TLMC5
Quinto Taller Latinoamericano de Materiales de Carbono

ABCarb
Brazilian Carbon Association

A small history of carbon materials from paint to scaffold biomaterials

(04.11.2024 – Monday – 09:45 – 10:45h)

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2024

Carbon ... It is one of the most versatile atom !

CH																He
CLi	CBe											CB	CC	CN	CO	CF	Ne
CNa	CMg											CAl	CSi	CP	CS	CCl	Ar
CK	CCa	CSc	CTi	CV	CCr	CMn	CFe	CCo	CNi	CCu	CZn	CGa	CGe	CAs	CSe	CBr	CKr
CRb	CSr	CY	CZr	CNb	CMo	CTc	CRu	CRh	CPd	CAg	CCd	CIn	CSn	CSb	CTe	CI	CXe
CCs	CBa		CHf	CTa	CW	CRe	COs	CIr	CPt	CAu	CHg	CTl	CPb	CBi	CPo	CAt	Rn
Fr	CRa		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

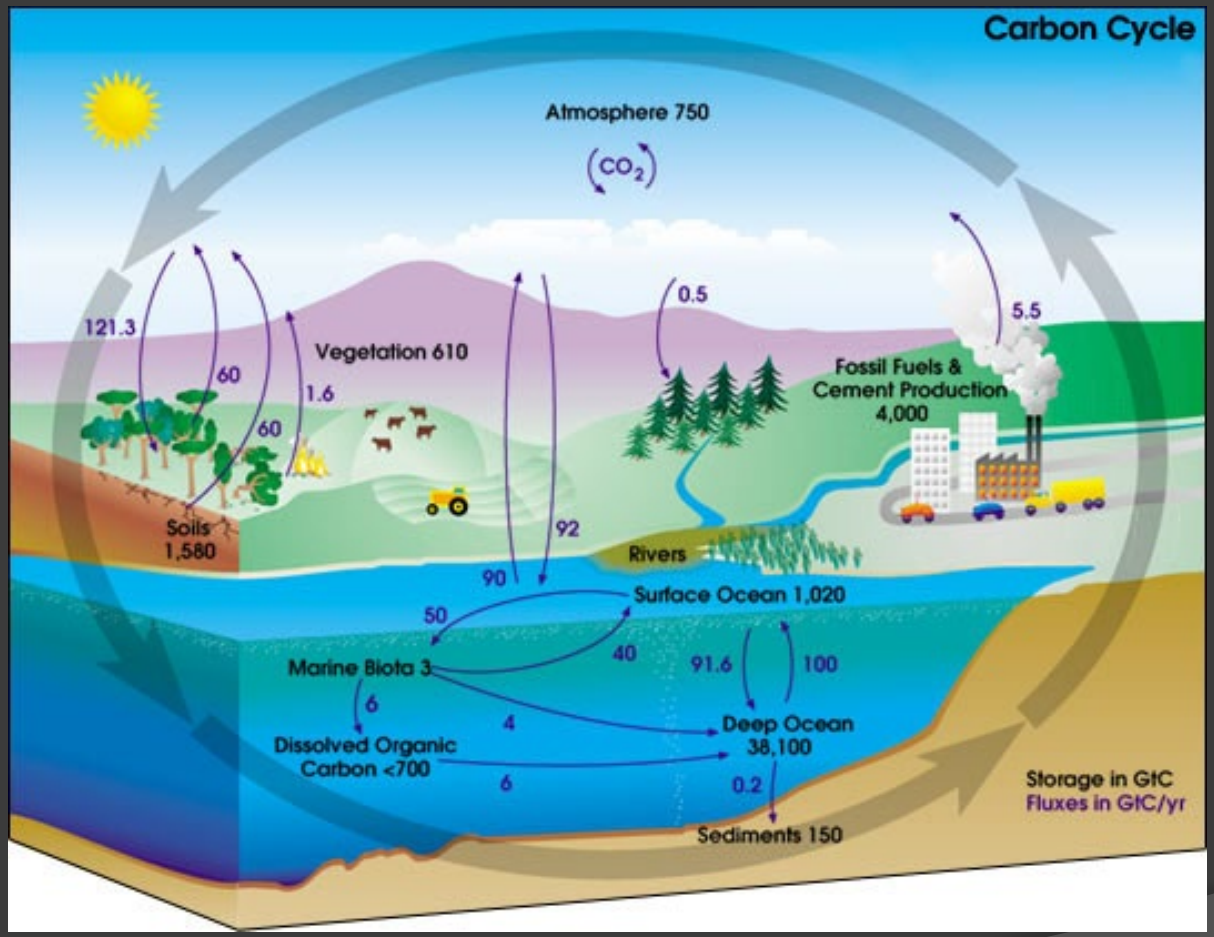
CLa	CCe	CPr	CNd	CPm	CSm	CEu	CGd	CTb	CDy	CHo	CEr	CTm	CYb	CLu
Ac	CTh	CPa	CU	CNp	CPu	CAm	CCm	CBk	Cf	CEs	Fm	Md	No	Lr

Chemical bonds to **carbon**

Core organic chemistry	Many uses in chemistry
Academic research, but no widespread use	Bond unknown / not assessed

- **Organic & inorganic compounds**
- **Allotropes (carbon nanotubes, fullerenes, diamond, graphite ...)**
- **18 wt.% of human body ; 19o. Element on Earth**

Everyday presence …
The good, …



- Photosynthesis
- Earth natural temperature control and maintenance (live planet !)

… the bad and the ugly !

https://bangkok.unesco.org/content/unesco-bangkok-marks-beat-plastic-pollution-mission-sense-urgency

Plastic and tyres pollution !

Carbon: origins and technological evolution

The word “carbon” came from Latin word: carbo that means: charcoal

15,000 BC – North of Spain

First black colour paint !

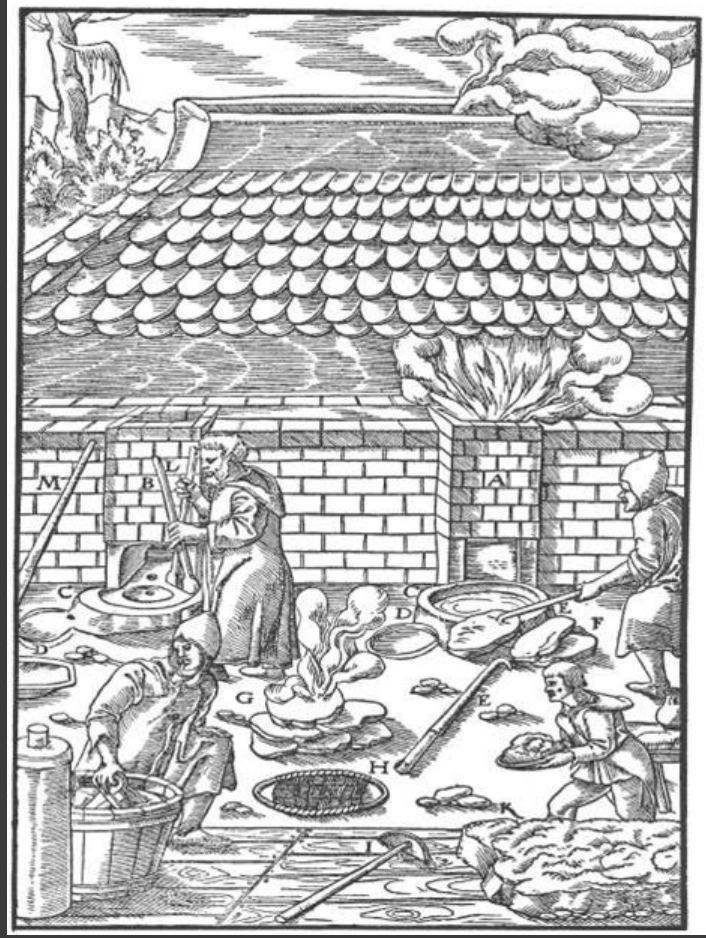
Carbon: origins and technological evolution

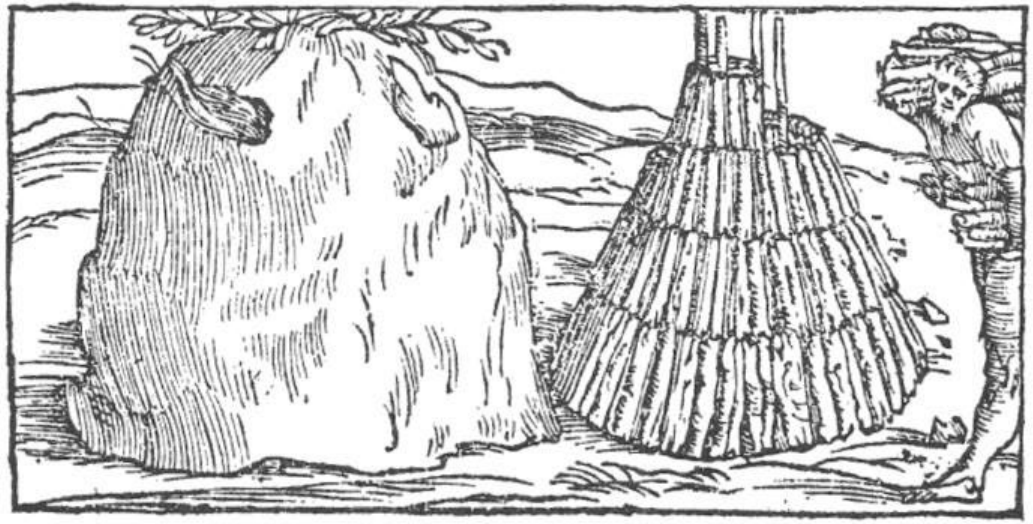
Essential for iron-carbon Development and Technology

The Iron Pillar of Delhi
(3rd ~4th Century)

Charcoal and the Middle age

The word “carbon” came from Latin word: carbo that means charcoal





Middle age: charcoal production for iron making

Source: The Pyrotechnia, VANNOCCIO BIRINGUCCIO; Year: 1540 edition

Carbon: and the pre-industrial revolution

The first blast furnace on coke

Abraham Darby I,
10 of January of 1709

Chemistry evolution … The first two allotropes: graphite and diamond

***John Dalton**. 1808; (Symbol of Carbon)*
New System of Chemical Philosophy.

Antoine-Laurent Lavoisier,
named the carbon element (C)

Diamond: 1,200 BC (from Hindu manuscripts).

Source: http://www.mineralminers.com/html/diamins.stm

MARVEL

ADAMANTIUM ! …

… it's came from ADAMAS

The origin of diamond word came from the Greek word: "Adamas" – that means: invincible !

WOLVERINE

Born with super-human senses and the power to heal from almost any wound, Wolverine was captured by a secret Canadian organization and given an unbreakable skeleton and claws. Treated like an animal, it took years for him to control himself. Now, he's a premiere member of both the X-Men and the Avengers. less

Real Name	James Howlett
Height	5'3"
Weight	(Without Adamantium skeleton) 195 lbs., (with Adamantium skeleton) 300 lbs.

http://marvel.com/characters/66/wolverine

http://www.slashfilm.com/new-logan-photo-effectively-shows-why-the-wolverine-sequel-will-be-r-rated/

Emma Frost

January Jones

X-man:
First Class

Tahyna Tozzi

X-man:
Origins (2009)

Carbon materials, from the SEM point of view

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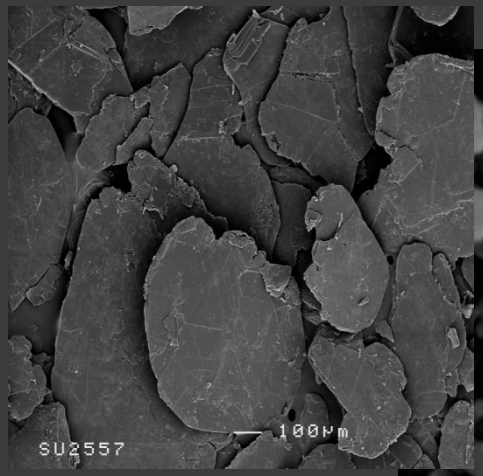
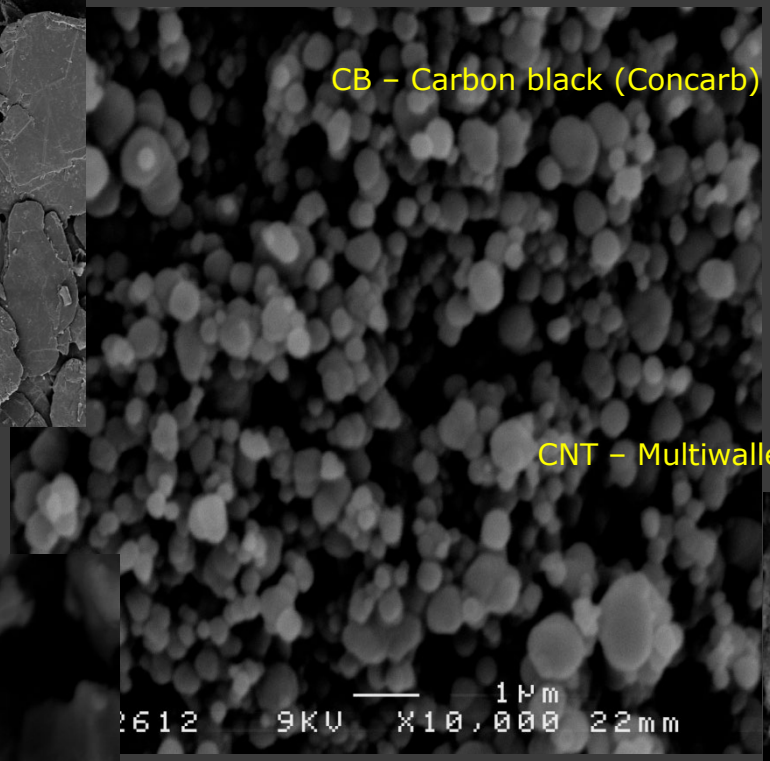
ABCarb Brazilian Carbon Association

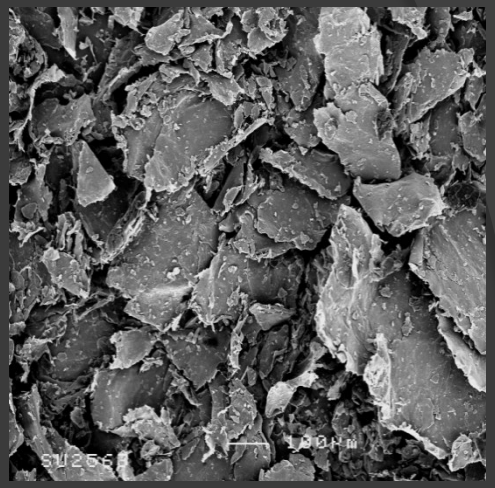
FG - Brazilian flake graphite (N. Grafite)



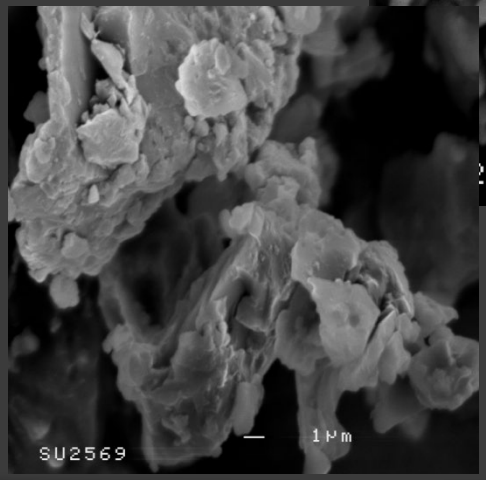
CB – Carbon black (Concarb)



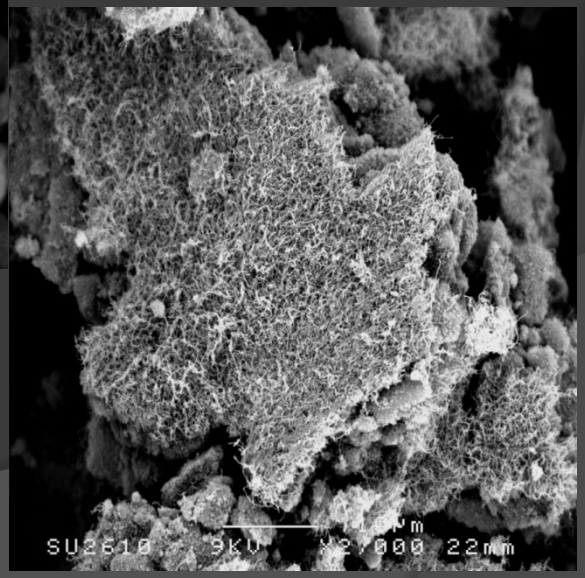
TG – Treated graphite (BSP 80)



SP – Solid pitch
(Carbores-P / Rutgers)

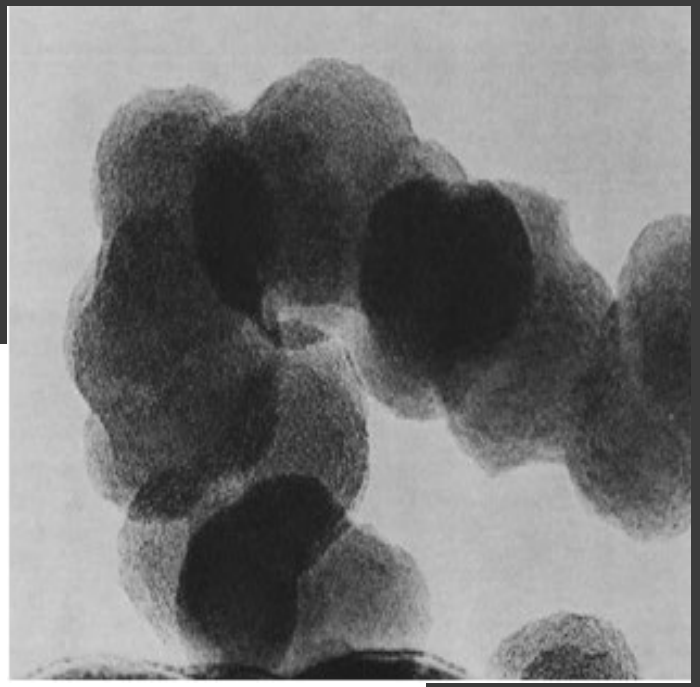


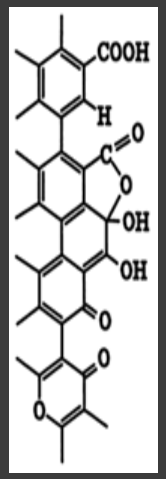
CNT – Multiwalled carbon nanotubes (Sigma – Aldrich)

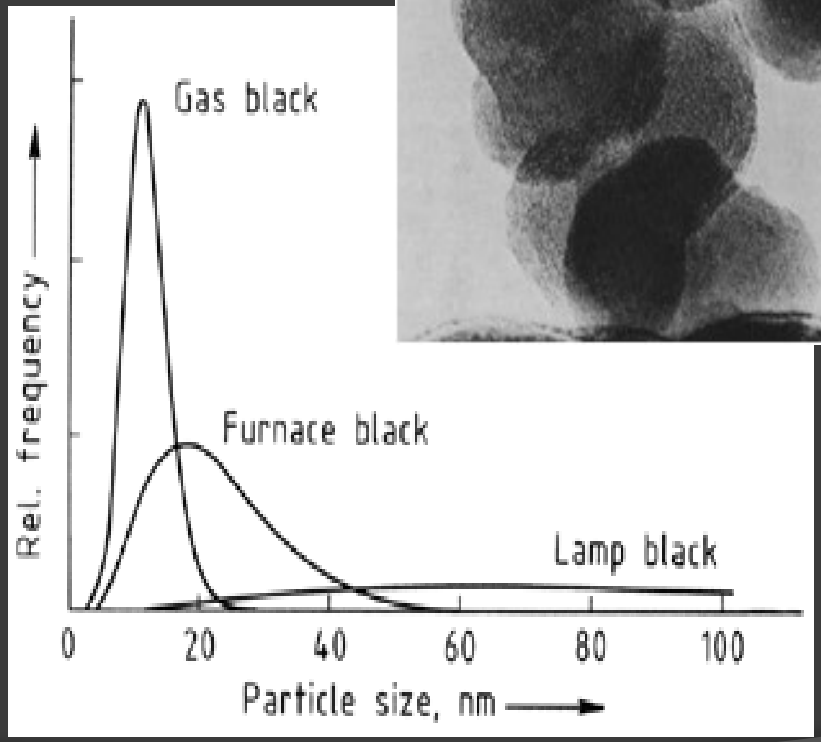


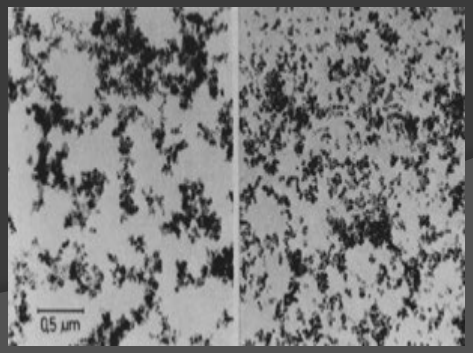
Prof. Guilherme Lenz images SEM – JEOL 6400 / Sorby Centre – University of Sheffield

Carbon blacks







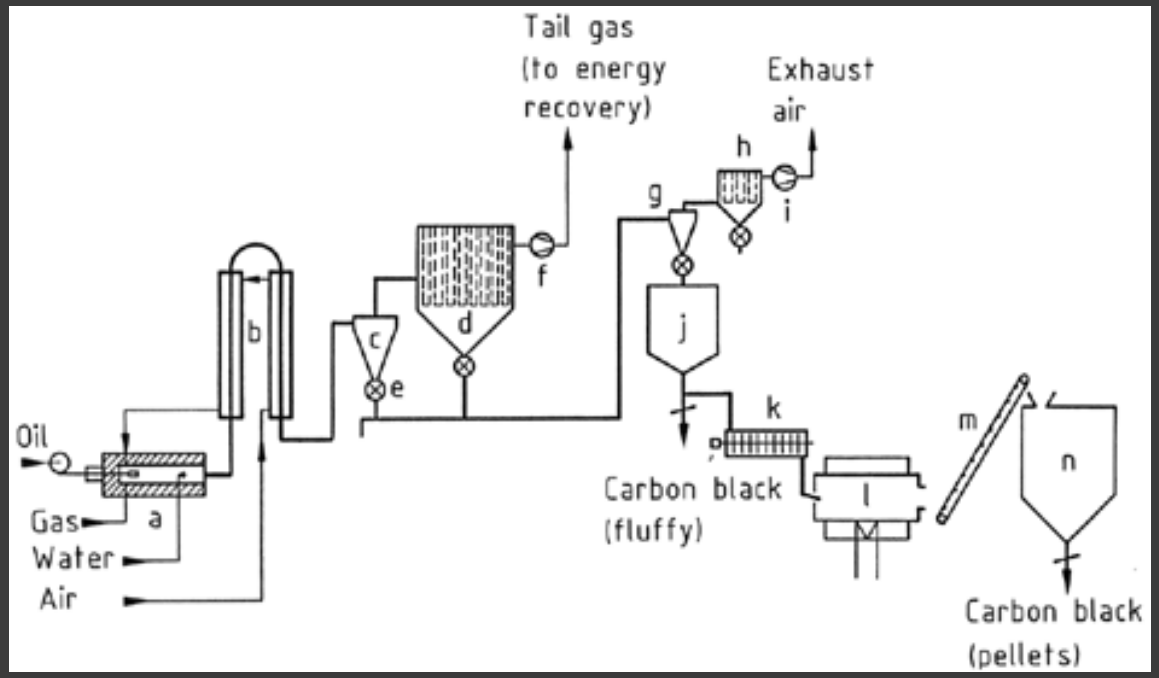


Applications:

- Pigments
- Structural reinforcement of rubber
- Refractories
- Paints (Black pigment and electrostatic /conductive) and coatings

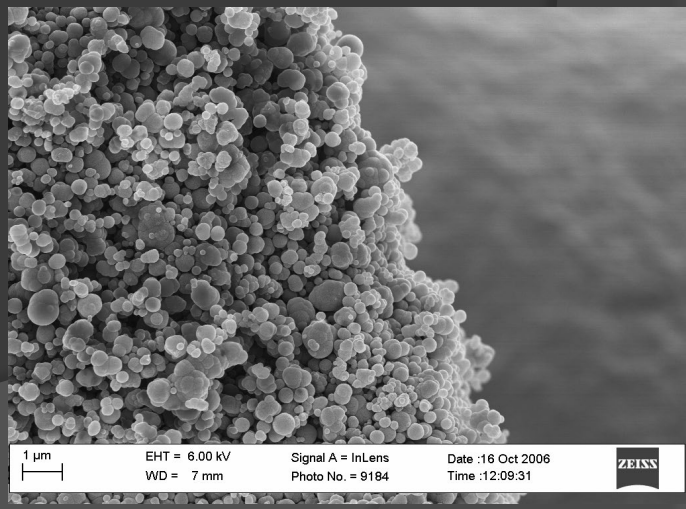
...

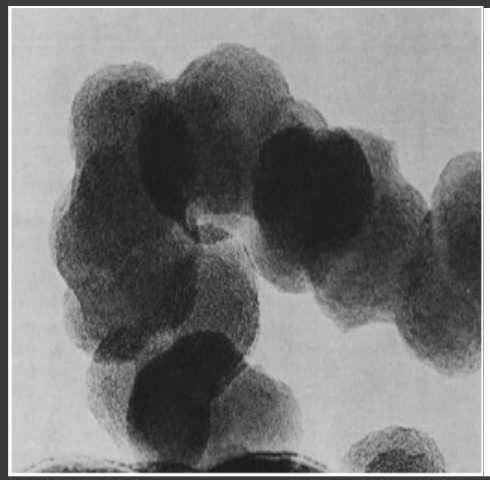
Carbon black production: from oil and/or gas incomplete combustion

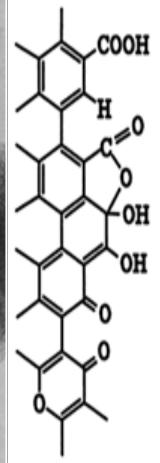


70% of world total production goes to tyres production

Up to 16 different types of carbon black on a tyre formulations.







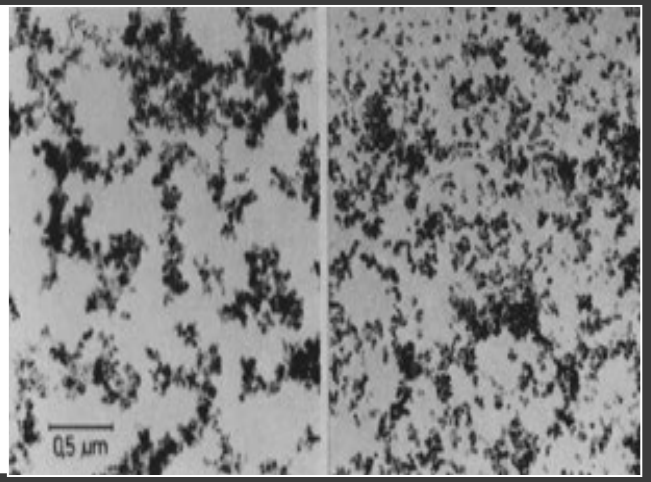
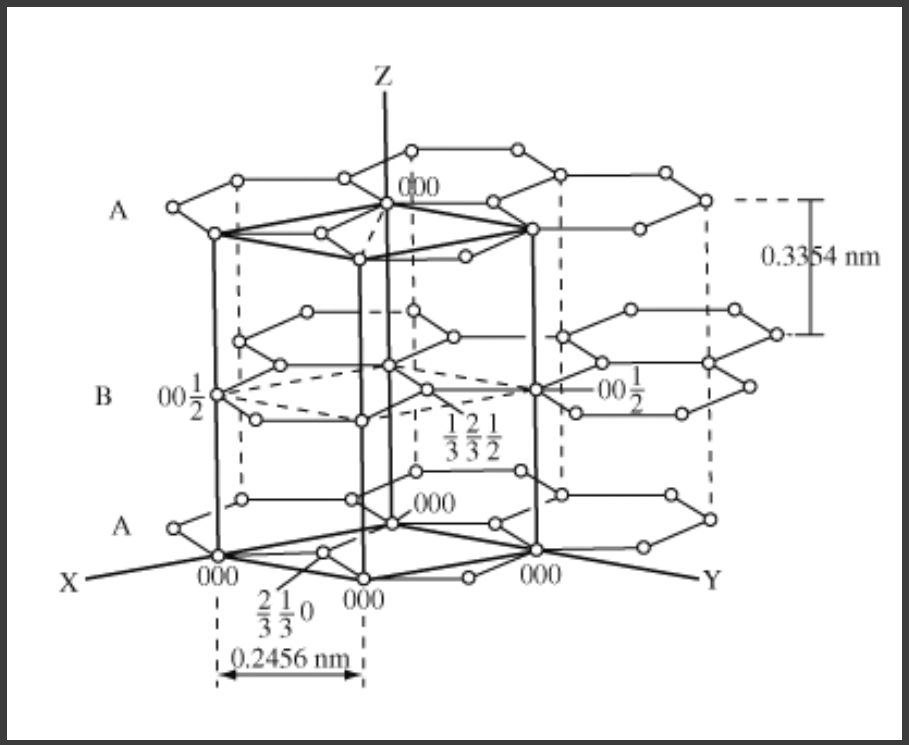
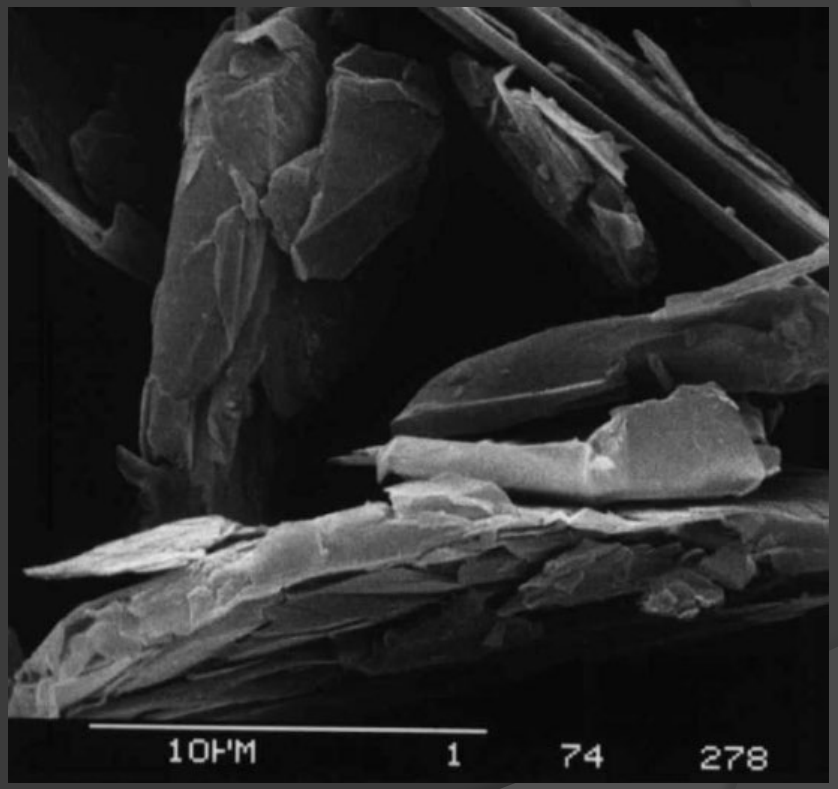


Figura 2: Estrutura do pneu de carj
Fonte: Brazil Tires, 2009

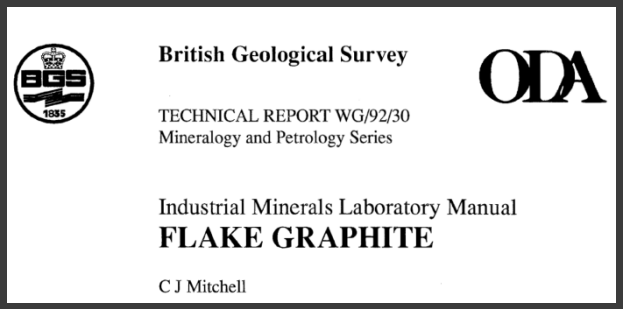
Natural Flake Graphite





Qingdao Kropfmuehl Graphite Co., Ltd

Application	Type	C content	Flake size	Comments
Refractories				
Magnesia graphite	F	85 - 90%	150 - 710 µm	Ash <2%, often up to 10%.
Alumina graphite	F	Min. 85%	150 - 500 µm	
Crucibles	AF	80 - 90%	+150 µm	Bulk density 48 - 54 g per 100 cm^3
Expanded graphite	F	Min. 90%	200 - 1700 µm	
Foundry additive	AFV	40 - 70%	53 - 75 µm	Sulphides and other readily fusible minerals undesirable
Foundry core and mould washes	AF	70 - 90%	~75 µm	
Brake / clutch linings	AFV	Min. 98%	<75 µm	
Bearings	FV	90 - 93%	+150 µm	
Lubricants	AFV	98 - 99%	53 - 106 µm	Free from sulphides, abrasive material and metallic contaminants.
Dry cell batteries	A	Min. 88%	85% <75 µm	No metallic impurities and S less than 0.5%
Alkaline batteries	AF	Min. 98%	5 - 75 µm	No impurities such as Cu, Co, Sb and As.
Recarburizing steel	A	98 - 99%	~5 µm	
Carbon brushes	AFV	95 - 99%	<53 µm	< 1% ash / silica. No abrasive or metallic contaminants.
Electrical	FV	93 - 95%	+150 µm	
Pencils	AF	95 - 97%	+150 µm	Free of gritty impurities
Conductive coatings	A	50 - 55%	<75 µm	May contain up to 25% silica, but free from gritty impurities.
Packing paints	FV	85 - 90%	<150 µm	
Polishes	AFV	85 - 90%	<150 µm	
Drilling mud (lubricating)	F	80%+	N/A	About 4lb per barrel of mud
Explosives (control of burning rate)	AF	65%	<150 µm	Free from sulphides and acids. Low moisture content
Nuclear reactors (moderators & reflectors)	F	93 - 95%	N/A	Free from high neutron absorbing elements, e.g. boron
Boilers (scale prevention)	F	50%+	N/A	



British Geological Survey

ODA

TECHNICAL REPORT WG/92/30
Mineralogy and Petrology Series

Industrial Minerals Laboratory Manual

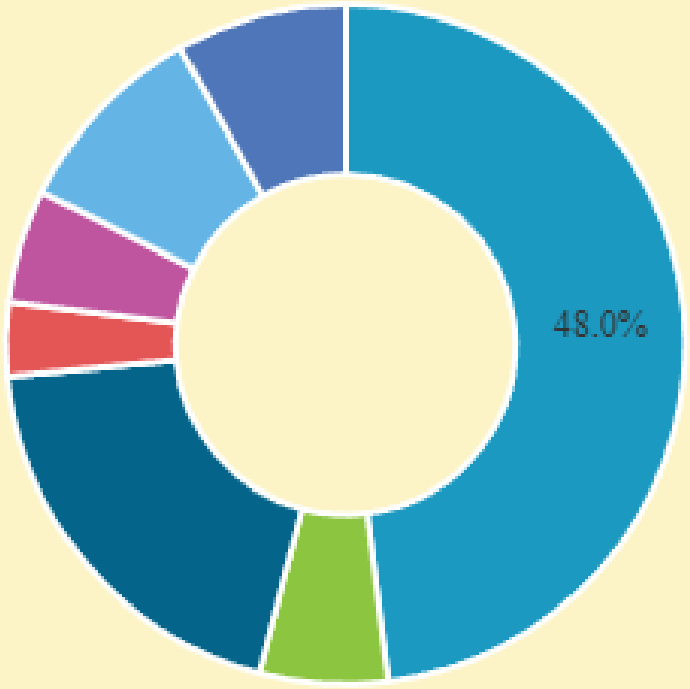
FLAKE GRAPHITE

C J Mitchell

	Flake	Vein	Amorphous
Description	Crystalline flakes; coarse >150 µm; fine <150 µm	Coarse crystals Mostly >4 cm	Microcrystalline <70 µm
Origin	Syngenetic; regional metamorphism	Epigenetic; regional metamorphism	Syngenetic; contact and / or regional metamorphism
Ore	5 - 30% graphite; strata-bound, tabular or lenses	98%+ graphite; veins and fractures	Seams, often folded and faulted
Product grade	75 - 97% graphite	98 - 99.9% graphite	60 - 90% graphite
Main uses	Refractories, brake linings, lubricants and batteries	Carbon brushes, brake linings and lubricants	Refractories, steel industry, paint and batteries
Major producers	China, Brazil, India, Madagascar, Germany, Norway, Canada and Zimbabwe	Sri Lanka.	China, S Korea, Czechoslovakia, Austria and N Korea

http://www.bgs.ac.uk/research/international/dfid-kar/WG92030_col.pdf

Global Graphite Market Share, By Application, 2023



www.fortunebusinessinsights.com

GRAPHITE MARKET

$7.32 Billion 2023

$7.80 Billion 2024

$13.35 Billion 2032

CAGR 6.9%

2024-2032

DRIVERS

Increasing Demand from the Refractory Industry

TRENDS

Trend of Battery Powered Vehicles

BY APPLICATION, 2023

Refractories 48.0%

Foundries | Batteries | Friction Products | Lubricants

Recarburising | Others

BY PRODUCT

Synthetic

Natural

CHINA, BY APPLICATION, 2023

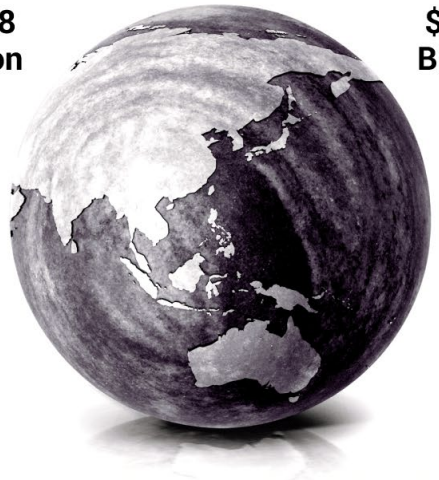
Refractories 48.3%

Foundries | Batteries | Friction Products | Lubricants

Recarburising | Others

ASIA PACIFIC

$3.78 Billion 2022



$4.08 Billion 2023

North America | Europe | Latin America | Middle East & Africa

KEY PLAYERS

Eagle Graphite · Tirupati Carbons & Chemical Pvt Ltd · Nacional de Grafite · Superior Graphite · Grafitbergbau Kaisersberg · sgl carbon · BTR · Imerys · Asbury Carbons · AMG Graphite · GK · MRC

INDUSTRY DEVELOPMENT

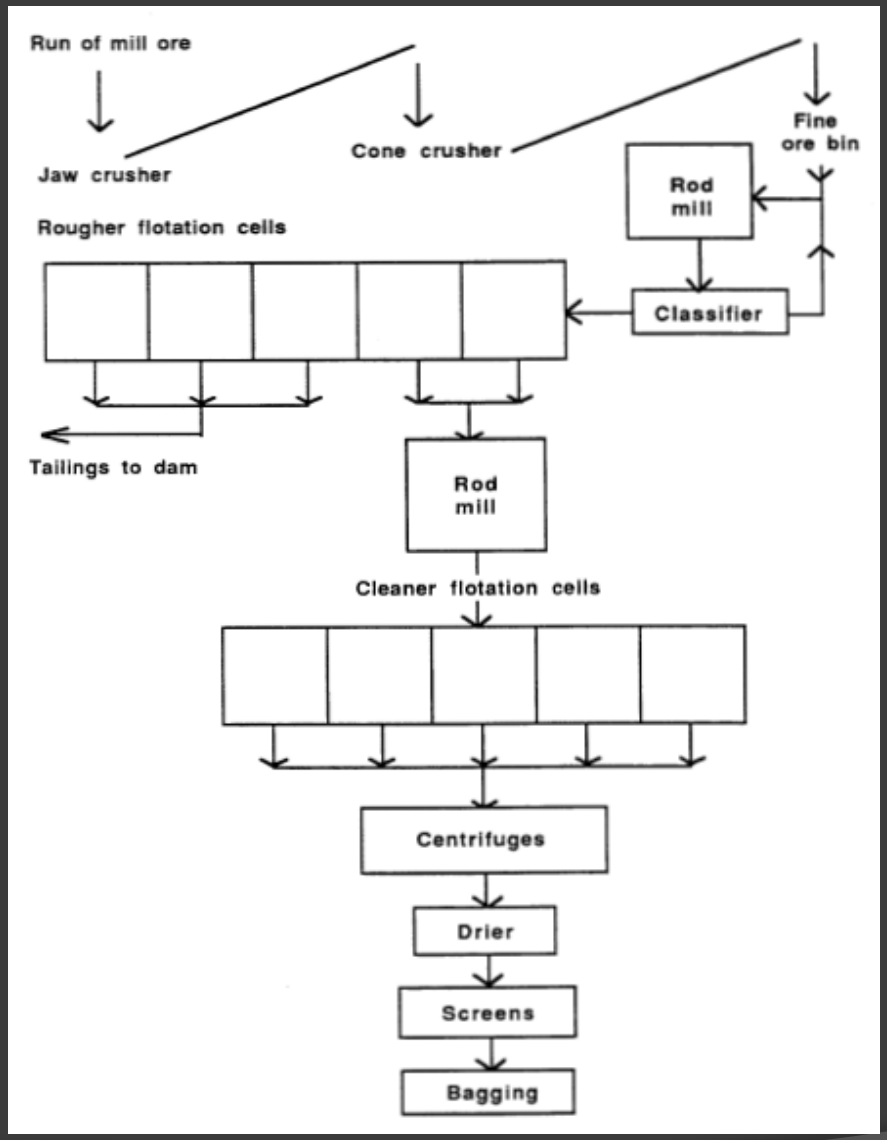
MARCH 2022

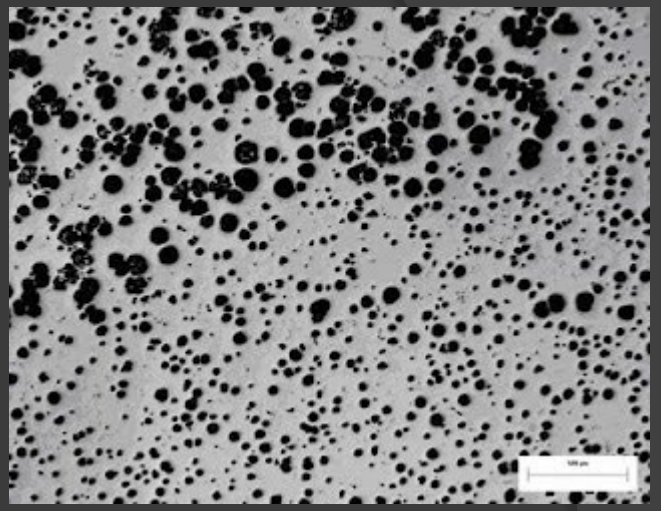
EagleGraphite announced its partnership with British Columbia to develop silicon-modified battery anodes.

LIST OF KEY COMPANIES PROFILED:

- AMG (Germany)
- Asbury Carbons (U.S.)
- Eagle Graphite (Canada)
- Grafitbergbau Kaisersberg GmbH (Austria)
- Imerys S.A. (France)
- Stoker Concast Pvt. Ltd. (India)
- BTR NEW Material Group Co., Ltd. (China)
- Nacional de Grafite (Brazil)
- SGL Carbon (Germany)
- Mineral Commodities Ltd. (Australia)
- Superior Graphite (U.S.)
- Tirupati Carbons & Chemicals Pvt. Ltd. (India)

Natural flake graphite processing flowchart
(Mine Lynx – Zimbabwe)

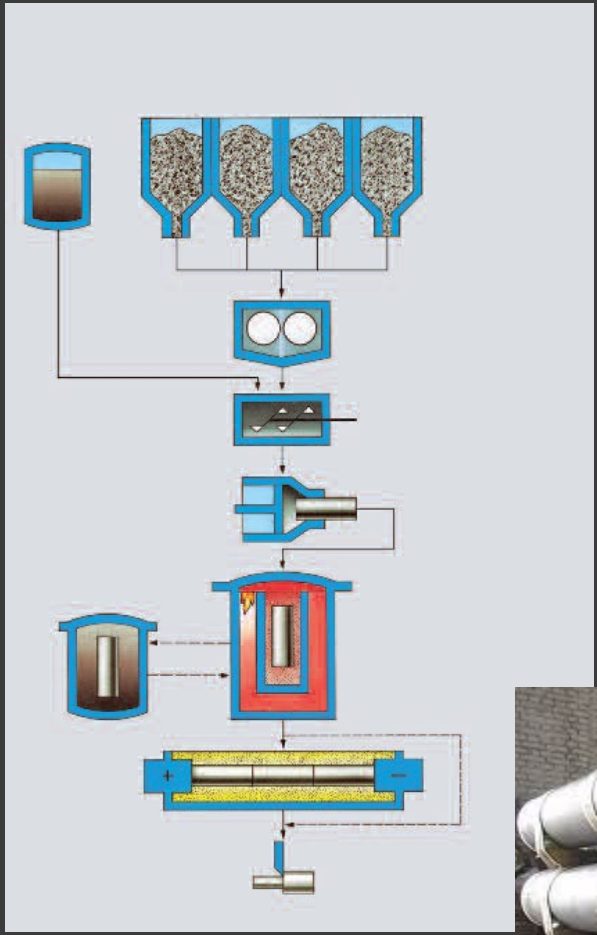


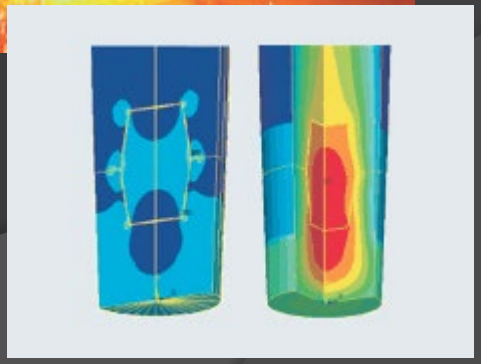


Flotation of natural graphite (Madagascar)

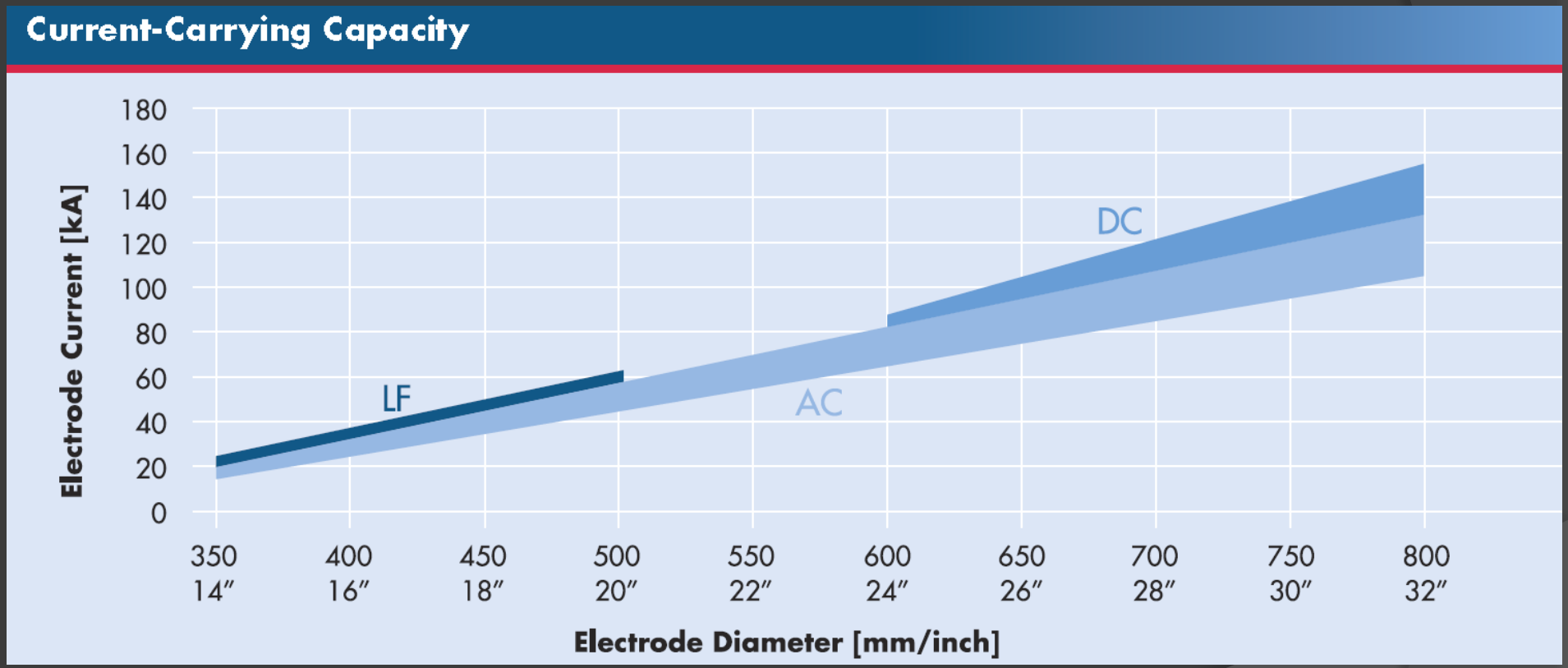
http://ets.gallois.pagesperso-orange.fr/index.htm

Electrodes for metal reduction and melting/scrap furnaces





Electrodes for different size equipment
Electrical current vs. electrode diameter



Carbon cathodes for metallic aluminum production from alumina reduction

Carbon blocks: calcined anthracite treated at 1,800 ºC

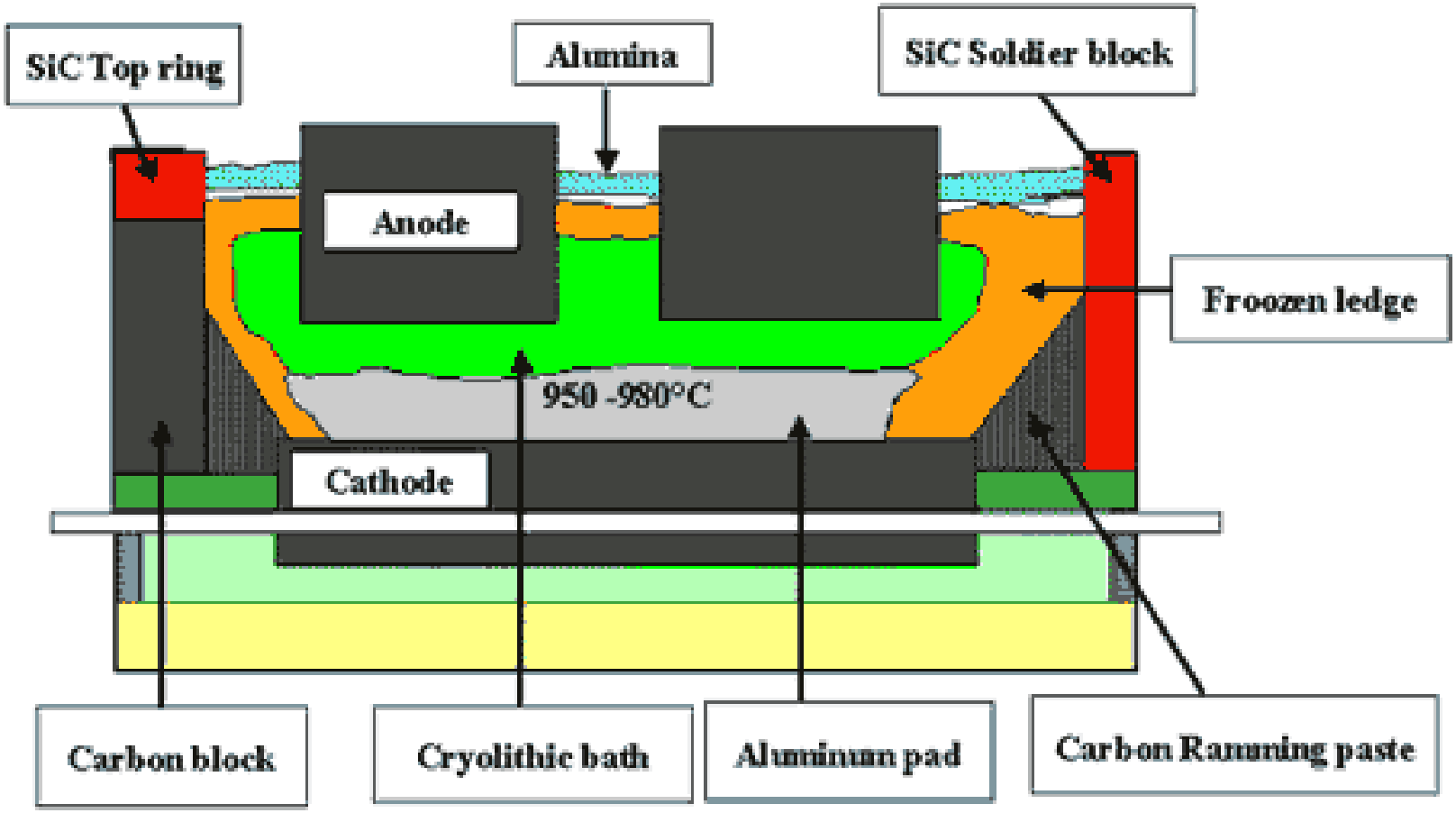
Graphite blocks: artificial graphite from oil/gas

Carbon blocks: from petro-coke .

No	Item		Unit	Partial Graphite	High Graphite	Graphite
1	Ash	≤	%	8	5	3
2	Resistance	≤	μΩ·m	43	35	32
3	Bulk Density	≥	g/cm3	1.54	1.52	1.52
4	Electrolytic Expansion	≤	%	1.0	—	—
5	Real Density	≥	g/cm3	1.88	1.90	2.06
6	Compressive Strength	≥	Mpa	30	28	26

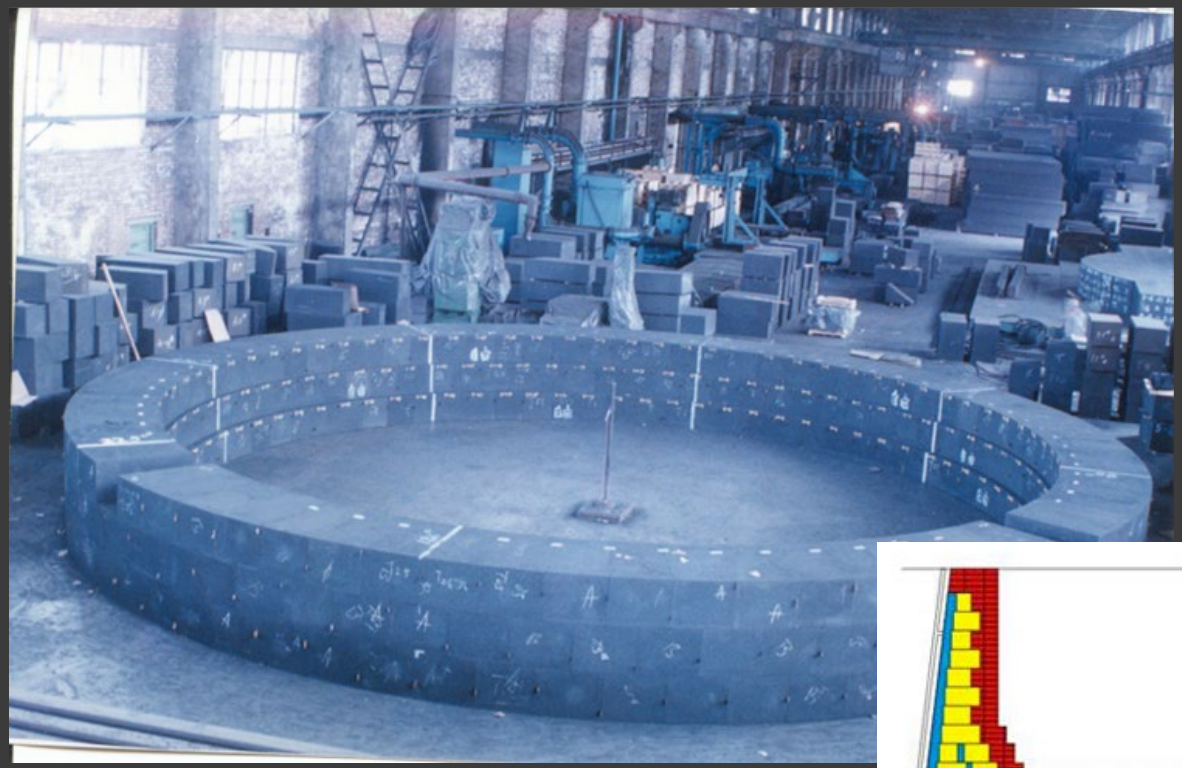
Fonte: http://www.fangdacarbon.com/en/product/a

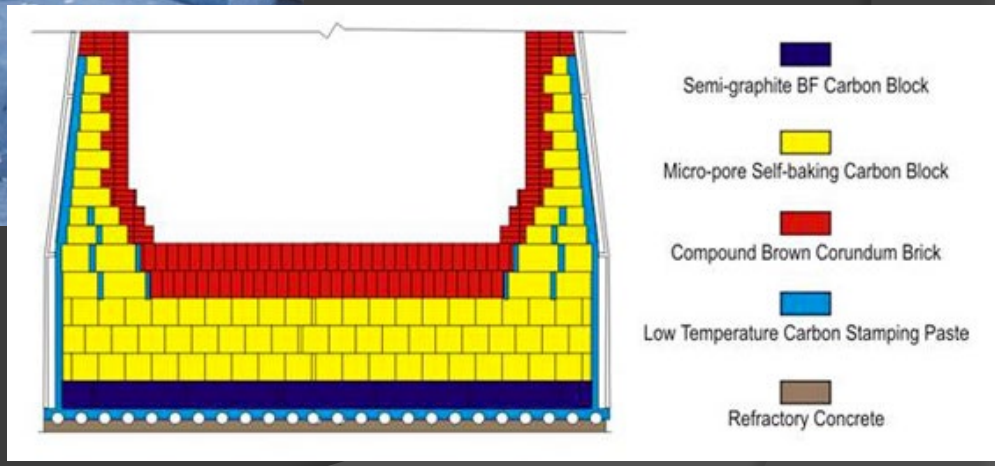
Hall-Heroult alumina reduction cell



Source: http://www.refractories.saint-gobain.com/Aluminium-Reduction.aspx

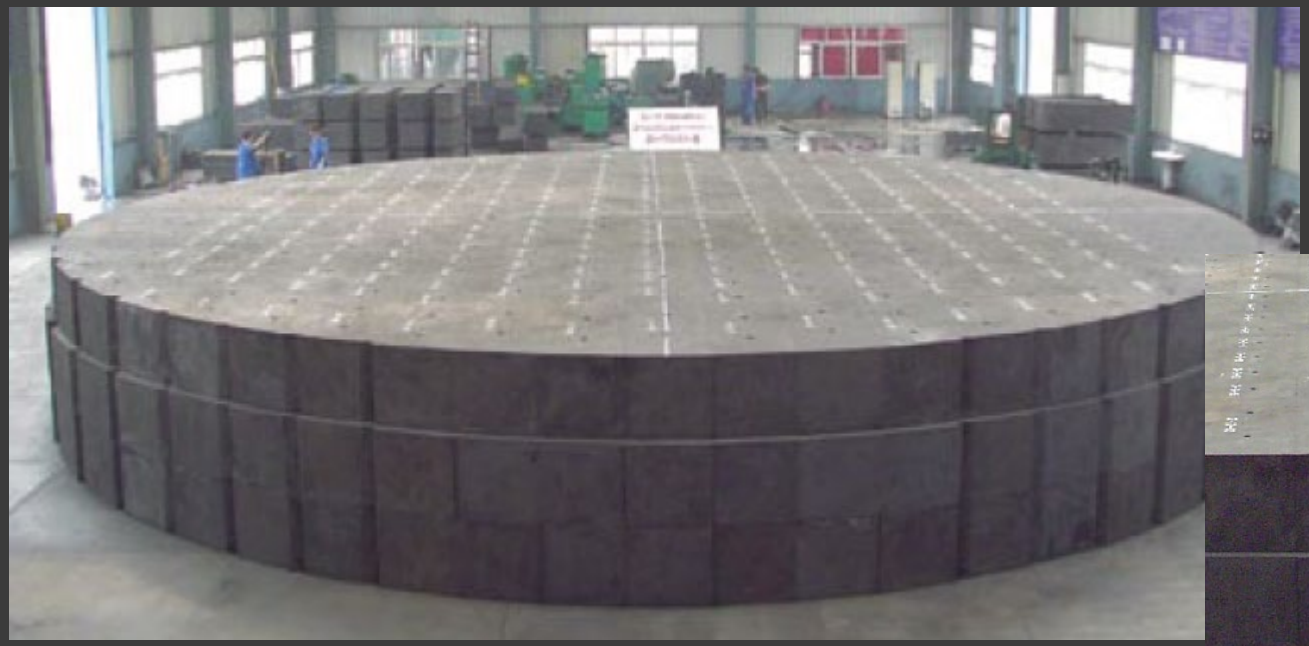
Carbon block – blast furnace for hot metal production

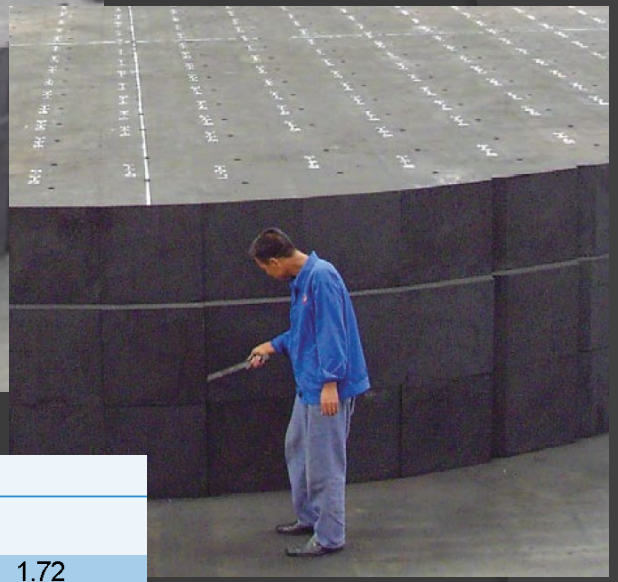




Super Micro-pore Carbon Block

Fonte: http://www.fangdacarbon.com/en/product/c/default.shtml





Bulk density	g/cm³	1.61	1.65	1.72
Apparent porosity	%	24.70	19.10	16.5
Compression strength	MPa	25.70	30.25	35.80
Bending strength	MPa	7.80	10.51	12.50
Thermal conductivity (room temp.)	W/m·k	42	84	128
Ash	%	0.48	0.39	0.28

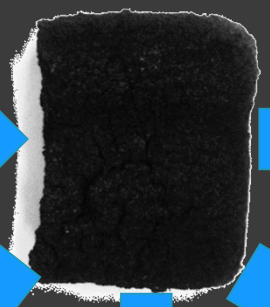
http://www.furnacelining.com/FangYuan/Literature_files/FangYuan_Blast_Furnace.pdf

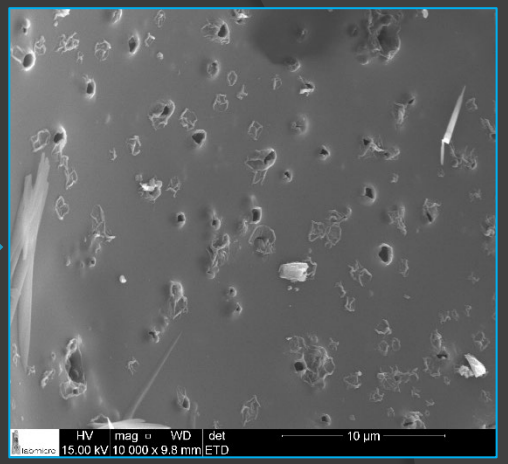
Sustainable Porous Carbons Materials

Kraft Black liquor

Crosslinker
PMMA
Resorcinol

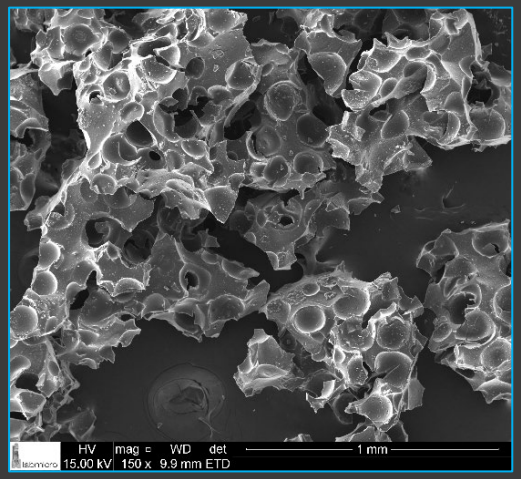
Polymerization/ Carbonization

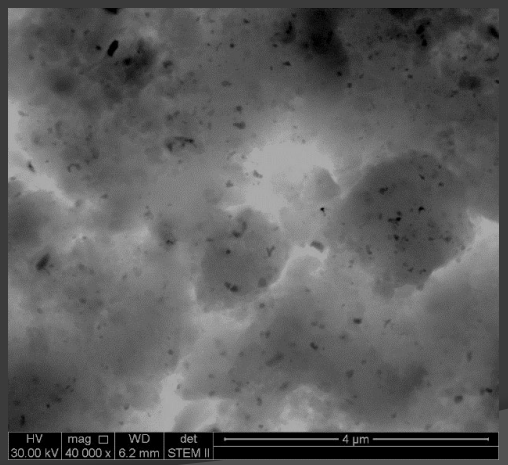


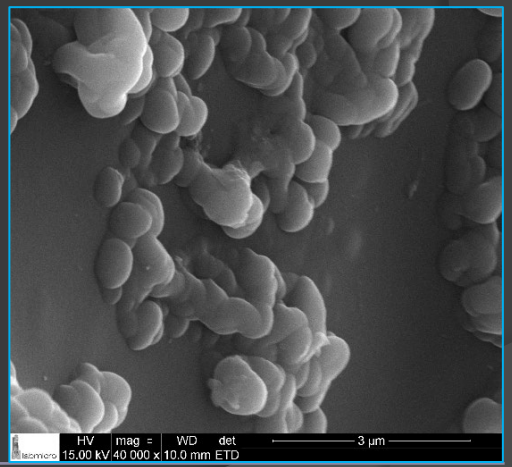


$Ni(NO_3)_2.5H_2O$

Nanoparticles





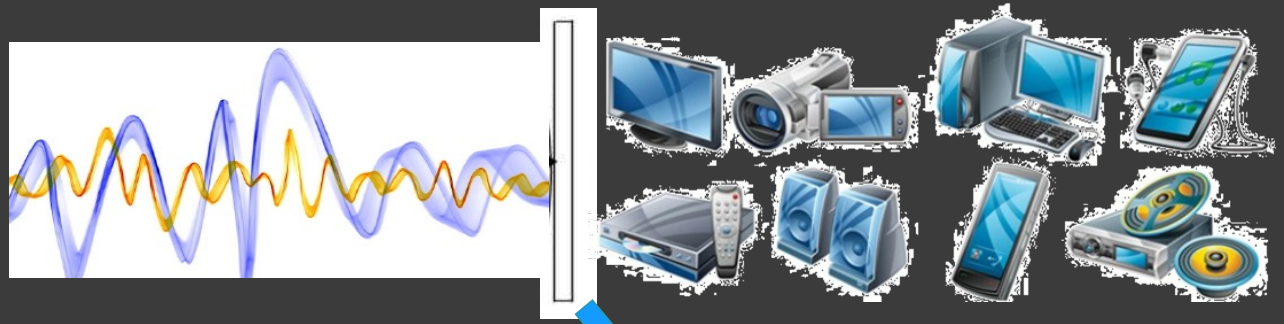


Bulk density (g/cm^3)	Porosity (%)
0.35-0.50	70-85

Several applications

Dra. Gisele Labat (former posdoc at LM²C²-PMT POLI – USP , now at INPE)

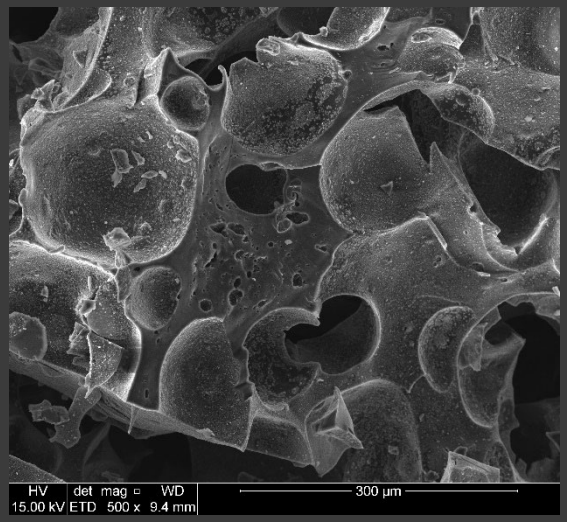
Electromagnetic Shielding

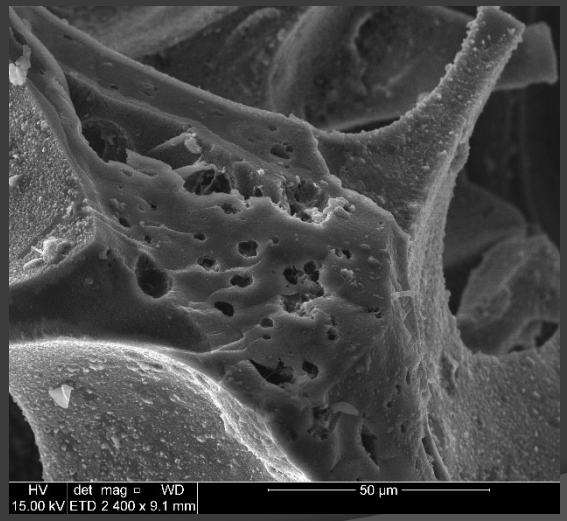


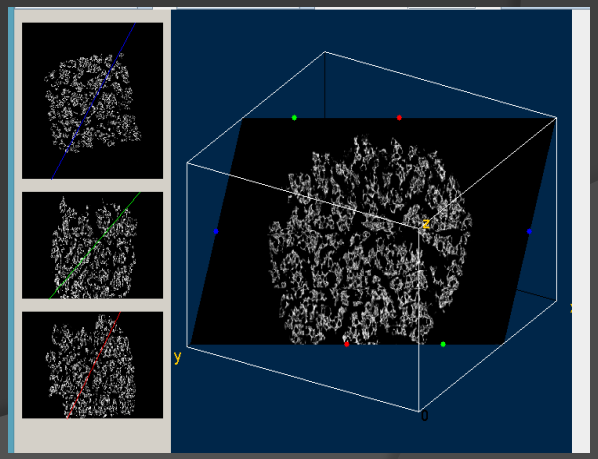
Aerospace field- radar

- ✓ High porosity
- ✓ Pore size (micron scale)

EMI- electromagnetic interference





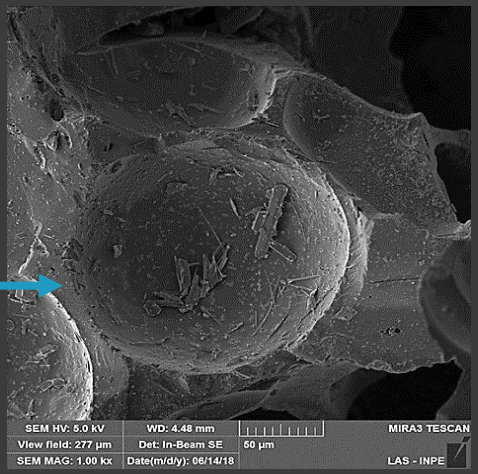


Dr. Alan Boss (former posdoc at LM²C²-PMT POLI – USP)

Shield by absorption

Vector network analyzer (VNA) in the frequency range from 8.2 GHz to 12.4 GHz (X-Band) for electromagnetic properties

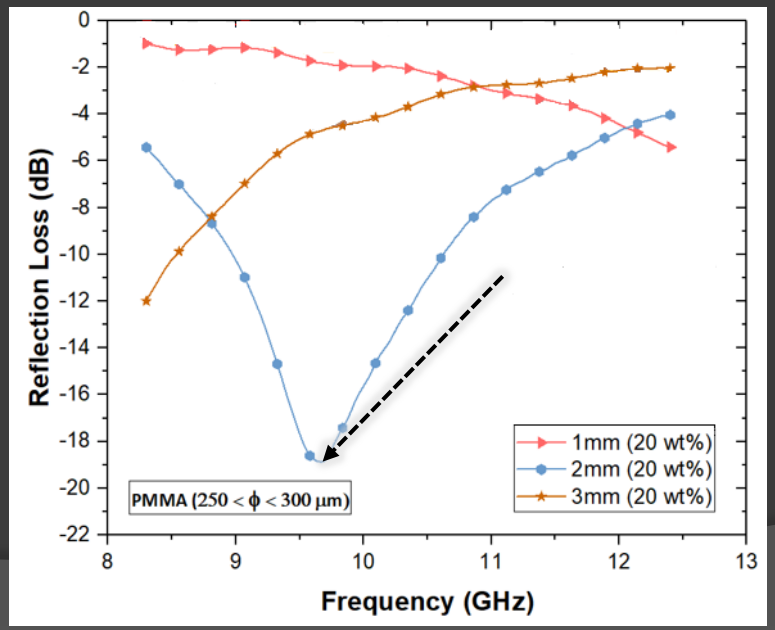
Dispersion in Silicon

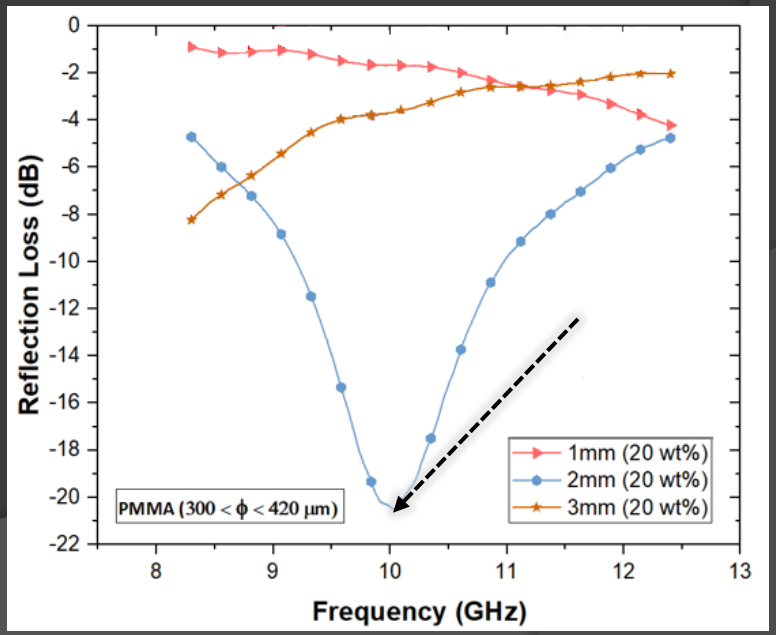


Particle size 250-420 µm

$$RL(\mathrm{dB}) = 10 \log_{10} \frac{P_\mathrm{i}}{P_\mathrm{r}}$$

99% of absorption

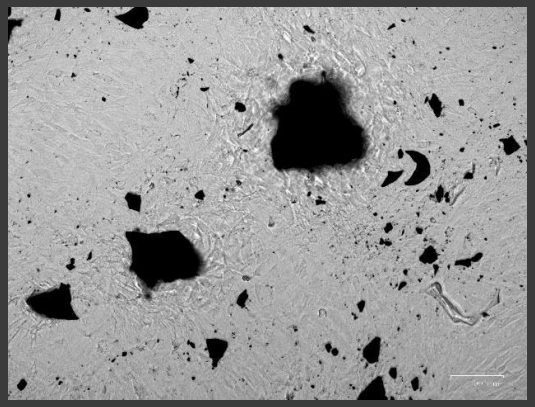


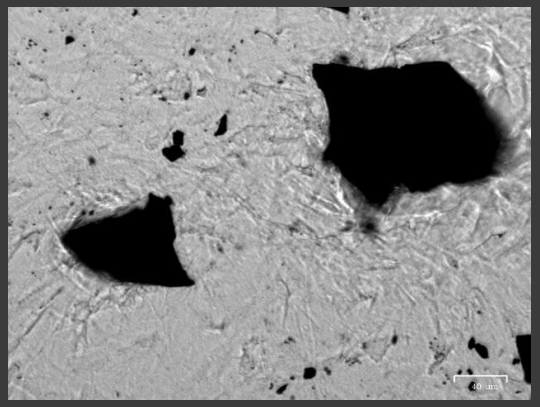


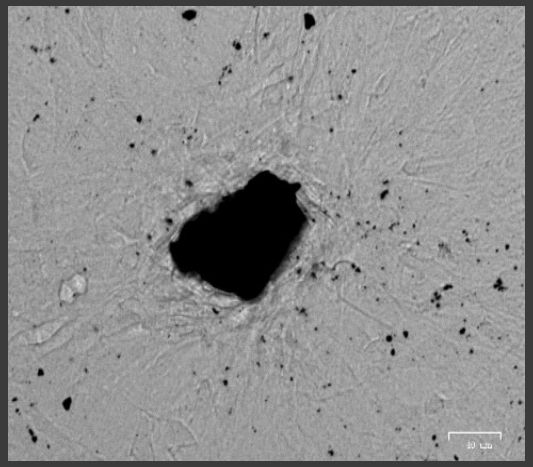
POROUS CARBON BIOMATERIAL (IN VITRO TESTS)

Osteoblasts cells culture

Biomaterial







Optical Microscopy

Biomaterial + Silver nanoparticles (600 ppm)

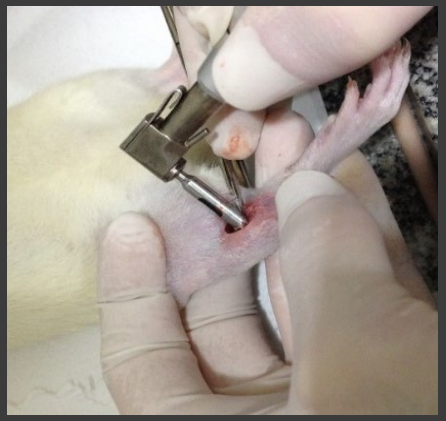
- Cell Adhesion

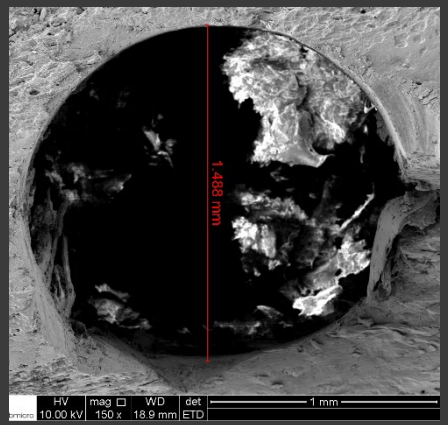
Bone X Biomaterial (structure)

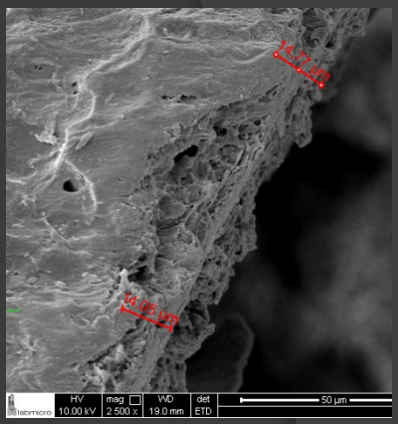
TLMC5 Quinto Taller Latinoamericano de Materiales de Carbono

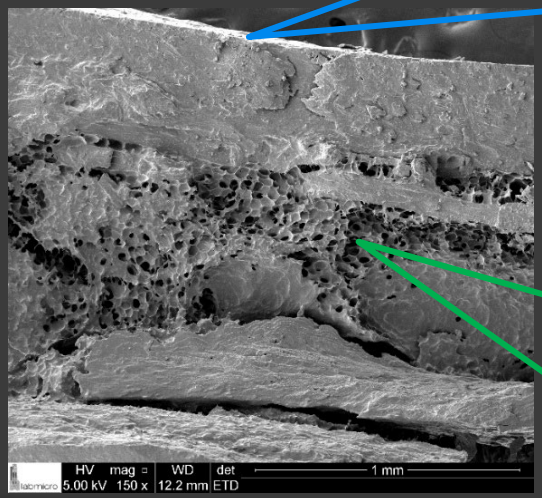
ABCarb Brazilian Carbon Association

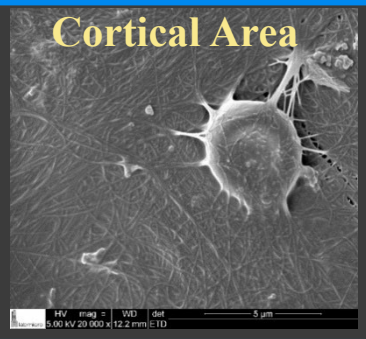
Tibia - Bone Defect (standard process)

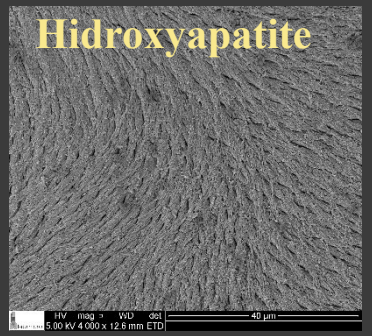


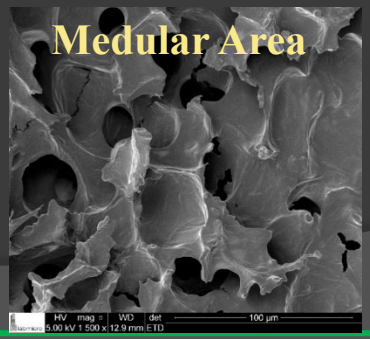


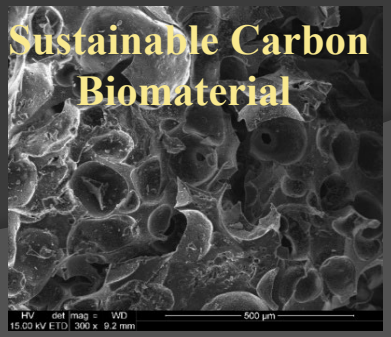








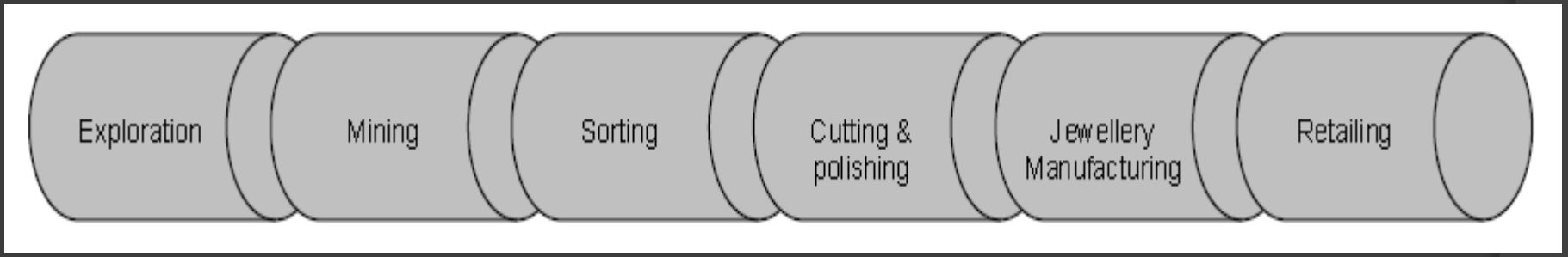




Dra. Patrícia Almeida
(Posdoc at LM²C²-PMT POLI – USP)

Synthetic and natural diamonds

- Market size (estimated): US$9 to 13 billions /year
- Jewelry: 30%
- Industrial grade: 70% (cut, drilling and polishing)



- Angola;
- Australia;
- Botswana;
- Canada;
- Congo;
- Namibia;
- Russia;
- South Africa.

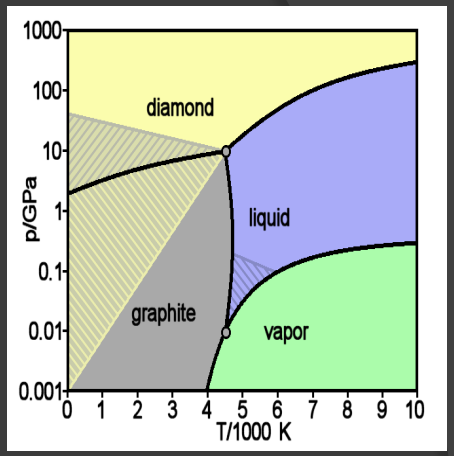
- Color;
- Size;
- Quality;
- Shape.

- Antwerp;
- Mumbai;
- Tel Aviv;
- New York;
- China;
- Thailand;
- Johannesburg.

- USA (50%);
- Japan (15%);
- Italy (5%);
- India (3%);
- China (2%);
- Middle East (2%);
- Others (23%).

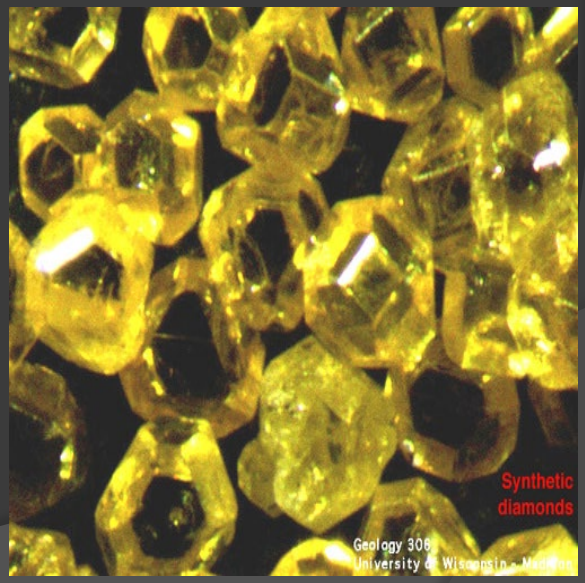
Synthetic diamonds

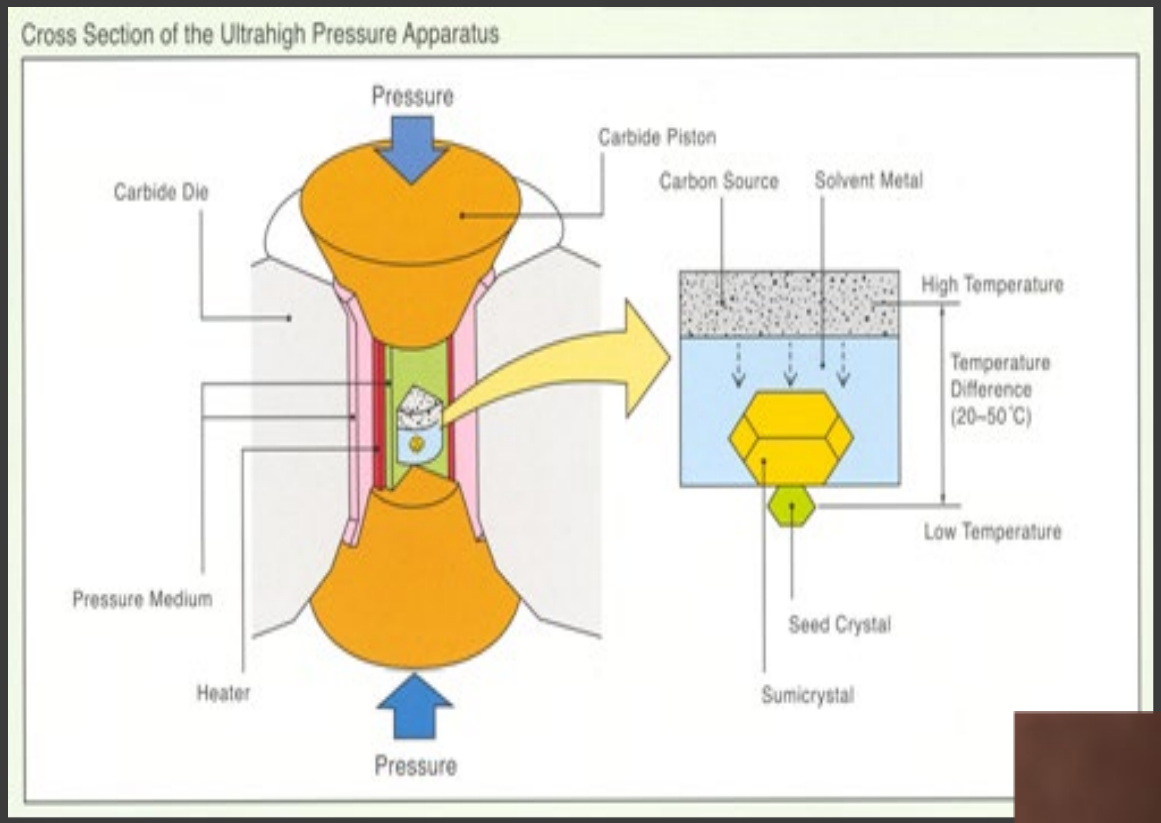
2 main synthesis routes: The first one was discovery by GE at 1955 . The second is by CVD (Chemical Vapor Deposition). Nowadays 100 million of carats of industrial grade diamonds are produced by year.



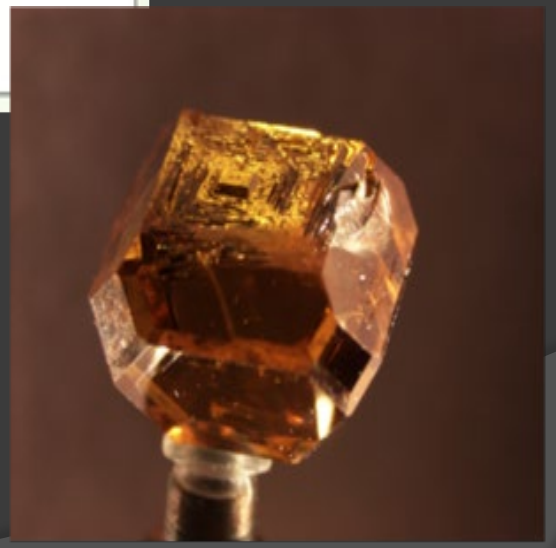
Carbon phase diagram

Synthetic Diamond Hydraulic Press





Artificial diamond

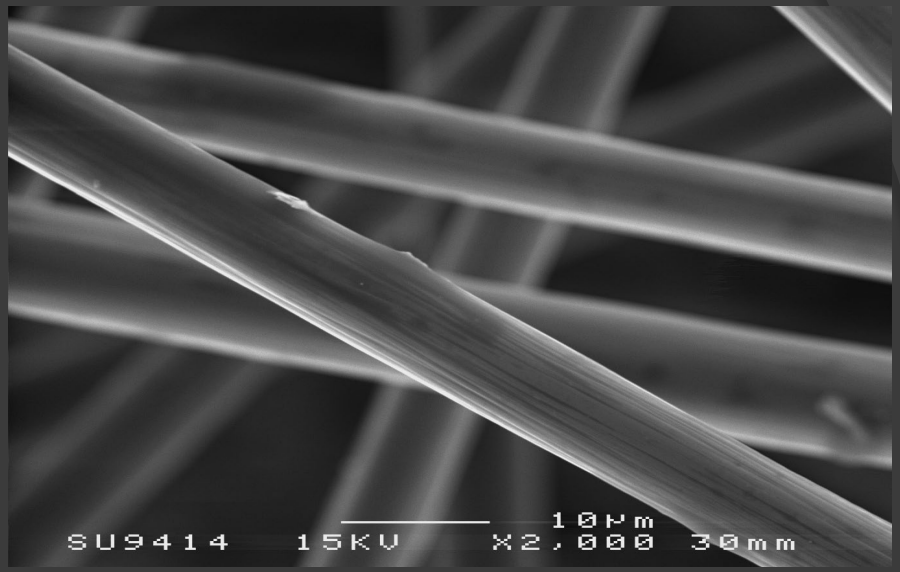


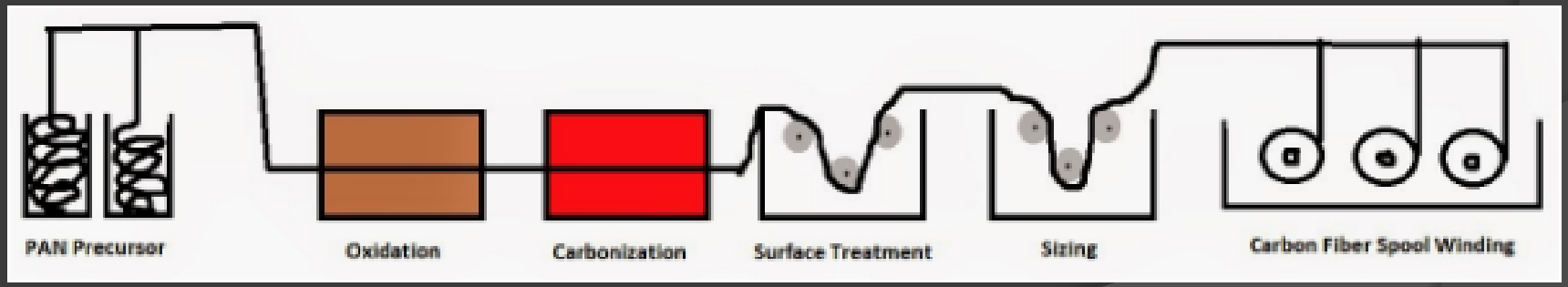
Carbon Fibers

Two dominant technologies: PAN and pitch.

SEM Image SEI mode: 7 microns High resistance fiber from: Toray/France

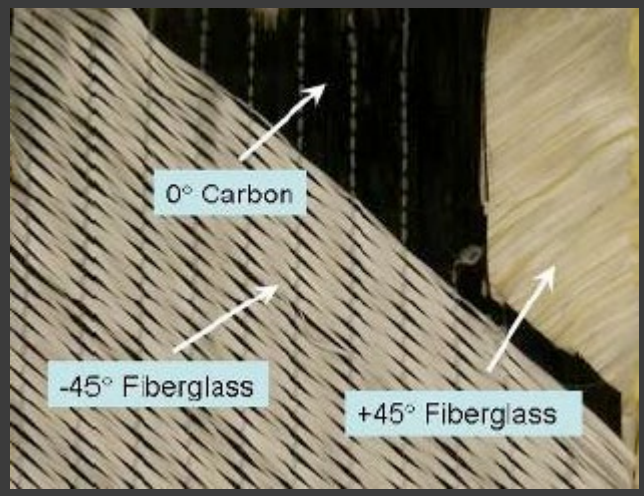
MEV JEOL 6400-F

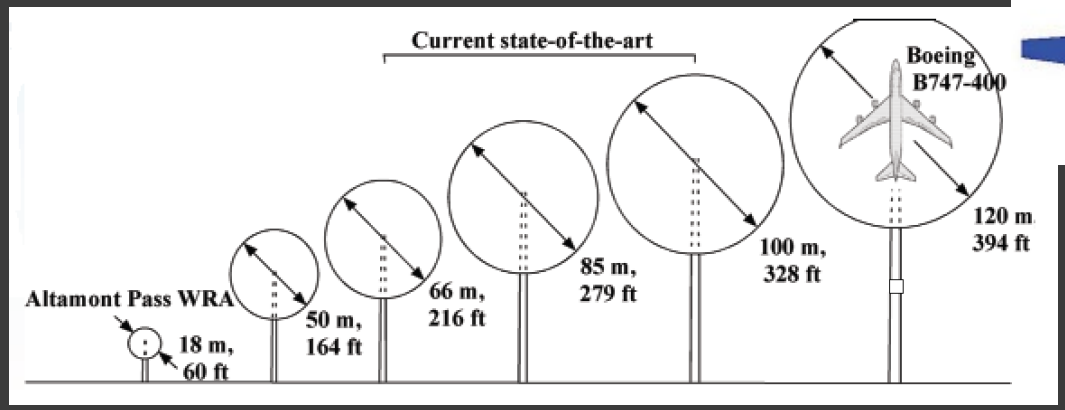


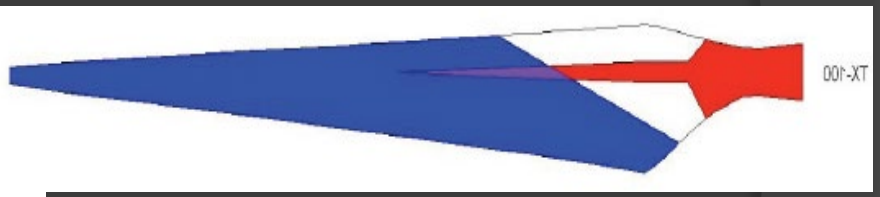


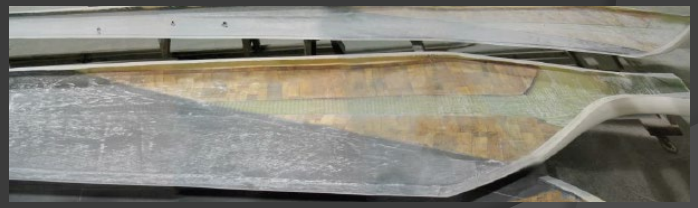
Typical carbon fiber production line from PAN precursor.

Composites: carbon f& glass fibers









Lamborghini – Sesto elemento

Cost: 2,2 Millions US$
(2nd more expensive car model in history !)

Boasting an extremely lightweight construction thanks to advanced carbon-fiber technology, the Lamborghini Sesto Elemento has an overall curb weight of just 999 kilograms (2,202 lb) - including V10 power unit and permanent all-wheel drive.

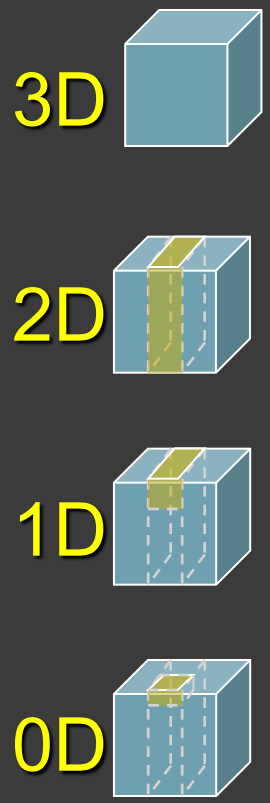
With its amazing output of 570 hp, sensational power-to-weight ratio of only 1.75 kilograms per hp and 0 to 100 km/h (0-62 mph) acceleration of only 2.5 seconds, the Sesto Elemento guarantees unparalleled driving fun.

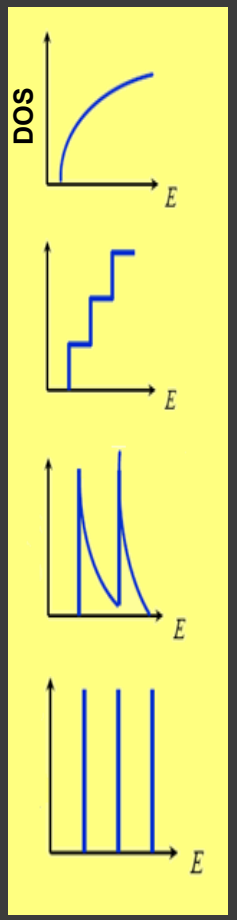
Partnership: Lamborghini & Boeing

The carbon big “new” family:

… from micro to nanosize materials !

What happens in the nano-size world?



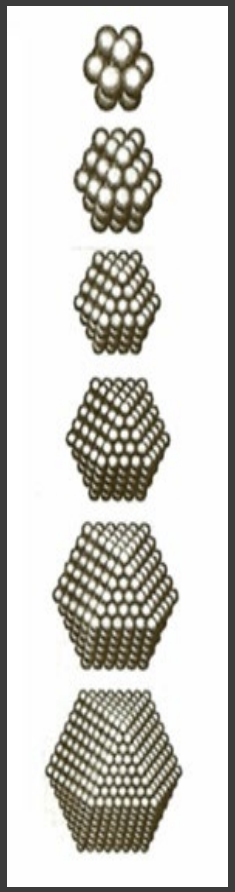


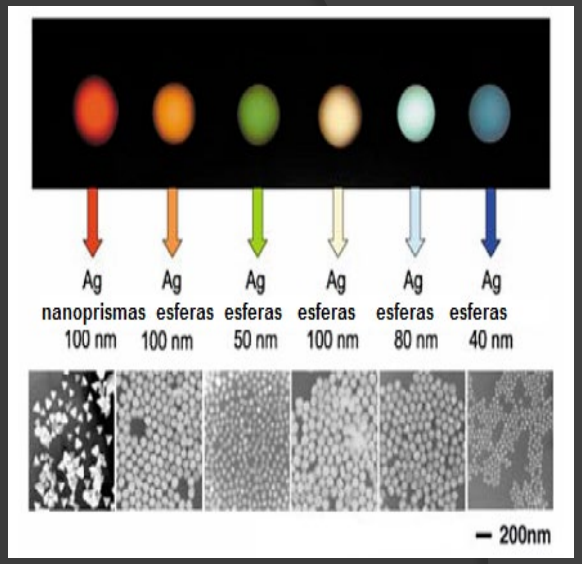
DOS : Density of states

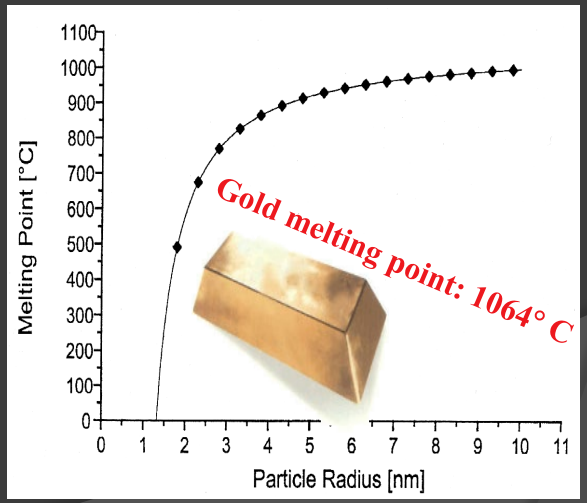
- High surface area
- Quantum size effects ;
- Changing on total energy : less bulk and more superficial energy;
- Defects of grains and nanoparticles;
- High catalytic properties due high surface area: particles and agglomerates;
- Optical properties;
- Mechanical properties; etc.

... Nano is the scale at which surfaces and interfaces play a large role in materials properties and interfaces

Agglomerate	Total number of atoms (%)	Surface atoms (%)
1 Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
6 Shells	1415	35



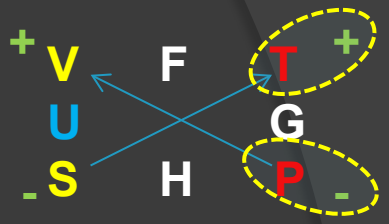




Source: K.J. Klabunde, 2001

Thermodynamics of surfaces

- U(S,V,N)
- dU=TdS –PdV + μdN or
- U=TS-PV + μN, Inserting the associated factor with superficial tension, we have:
- U=TS - PV+ μN + **γA**, where:



U = f(**S** and **V**), than:
U = +**T** dS - **P** dV

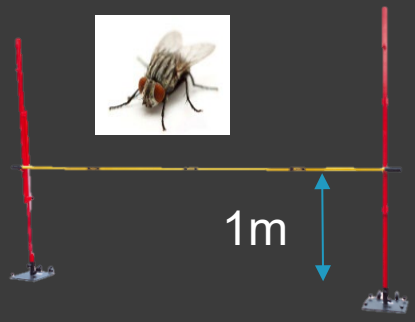
U – Internal energy
T – Temperature
S – Entropy
P – Pressure
V – Volume
μ - Chemical potential
N – Number of moles
γ - Superficial tension
A – Surface area

Surface & energy !

"**V**alid **F**acts and **T**heorical **U**nderstanding **G**enerates **S**olutions of **H**ard **P**roblems"

Let's make an exercise calculation !

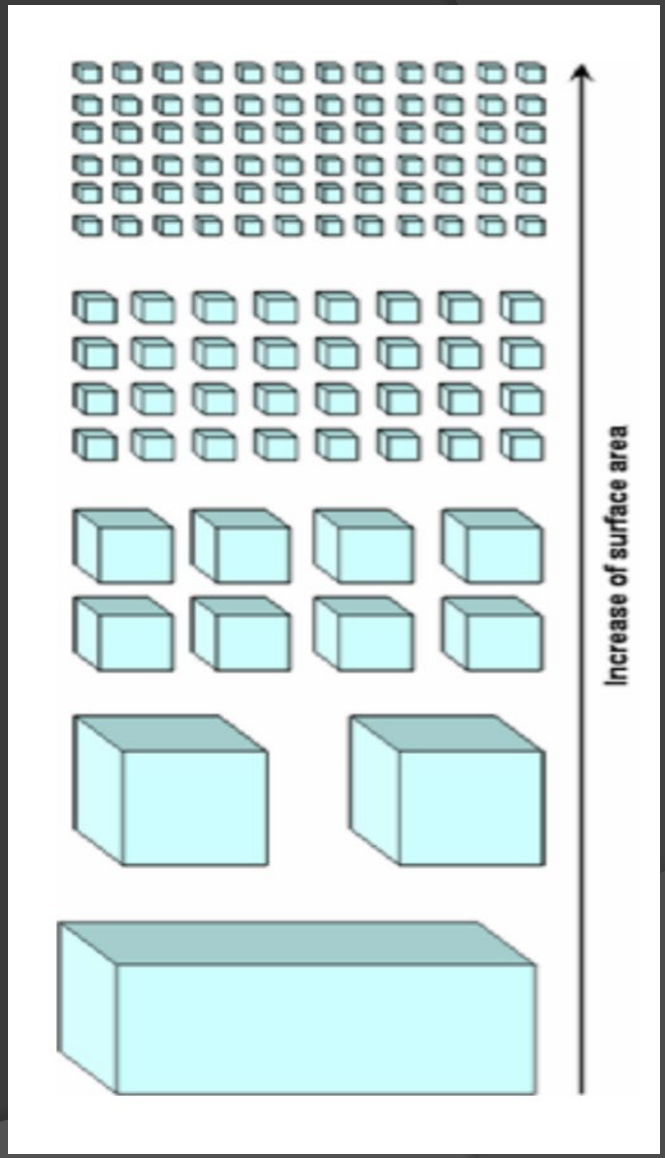
Potential energy
(mgh) = g * mass * height …
$9,8*12x10^{-6}*1 =$ **$1,176x10^{-7}J$**



Fly (*Musca domestic*)
Mass: 12 mg
Velocity: 7.2 km/h = 2m/s
www.speedofanimals.com

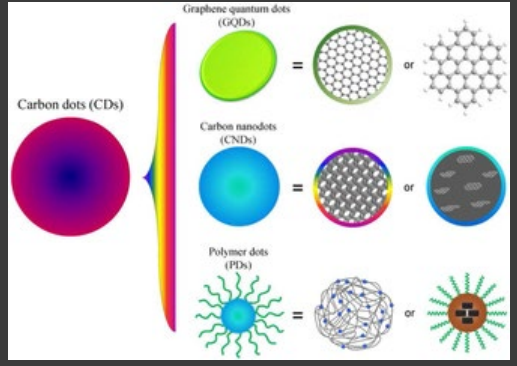
Remembering ….
1 erg = 10^{-7} J and 1 erg/s = 10^{-7}W

Eg: Bonding rupture energy in a single crystal is about : γ ~1.200 erg.cm^{-2}

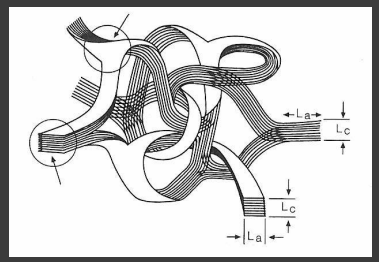


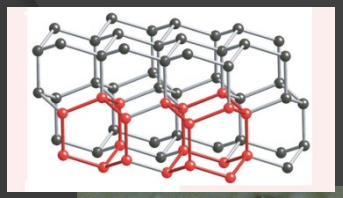
http://www.nanocap.eu/Flex/Site/Download07ab.pdf?ID=2256

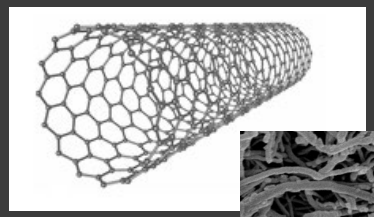
The carbon family !



Amorphous & carbon black





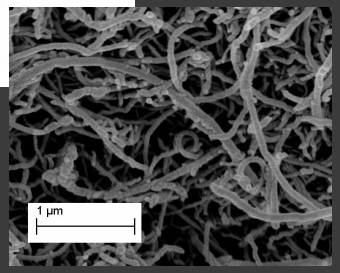


CNT

SWCNT

DWCNT

MWCNT

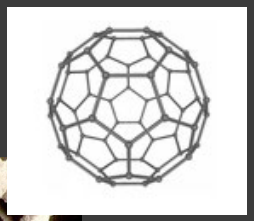


Carbon dots

(Glassy Carbon Model - Jenkins G. M. and Kawamura, K. - 1976)

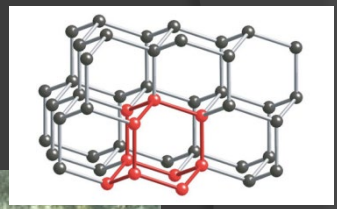
Lonsdaleite

http://webmineral.com



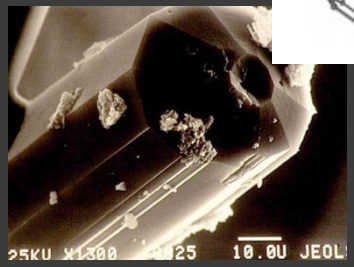
Carbon Structures (Hybridization)

Diamond



http://www.nature.com

http://www.musee.ensmp.fr

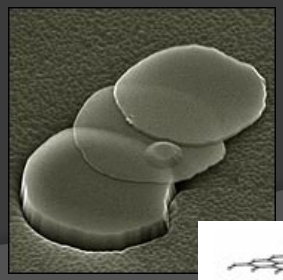


http://www.cite-sciences.fr

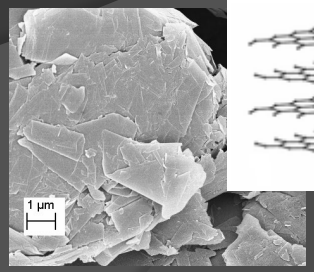
Fullerenes

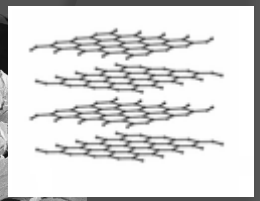
C_{60}, C_{70}, C_{540}, etc.

Graphene, r-GO, FLG



Graphite



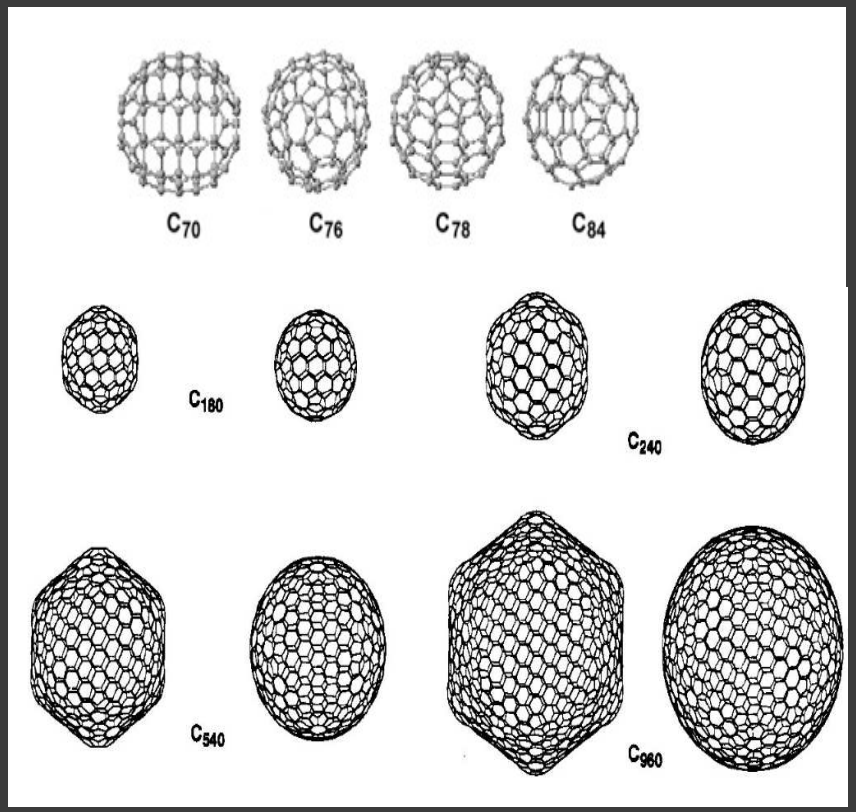


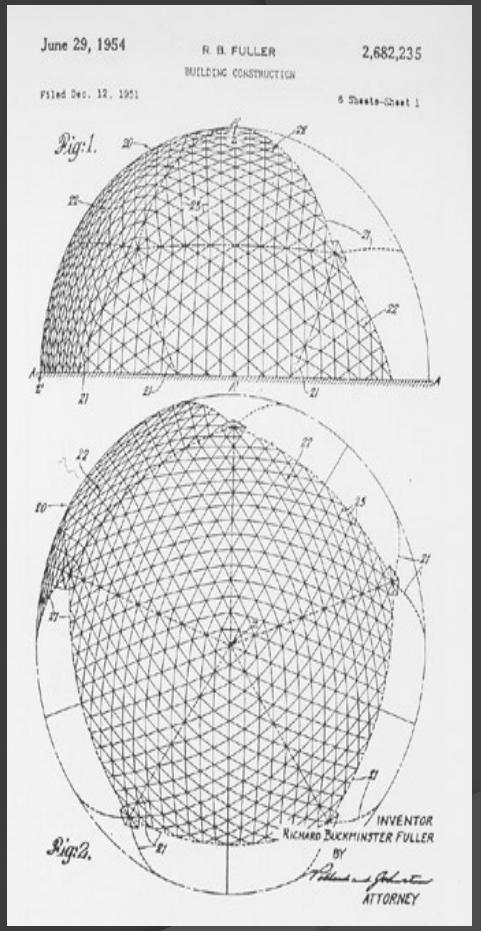
Carbon cones & onions

Carbyns & carbolite

$R\text{-}[\text{-}C{\equiv}C\text{-}]_n\text{-}R$

Fullerenes



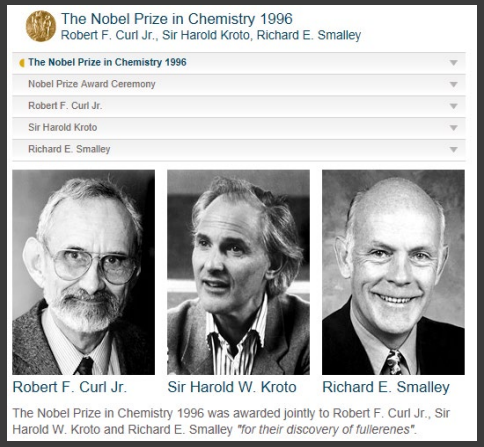


Buckminster Fuller,
Ford rotonde du dôme, 1953

”The most symmetrical large molecule”

- Discovered in 1985

  - Nobel prize Chemistry 1996, Curl, Kroto, and Smalley



Pure Appl. Chem., Vol. 77, No. 5, pp. 843–923, 2005.
DOI: 10.1351/pac200577050843

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

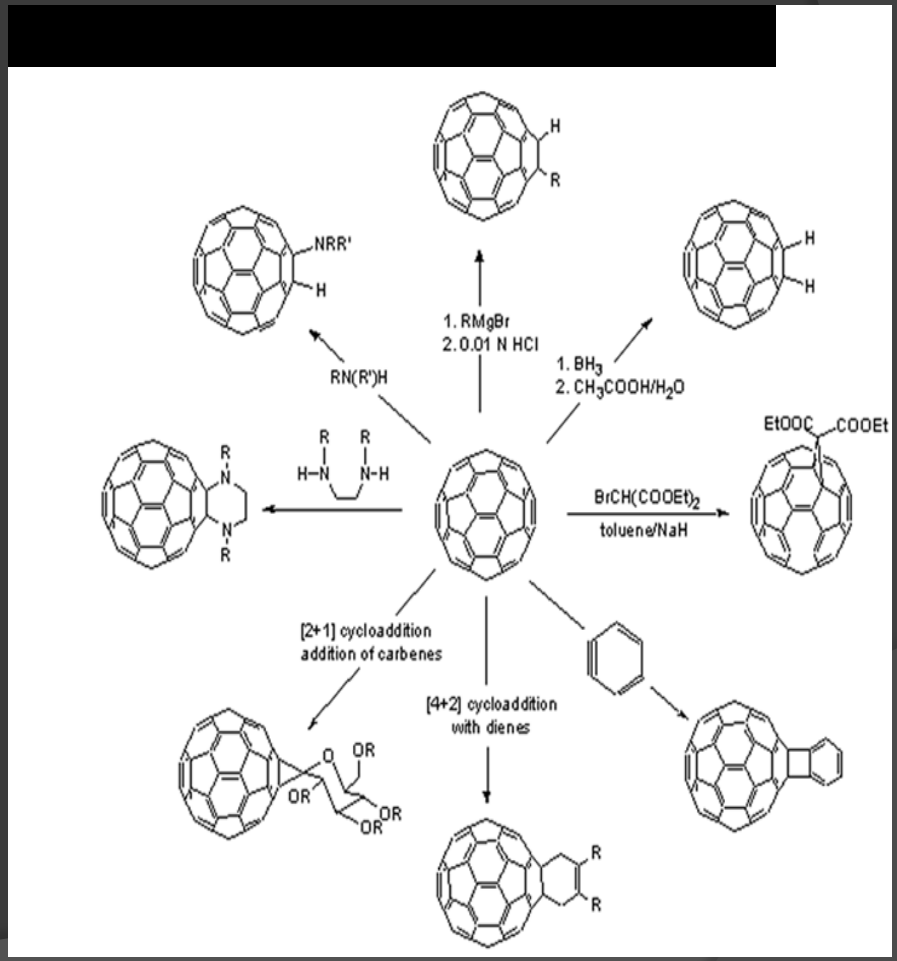
CHEMICAL NOMENCLATURE AND STRUCTURE REPRESENTATION DIVISION*

NUMBERING OF FULLERENES

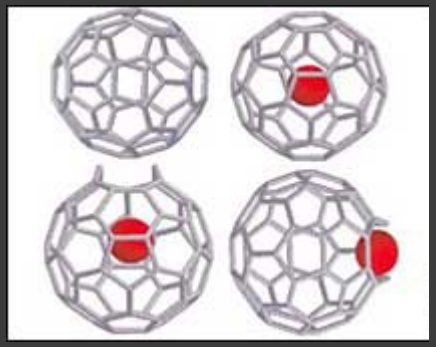
(IUPAC Recommendations 2005)

F. COZZI[1], W. H. POWELL[2,‡], AND C. THILGEN[3]

[1]*Dipartimento di Chimica Organica e Industriale via Golgi, 19-I-20133, Milano, Italy;* [2]*1436 Havencrest Ct., Columbus, OH 43220, USA;* [3]*Laboratorium für Organische Chemie - ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093, Zürich, Switzerland*

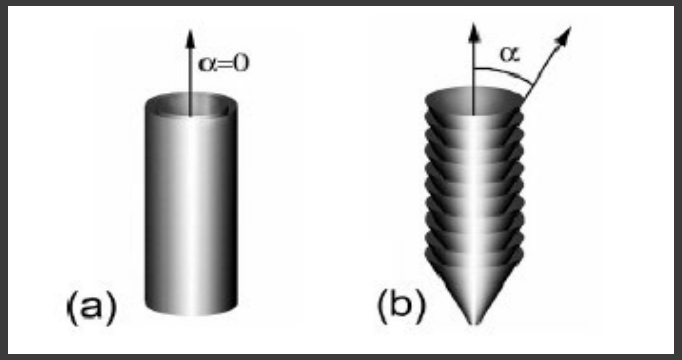


- Symmetric shape
  → lubricant
- Large surface area
  → catalyst
- High temperature (~500°C)
- High pressure
- Hollow
  → caging particles
- Ferromagnet ...
  - polymerized C_{60}
  - up to 220°C
- Chemically stable as graphite
  - most reactive at pentagons
- Crystal by weak van der Waals force
- Superconductivity: - K_3C_{60}: 19.2 K and - $RbCs_2C_{60}$: 33 K



Slide and images from:
Kai de Lange Kristiansen

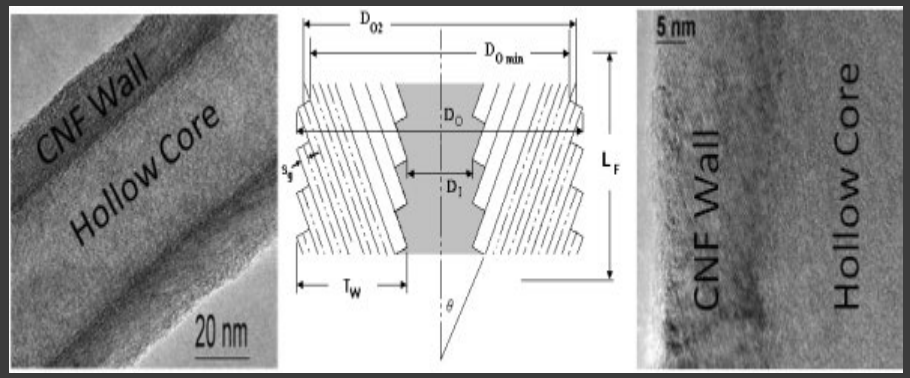
Carbon nanotubes and carbon nanofibers …

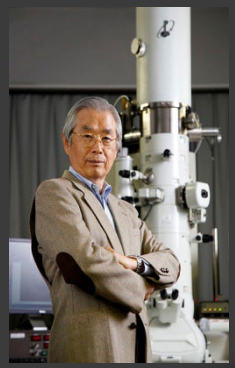


CNT first discovered by L. V. Radushkevich and V. M. Lukyanovich at: **1952** (*Journal of Physical Chemistry, 62:88-95)*;

- Observed by Endo, Koyama and Oberlin in **1976** and;
- Finally described by Iijima at **1991**.

Nanofibres: **discovered in 1889**, US patent number: 450 e 480, by Hughes and Chambers.





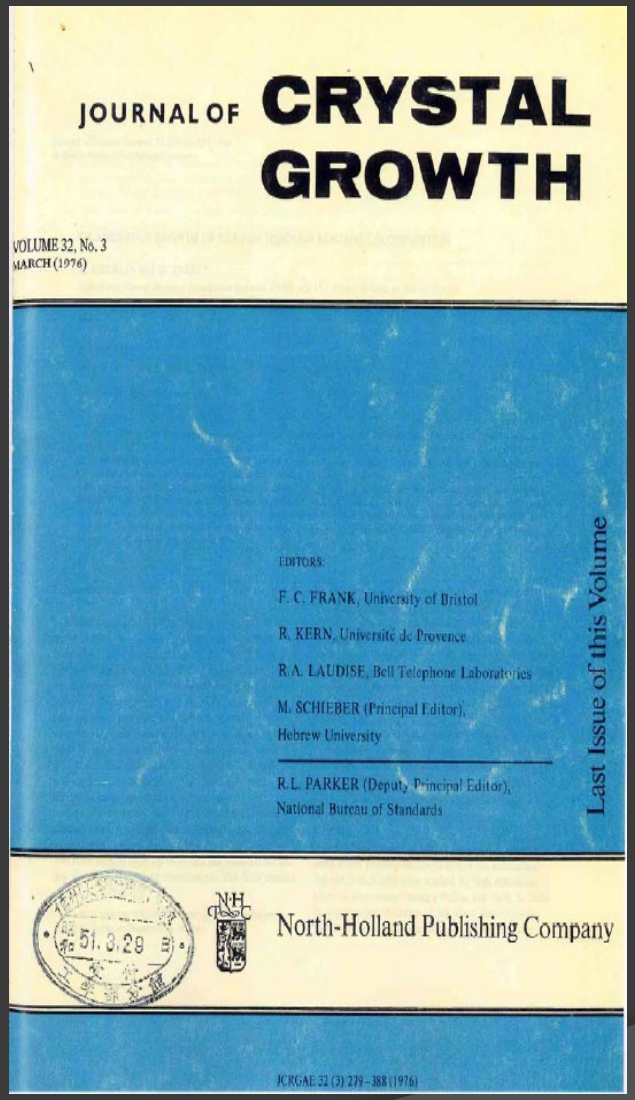
Iijima

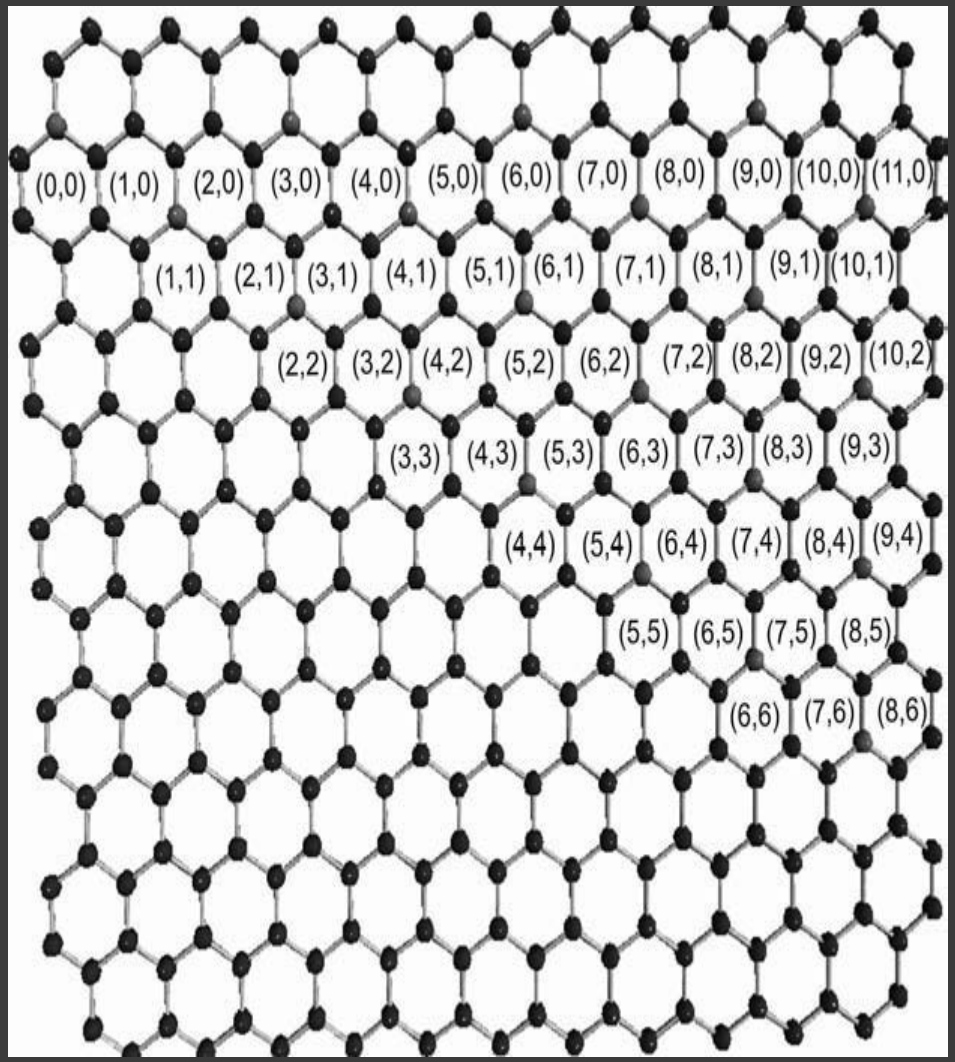
VGCF: Vapor growth carbon fibers

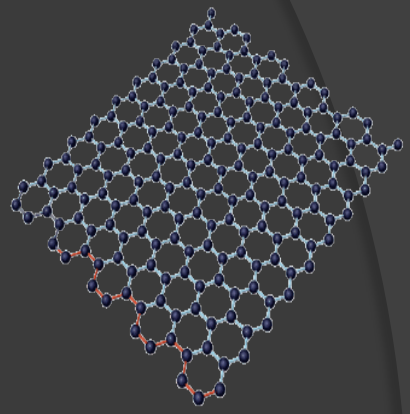
J. Cryst. Grow. 32
（1976）335-349

A. Oberlin,
M. Endo, e
A. T. Koyama

Morinobu Endo

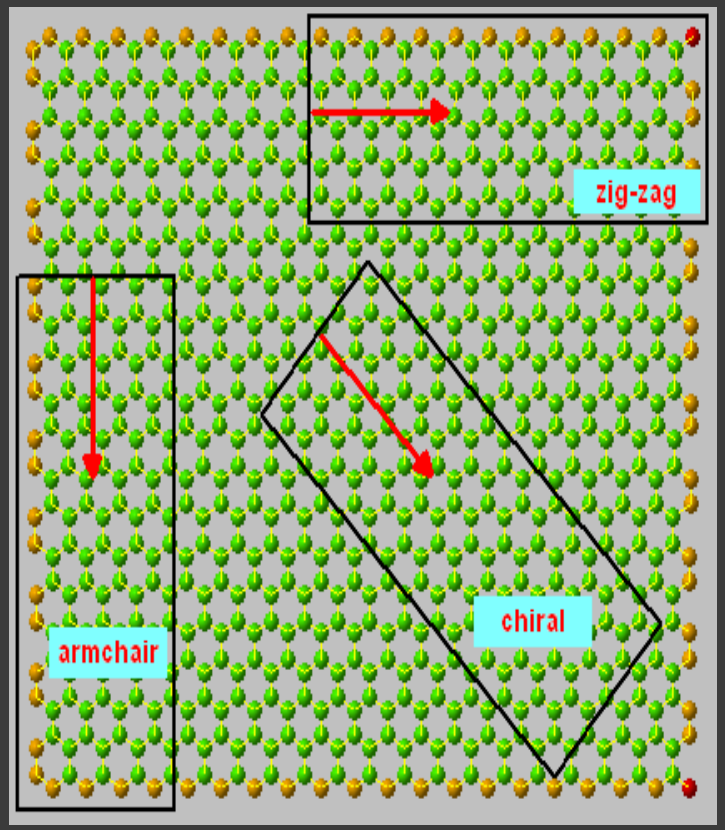


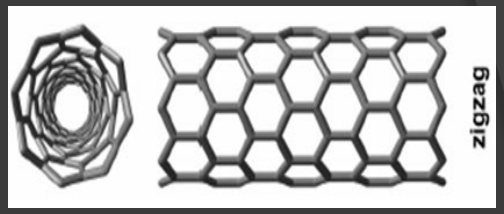




Animation courtesy H. Nakahara and Saito Lab

M. Endo, Ph.D. Thesis (1975)

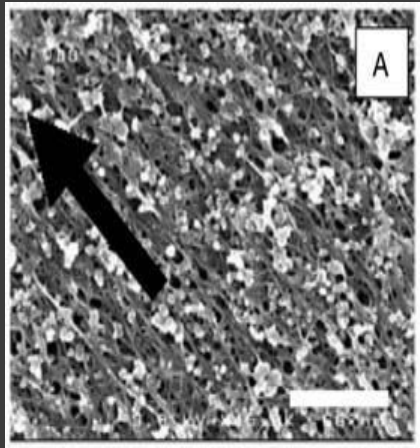


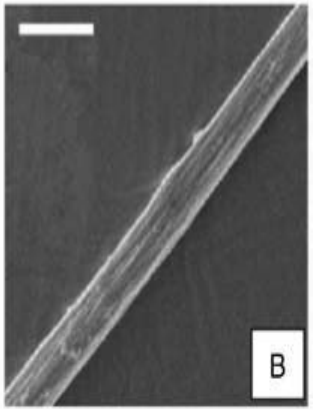


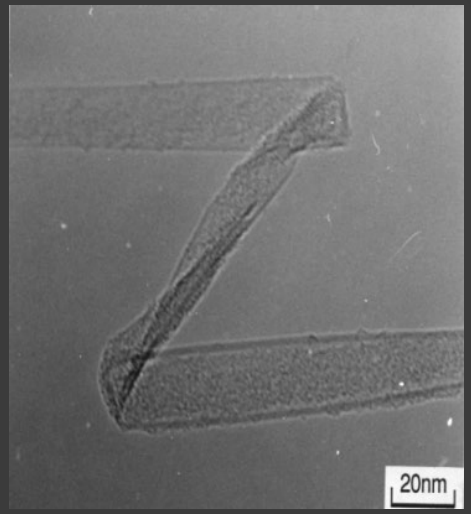
Zigzag: (n,0)

Armchair: n = m

Chiral: (n,m) m0







M. Endo, K. Takeuchi, K. Kobori, K. Takahashi, H. W .Kroto and A. Sarkar, Carbon, 33, 873-881 (1995).

Scanning electron micrographs (SEMs) of a SWNT ribbon (scale bar = 667 nm)

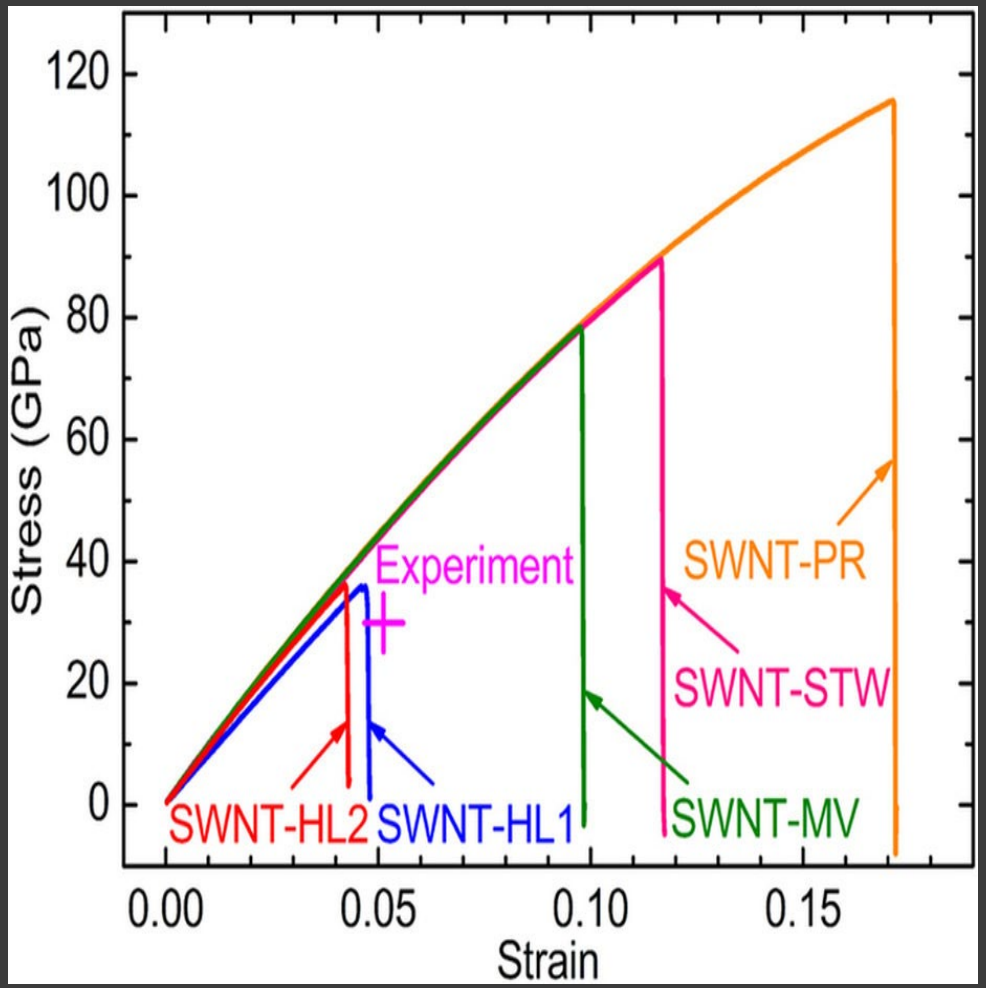
(a) and a SWNT fiber (scale bar = 25 μm)
(b) each showing the alignment of the SWNTs within the structure.
(c) An optical micrograph of a SWNT fiber tied in a knot showing the high flexibility and resistance to torsion (fiber diameter = 15 μm).

From B. Vigolo, A. Pénicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, and P. Poulin. Macroscopic fibers and ribbons of oriented carbon nanotubes, *Science*, 290, 1331–1334, 2000.

- Young Modulus (stiffness):
  - Carbon nanotubes 1250 GPa
  - Carbon fibers 425 GPa (max.)
  - High strength steel 200 GPa

- Tensile strength (breaking strength)
  - Carbon nanotubes 11- 63 GPa
  - Carbon fibers 3.5 - 6 GPa
  - High strength steel ~ 2 GPa
- Elongation to failure : ~ 20-30 %
- Density:
  - Carbon nanotube (SW) 1.33 – 1.40 gram / cm^3
  - Aluminium 2.7 gram / cm^3

Yield strength limit: real (experimental) versus theory (simulated)



SCIENTIFIC REPORTS

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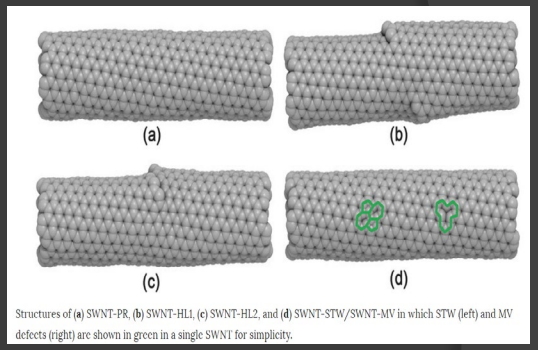
(2106)



Structures of (a) SWNT-PR, (b) SWNT-HL1, (c) SWNT-HL2, and (d) SWNT-STW/SWNT-MV in which STW (left) and MV defects (right) are shown in green in a single SWNT for simplicity.

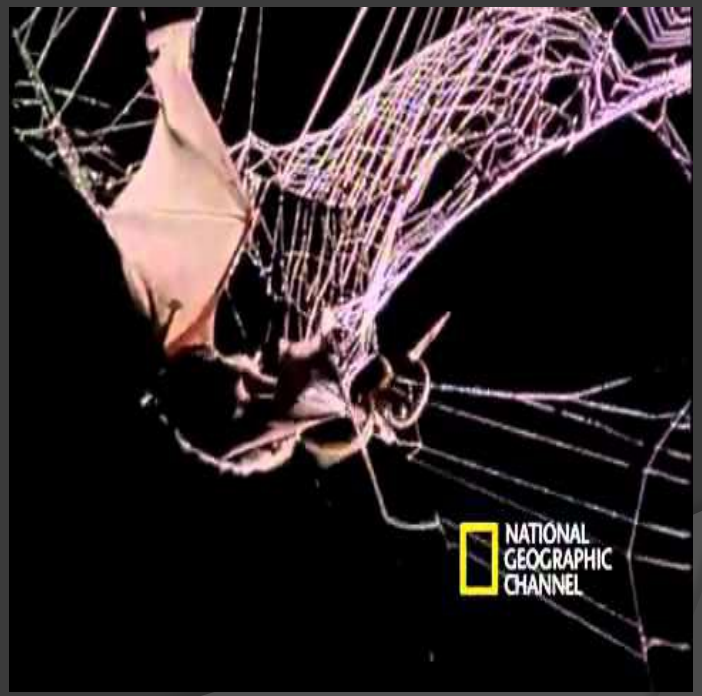
MV - monovacancy;
STW - Stone-Thrower-Wale defects (created during processing)
PR - "Pristine" (without defects)

http://www.nature.com/articles/srep20324/figures/3
http://www.nature.com/articles/srep20324/figures/2

Mechanical properties of materials:

- Steel: 0,2 a 2 GPa
- Spider silk: 1 GPa (one specimen): https://phys.org/news/2013-06-spider-silk-nature-stronger-steel.html)
- Carbon nanotubes filaments: 1,3 GPa
- Single wall carbon nanotubes (with helicoidally defects): 30-45 GPa ,
  (http://www.nature.com/articles/srep20324)

https://phys.org/news/2013-01-nanotube-fibers-unmatched-combination-strength.html



https://i.ytimg.com/vi/AyYH0LNW8yo/hqdefault.jpg

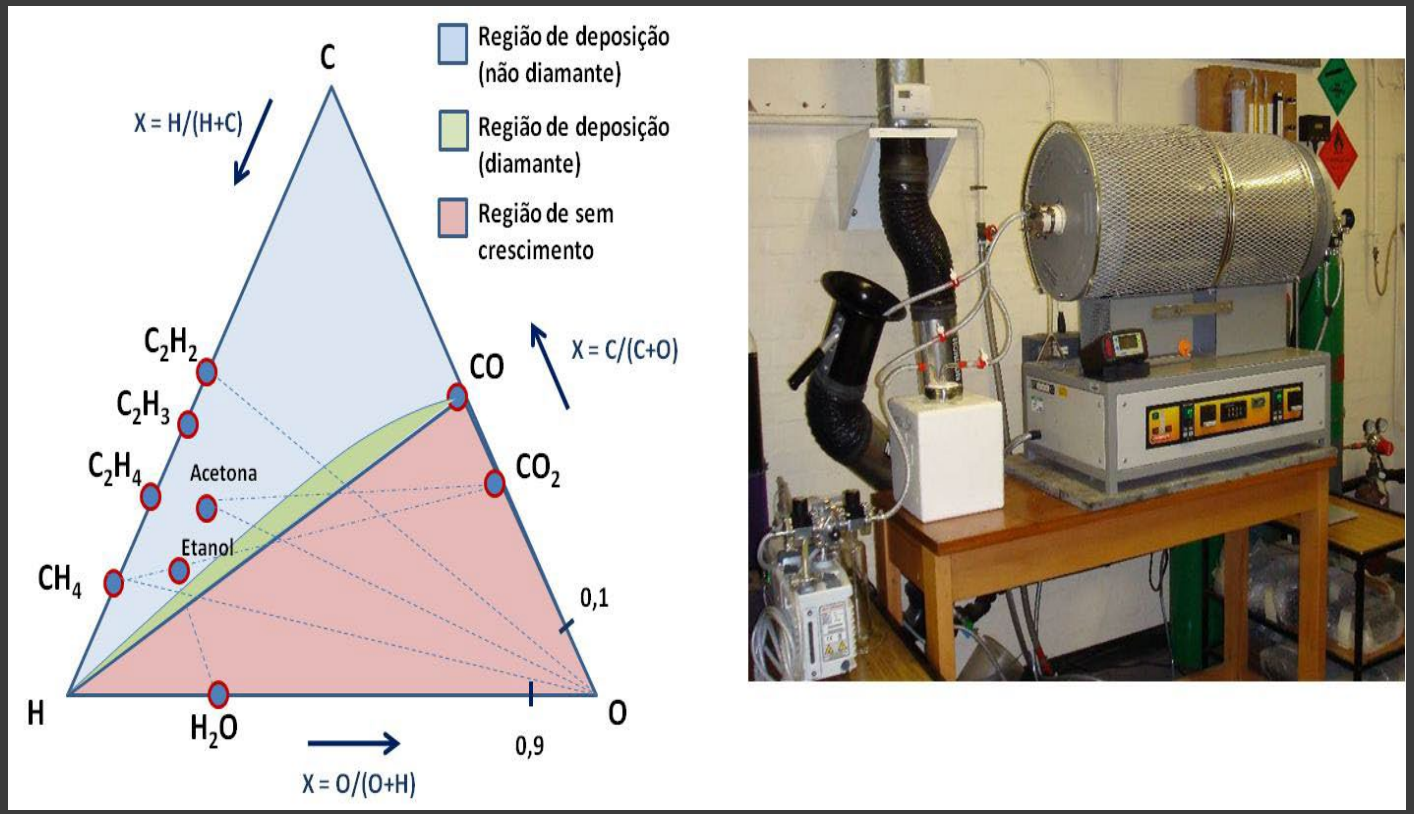
Synthesis methods

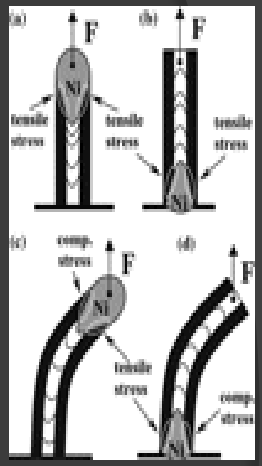
Large number of methods:

- CVD
- Catalytic combustion;
- Laser ablation
- Plasma

...

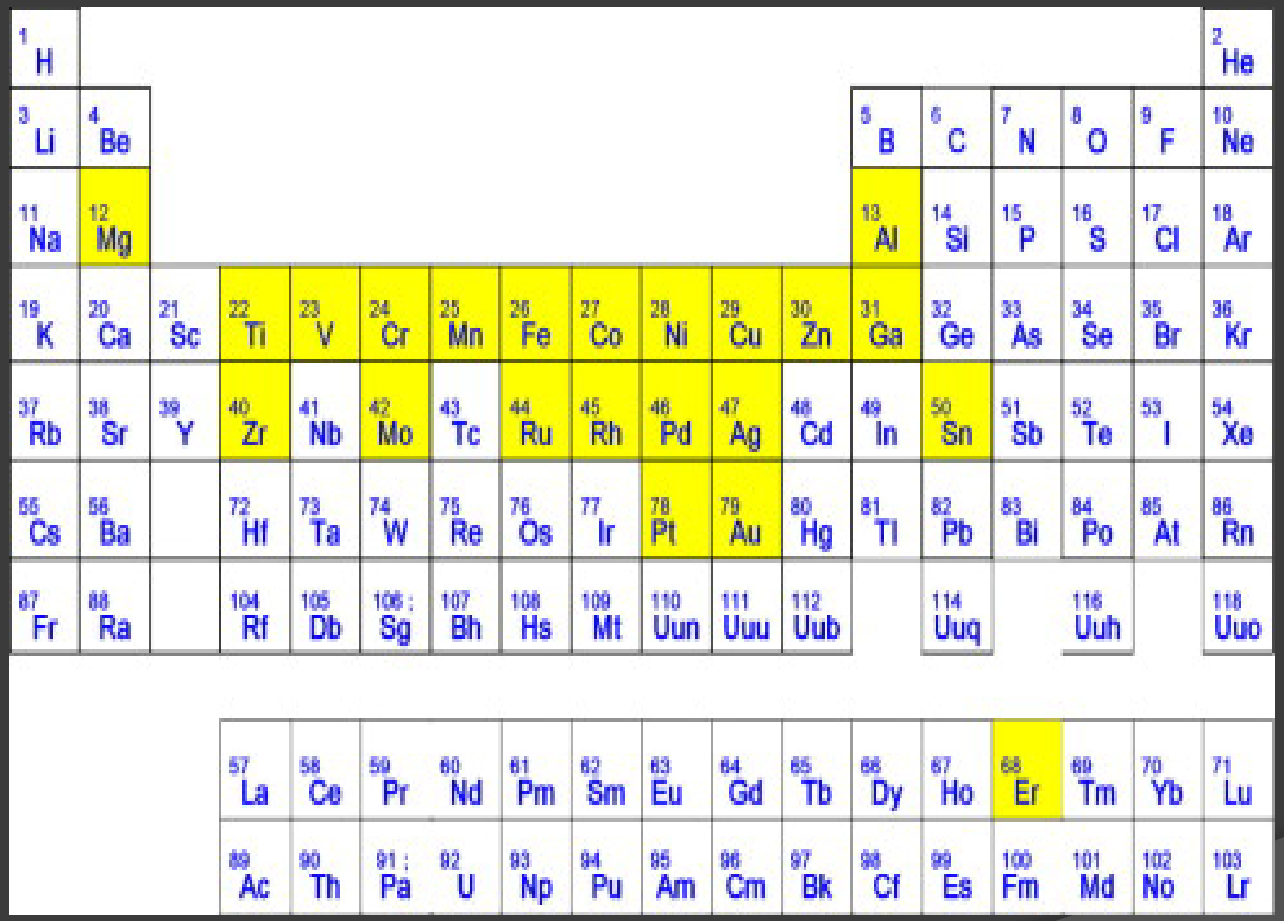
CVD – Chemical Vapor Deposition





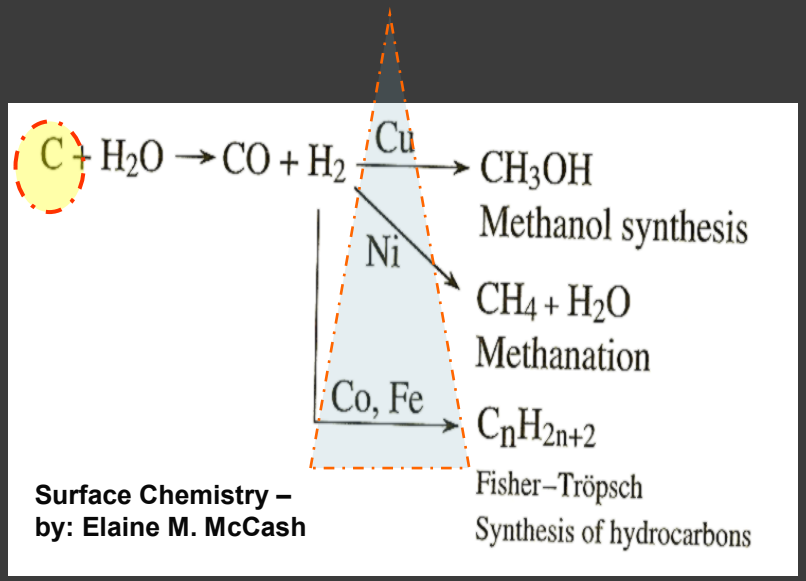
Reactor atmosphere
Thermal gradient (temperature)
Type of catalyzers
Source of carbon (chemical compounds)
Pressure …

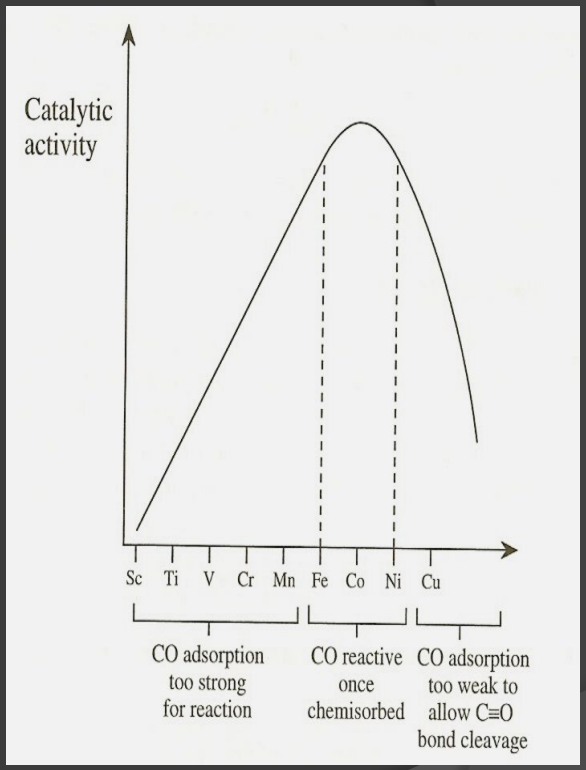
Catalyzers


1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
104 Rf
105 Db
106 : Sg
107 Bh
108 Hs
109 Mt
110 Uun
111 Uuu
112 Uub
114 Uuq
116 Uuh
118 Uuo
57 La
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
89 Ac
90 Th
91 : Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr

“Volcano curve”: Catalyzer and CO (g) bonding - (Fisher-Tropsch reaction)

Catalyzers





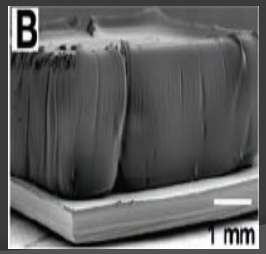
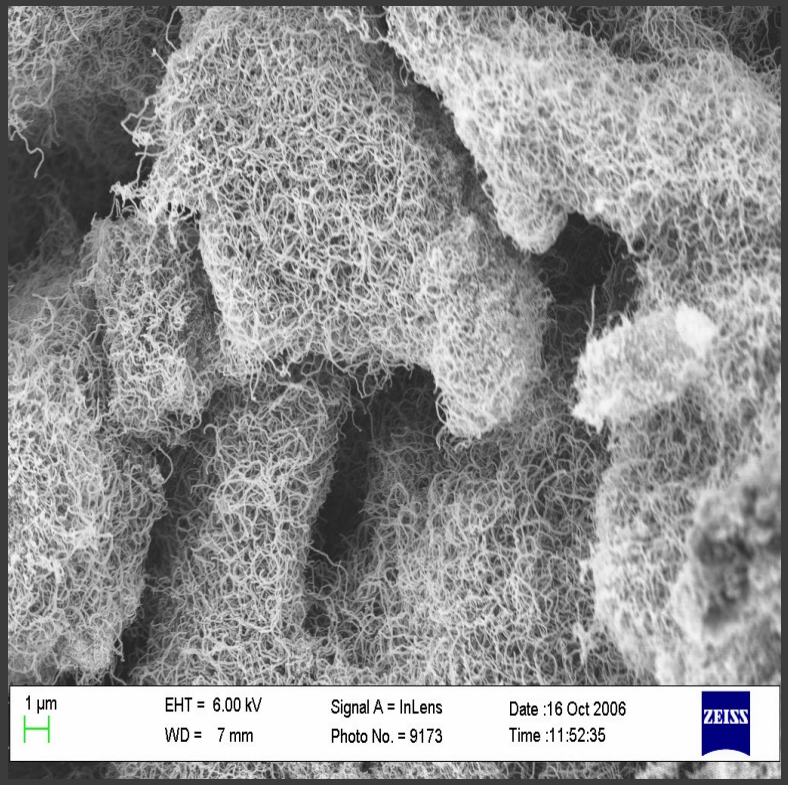
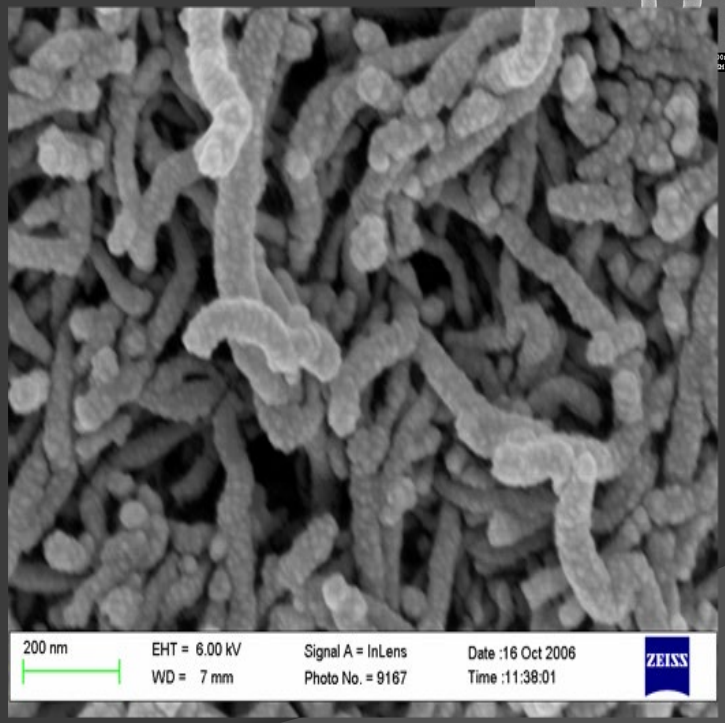


Fig. 1. SWNT forest grown with water-assisted CVD. (A) Picture of a 2.5-mm-tall SWNT forest on a 7-mm by 7-mm silicon wafer. A matchstick on the left and ruler with millimeter markings on the right is for size reference. (B) Scanning electron microscopy (SEM) image of the same SWNT forest. Scale bar, 1 mm.

Science 306, 1362, Hata et al.

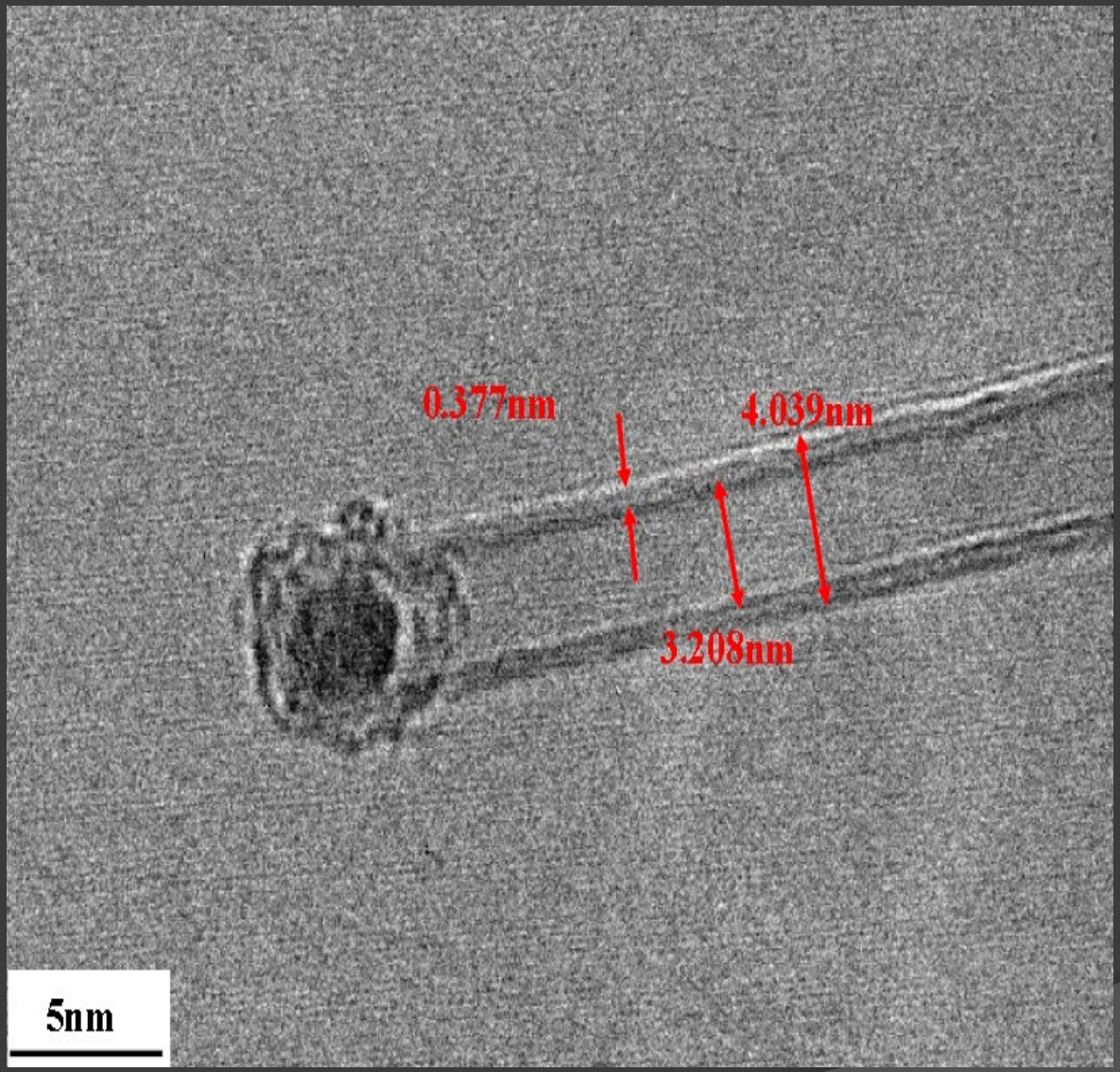
Mutiwall carbon nanotubes



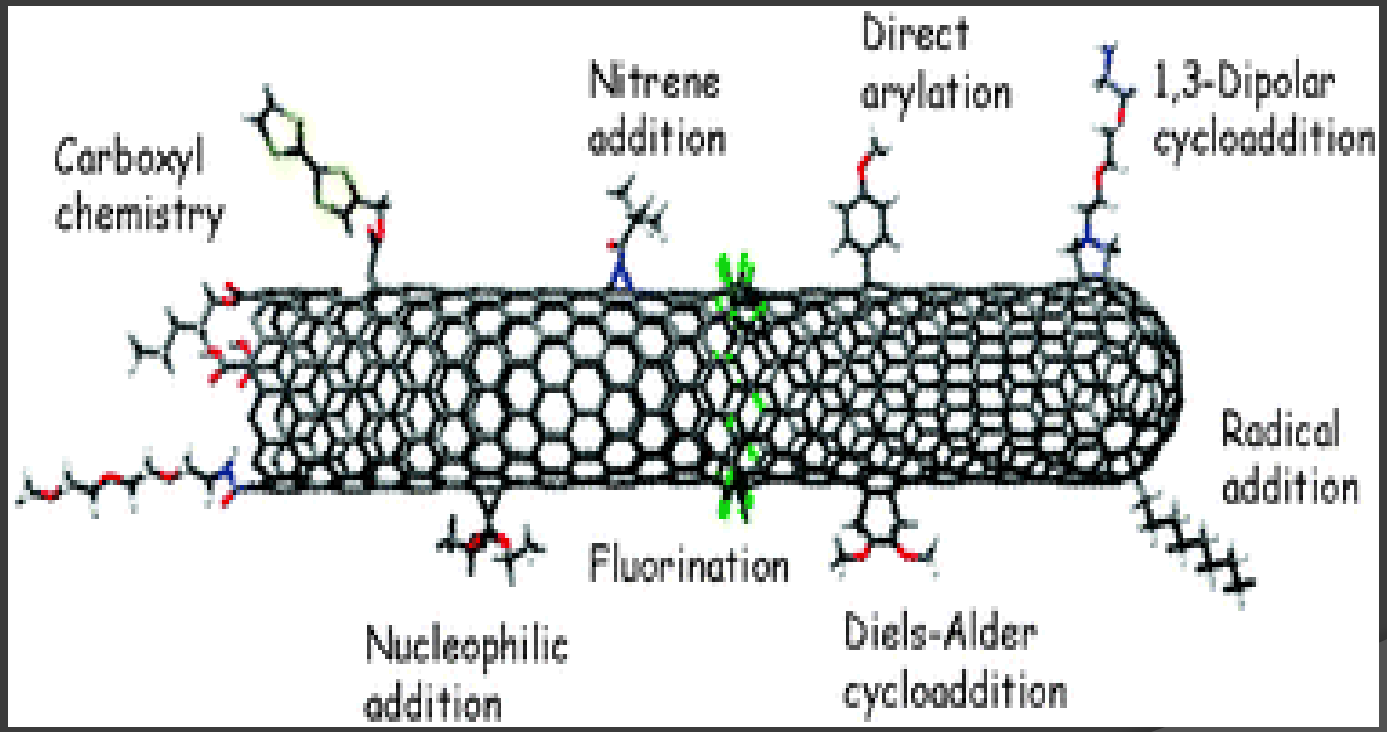


CVD – MWCNT
(Industrial grade): +/- 95% purity

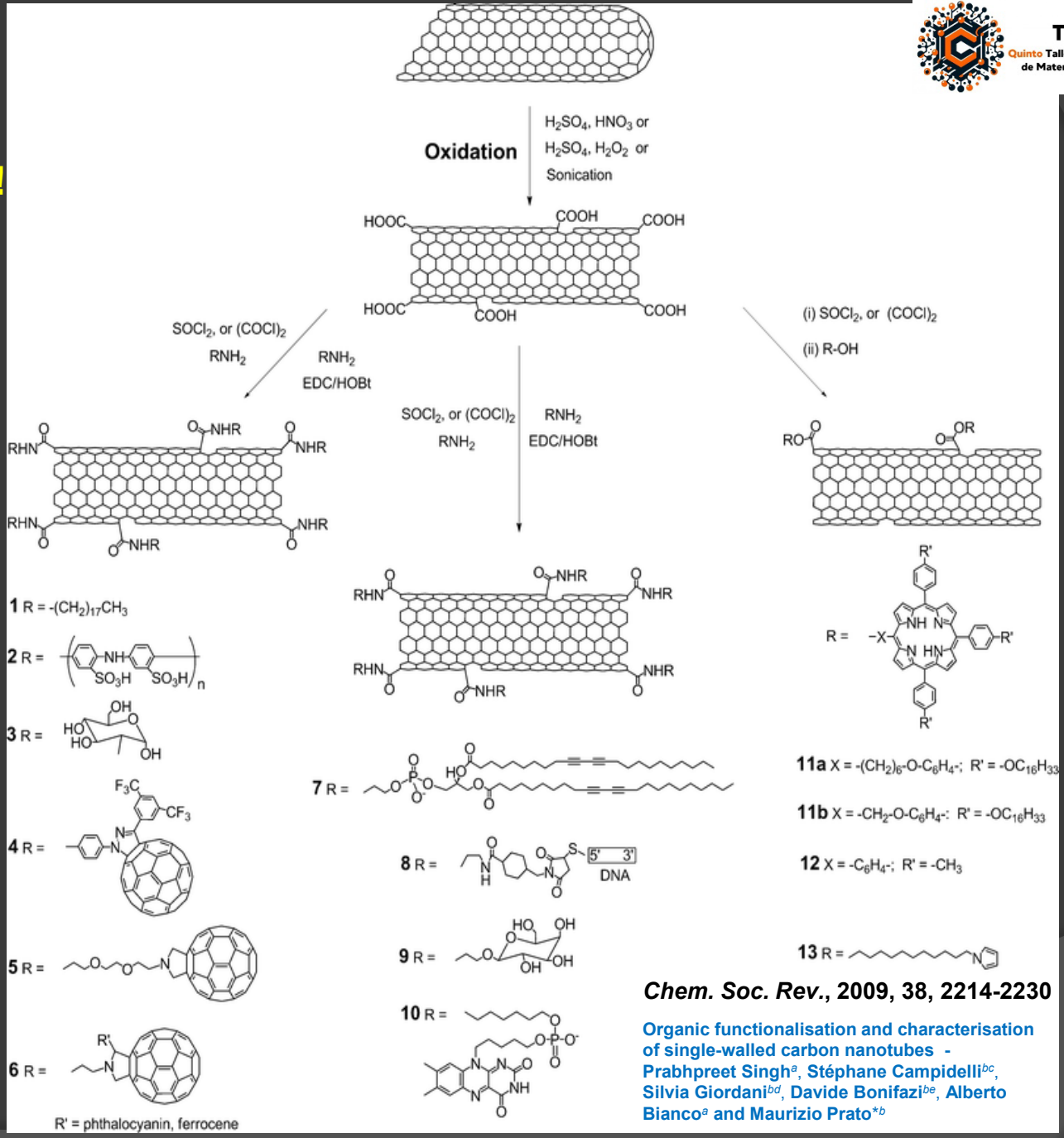
Purification step !!!



Functionalization:



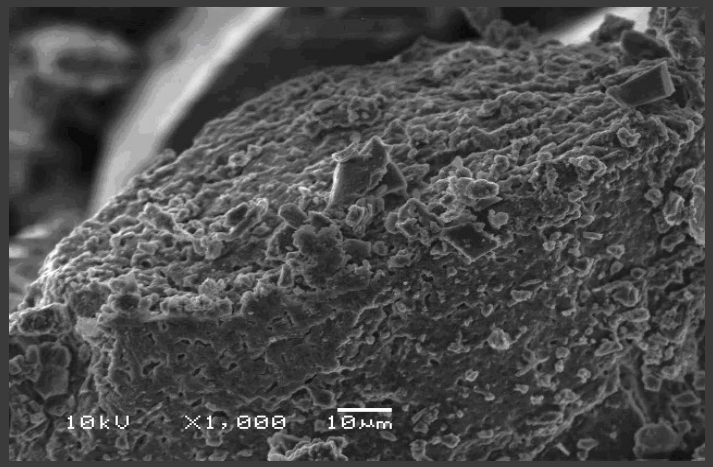
… More than 35 examples !



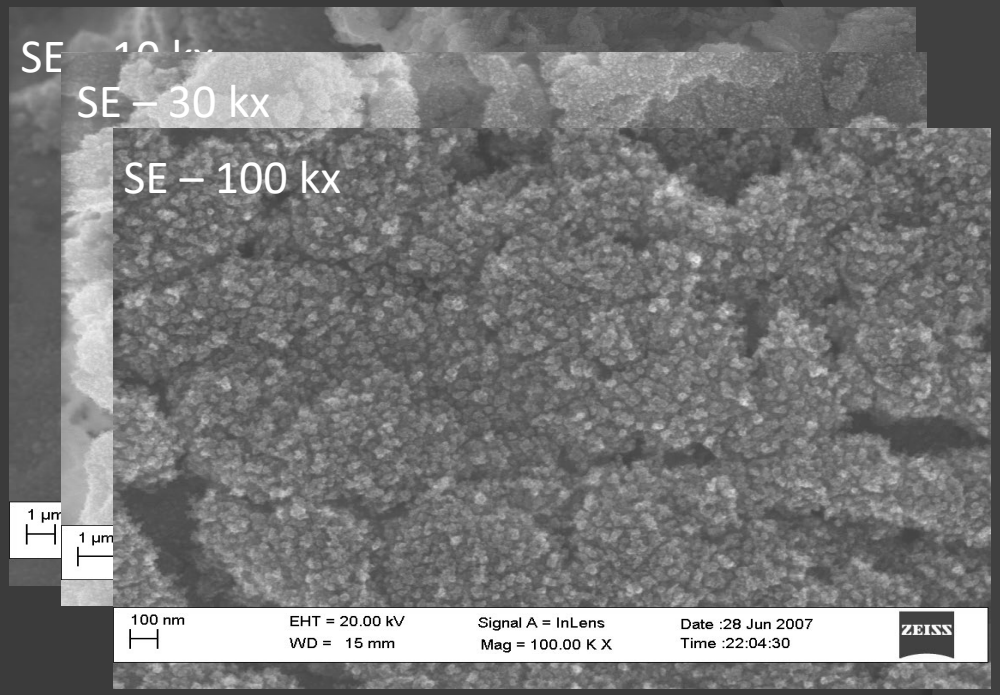
***Chem. Soc. Rev.*, 2009, 38, 2214-2230**

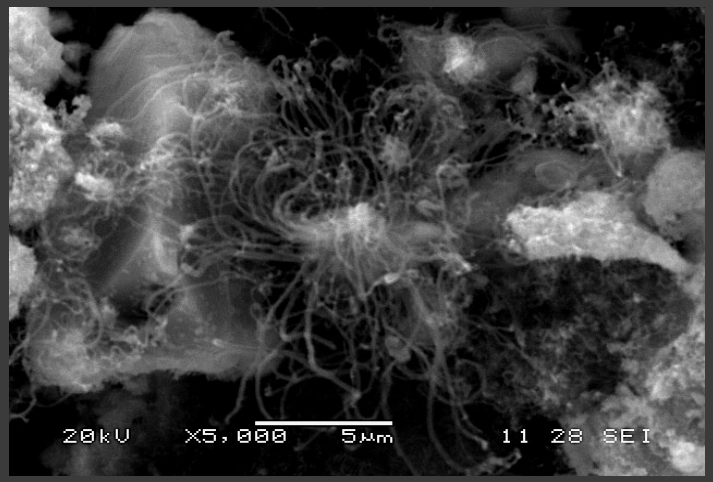
Organic functionalisation and characterisation of single-walled carbon nanotubes - Prabhpreet Singh[a], Stéphane Campidelli[bc], Silvia Giordani[bd], Davide Bonifazi[be], Alberto Bianco[a] and Maurizio Prato*[b]

Chemical Vapour DEPOSITION

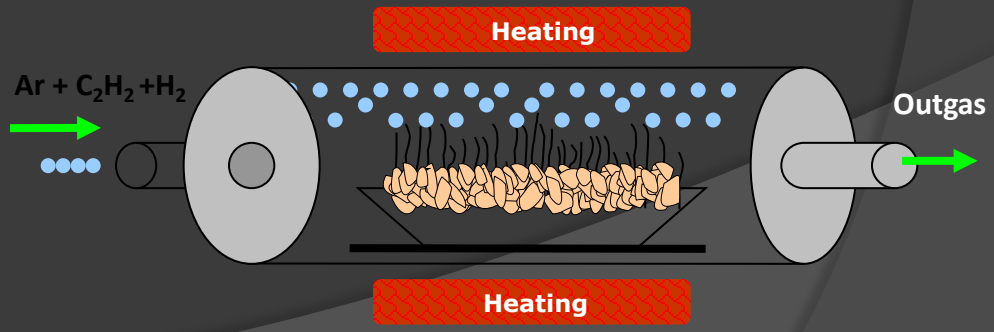


SE image of a MgO grain coated with catalyst



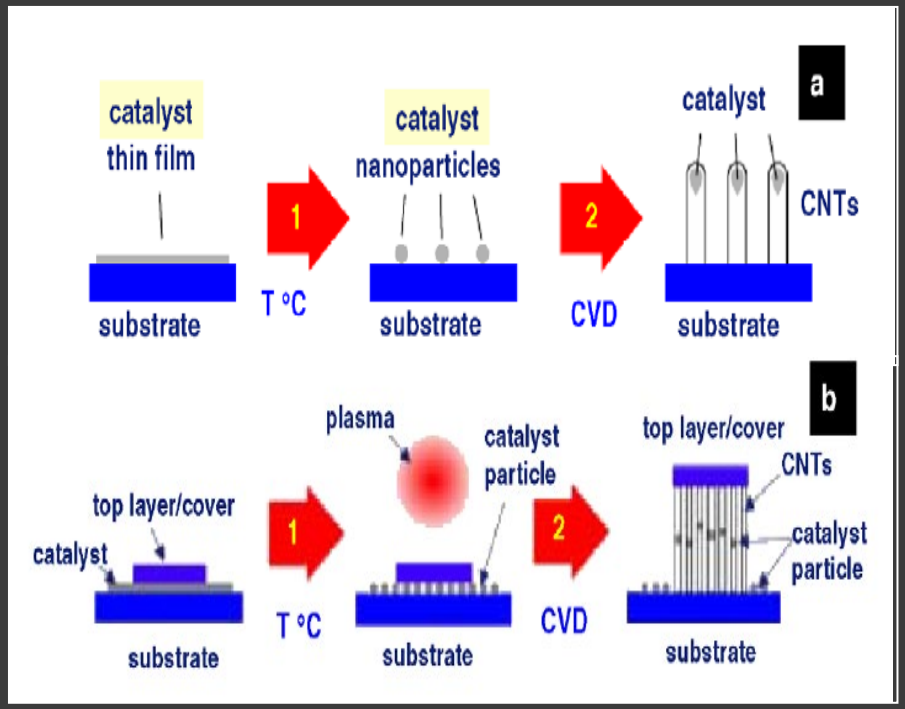


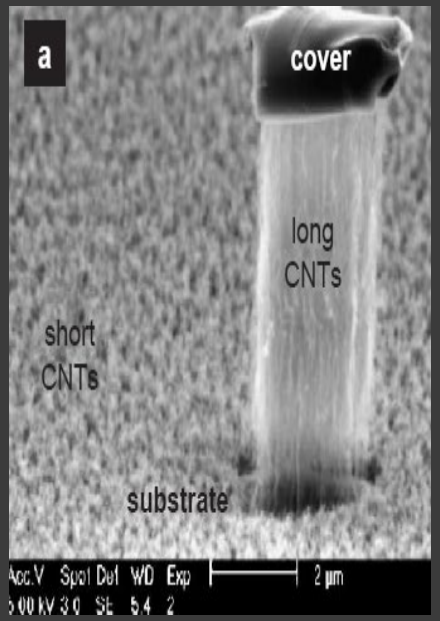
SE image of catalyst particles and CNTs



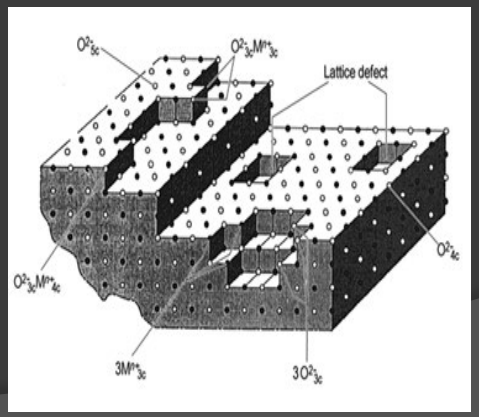
Guilherme Lenz (Pos-doc Program) & Rafael Sá, PhD Thesis (IC London) - 2006/2009

Substrate a “sandwich” of surfaces

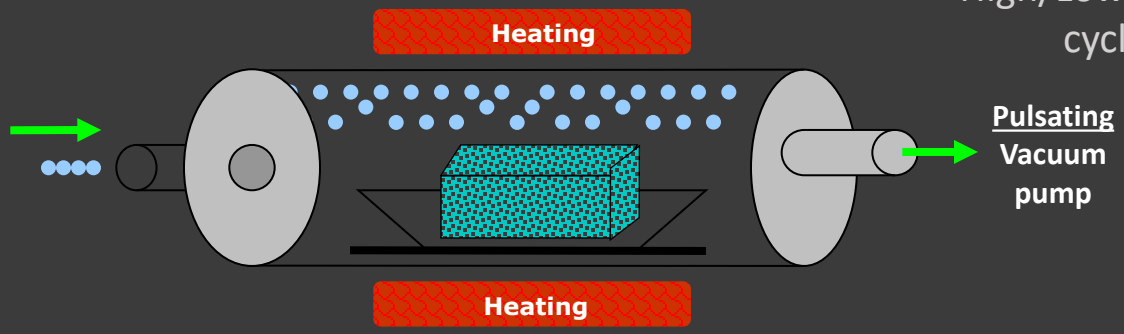




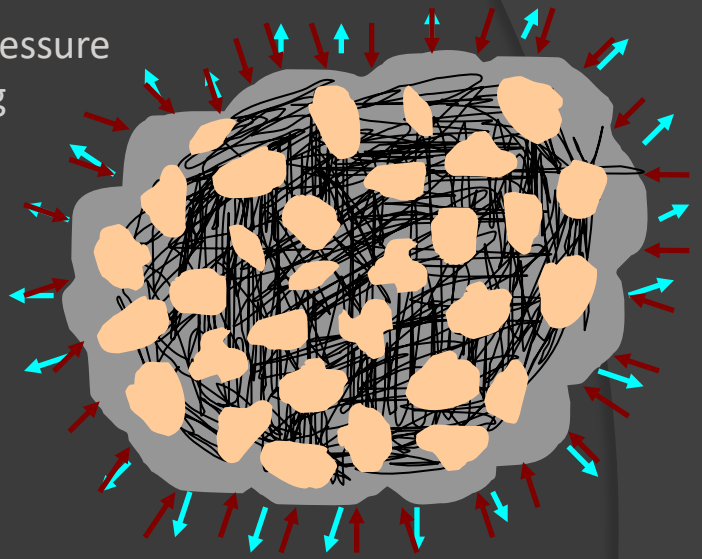
Z. Chen et al. / Diamond & Related Materials 15 (2006) 104–108

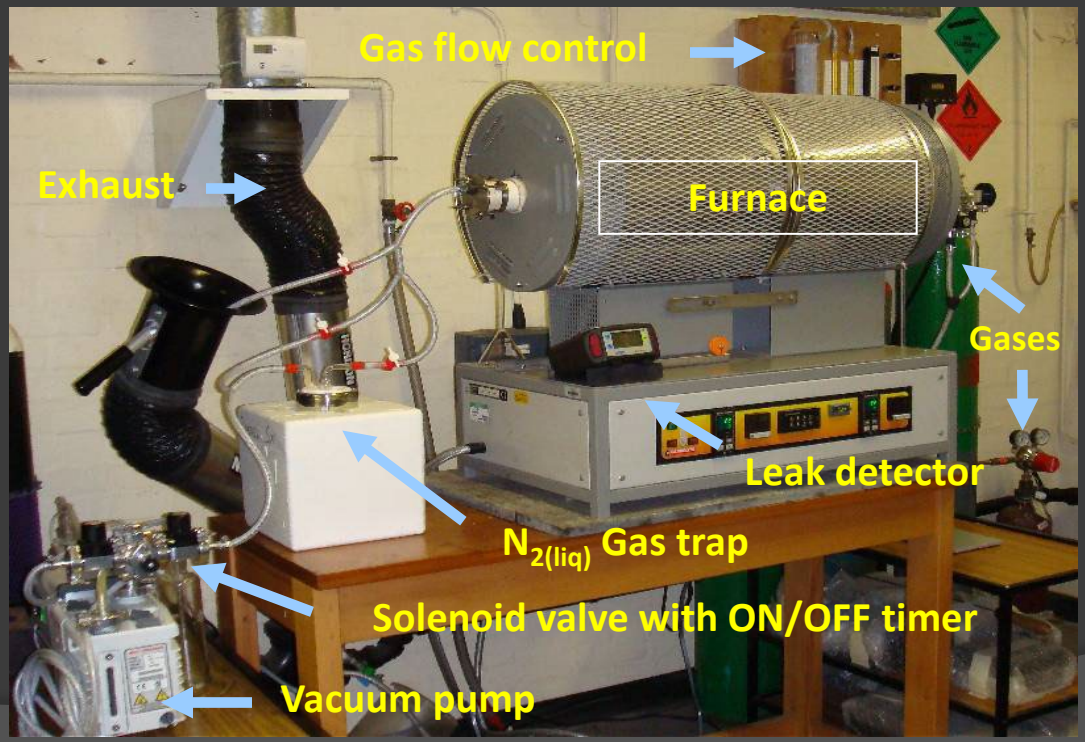


In-situ Formation: CVI



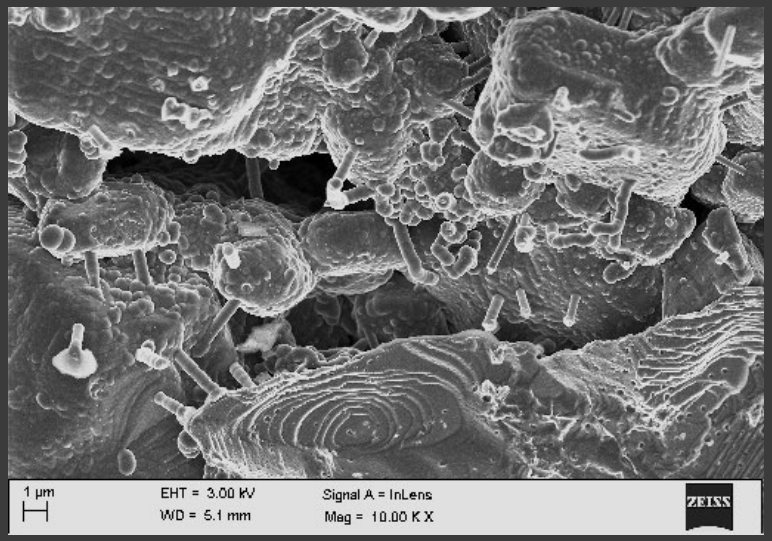
High/Low pressure cycling

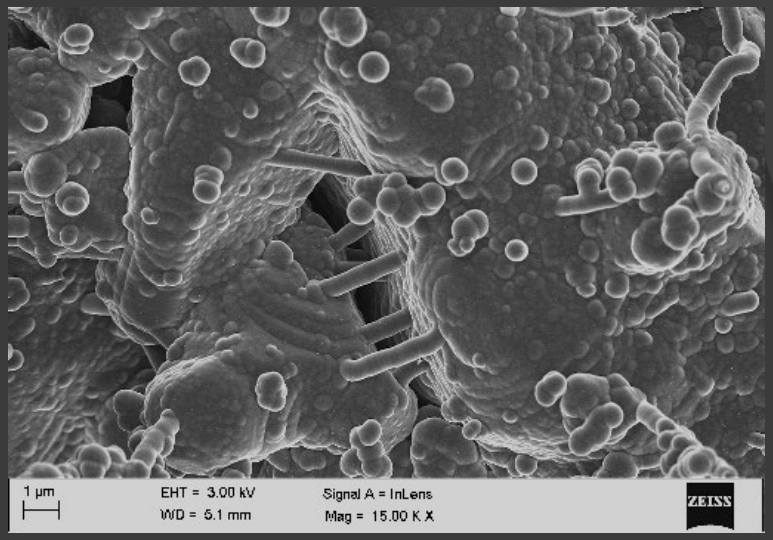


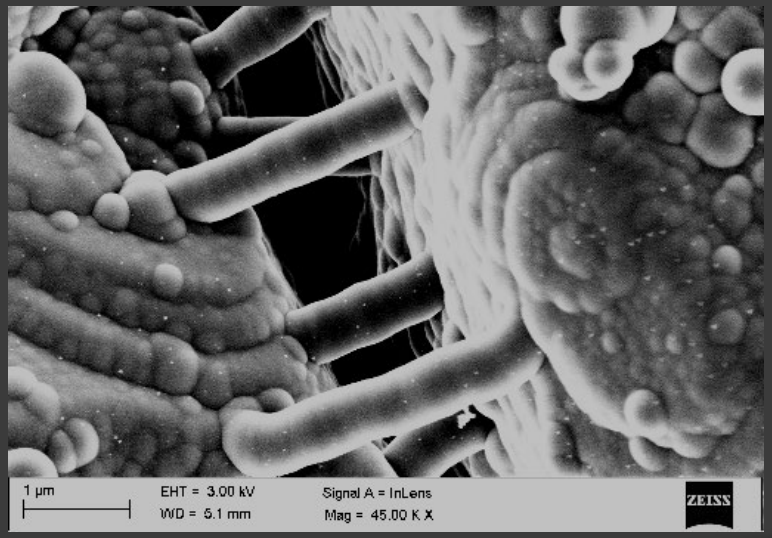


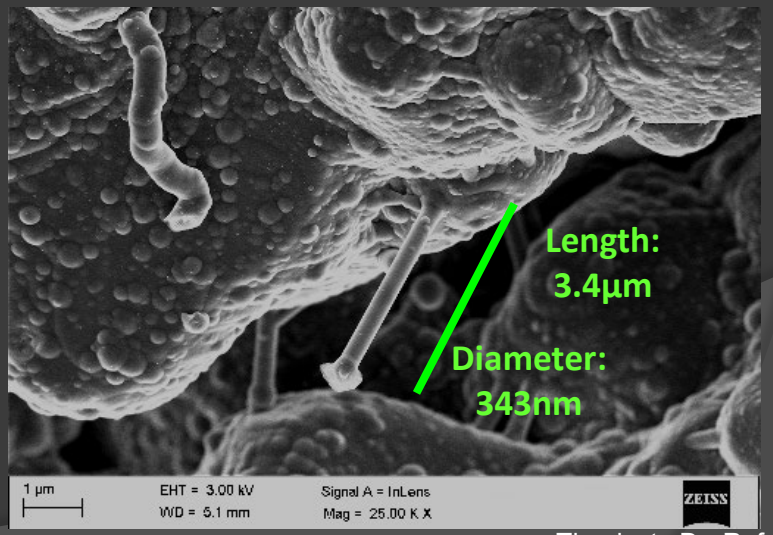
Detail of gas mixture and flow controls

In situ: MgO – MWCNT (CVI process)







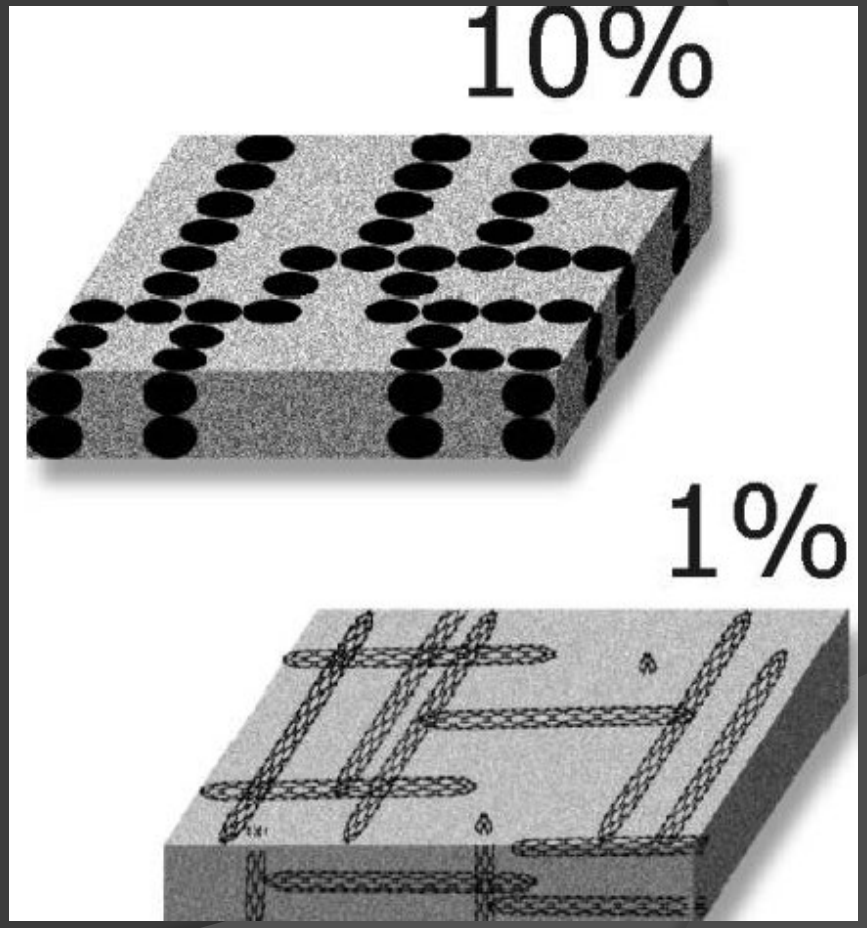


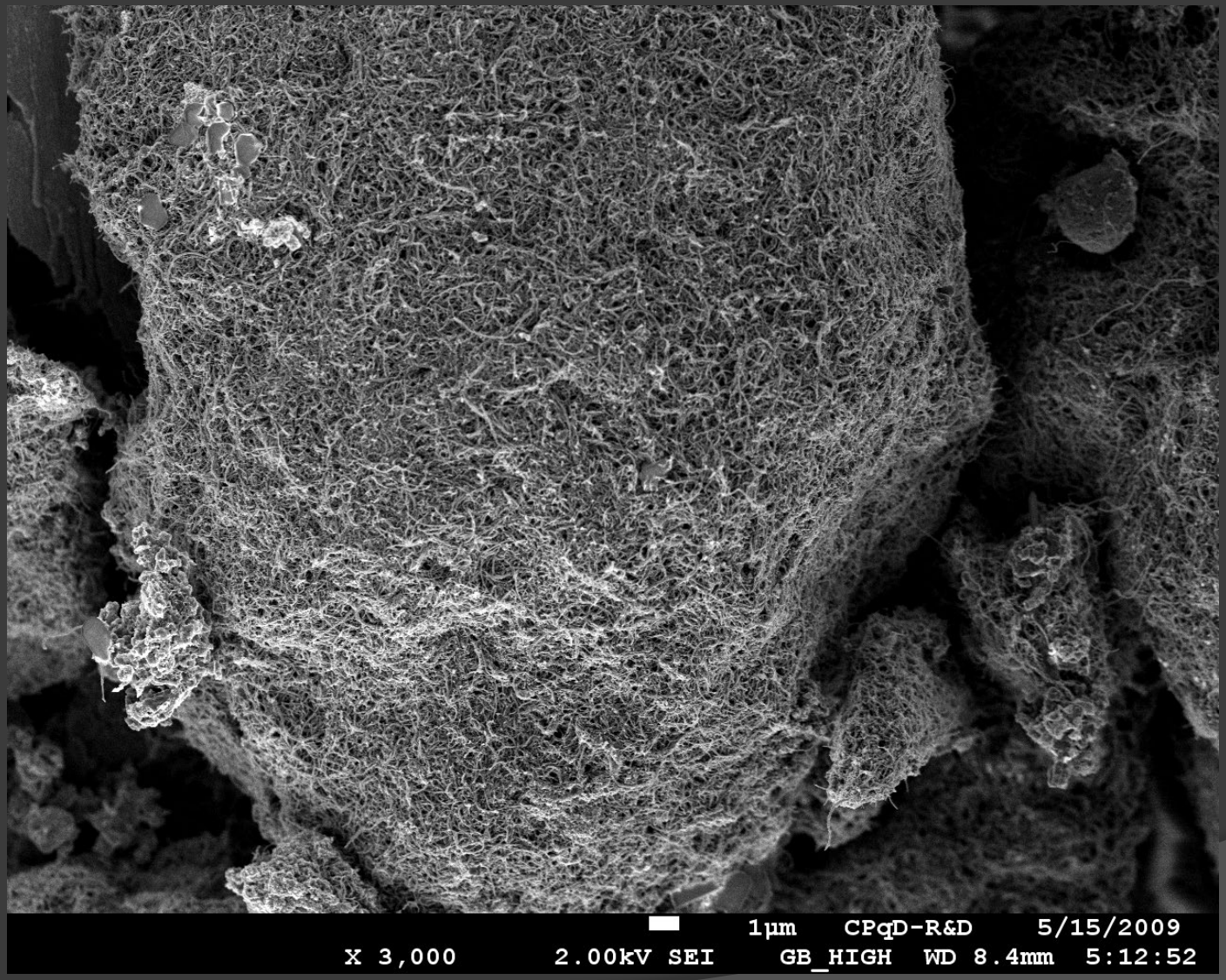
Thanks to Dr. Rafael G. de Sá

CNT / polymer composite

- Current technology
  - carbon black
  - 10 – 15 wt% loading
  - loss of mechanical properties

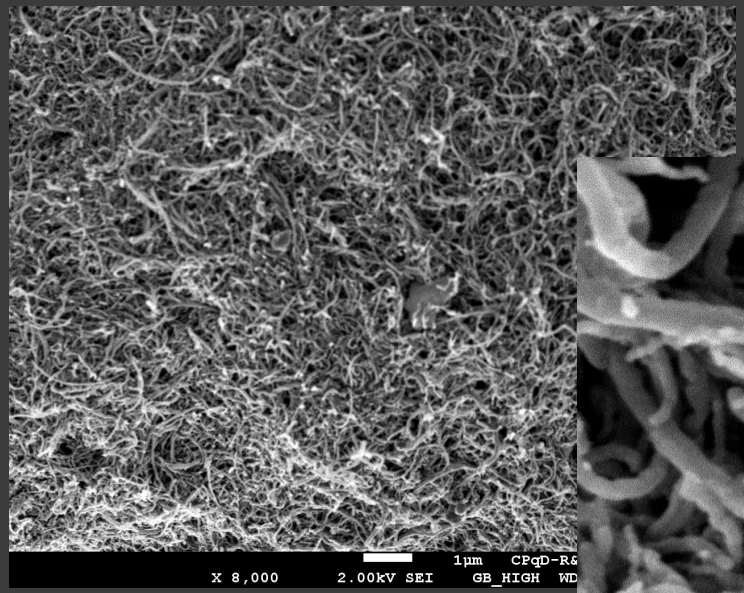
- CNT composites
  - 0.1 – 1 wt% loading
  - low perculation treshold

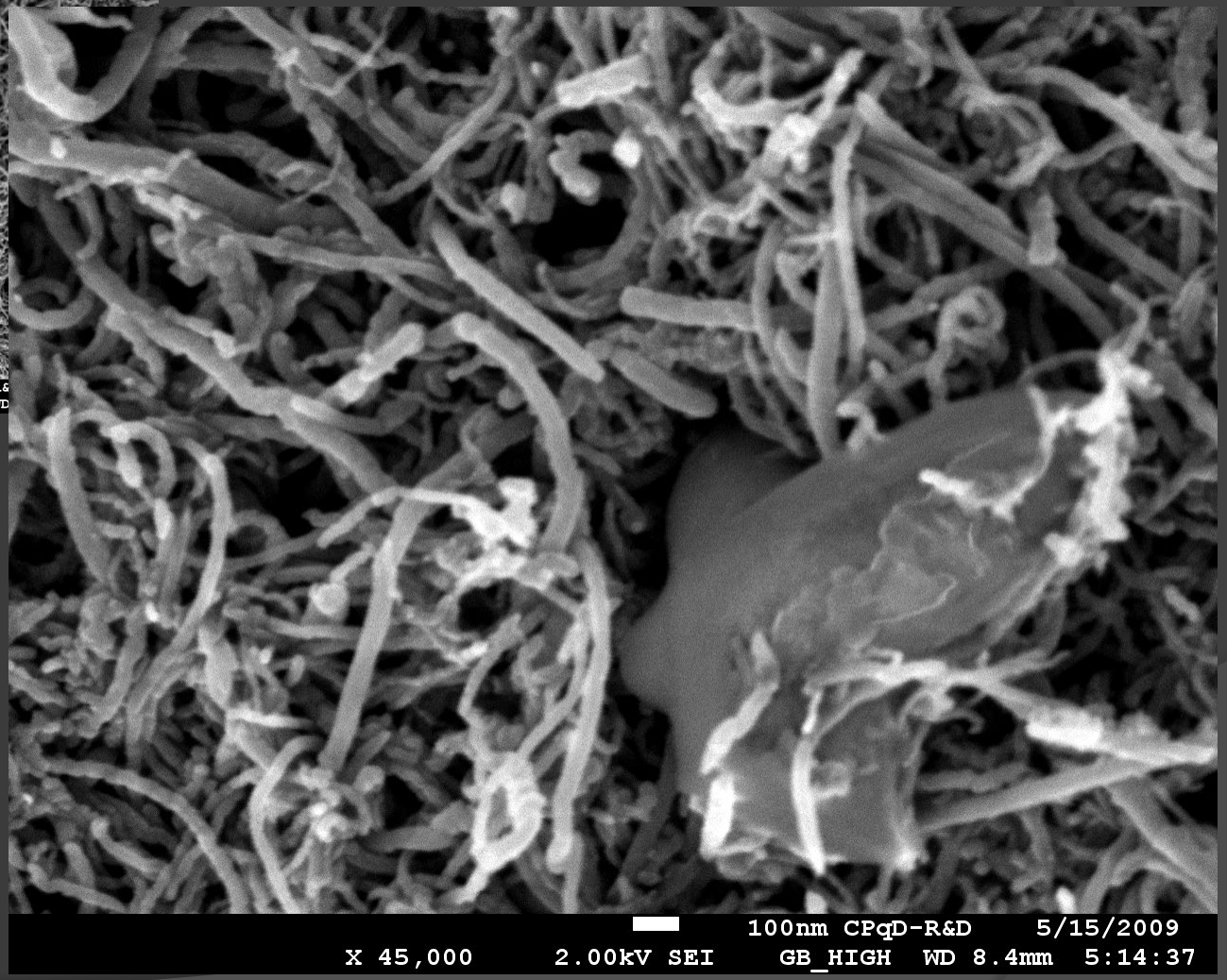




MWCNT
(50 nm)

Surface treated
(-OH)

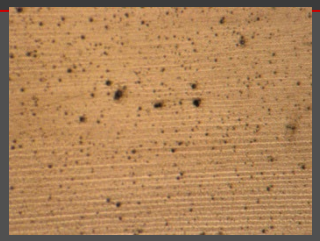
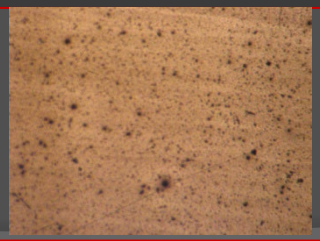




MWCNT
(50 nm)

Surface treated
(-OH)

CNT + phenolic resin + dispersants

A3 1%wt CNT			
A4 1%wt CNT			
A5 1%wt CNT			
A6 2,5 %wt CNT			
A7 2,5%wt CNT			

Key aspects:

viscosity;

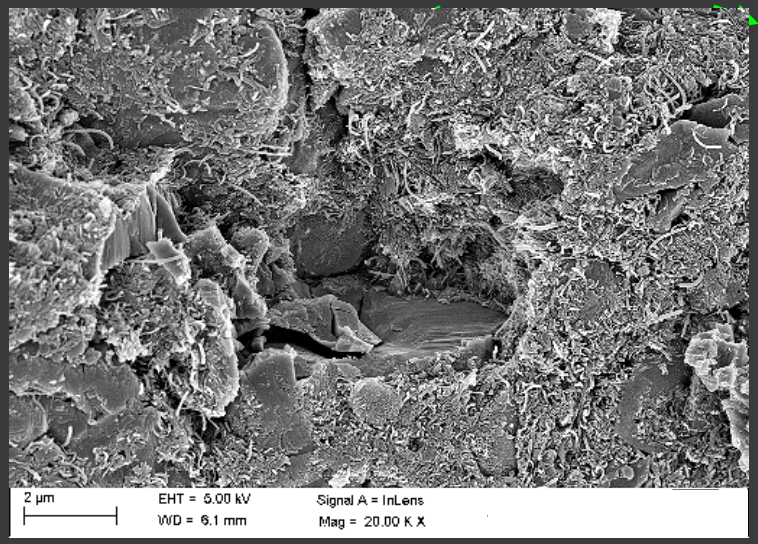
dispersant chemistry;

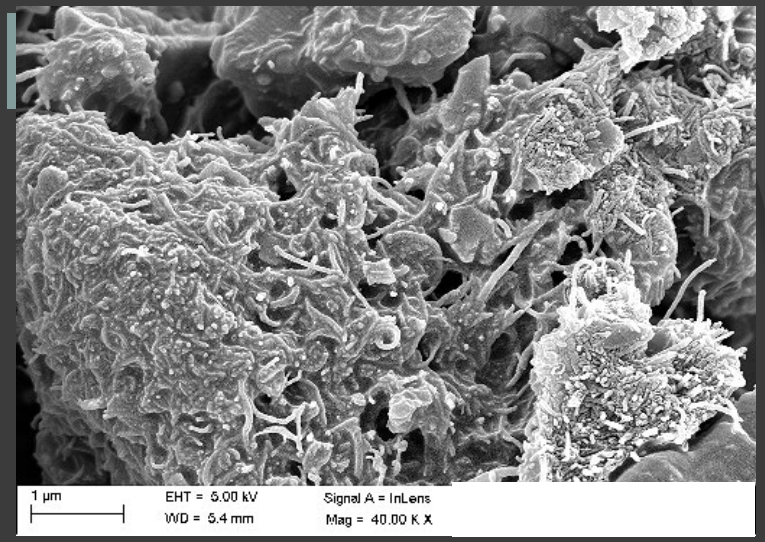
temperature control;

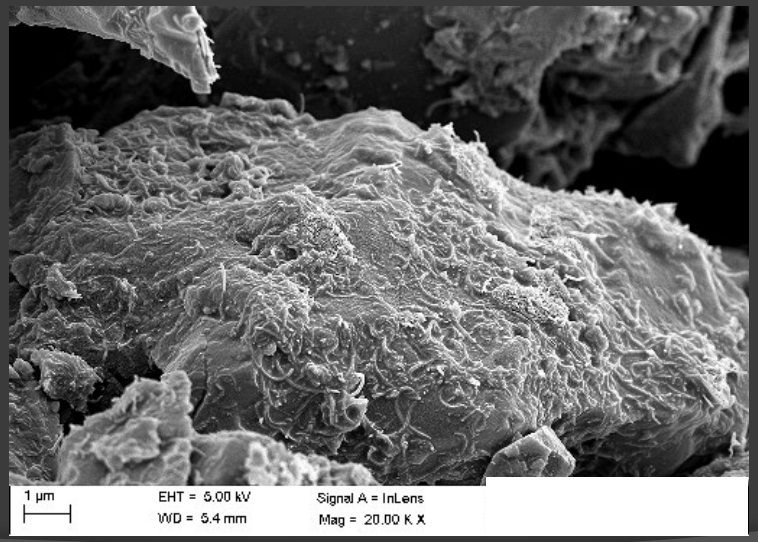
& mixing equipment

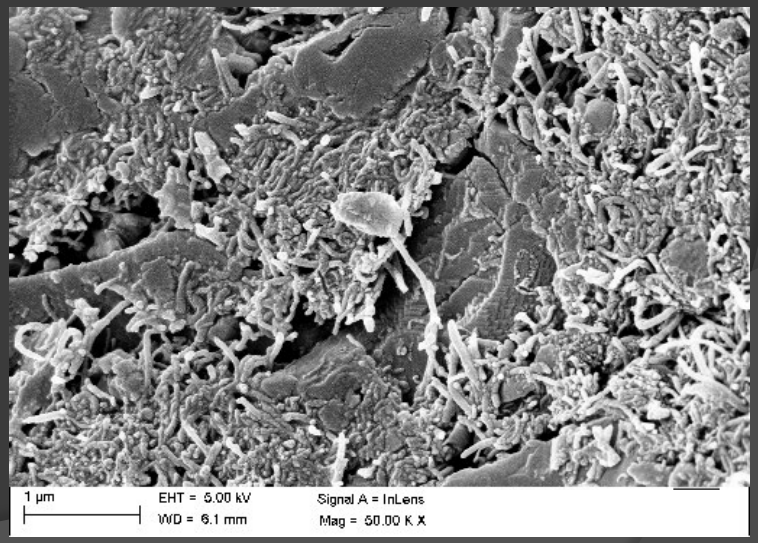
CNT Dispersed in Phenolic Resin

CNTs in binder



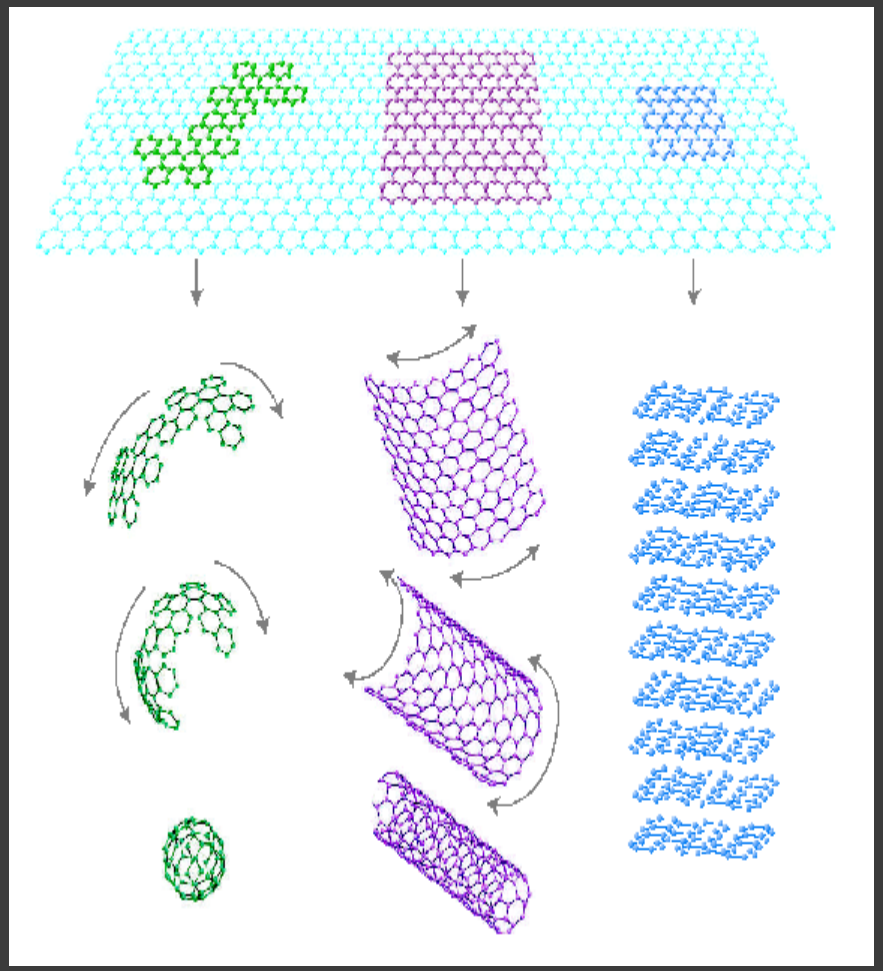






Thanks to Dr. Rafael G. de Sá

Graphene



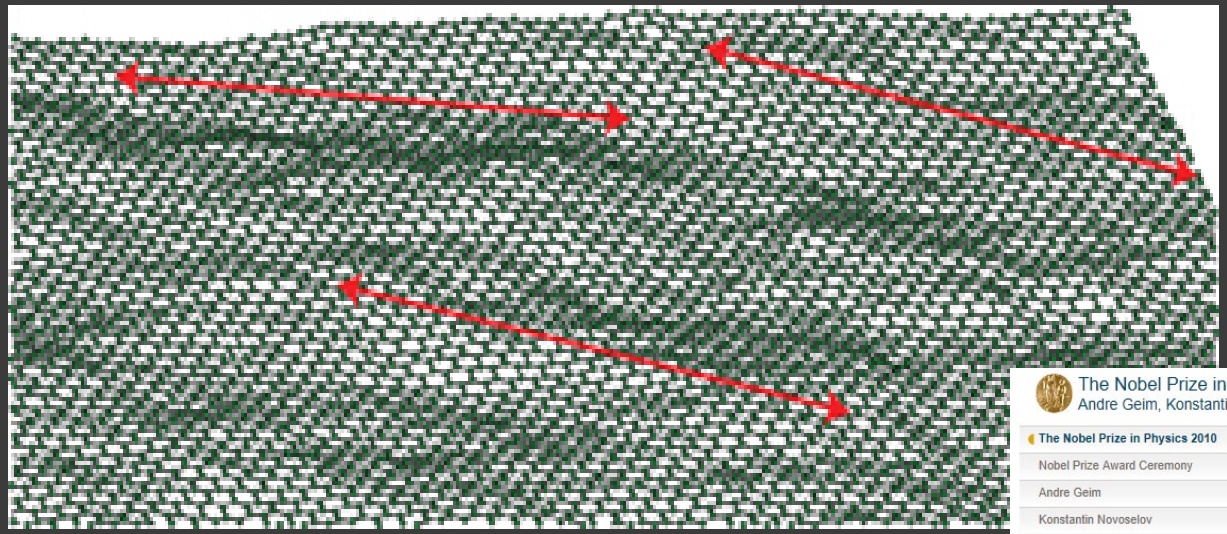
Graphene

Grafite

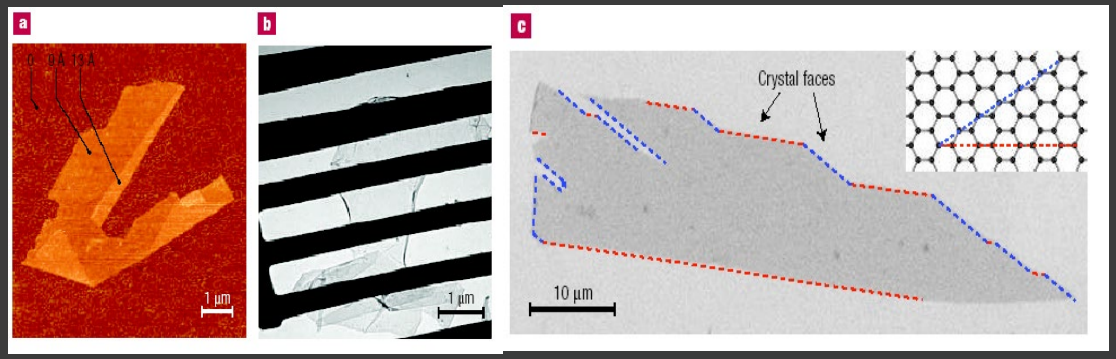
Fulerenos

Nanotubos

The stability of graphene 2D? ... Came from the surface curvature !!



Red size:
~800 nm



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010
Nobel Prize Award Ceremony
Andre Geim
Konstantin Novoselov


Photo: U. Montan
Andre Geim

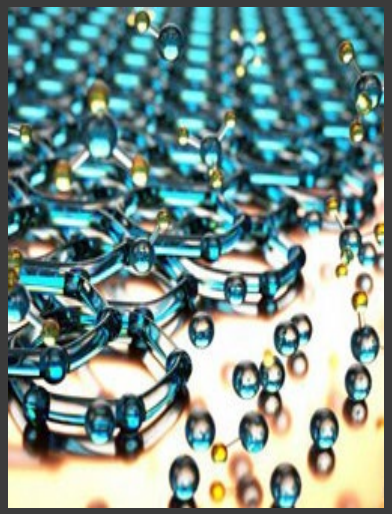

Photo: U. Montan
Konstantin Novoselov

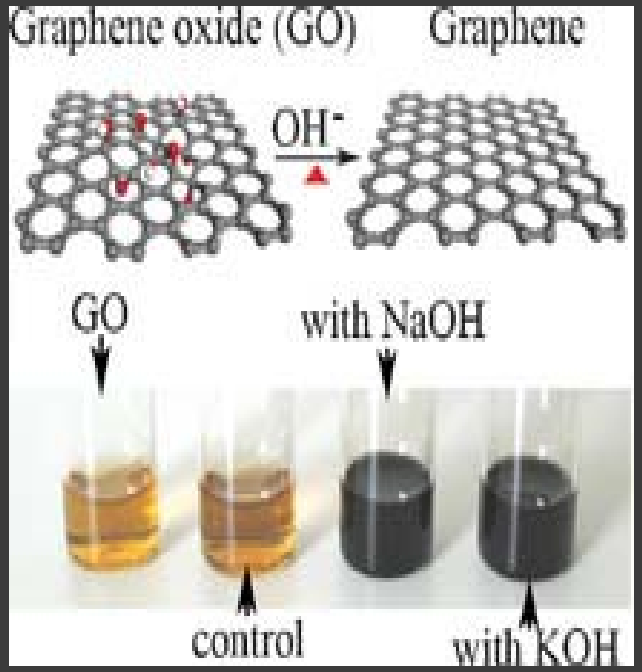
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

http://www.nature.com/nmat/journal/v6/n11/fig_tab/nmat2011_F1.html#figure-title

A. K. Geim & K. S. Novoselov. The rise of graphene. ***Nature Materials Vol 6*** 183-191 (March 2007)

Graphene synthesis



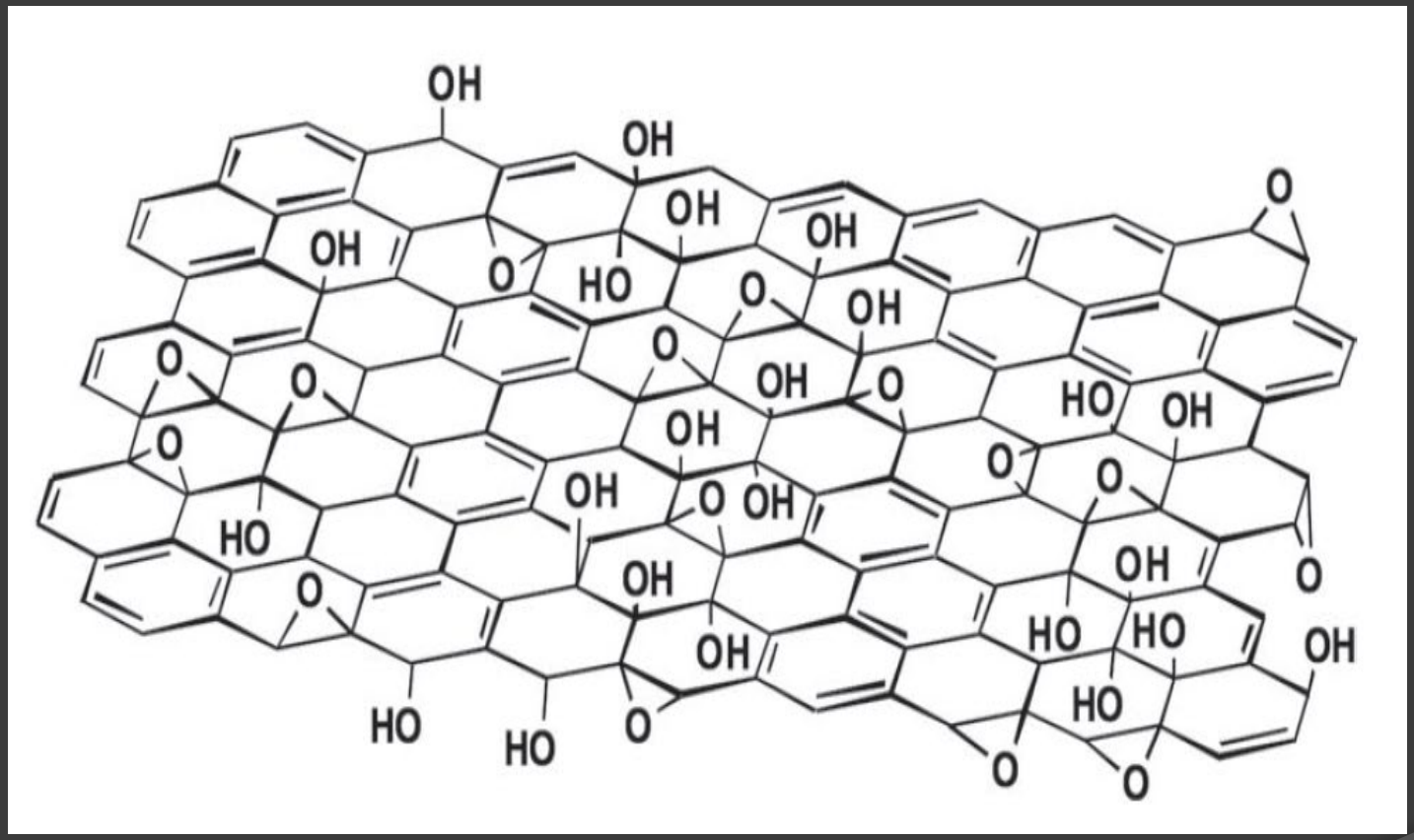


1) Exfoliação mecânica
2) Exfoliação química
3) CVD (sobre cobre)
4) Remoção do silício do carbeto de silício

Fan, X., Peng, W., Li, Y., Li, X., Wang, S., Zhang, G. and Zhang, F. (2008), Deoxygenation of Exfoliated Graphite Oxide under Alkaline Conditions: A Green Route to Graphene Preparation. Advanced Materials, 20: 4490–4493

Sais de potássio: inflamabilidade ao GO

GO chemical model

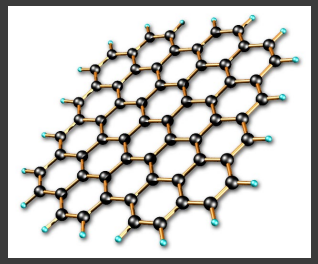


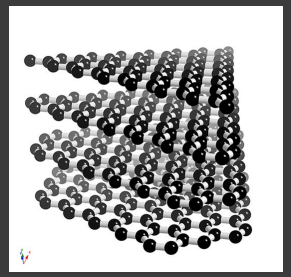
Lerf-Klinowski model

Chem. Phys. Lett., 1998, 287, 53–56

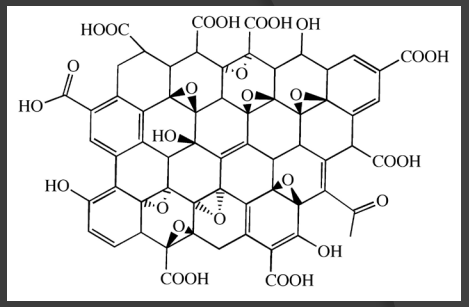
Graphene & GO

Natural Flake graphite





Exfoliated Graphite
-Chemical
-Thermochemical



Schematic of GO monolayer

Strong acids, nitrides, perchlorates, alkaline neutralization, etc...

-Graphene oxide (-OH, COO, COOH, etc...)

- **S**ingle-atom-thick sheet of carbon with oxygen containing functional groups decorating its basal plane and edges sites
-Water soluble/monolayer (hydrophilic)
-Widely used as precursor for graphene synthesis
-Area/mass: 2650 m^2/g

where ρ ~ 1.8 g/cm³ (GO density)
d ~ 0.42 nm (GO thickness)

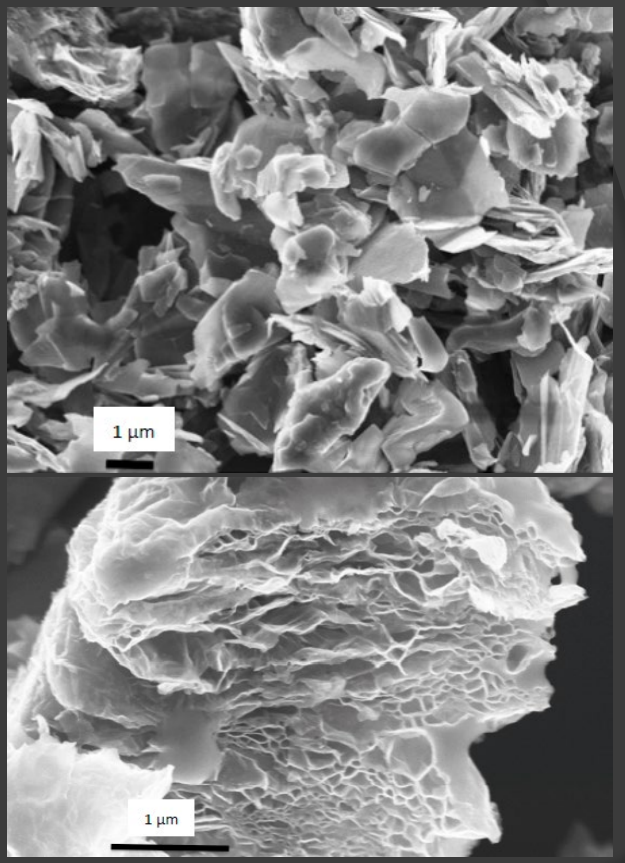
$$\frac{Area}{mass} = \frac{2LW}{\rho LWd} = \frac{2}{\rho d}$$

Dinkin et al. Nature 448(26),2007

New opportunities for castables, resin integration, pre-mixing, etc.

New opportunities for Improvements on thermal conduction of carbon-oxides refractories.

Material/Chemical	Chemical application	Decomposition enthalpy, [Jg^{-1}]
GO	Precursor for rGO	1,400-1,700
Benzoyl peroxide	Industrial chemical	1,602
Cumene hydroperoxide	Industrial chemical	1,219
Ethyl oleate ozonide	Industrial chemical	684
Trinitrotoluene (TNT)	Monopropellant and explosive	2,305
Hydrazine	Monopropellant and explosive	2,980-4,906
Nitrocellulose	Monopropellant and explosive	1,900-2,400

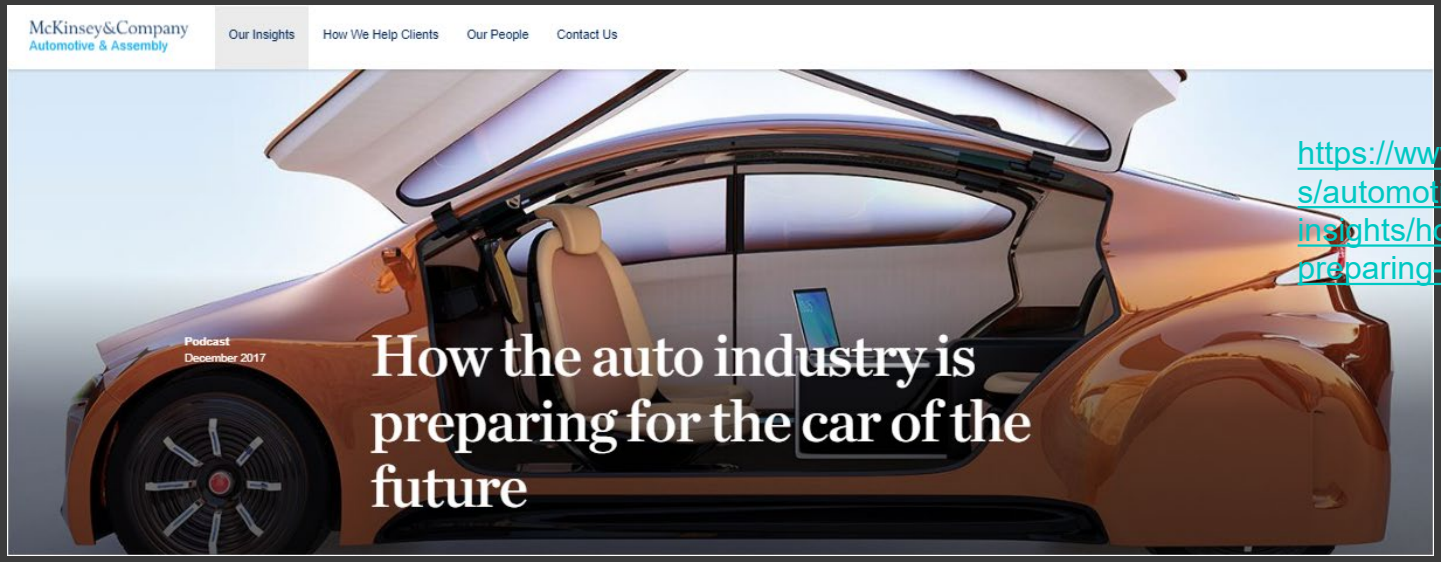


Qiu et al., Explosive thermal reduction of graphene oxide-based materials: Mechanism and safety implications, Carbon 72; 215-223, 2014.

r-GO before and after thermal explosive reduction.

Thanks to Dr. Indrek Kulaots and Yang Qiu

Automotive technology ...
And the future of automobilist industry



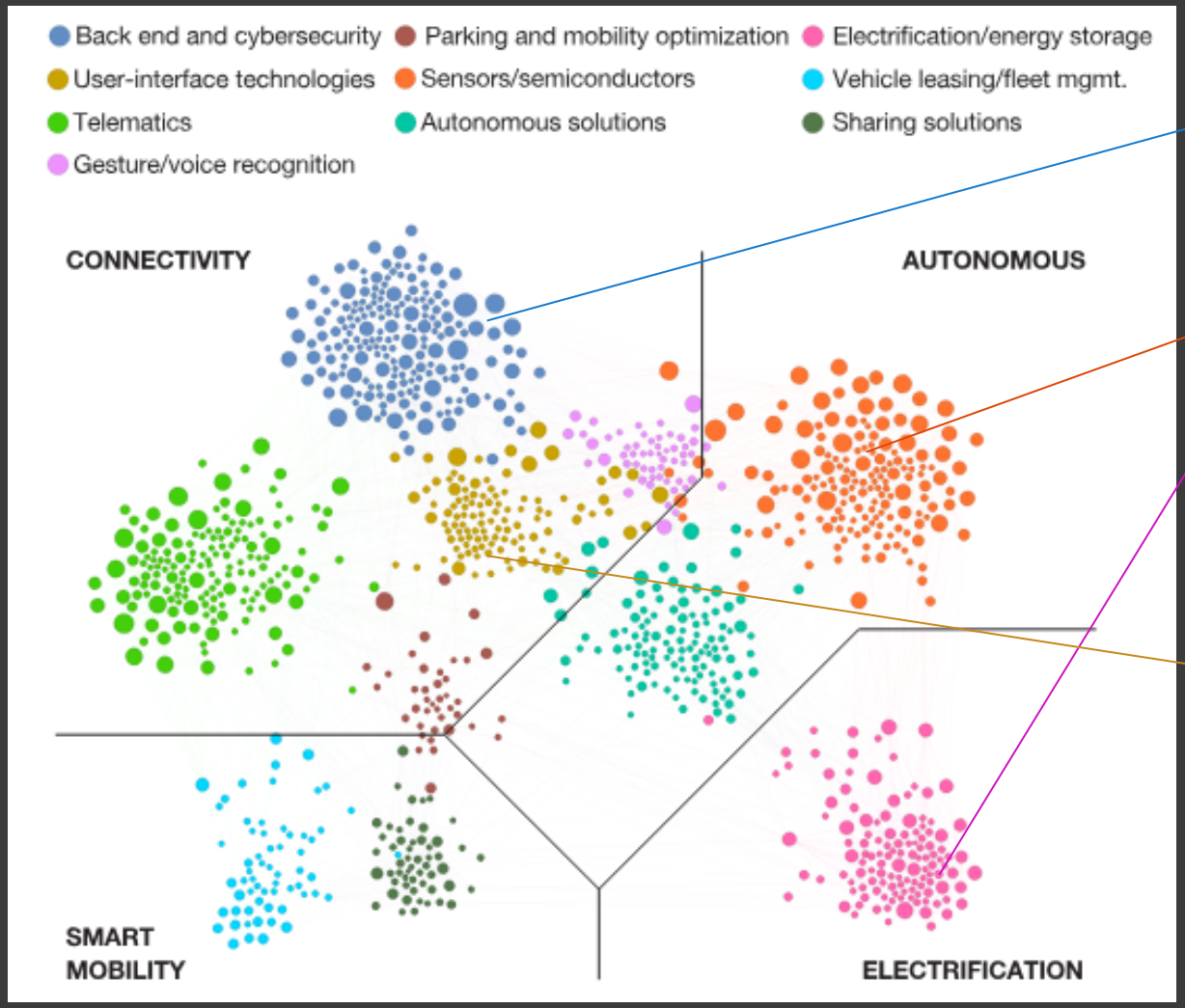
https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/how-the-auto-industry-is-preparing-for-the-car-of-the-future

Autonomous / Connectivity / Electrification / Smart Mobility

- Fuel economy & autonomy: Better engine + Better electronic control systems
- Combustion engines are changing to hybrids and electrical (Flexibility)
- Smart and software control
- Self driving technologies: more specialized + fast control (sensors & software)
- Safety

Hardware & Materials

Software



New materials:

Reliable materials:
- **electromagnetic shield;**
- **fast devices;**

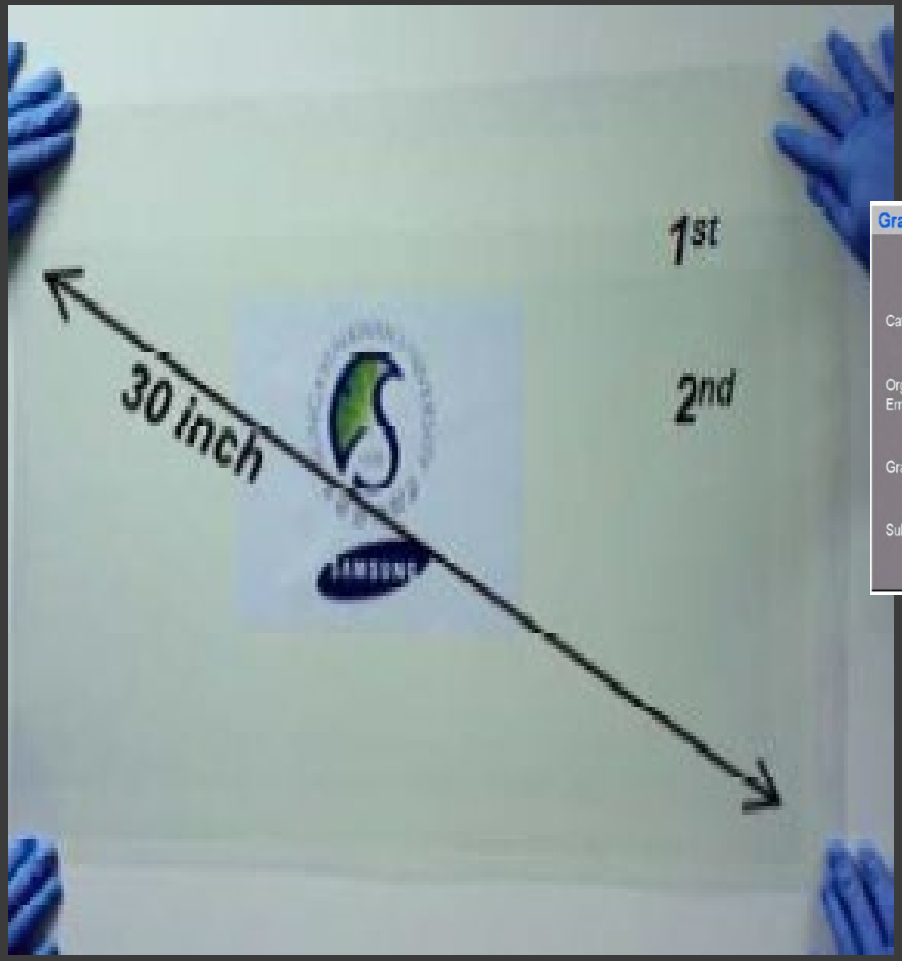
New sensors:

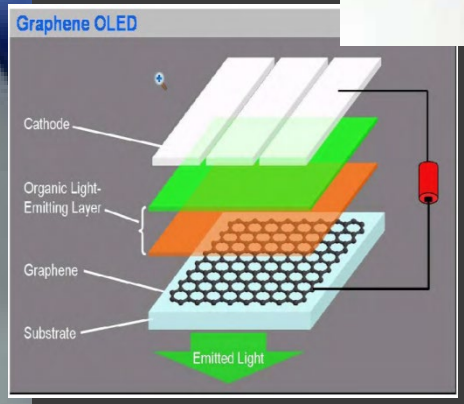
Recovery energy, autonomy & power:
- batteries & supercapacitors;

Smart coatings: touch technology
- smart glass (Man-Machine interfaces)

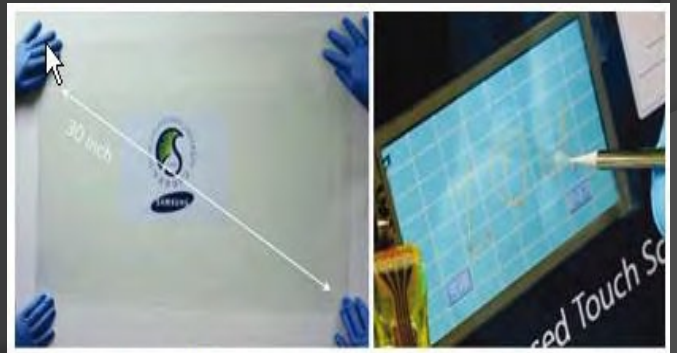
(nano)-carbon based materials !

Touch capacity and sensibility



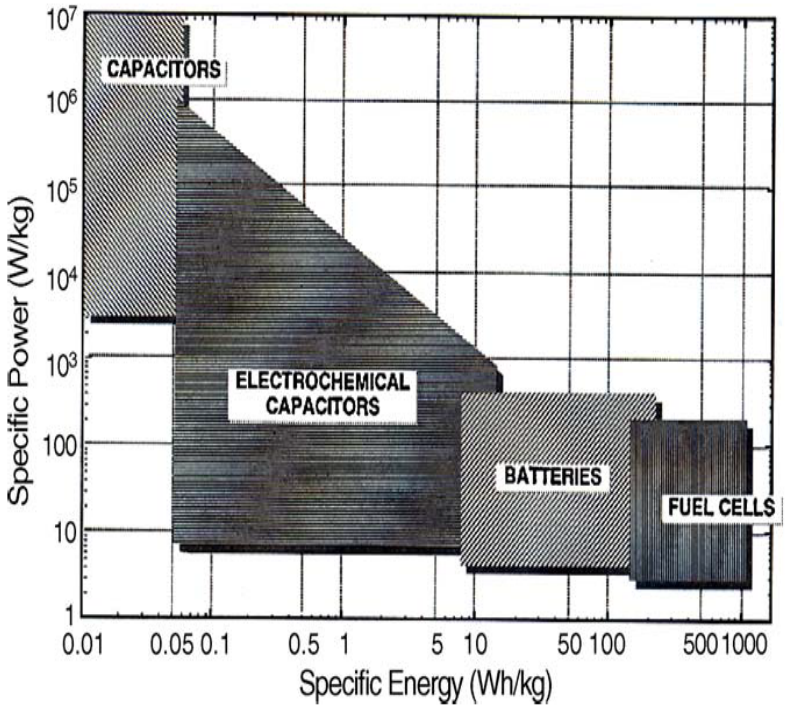


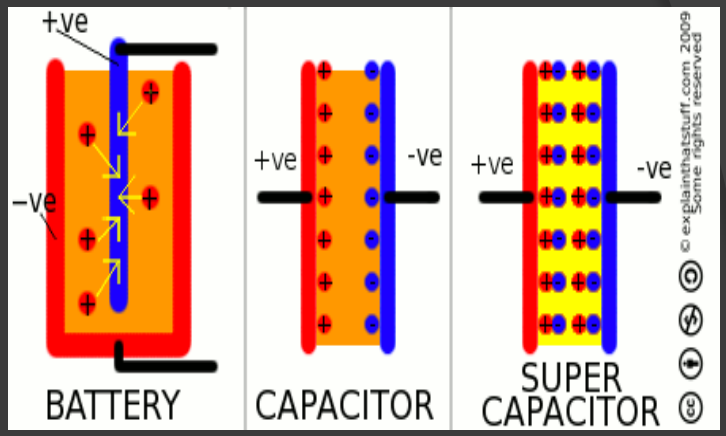
Carbon-Based Supercapacitors Produced by Activation of Graphene
Science ***24 June 2011: 1537-1541.DOI:10.1126/science.1200770***



Left: A transparent graphene film transferred on a 35-inch PET sheet. Right: A graphene-based touchscreen panel connected to a computer

Batteries, capacitors and supercapacitors





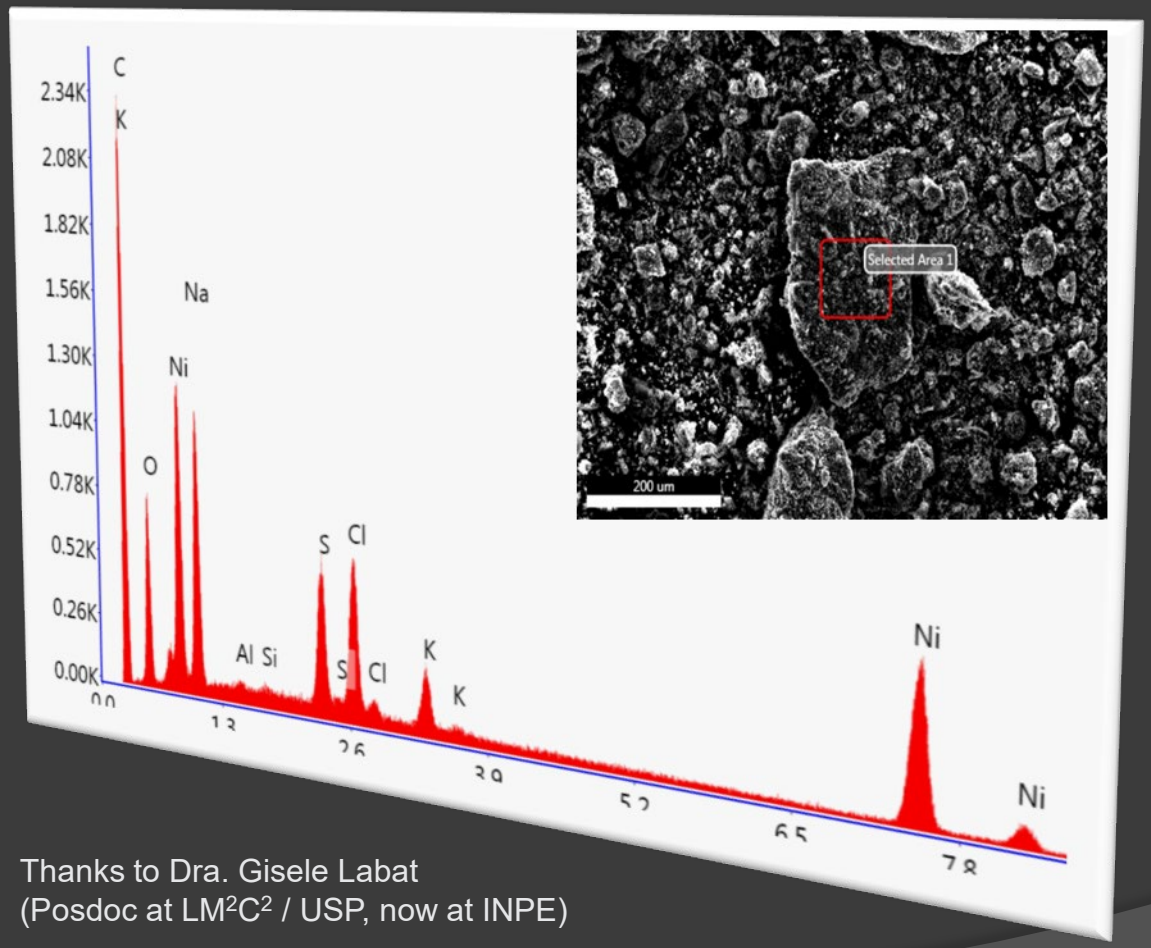
Energy density

Power density

Characteristic	Electrolytic capacitor	Carbon supercapacitor	Battery
Specific energy ($Wh\,kg^{-1}$)	<0.1	1–10	10–100
Specific power ($W\,kg^{-1}$)	≫10000	500–10000	<1000
Discharge time	10^{-6} to 10^{-3} s	s to min	0.3–3 h
Charging time	10^{-6} to 10^{-3} s	s to min	1–5 h
Charge/discharge efficiency (%)	~100	85–98	70–85
Cycle-life (cycles)	Infinite	>500000	~1000
Max. voltage (V_{max}) determinants	Dielectric thickness and strength	Electrode and electrolyte stability window	Thermodynamics of phase reactions
Charge stored determinants	Electrode area and dielectric	Electrode microstructure and electrolyte	Active mass and thermodynamics

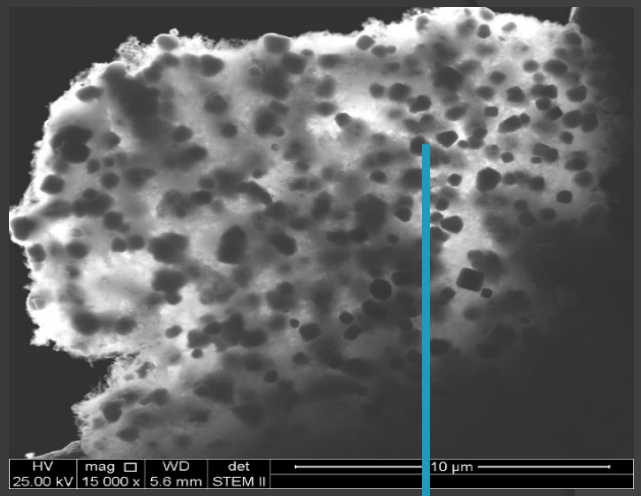
Catalyst support (Fuel Cells)

SEM + EDX

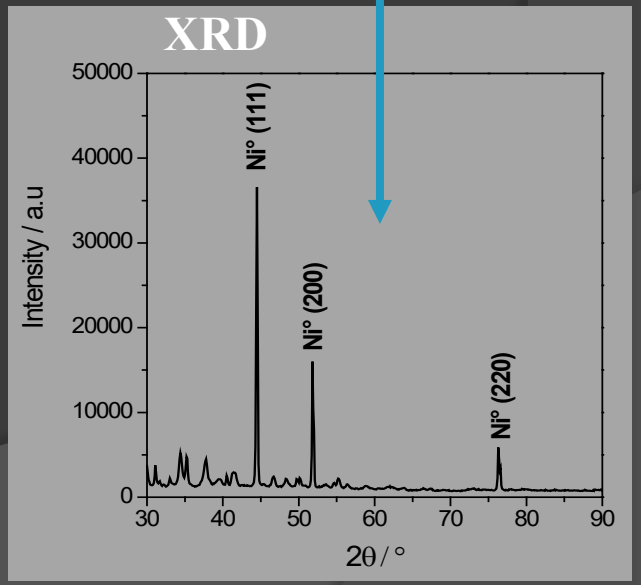


Thanks to Dra. Gisele Labat
(Posdoc at LM²C² / USP, now at INPE)

STEM

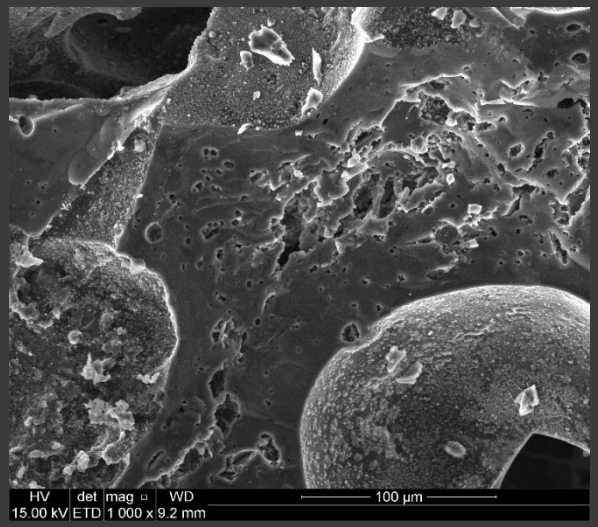


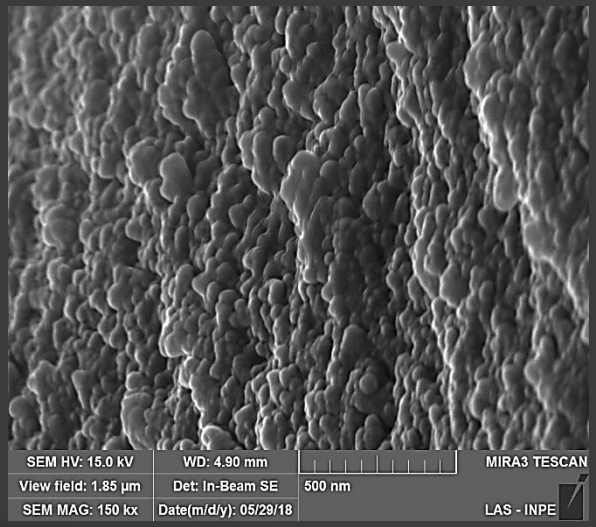
XRD

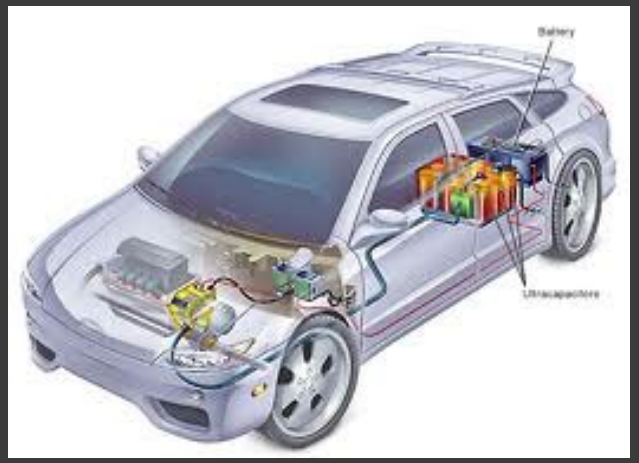


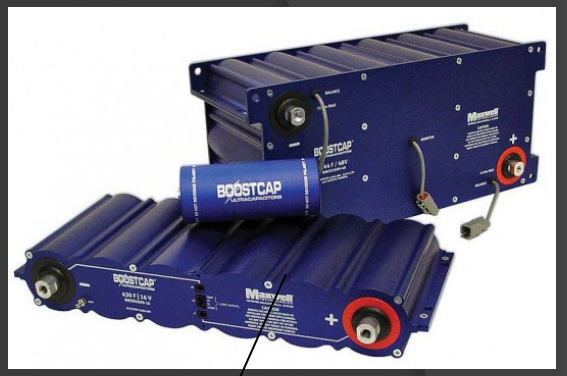
Energy storage (supercapacitors)

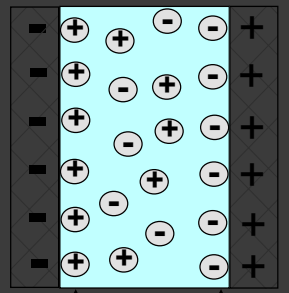
Structured Activated Carbon from Black liquor-lignin carbonization











Electric double-layer

First results

80 – 110 F/g

*Commercial activated carbon (28-100 F/g)
Carbon xerogels from resorcinol (10-200 F/g)

*Obreja *et al*, International Review of Electrical Engineering, 2010 5(1):272-282

Carbon application and future

Smart glasses

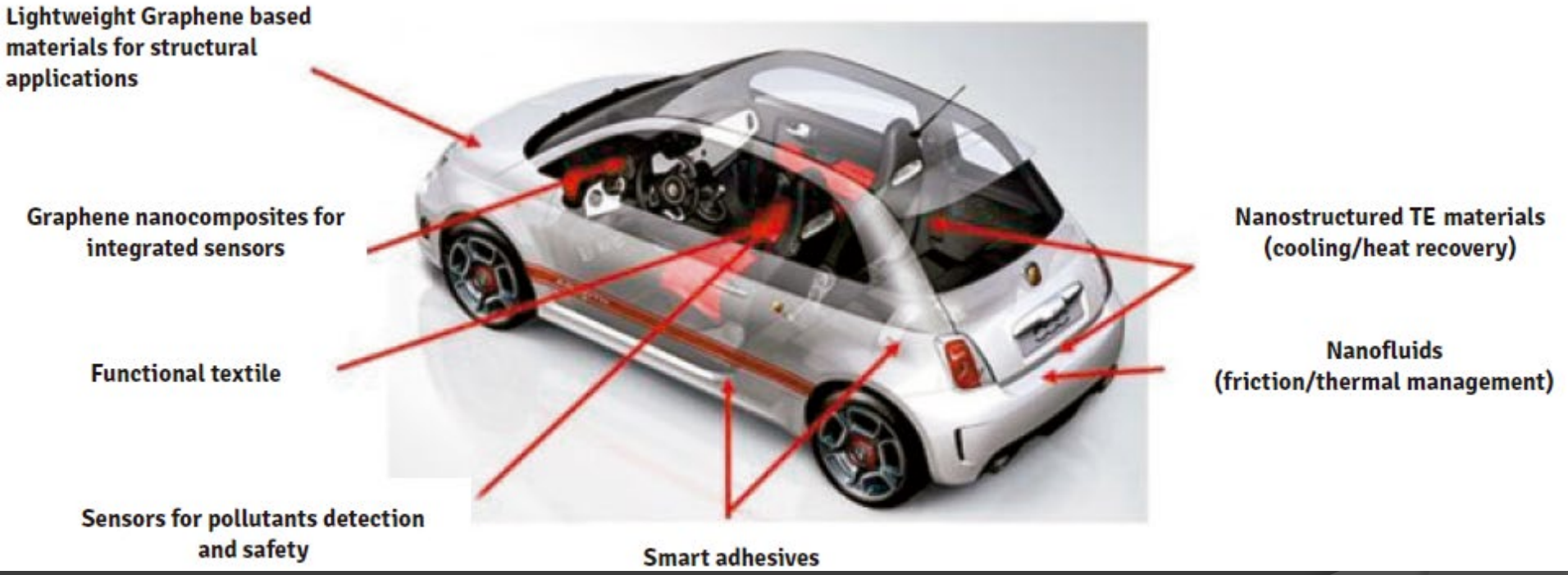
Energy storage

Structural composites

Sensors

Graphene in automotive industry ...

Lightweight graphene based components by Fiat

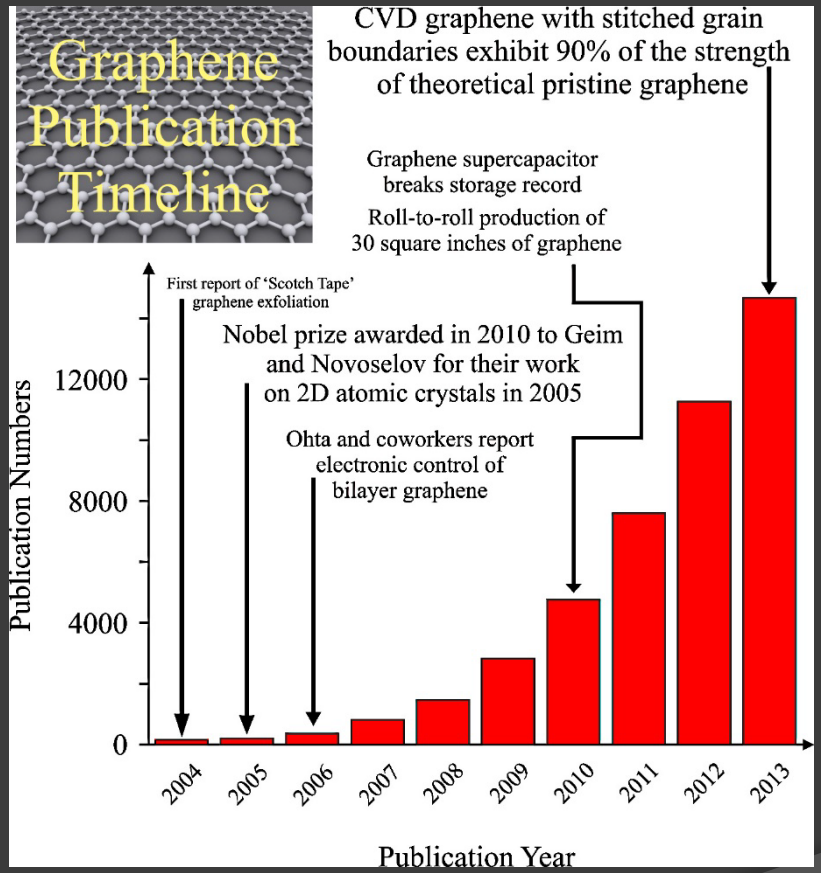


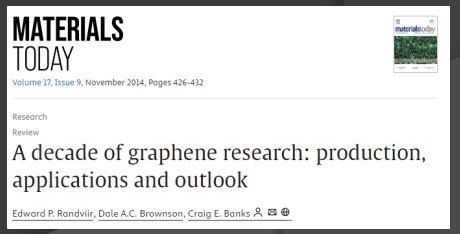
Graphene ... 10 years ago

10 year ago …

Applications:

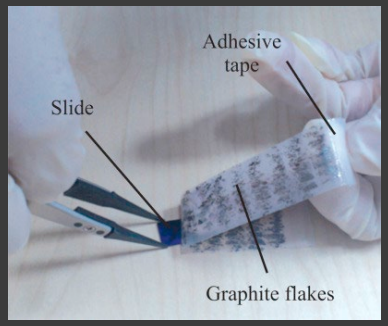
- High speed electronics
- Data storage
- LCD smart windows and OLED displays
- Supercapacitors
- Solar cells
- Electrochemical sensing





https://www.sciencedirect.com/science/article/pii/S1369702114002144

Graphene ... now



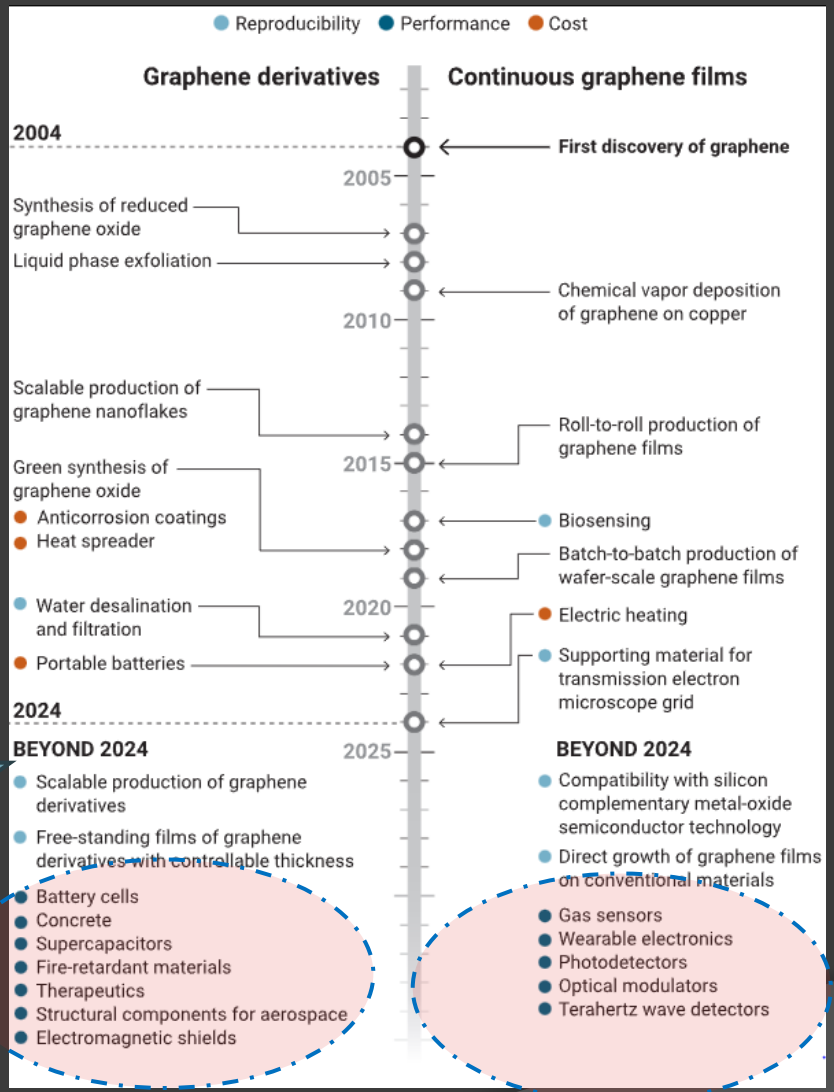
R. Van Noorden
Nature, 483 (2012), p. S32

Creativity, Ingenuity, Serendipity

~ 10 years of hard work on science & technology approach to scale up and industrial ramp-up !

New materials and increasing market share of graphene-based products … ~20 years !

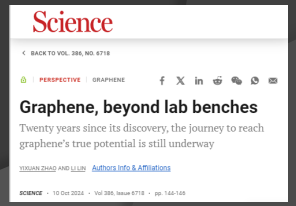
Wide range of new products compared 10 years ago !



Now …

From lab to the market …

- Universities
- Center of technology for industrial applications
- Spin offs
- Start ups
- New companies
- Big techs …



https://www.science.org/doi/10.1126/science.ads4149

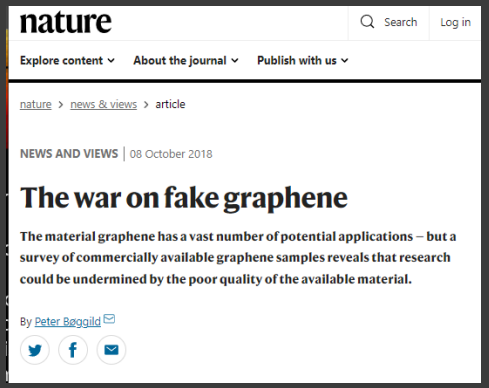
What changed …
(after 20 years of graphene discovery !)

From lab to industry: new products and new production capability ! …. Lowering price …new applications !

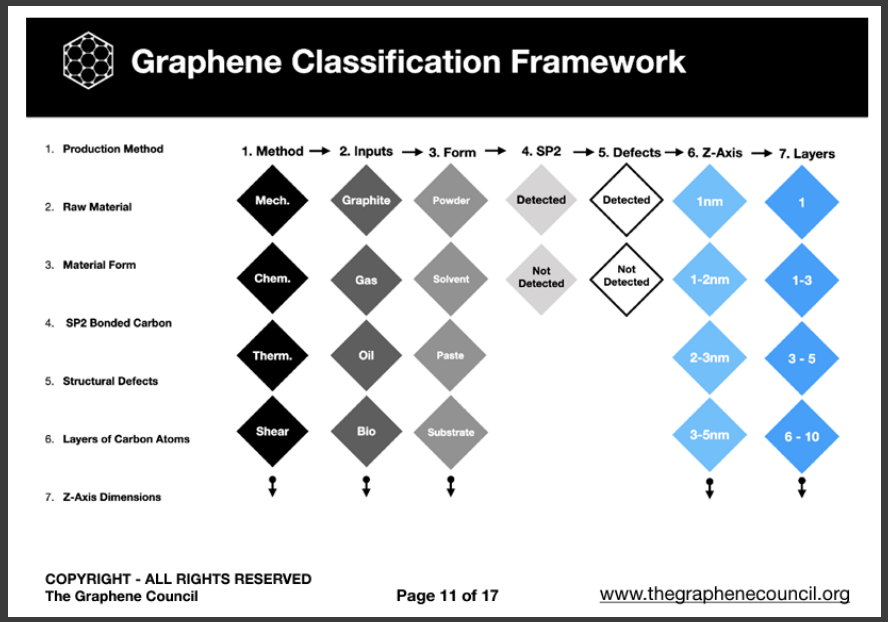
Understanding of graphene properties & applications … “New graphene” material types/specifications

From pristine monolayers materials to dozen of “graphene family” materials …mono, bi, last then 10 layers, more than 10 layers, nano graphite , oxidized graphite (many oxidation grades), GO, reduced GO, and so on !

https://www.nature.com/articles/d41586-018-06939-4



The Graphene Council
Research, Development and Application



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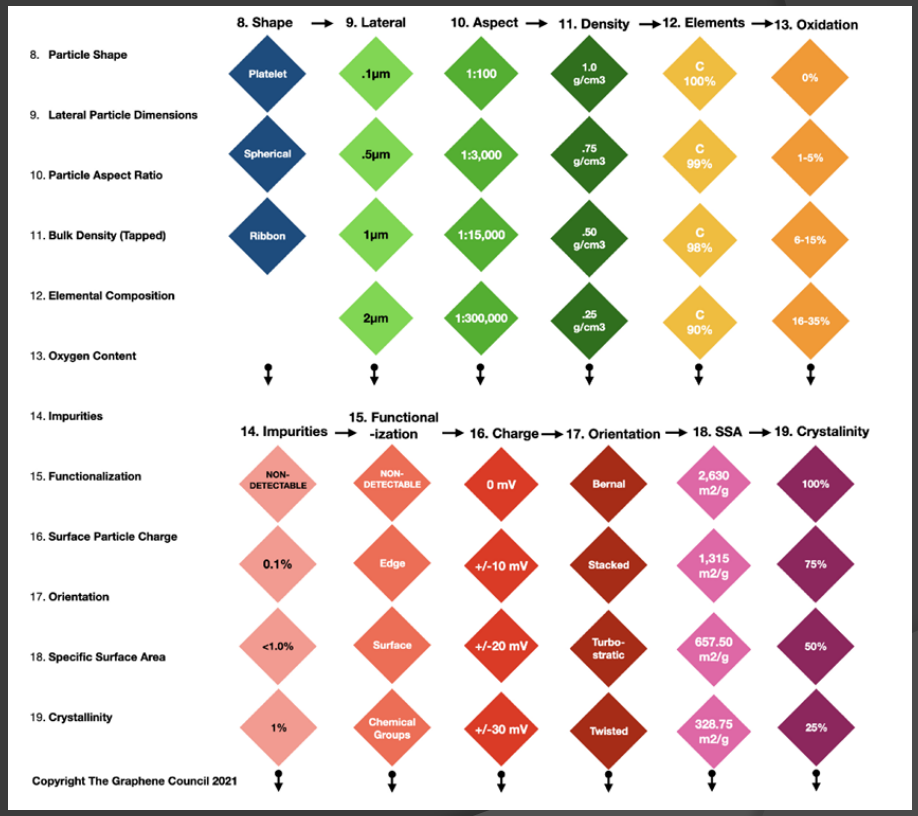
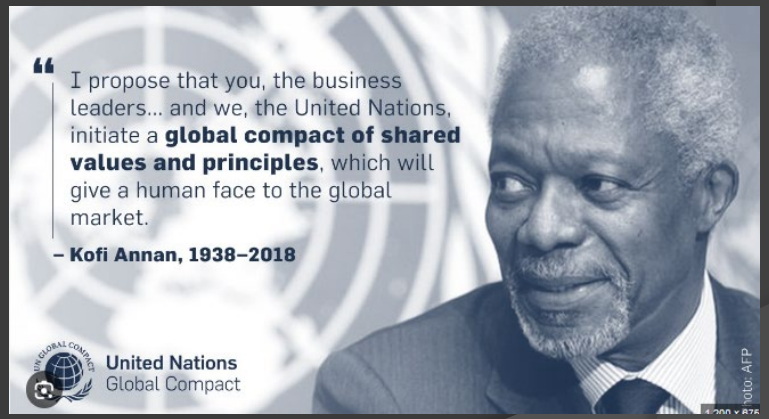


ESG : Environmental, Social & Governance

ESG is a 20 years old concept !

It's came from UN (Kofi Annan UN secretary general)



2004 report titled **"Who Cares Wins"**,

ESG give to the business:

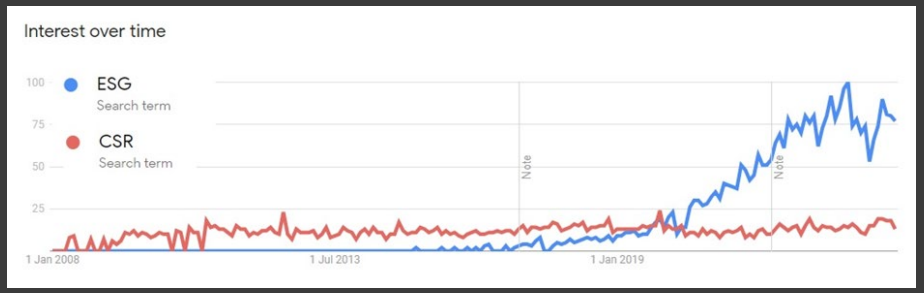
- Clear PURPOSES
- LONG TERM VISION
- INTREGRATED VISION
- VISIBILITY

People & Community

Planet

Business performance

Companies that perform better about these issues can increase shareholder value



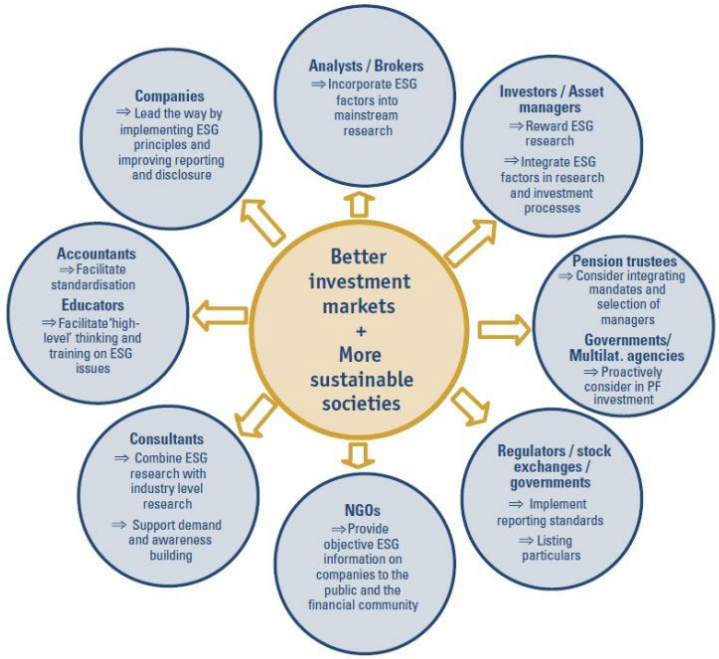
ESG: Environmental, Social & Governance
CSR: Corporate Social Responsibility

Financial Sector Initiative
Who Cares Wins

Graphical summary of key recommendations

Overall goals:

- Stronger and more resilient financial markets
- Contribution to sustainable development
- Awareness and mutual understanding of involved stakeholders
- Improved trust in financial institutions



S - Social

- Race/Colour Diversity
- Women in Management
- Inclusion
- Health
- Equity
- Training
- Safety
- Inequality

G - Governance

- Government/Regulation
- Corporate Governance
- ESG Investments
- Innovation
- Compliance
- Risk Management
- Accountability

E - Environmental

- Environmental Education and Carbon Market
- Reforestation
- Renewable Energies
- Decarbonization
- Climate Effects
- Recycling
- Environmental Preservation
- Energy Efficiency

The balance between E & S. The key point of G!

Remember … ESG came from a vision of UN working together of most influential finance companies, bank and market people, such like: ABN AMRO Bank N.V. AXA, Banco do Brasil , Sarasin & Partners LLP, BNP Paribas, Credit Suisse, Deutsche Bank, Goldman Sachs HSBC , Morgan Stanley , UBS and Westpac with more than 500 representatives from business and civil society !

Governance is the key point to evaluate, control and give vision and directions for the ESG platform. It is the balance for a good implementation of S (Social) and E (Environmental) programs based on accountability, performance, measurements, goals and achievements !

Without metrics and vision, it is impossible to implement a coherent ESG program!

SUSTAINABLE DEVELOPMENT GOALS

https://www.un.org/sustainabledevelopment/news/communications-material/

New plastic composites: high mechanical properties, less material use, recycling technologies based on graphene materials: chemical adsorbents for metal recovery

SUSTAINABLE DEVELOPMENT GOALS

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

11 SUSTAINABLE CITIES AND COMMUNITIES

New electronic materials: Sensors, resistive memories, smart screens, etc.

3 GOOD HEALTH AND WELL-BEING

New medical treatments: graphene-based scaffolds (bone replacement with stein cell technology, graphene tissue engineering,
Soft 3D printed human tissue, etc.

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

8 DECENT WORK AND ECONOMIC GROWTH

New materials: OPC (ordinary Portland cement) with graphene

New companies, tech business, new products, new materials & Applications

ESG – SDG & Graphene Applications

High efficiency membranes for water filtration and treatment

Graphene for wind blades composites
Graphene based solar cells
(…)

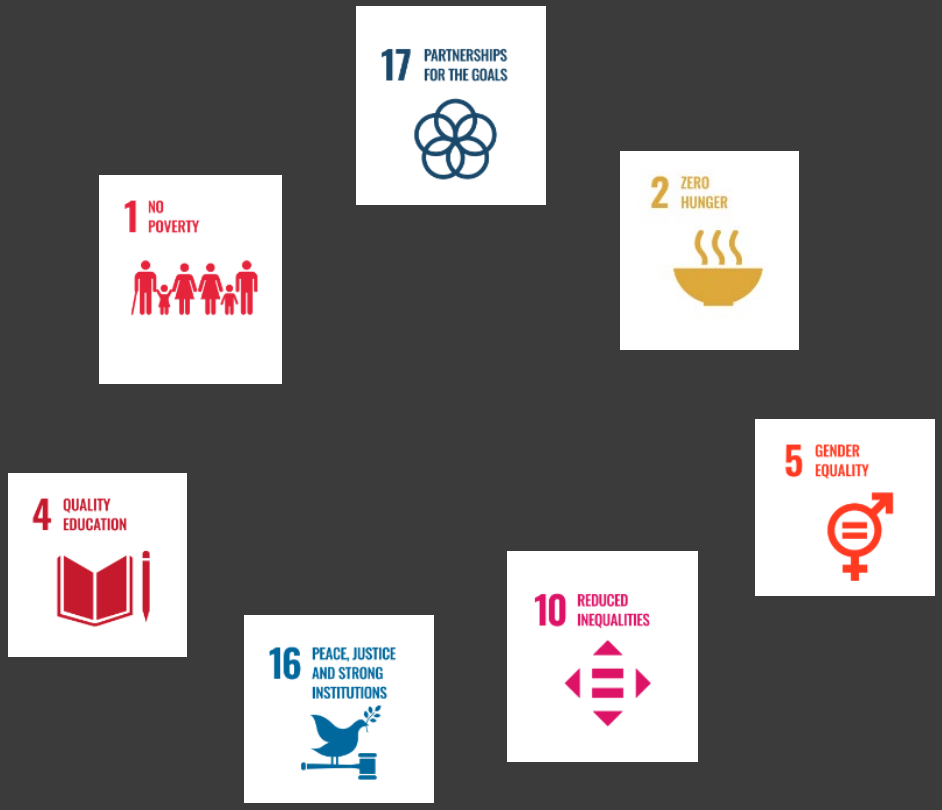
Low carbon footprint technologies: solar cells, New batteries, carbon capture & storage, Synthetic photosynthesis, …

Graphene for pollutes removing & treatment , soil fertilizing, …

Water pollution control technologies

And here ? … It is about good **Leadership & Vision** !

… Simple like that !!!!!



Communication
Ethics
Responsibility
Empathy
Actions
Integrity

There is only one Earth ! …

You should know by now …

2013: Earth as seen through Saturn's rings (Cassini)

Image Credit: NASA/JPL-Caltech/Space Science Institute

Earth as seen from Saturn's rings looks like a blue luminescent carbon dot ! ! !

There is no plan B !

Image Credit: NASA/Goddard/Arizona State University

2015: Earthrise 2.0 (Lunar Reconnaissance Orbiter)

https://explorer1.jpl.nasa.gov/galleries/earth-from-space/

TLMC 5

Quinto Taller Latinoamericano de Materiales de Carbono

Thanks
धन्यवाद
Aloha
Merci
Gracias
谢谢
Danke
Grazie
Teşekkürler
Dziękuję
Спасибо (Spasibo)
Obrigado

Let´s talk with us about carbon ! https://abcarb.org.br/

ABCarb

Education changes people
People change the world !

Brazilian Carbon Association / ABCARB – President
Senior Member of AIChE – American Institute of Chemical Engineers
Strategic Decision and Risk Management Certificate Professional (Stanford University)
Visiting Scholar at Brown University (LEHN / School of Engineering)
Academic Visitor at Imperial College London (Department of Materials)
Postdoctoral Fellow at the University of Sheffield/UK (Department of Materials Science & Engineering)
Ph.D in Materials and Metallurgical Engineering from University of São Paulo (USP)
MBA in Environment Technologies & Management from Polytechnic School of Engineering (POLI-USP)
Certified Safety Professional from Federal University of Minas Gerais (UFMG)
Metallurgical Engineer from Federal University of Minas Gerais (UFMG)