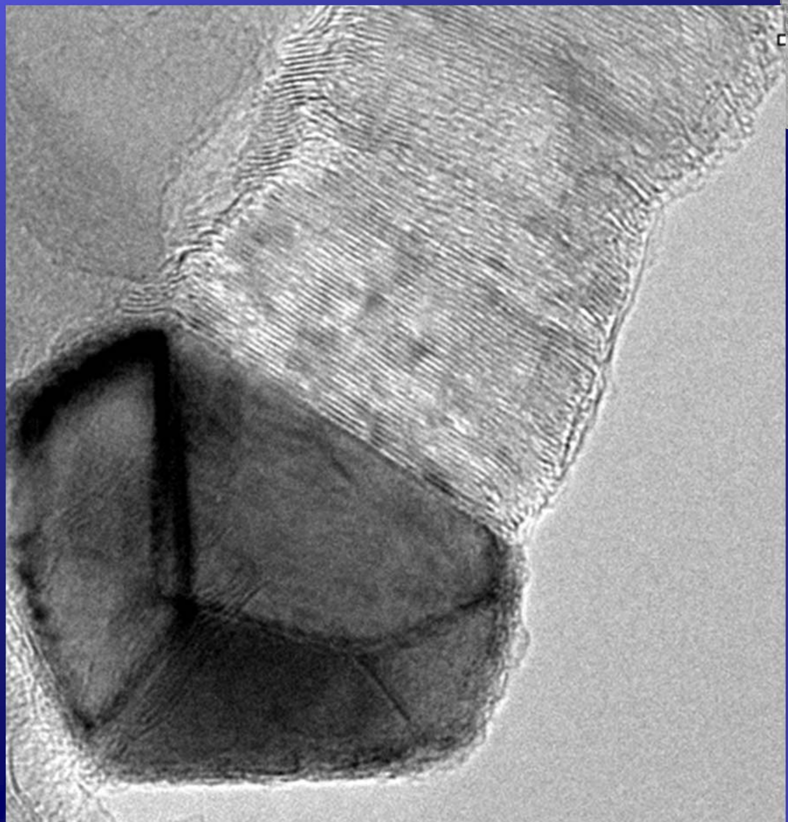
(Multi-wall) Carbon NanoFibres

Concentric

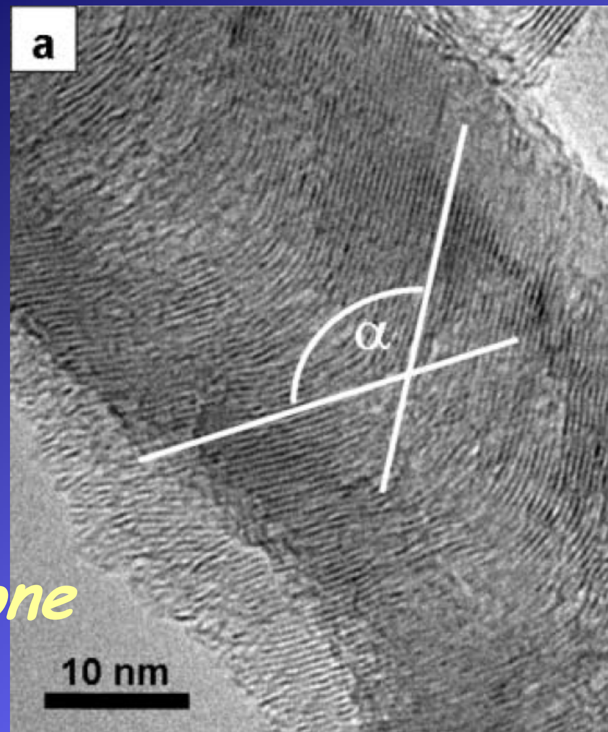
Zhao et al,
Phys Rev Lett
92(2004)125502



Platelet

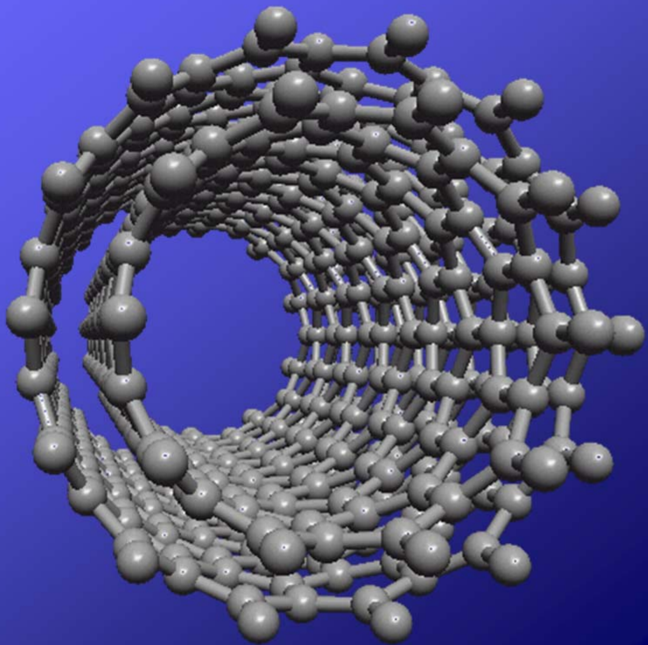


Monthioux
et al,
J Mater chem 17
(2007) 4166



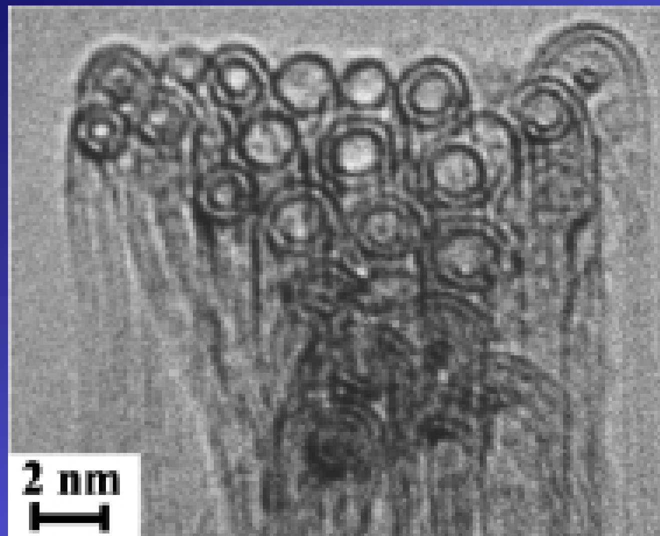
herringbone

DWCNTs: the ideal compromise?

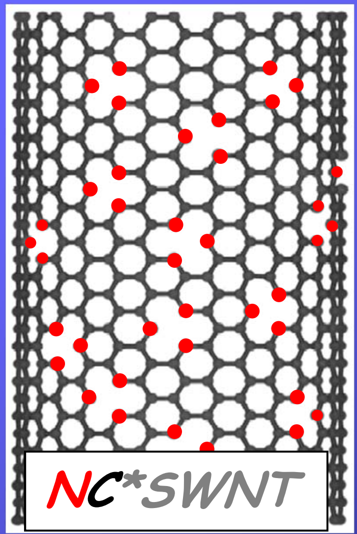


Smith, Monthioux, Luzzi CPL315(1999)31

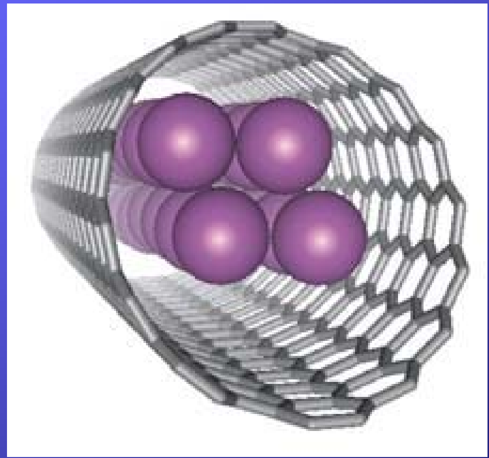
- *The smallest MWCNT*
- *May combine advantages of SWCNT and MWCNT*



Flahaut et al, Chem Comm(2003)1442

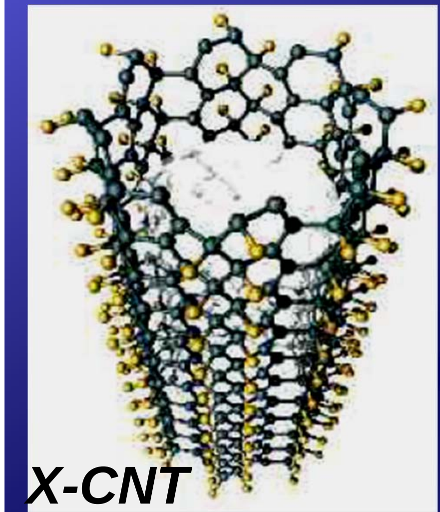


Hetero-nanotubes

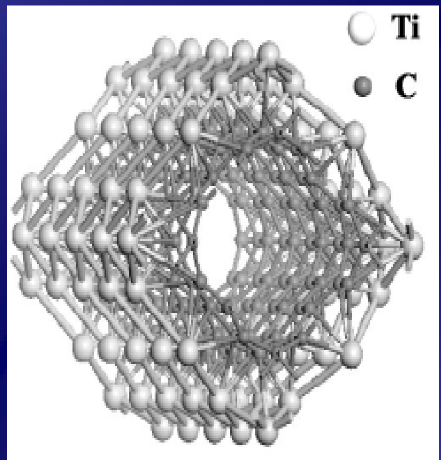


X@CNT – X:CNT

Filled / doped nanotubes



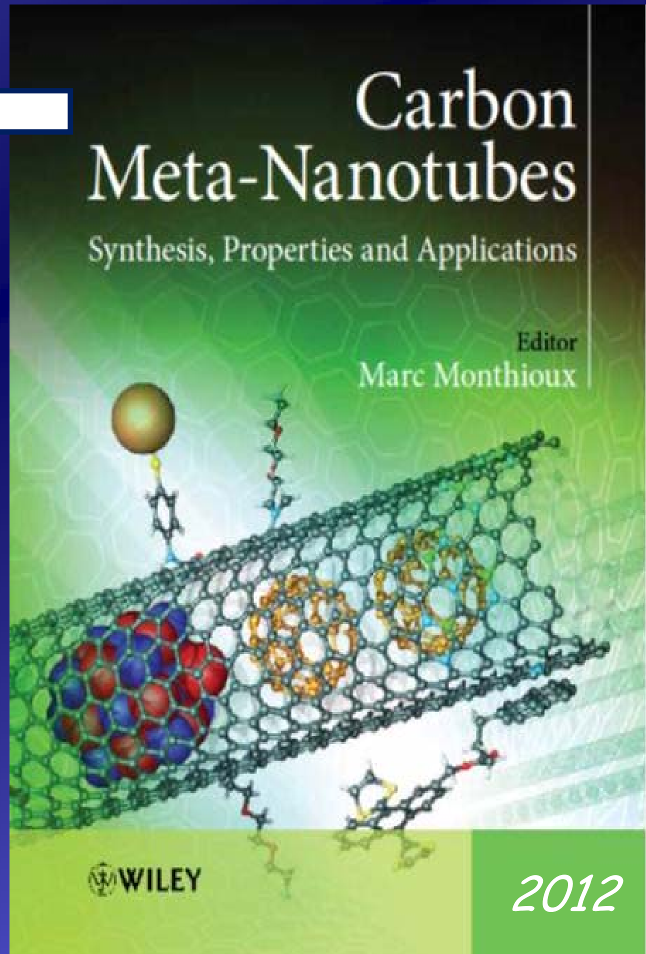
Functionalised nanotubes



X/CNT

Coated nanotubes

= CNT + X (component)



New materials

New or improved properties

Fixing problems of pristine nanotubes

SUMMARY

Describing carbon nanotubes-nanofibres

SWCNT

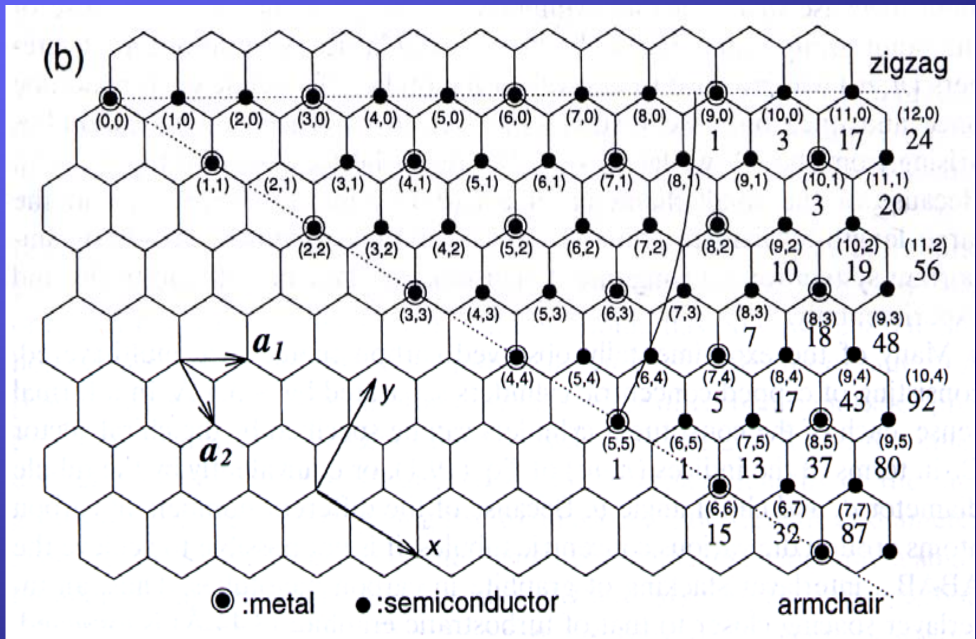
(m,n)

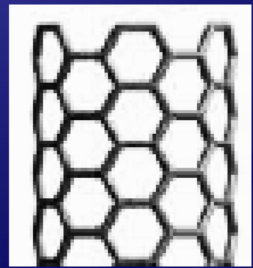
MWCNT

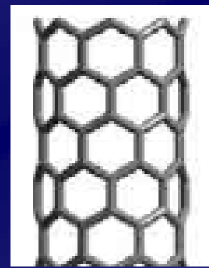
The description chart of multigraphene carbon nanofilaments

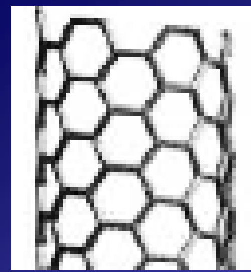
1. Outer morphology (SEM)	Regular, coiled, branched, conical, …	
2. Inner morphology (TEM)	NanoFibre (*CNF*)	NanoTube (*MWCNT*)
3. Texture (TEM)	Platelet (*p*-) Concentric (*c*-) Herringbone (*h*-) Bamboo (*b*-)	
4. NanoTexture (HRTEM)	L_1, L_2, N, β parameters	
5. Structure (diffraction)	turbostratic → graphitic d_{002}, *hkl* with h and/or $k \neq 0$, and $l \neq 0$	

SWCNTs: Importance of molecular structure (helicity)









Armchair (n,n) → ◉ **Metal**

Zigzag (n,0) → ● **Semi-conductor**

Helical (n,m) → ● **Semi-conductor**

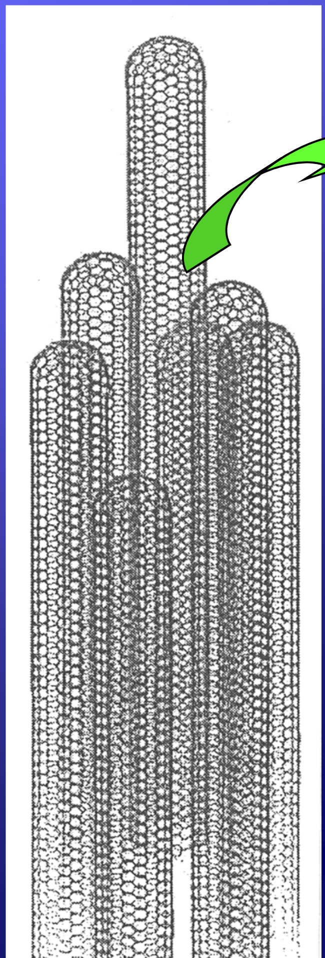
Semi-conductor → *(n-m) = 2i* *(i = integer)* → *small gap* → Metal (1/3)

Semi-conductor → *large gap* (2/3)

*Selectivity of helicity has a **dramatic effect** on **electrical** properties*

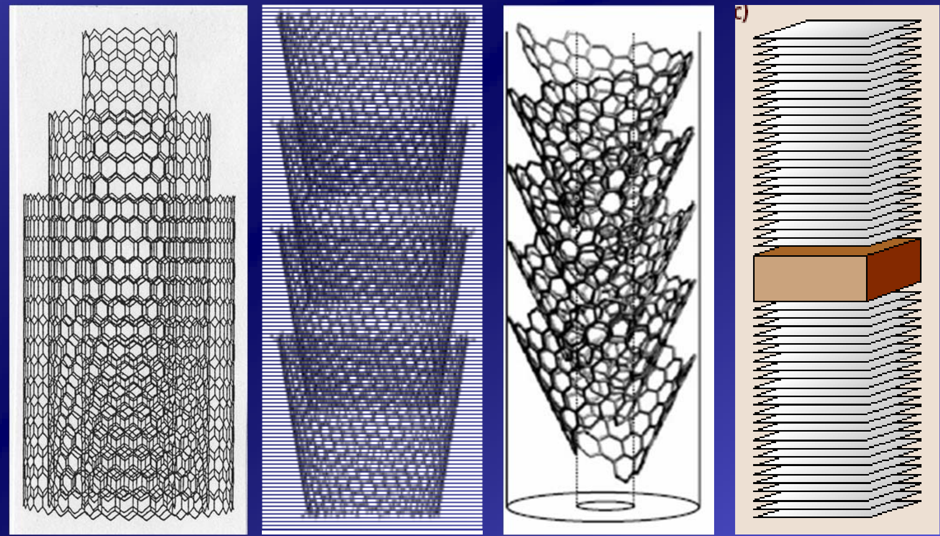
No more discrimination for diameter > 14 nm (= all metal type)

SWCNTs,
CNFs and MWCNTs: Importance of texture



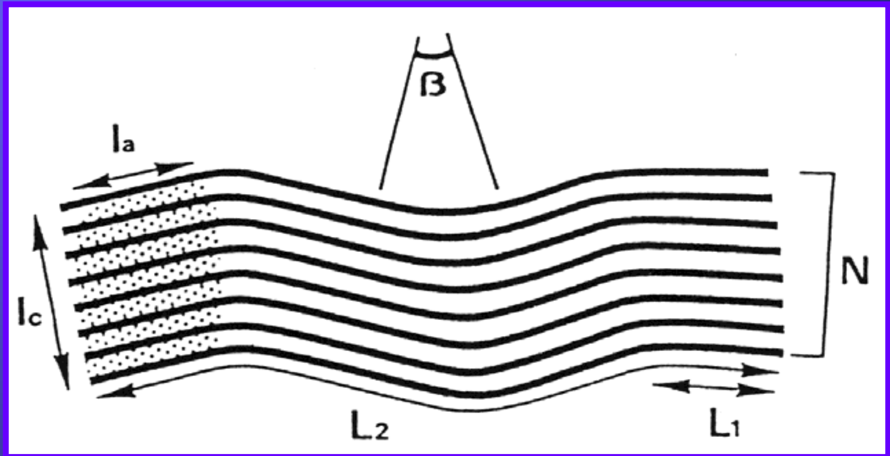
Weak interactions (van der Waals) between SWCNTs

Detrimental effect to collective mechanical properties and thermal stability



dramatic effect on most of properties (electrical, mechanical, thermal,…)

MWCNTs: Importance of nanotexture



Closely relates to most of MWCNT PROPERTIES (thermal, mechanical, electrical, ...)

since related to graphene perfection

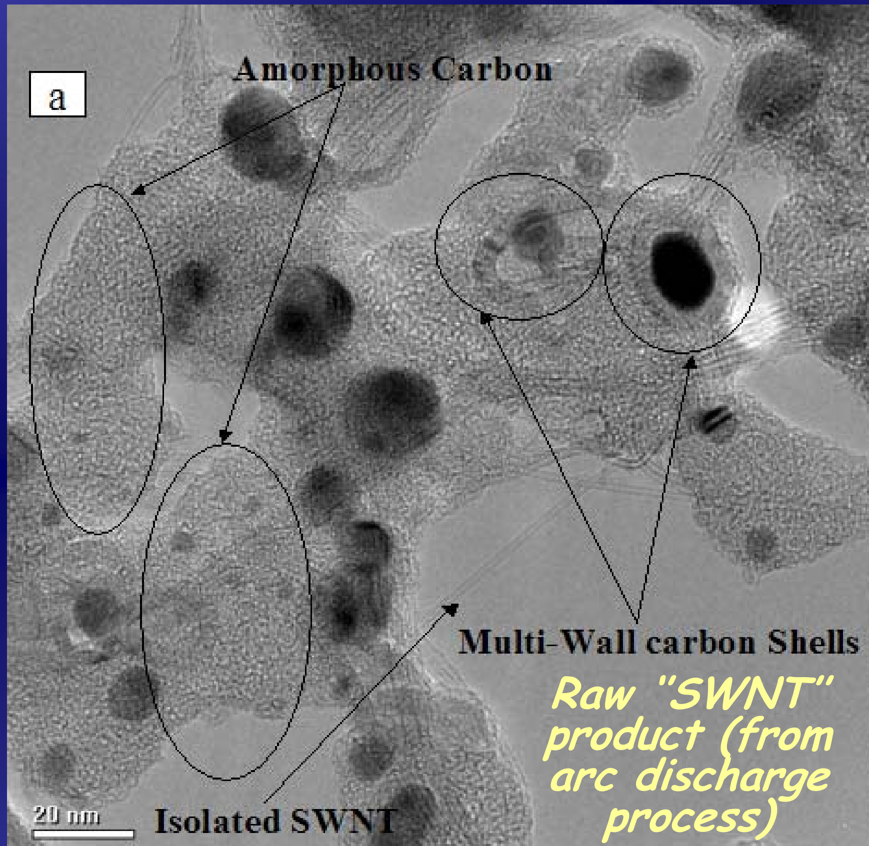
As opposed to NANOTEXTURE and TEXTURE, STRUCTURAL aspects (graphitic *vs* turbostratic) have a limited direct impact on physical properties of MWCNTs

Possible limitations of nanotubes

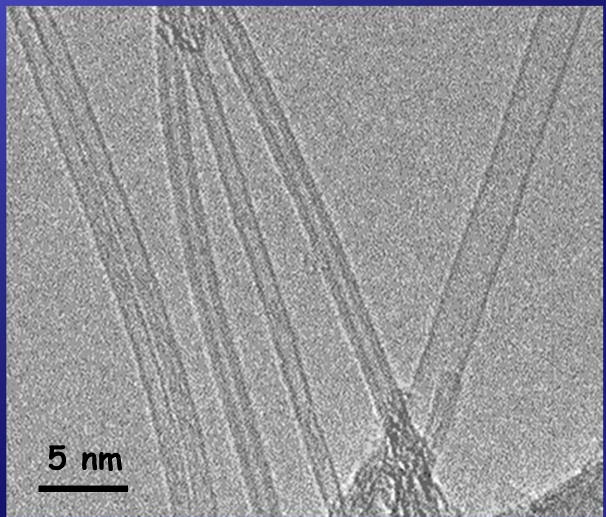
1. Quality

- **Low purity** for many marketed CNT grades

(Non-nanotube carbon phases, catalysts, residual solvents,…)



Raw "SWNT" product (from arc discharge process)



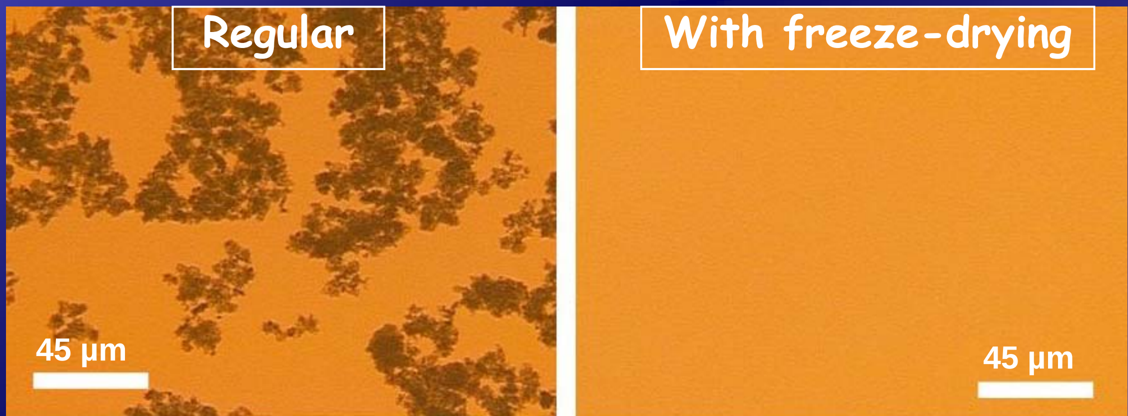
Purified "SWCNT" product (from a CCVD process)

- **Poor selectivity** in most of marketed CNT grades

(Metallic/semi-conductor type, number of walls, diameter distribution…)

2. Processing

- **Mostly: Poor dispersion in (liquid) matrix precursor**
  - *Clumping due to CNT-CNT weak force interactions*
  - *Entanglement preventing regular mixing procedure*

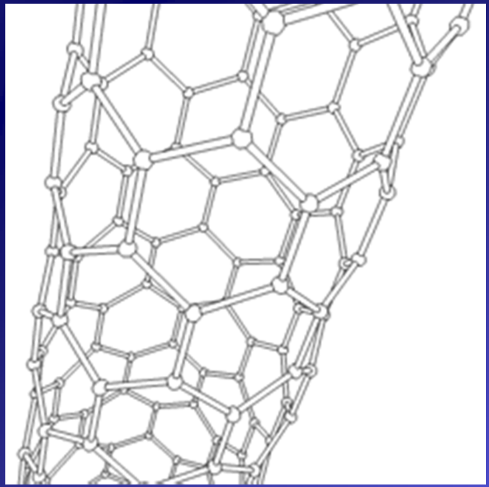


Maugey, et al
J Nanosci Nanotechnol
7 (2007) 2633

Purified "SWCNT" product (from arc discharge) in SDS-added water

3. Low surface reactivity

Perfect outer graphene = chemical inertness
(➔ no bond possible)



- **Limited matrix or medium / CNT interactions (e.g., mechanical: stress transfer in composites)**
- **Limited CNT/CNT connectibility (e.g., for CNT-based fibres)**

Not a drastic requirement for electrical and thermal management applications

Potential use for composites: is "Nano" beautiful?

Carbon nanotubes *versus* carbon (micro)fibres

Higher aspect ratio	*. Lower percolation threshold*
Higher surface area	*. Higher surface of interaction*
Better structural perfection	*• Ultimate properties*
Much simpler fabrication processes	*• Affordable technology*
Much convenient feedstock (constant quality, easy availability)	*. Low cost*

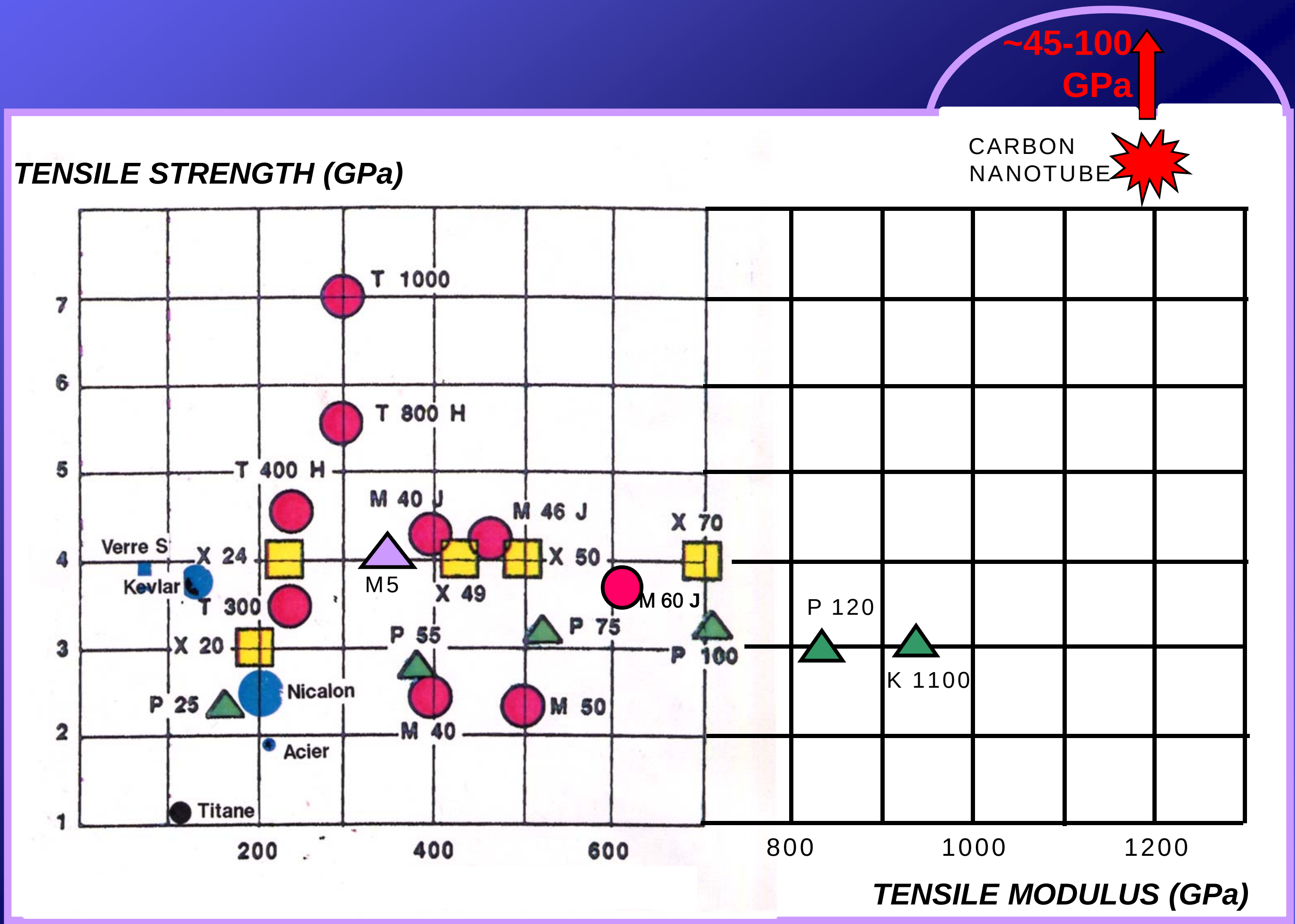
CNT-CNF Properties

"Extreme" and "performance" are the rule!

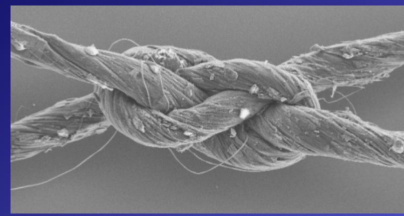
Properties	Values	Comments
Aspect ratio	~1 000 – 10 000	*Possibly higher*
Specific surface area	~2 780 m^2/g	*When considering both surfaces of open SWCNTs*
Tensile strength	> 45 GPa	*Other values up to 100 Gpa can be found in the literature*
Tensile modulus	1 to 1.3 TPa	*Independent on diameter when > 1 nm*
Tensile strain	> 40%	*Provides toughness values higher than that of spider web*
Flexural modulus	1.2 TPa	
Thermal stability	> 3000°C	*In oxygen-free atmosphere*
Electrical conductivity	10^4 – 10^7 S/cm	*Better than copper* (~60 10^4 S/cm)
Transport regime	Ballistic, up to superconductivity	$T_c < 1$ K
Thermal conductivity	~6 000 W/mK	*Better than diamond*
Electron emission	10^6 - 10^9 A/cm^2	*Highest current density*

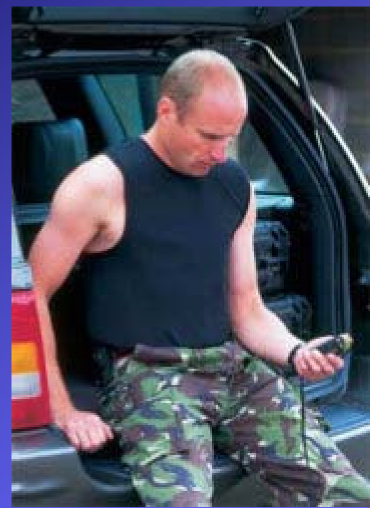
All valuable for use in composites (but electron emission)

CNTs in composites:
Mechanical reinforcement



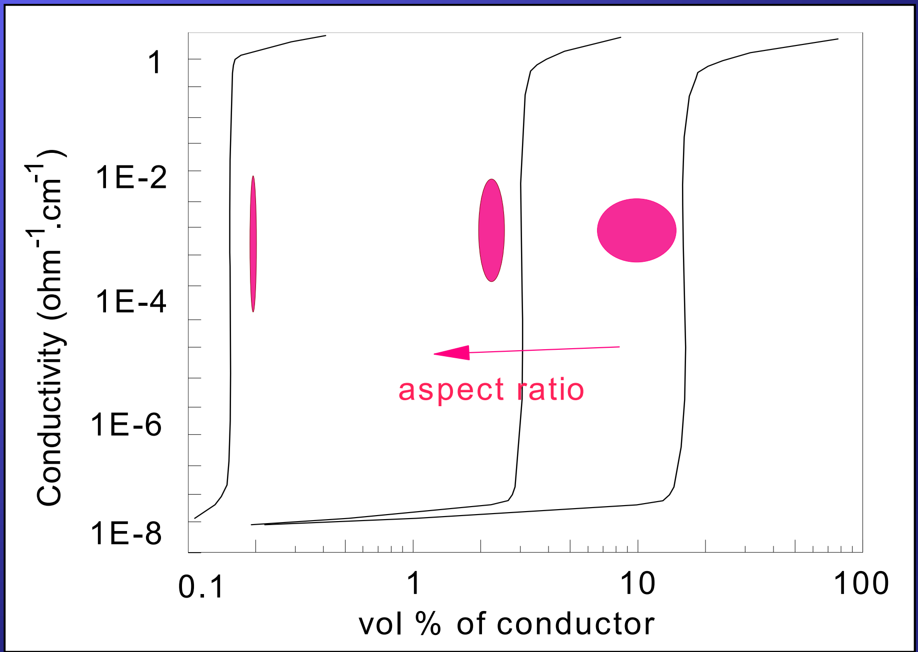
Field: structure parts in transport and space vehicles,…





Nanotube-based bullet-proof jacket

CNTs in composites:
Electrically conductive filler



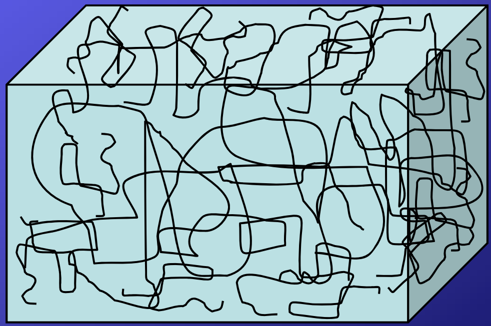
Percolation threshold:

~15% for carbon blacks

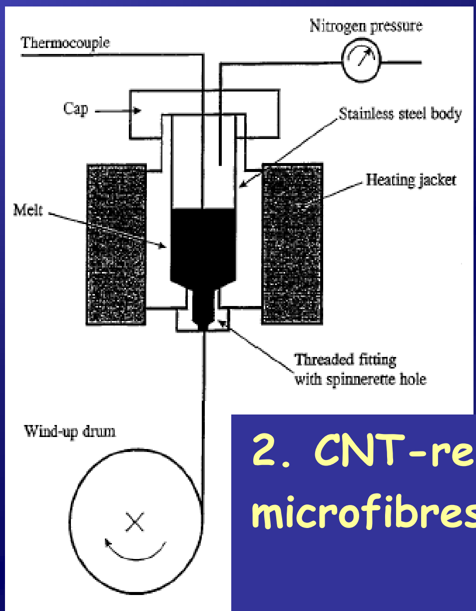
Black, non-transparent resulting materials

< 0.5% for CNTs

The various ways to use CNTs in composites

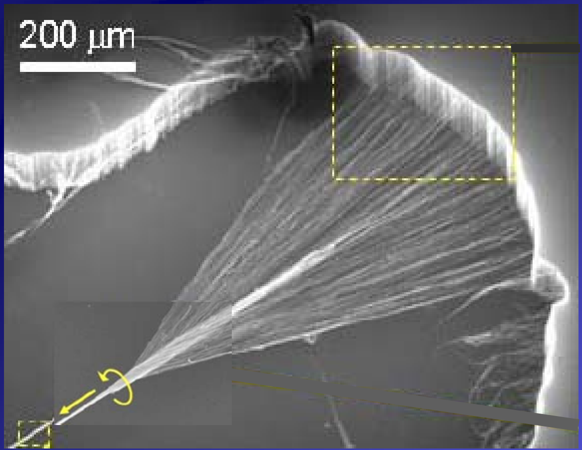


1. CNTs as direct filler

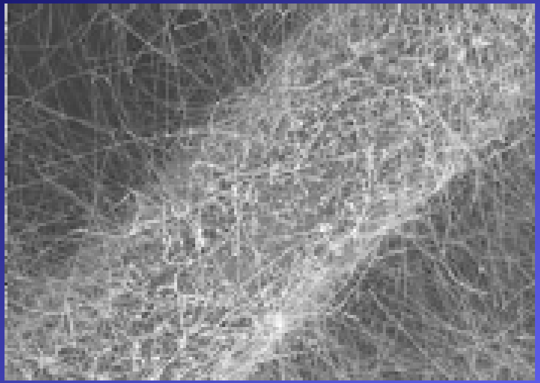


2. CNT-reinforced microfibres

Zhang et al Science 306(2004)1356



3. CNT-based microfibres



4. CNTs as interphase

Sun et al CPL394(2004)266

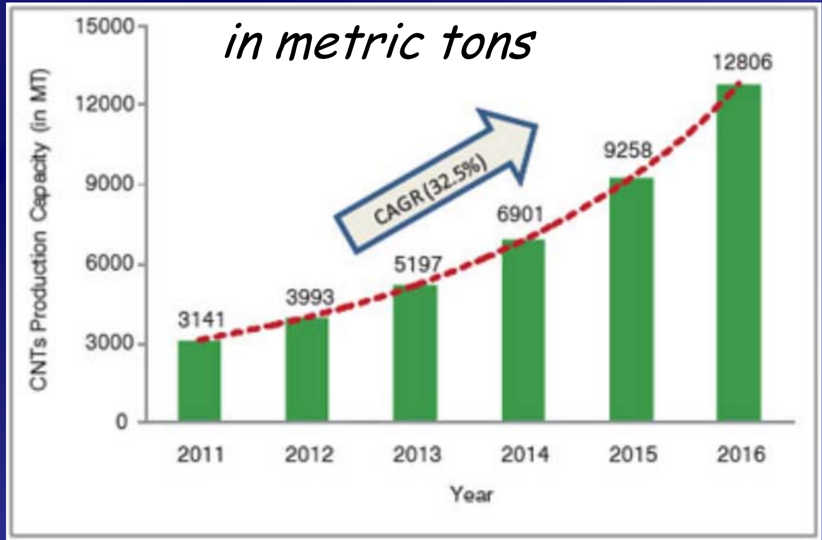
CARBON NANOTUBES-NANOFIBRES

Synthesis methods:
. Thermal decomposition of gaseous or vaporised hydrocarbons (CCVD) (or CO disproportionation) + catalyst
. Electric arc + catalyst

Capacity production:
ton scale

2010:
44.2% Asia,
29.2% USA,
24% EU

Patel, Nanotech Insights (2011)



Average market price:
. SWCNTs: 80 000 – 2 000 000 US $/kg
. MWCNTs: < 50 US $/kg

Depending on processes and post-treatments

(low grade PAN-based carbon fibre: ~20 US $/kg)

2010	Manufacturers	Annual production capacity (Metric tonnes)	Processing routes	Country
SWCNTs	Unidym, Inc. (acquired by Wisepower Co.), http://www.unidym.com	1500	High-pressure carbon monoxide (HiPco)	USA
	Toray Industries, Inc. http://www.toray.com	1500	CCVD	Japan
	Mitsubishi Rayon Co. Ltd. http://www.mrc.co.jp/english/index.html	1200	CVD	Japan
	SouthWest NanoTechnologies Inc. http://www.swentnano.com	1000	Cobaltmolybdenum catalyst (CoMoCAT)®	USA
	Kleancarbon Inc. http://www.kleancarbon.com	1000	CVD	Canada
MWCNTs	Showa Denko K.K http://www.sdk.co.jp/english	500	CCVD	Japan
	CNano Technology Limited http://www.cnanotechnology.com	500	CCVD	USA
	Nanocyl S.A., http://www.nanocyl.com*	400	CCVD	Belgium
	Bayer MaterialScience AG http://www.bayermaterialscience.com	260 3000 by 2013	CCVD	Germany
	Arkema Inc. http://www.arkema-inc.com	50 400 by 2011	CCVD	France
	Hyperion Catalysis International, Inc. http://www.hyperioncatalysis.com	50	CVD	USA
	Eden Energy Ltd	< 50		Australia
	Nanocomp Technologies Inc., Applied Science Inc.	< 50		USA
	Iljin Nanotech	< 50		South Korea
	NanoCarbon Technology, UBE Ind.	< 50		Japan

Suppliers

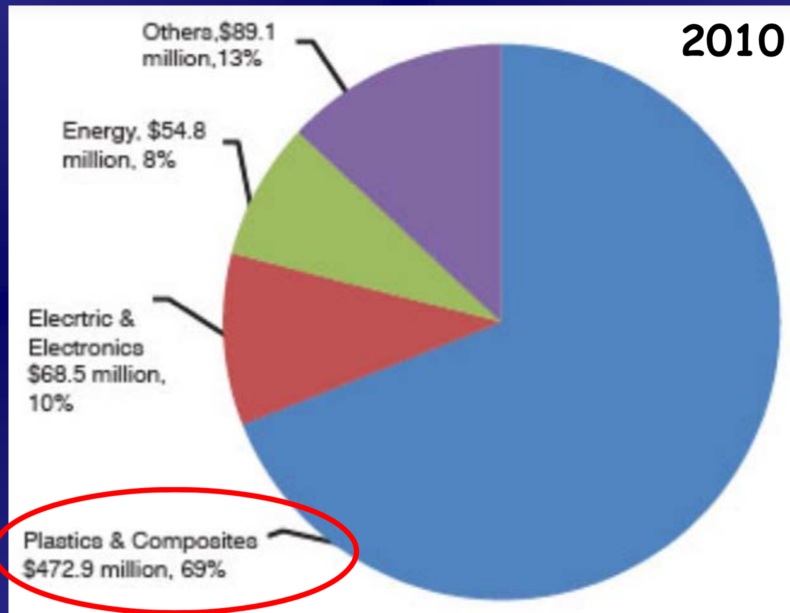
(not exhaustive!)

Patel, Nanotech Insights (2011)

Potential/real use in composite systems:

More than 100 companies are manufacturing CNTs, 200 expected by 2016

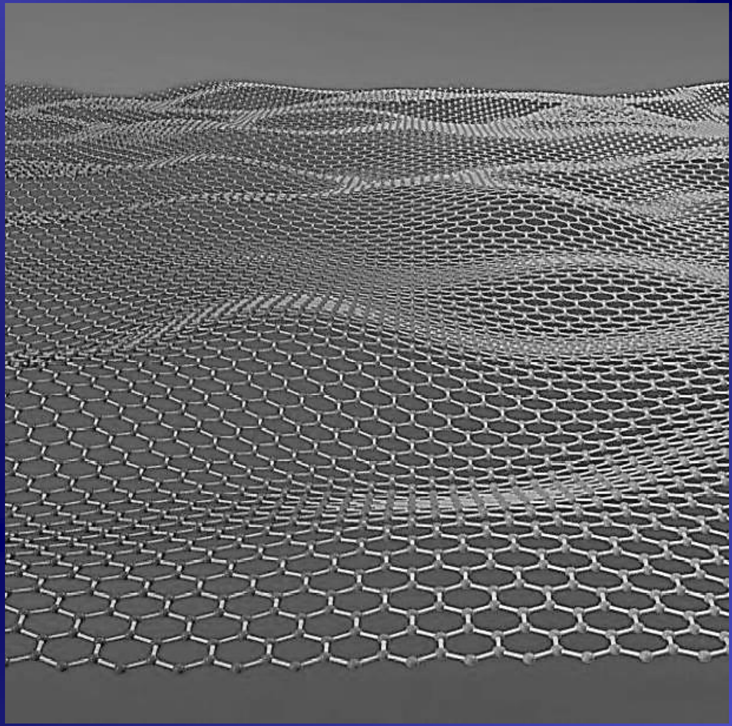
- Sport goods
  (mechanical properties)
- Built-in sensor for composite damaging
- TRANSPARENT, Conductive plastics (antistatic containers and surfaces, electro-painting, …)
- Power cables
- Pigments (inks)
- Flexible, transparent display



Patel, Nanotech Insights (2011)

GRAPHENE *(single)*

Acknowledged as such: in the late 80'
Isolated: 2004 (Geim & Novoselov)

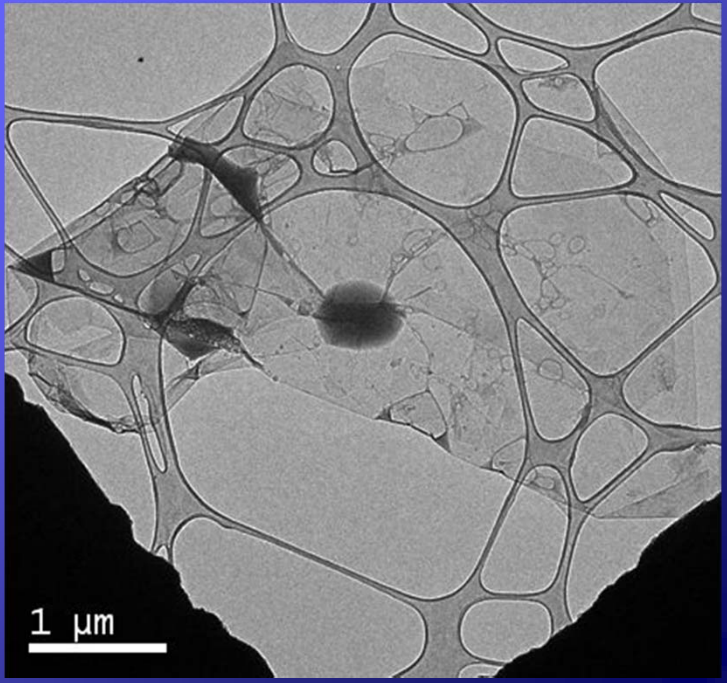


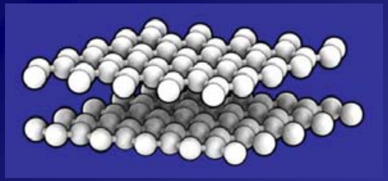
If perfect:
full benefit of the specificities of the graphene lattice

- mechanical properties: σ = 100 Gpa, E = 1 TPa
- transport properties (mass-less electron conduction: electron velocity = 1000 km/s, i.e., 150x higher than in silicium)
- Thermal conductivity: ~6000 W/m.K (~10x better than silver, copper…)

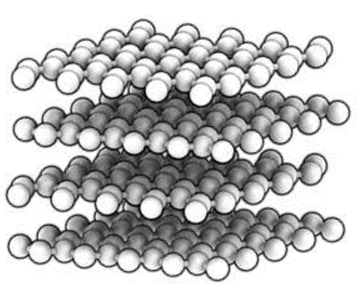
→ **Similar to SWCNT**

GRAPHENE NANOPLATELETS (flakes, FLG,…)





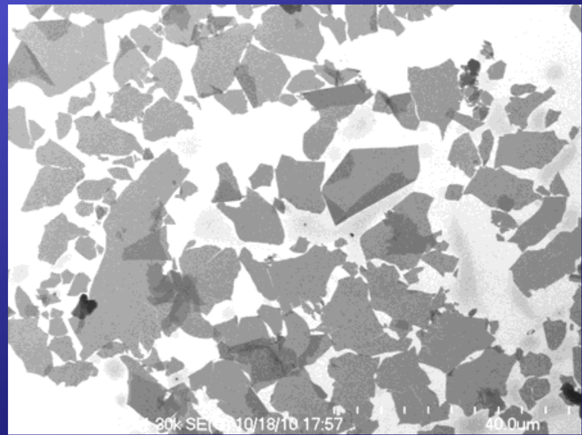
Specificities decrease as the number N of graphenes increases



Similar to graphite from N ≈10

Available on market:

1. Powder



Synthesis method:
Graphite exfoliation → powder

Market price: ~250 US $/kg

(NOT single graphene)

2. Film

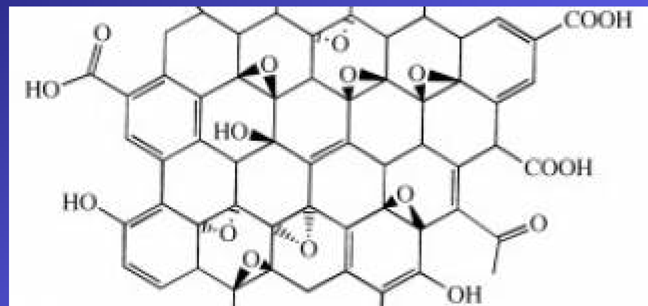
Synthesis method:
Epitaxial graphene on Cu foil → Polycrystalline film

Market price: single graphene (10x10 mm^2): 100 US $

3. Solution

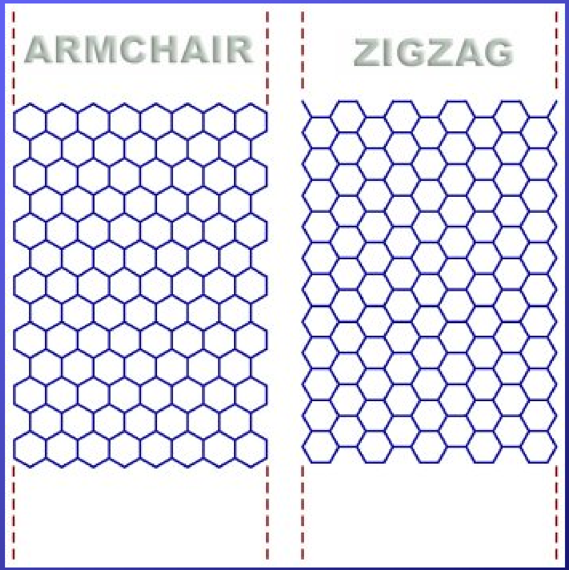
Synthesis method:
Oxidation of graphene → **graphene oxide** (~50%C !) → powder or soluble OR **reduced graphene oxide** rGO

Market price (solution): ~130 000-400 000 US $/kg



SUPPPLIERS: EU: graphenea - **USA:** Graphene SuperMarket, Angstron Materials, Harp Engineering… **- Asia:** Sinocarbon, etc.

GRAPHENE NANORIBBON

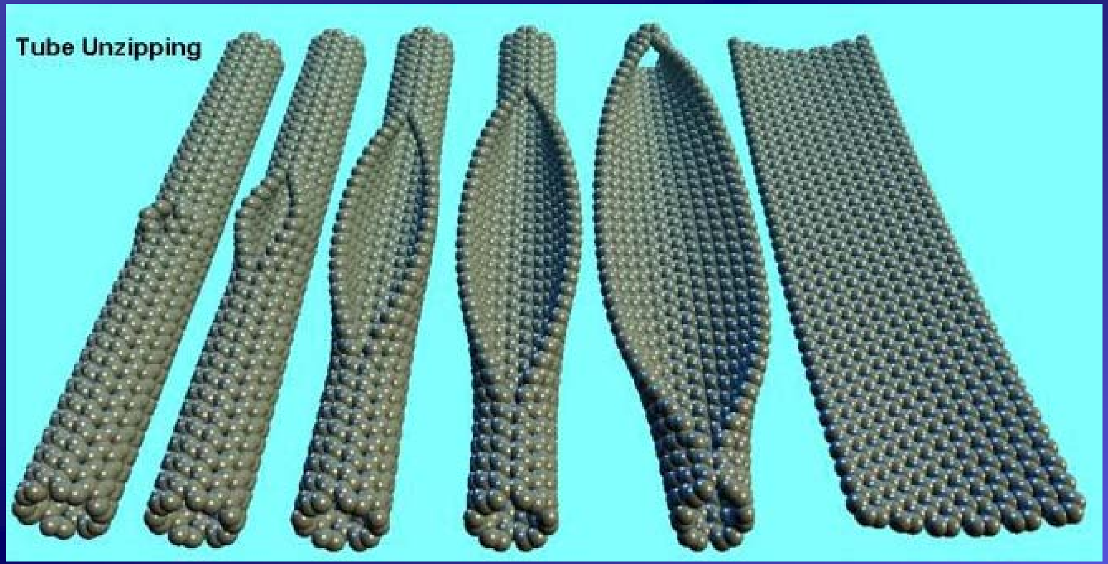


Orientational discrimination similar to SWCNTs

+ reactive edges

Metallic, semi-conducting, possibly ferro-magnetic (if doped)

Synthesis method:
- Etching of graphene
- Unzipping of CNTs

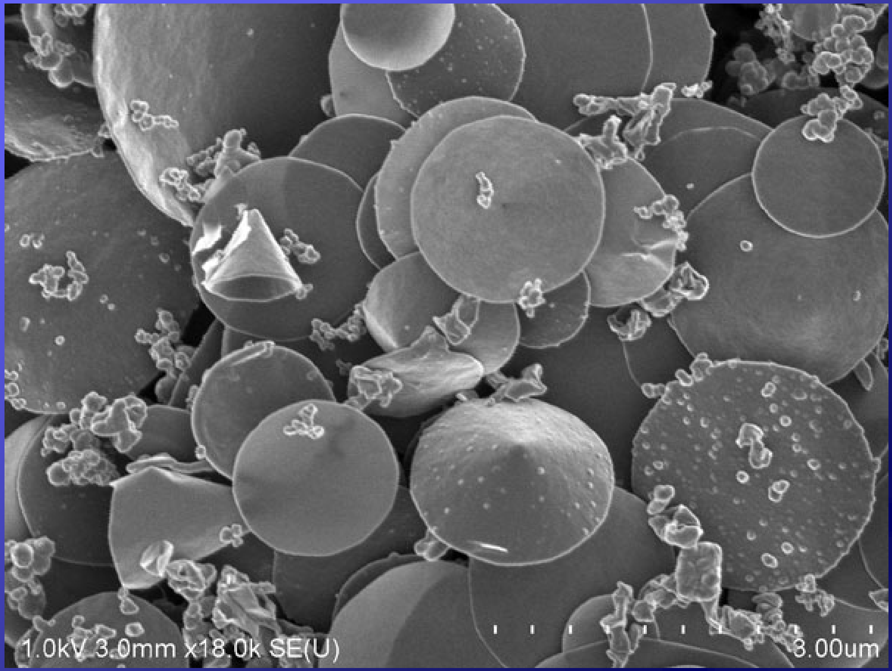


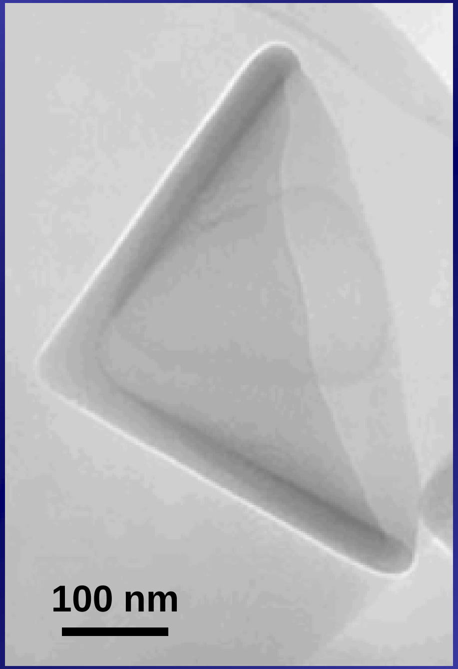
Not available on market (lab-made)

Kosynkin et al, Nature 458(2009)872

GRAPHENE cones and discs

Discovered: 1997 (Krishnan et al)





Diameters:
0.8 – 3 μm

Thickness:
20-50 nm

Synthesis method:
Thermal cracking of vaporised heavy oils (+ Post-HTT)

Capacity production: kg scale (for lab use only)

Average market price: ~130 000 US $/kg
(STREM chemicals Inc, n-TEC…)

Potential use of graphene / nanoplatelets / nanoribbons / nanodiscs in composite systems:

- Same use as CNTs

Advantages:

- High conductivity
- High surface area
- Functionalisability → large compatibility
  → tunable reactivity

Better than CNTs?

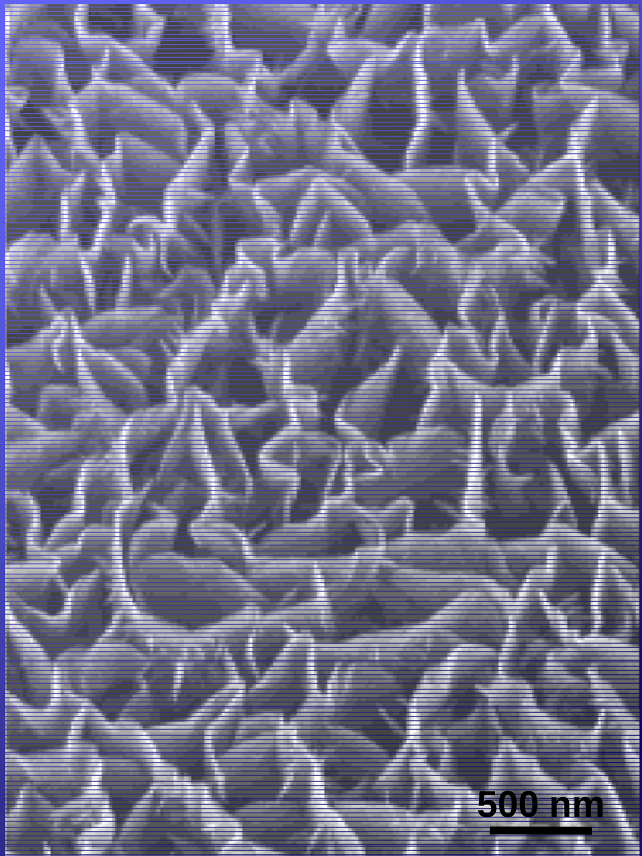
Issues:

- Multi-graphene: increasing contribution of the weak strength of van der Waals bond as N increases
- aspect ratio not favourable for percolating network (but for nanoribbons)
- 2D orientation
- Dispersibility, processability
- Graphene oxide NOT conducting
- Reduced graphene oxide ≠ graphene
- Cost

"Modulus, ultimate strength and thermal stability follow a similar trend, with values for functionalized graphene sheet–poly(methyl methacrylate) ***rivaling those for single-walled carbon nanotube–poly(methyl methacrylate) composites"***

Ramanathan et al, Nature Nanotechnol 3(2008)327

GRAPHENE NANOWALLS



Wu et al, J Mater Chem 14(2004)469

Synthesis method:
- Plasma enhanced CVD

Not available on market (lab-made)

Potential use in composite:
As material of interphase, to grow on, e.g., carbon fibres instead of CNTs
→ increase of specific surface area
→ increase of fibre/matrix interaction
→ Increase of fibre surface reactivity

HEALTH AND SAFETY

Toxicity of CNTs towards cells is supposed to increase

- *as aspect ratio increases ("Asbestos syndrom")*
- *as chemical reactivity increases*

but NO CERTAINTY REGARDING CYTO- AND ECO-TOXICITY OF CNTs YET

- *Too large variety of CNTs*
- *No standard investigation procedures*
- *Role of impurities*
- *Low reactivity of graphene surfaces*

Investigations are in progress worldwide for all kinds of nanocarbons (including carbon blacks)

Benefits might overcome hazards

CONCLUSION

- Many types of nanocarbons → large variety of potentialities
- 'Nano' is beautiful (but expensive!)
- Perfection is not necessarily a must
- The superiority of graphene over CNTs is not absolute
- Graphene and CNTs will be complementary instead of competitor (as other nanocarbons will as well)
- Attention not to rediscover graphite