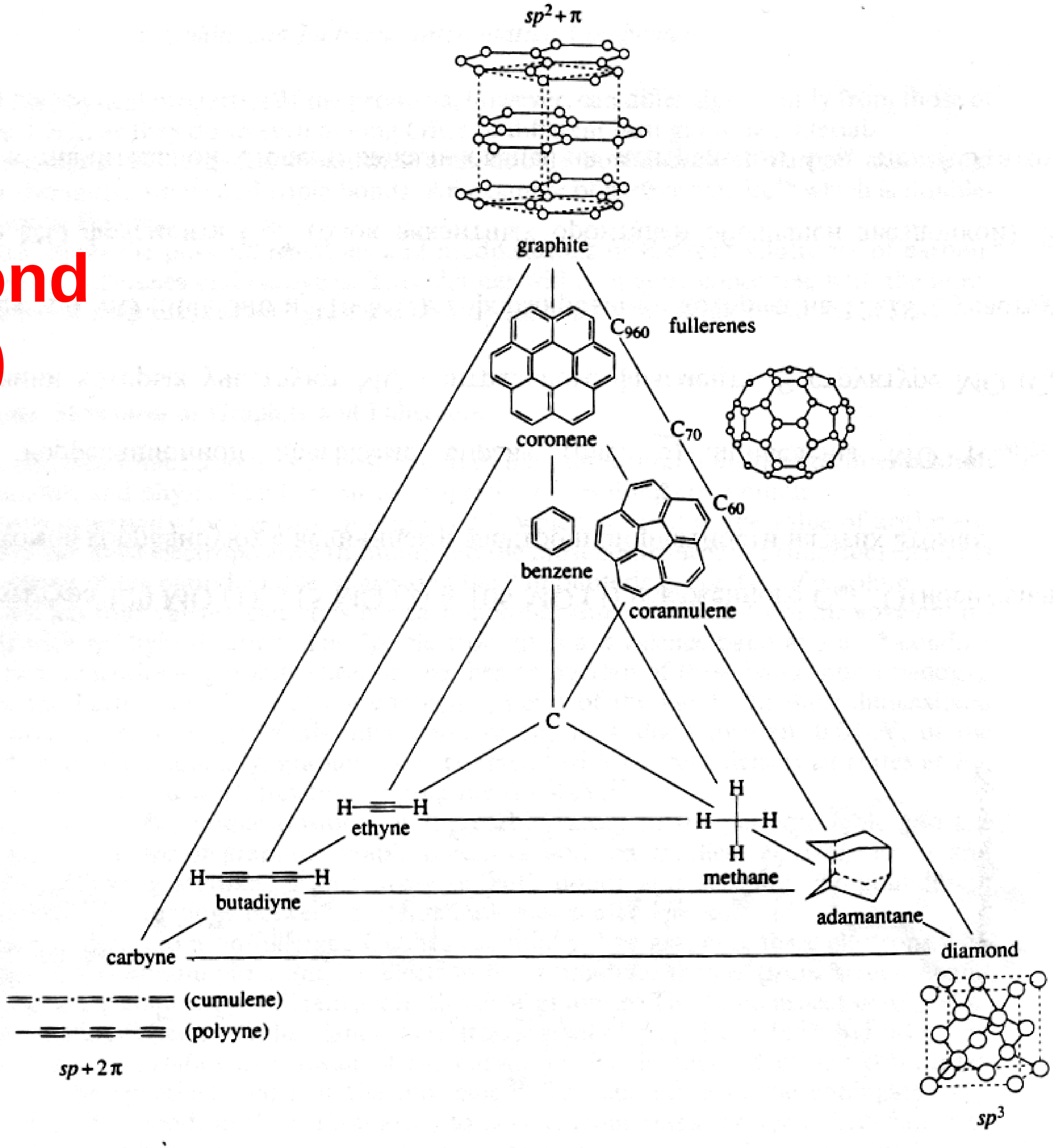
Carbon nanomaterials:

Fullerenes
Nanotubes
Graphenes
Nanodiamonds

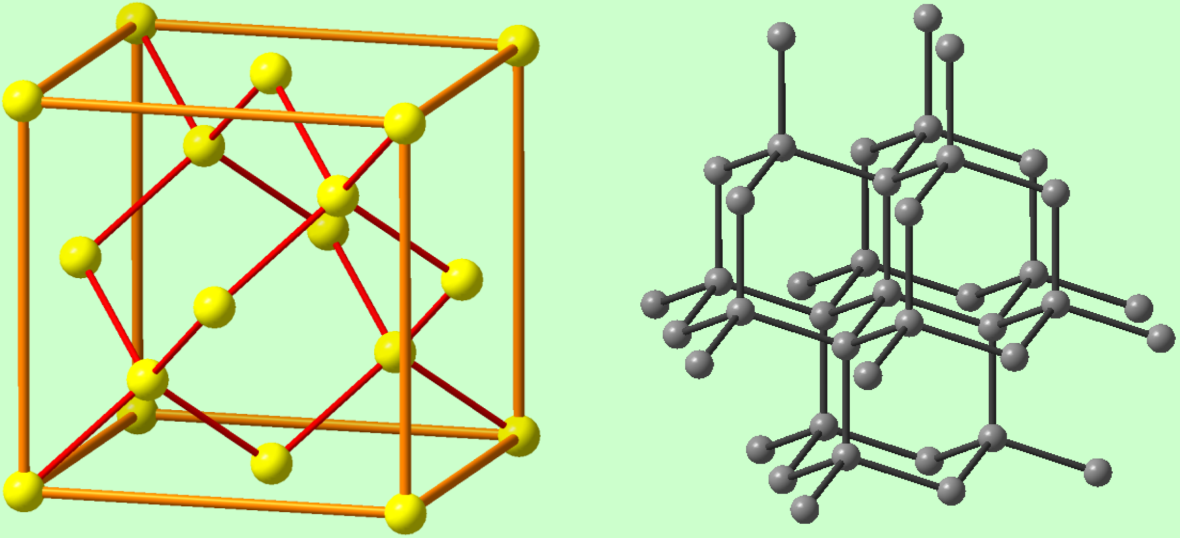
Carbon (chemical bond and forms)



Diamond
Synthesis, structure, properties

Diamond

Diamond – carbon modification with tetrahedral (*sp*^{3}) carbon atoms in the lattice



Crystal structure of the diamond

History

- 0000 - Known as a gemstone.
- 1796 - found to be composed of carbon.
- 1953 - synthesized in Sweden, the results were not published.
- 1955 - GE announces synthetic diamond synthesis.

~ 25 – 30 ton of diamonds are mined annually (SA, Russia, Australia, Canada)
~ 100 ton are synthesized

Properties

Density 3.5-3.53 g/cm3, refractive index n = 2.417

- Mechanical hardness ~98 Gpa (Mohs hardness 10)
- Compressive Strength > 110 GPa
- Highest bulk modulus- $1.2*10^{12}$ N/m^2
- Lowest Compressibility- $8.3*10^{-13}$ m^2/N
- Highest thermal conductivity- $2*10^3$ W/m/K
- Optically transparent from deep UV to far IR
- Good electrical insulator- R~10^{16} Ω
- Resistant to corrosion by acid or base
- Negative electron affinity

Stability

If graphite is more stable, then why don't diamond rings turn into graphite?

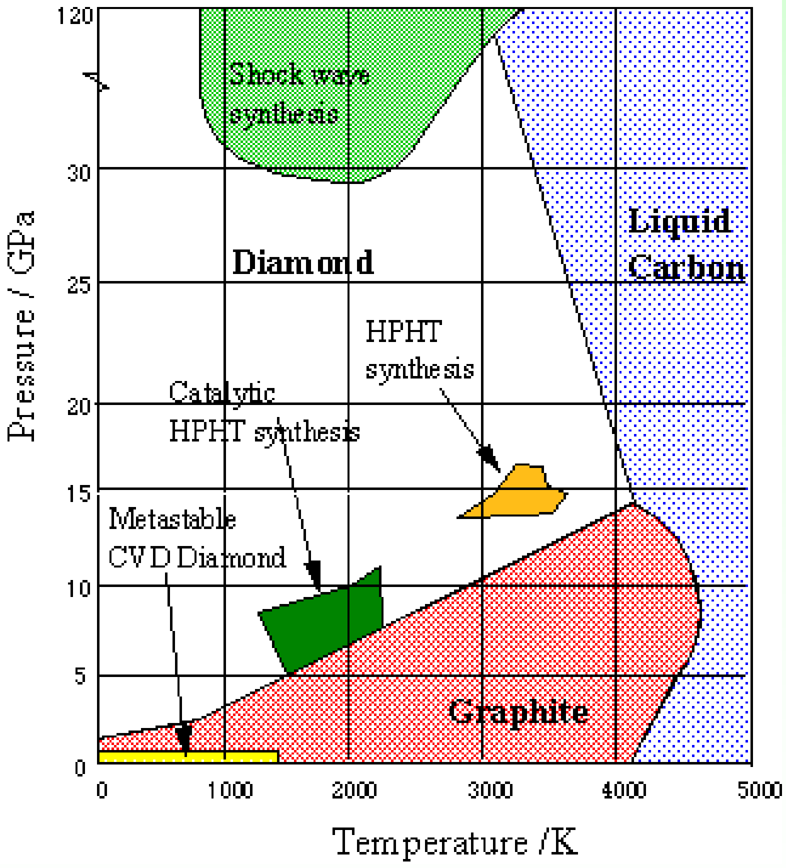
A diamond is formed deep inside the earth at extreme temperatures and pressures.

The activation energy for the transition reaction is almost the same as the energy of the diamond latticeю

Diamond is a metastable phase, which is defined as not thermodynamic, but kinetic stability.

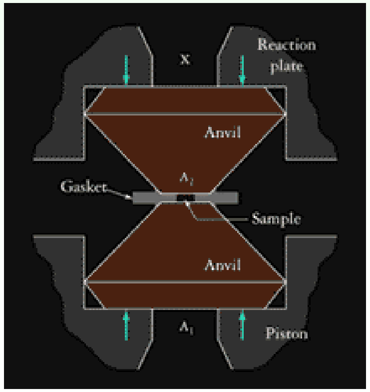
Carbon phase diagram

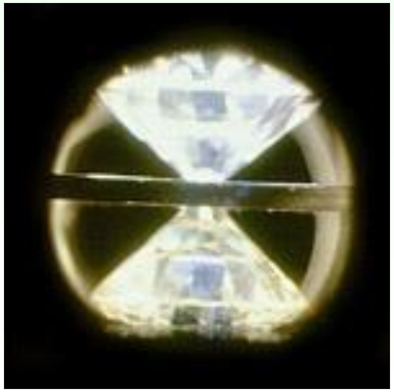
- Under normal conditions, a stable form of carbon is graphite.



Applications

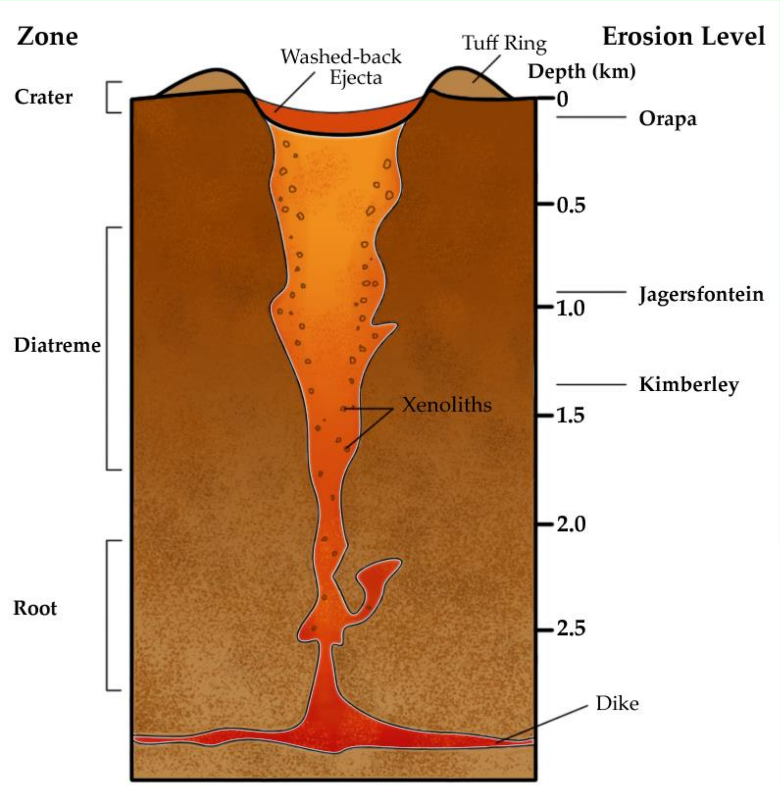
- Great abrasive.
- Windows for optical sensors. Used for infrared sensors of cruise missiles.
- Potentially useful semiconductor: band gap 5.4 eV.
- Low friction, no wear - mechanical hinges and bearings
- High pressure cells (RAMAN, X-ray)
- Cutting tool (but not iron!)
- Heat sink in electronic chips.





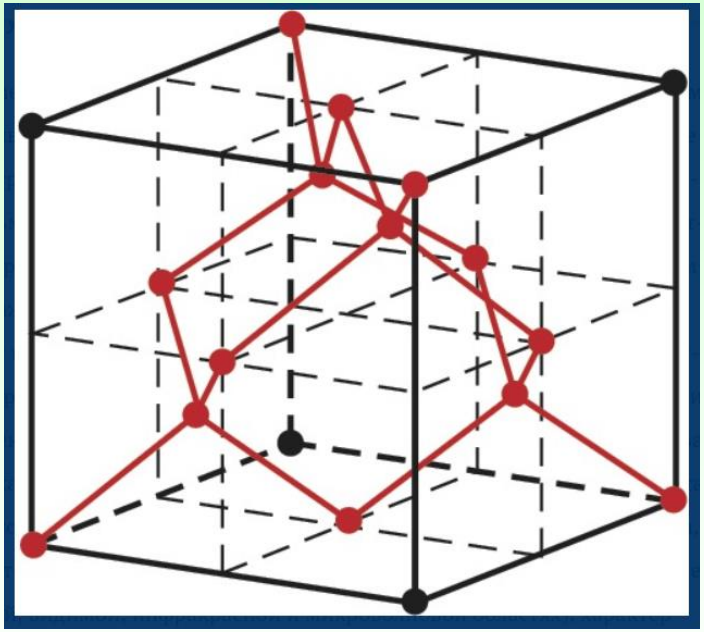
P ~ 4.5 million atmospheres

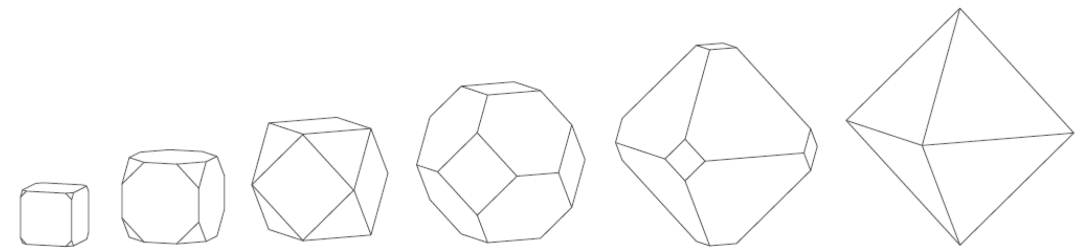
Synthesis of diamonds in nature



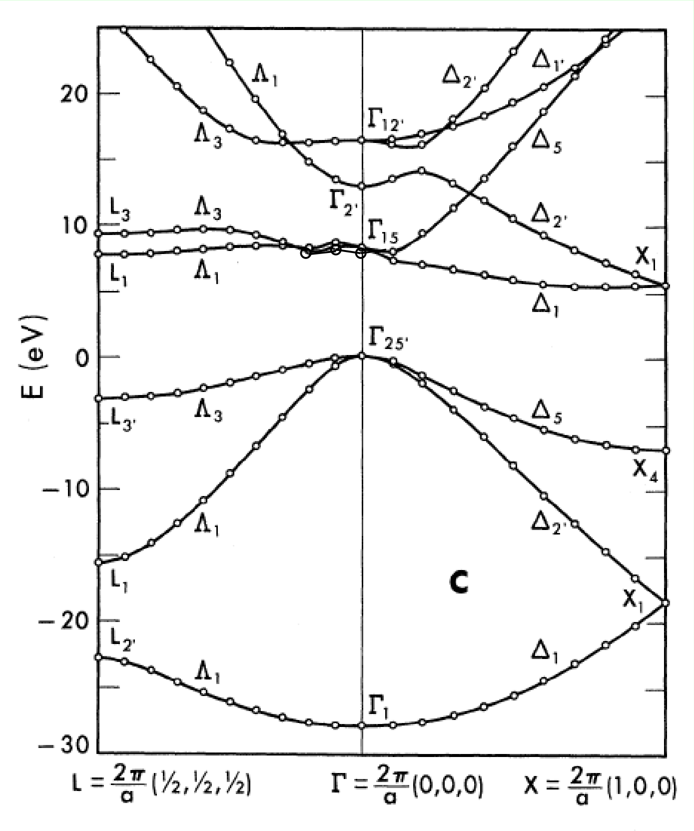
The age of deposits up to 1 billion years.

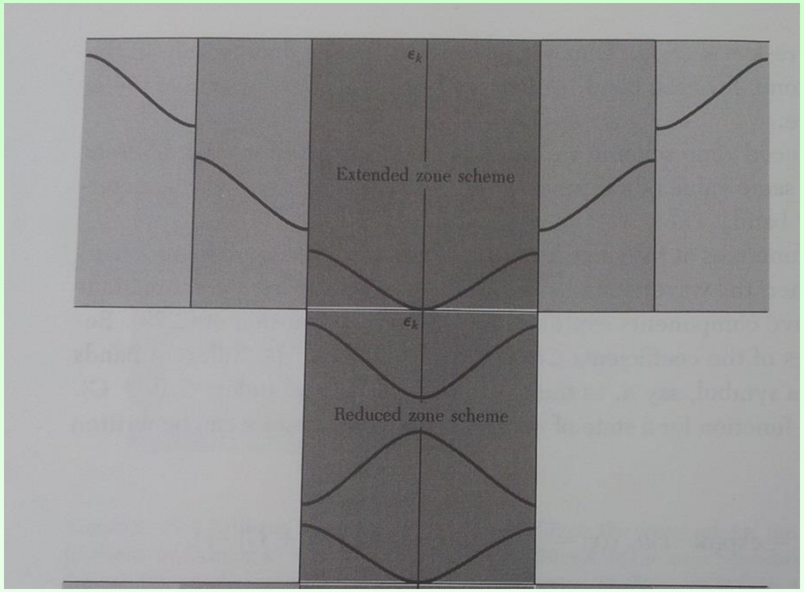
300 kg per year?





Diamond band structure





This bandstructure is simple considering there are ~10^{22} atoms!

Newton's 2nd law:
Force = mass × acceleration

For an electron in a crystal:
Force = *effective* mass × acceleration

Effective mass, $m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$

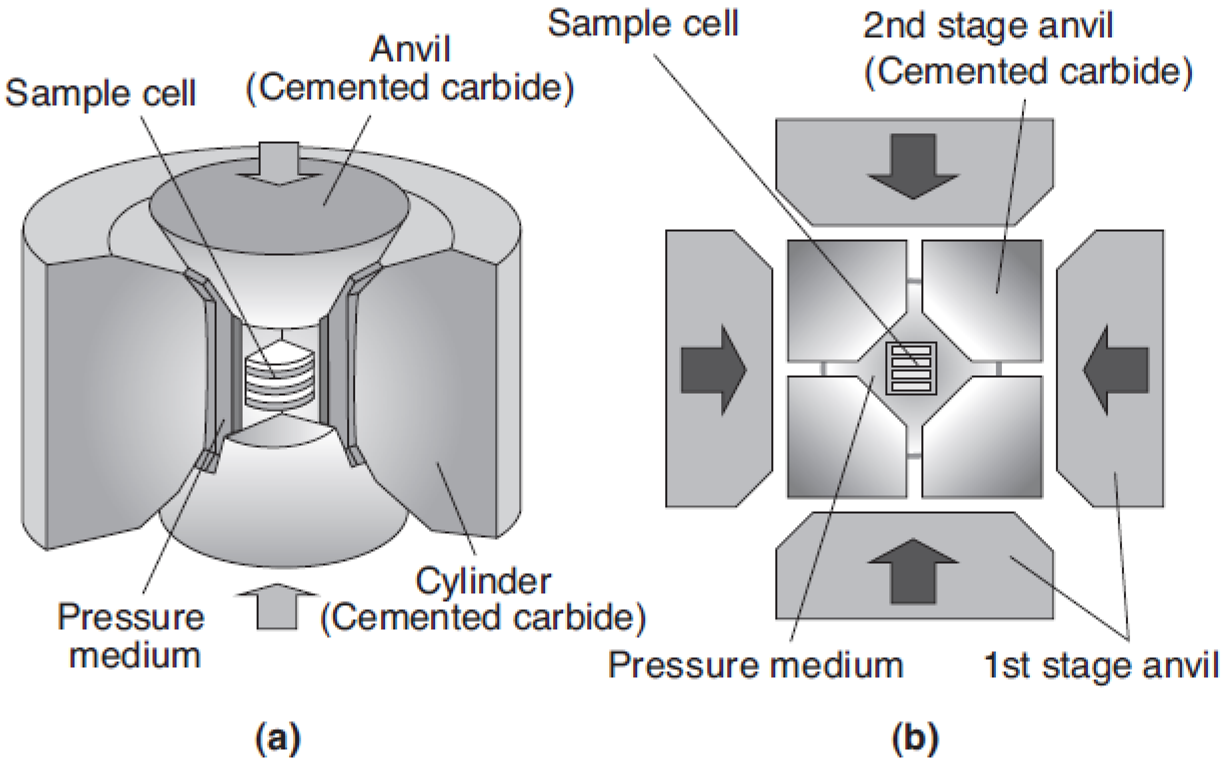
Natural diamonds (morphology)

Diamond "Leonid Vasilyev" weighing 54.05 carats.

Diamond crystal (6 mm) with the inclusion of garnet. Yakutia.

Octahedra, rhombododecahedra, and cubes, as well as their combinations, prevail. Sometimes there are rounded surfaces. Often, diamond crystals grow together, or grow into each other.

Diamond growth under pressure



Institute of Geology and Mineralogy SB RAS

Prof. Yu.N. Palyanov

P = 60.000 atm, temperature 1500 °C.

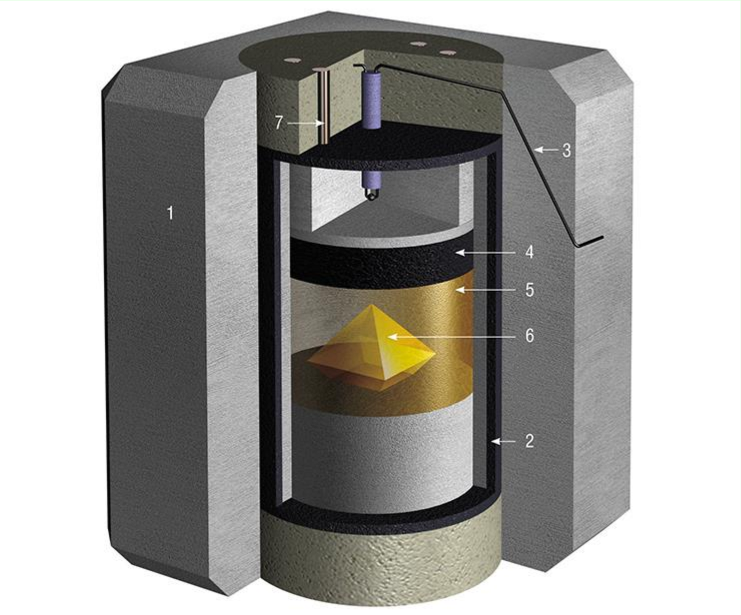


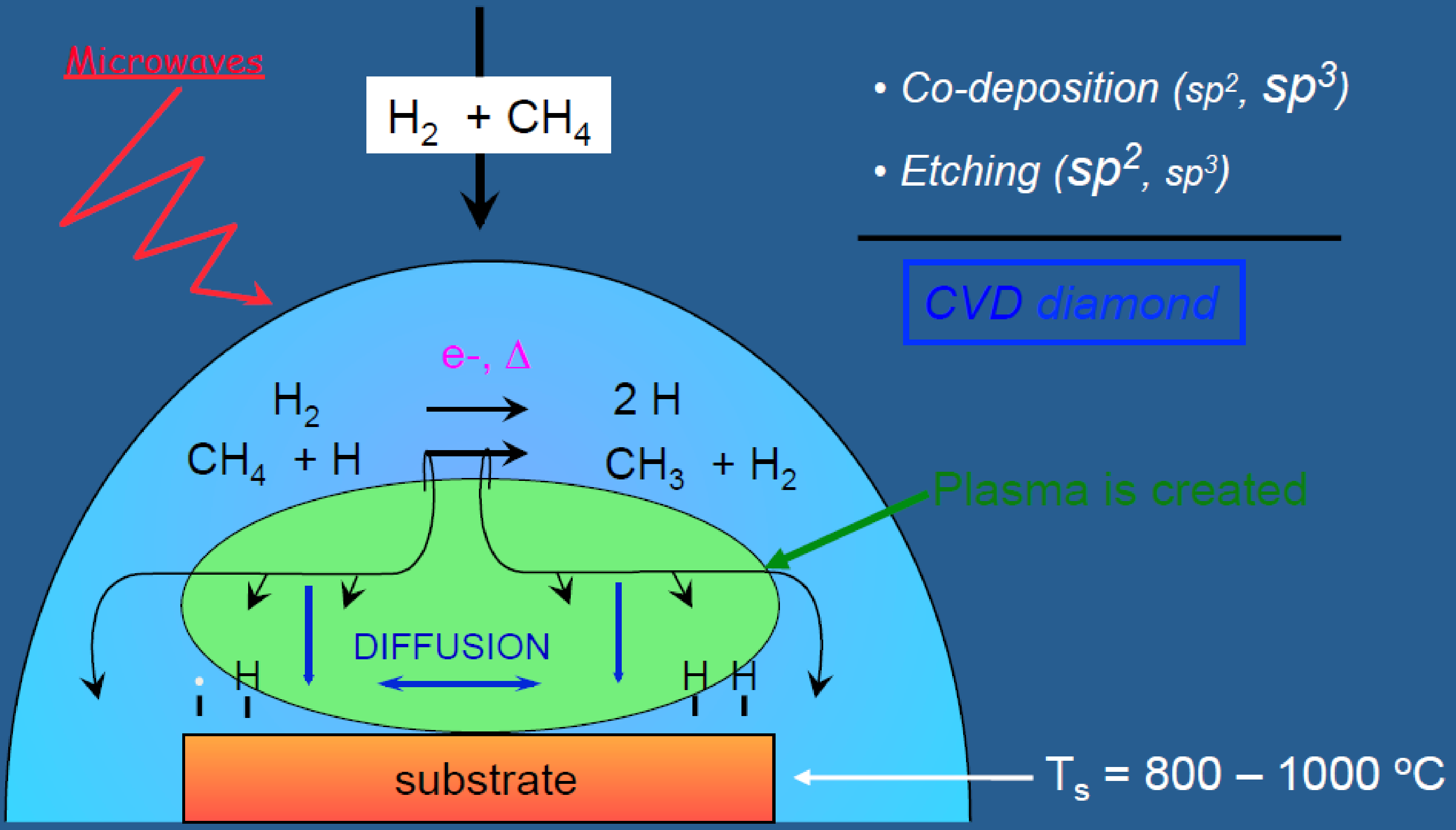
Diagram of high pressure cell for diamond growth

Synthesis of Diamond

Low-pressure, metastable synthesis: chemical vapor deposition (CVD)

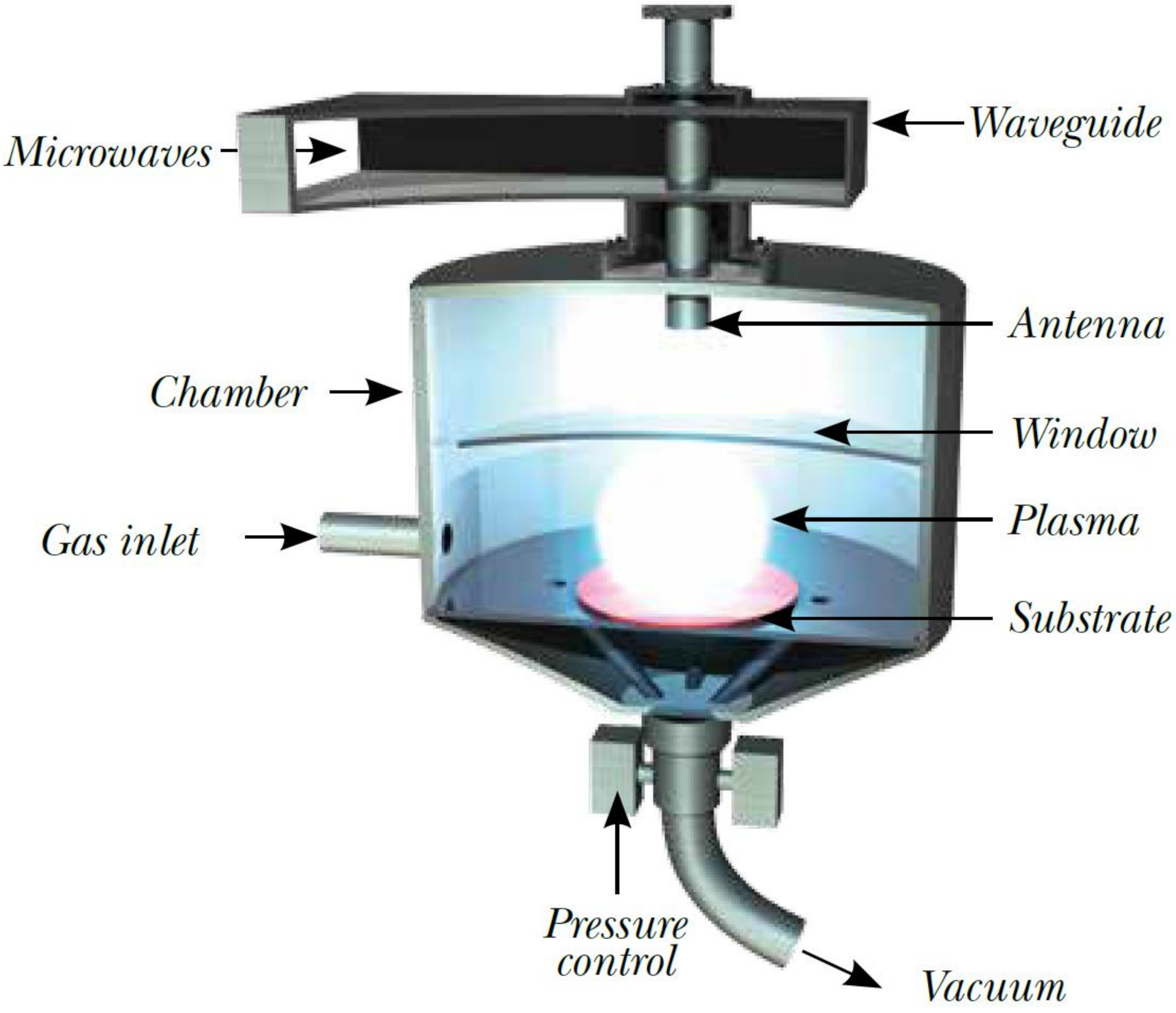
- Begun in early 1980's
- Polycrystalline films
- Growth rates ~1 μm/hr

CVD diamond is synthesized in metastable temperature and pressure conditions. Atomic hydrogen is key to diamond deposition.

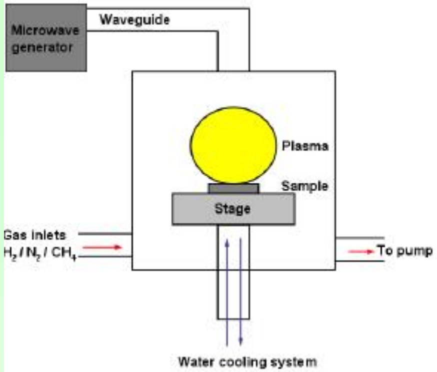


- *Co-deposition (sp^2, sp^3)*
- *Etching (sp^2, sp^3)*

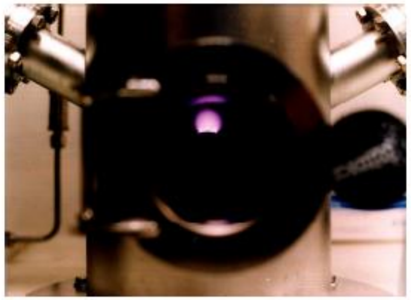
CVD diamond


Microwaves
Waveguide
Antenna
Chamber
Window
Gas inlet
Plasma
Substrate
Pressure control
Vacuum

CVD techniques have enabled new diamond technology

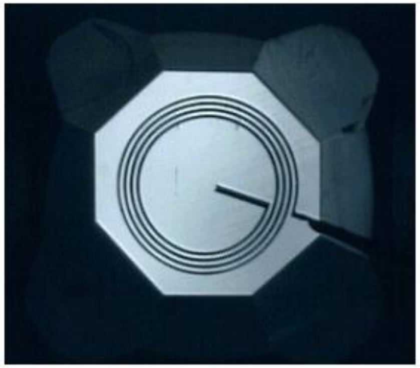


Diamond Growing in a Plasma Reactor



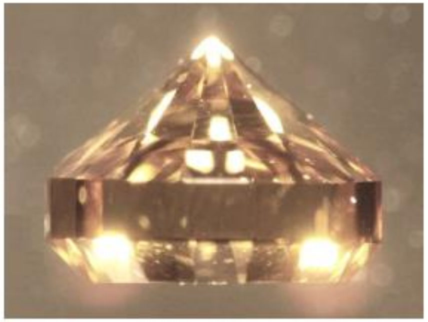
Microwave Plasma CVD: 100-200 torr H_2 pressures

[Yan *et al.*, *Proc. Nat. Acad. Sci.* (2002)]



“Designer Anvils”

[Vohra & Weir, *High Pressure Phen.* (2002)]



Production of regular diamond anvil
- 2.45 mm high
- 0.28 carats
- Grown in 1 day

[Yan *et al. Phys. Stat. Sol.* (2004)]

[Ho *et al.*, *Industrial Diamond Rev.* (2006)]

Half-inch single crystal

CVD synthesis of the diamond film and coatings

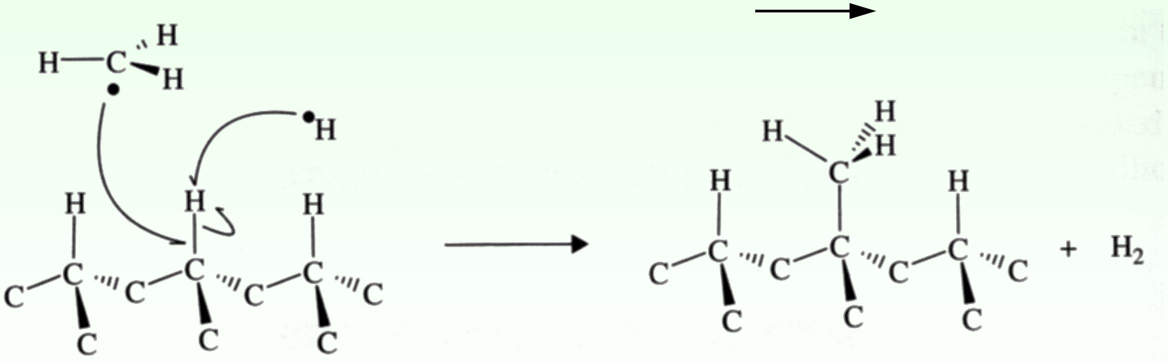
Synthetic conditions:

- CH_4, C_2H_2 (as carbon source) + H_2 (assistant gas)
- Support temperature 700 – 1000 °C
- Pressure 0.1 bar
- Plasma-assisted CVD reactor
- coating growth rate: ~ 1 – 10 μm/h

Possible mechanism:

1) initiation: $H_2 \longrightarrow 2H\bullet$; $H\bullet + CH_4 \longrightarrow CH_3\bullet + H_2$

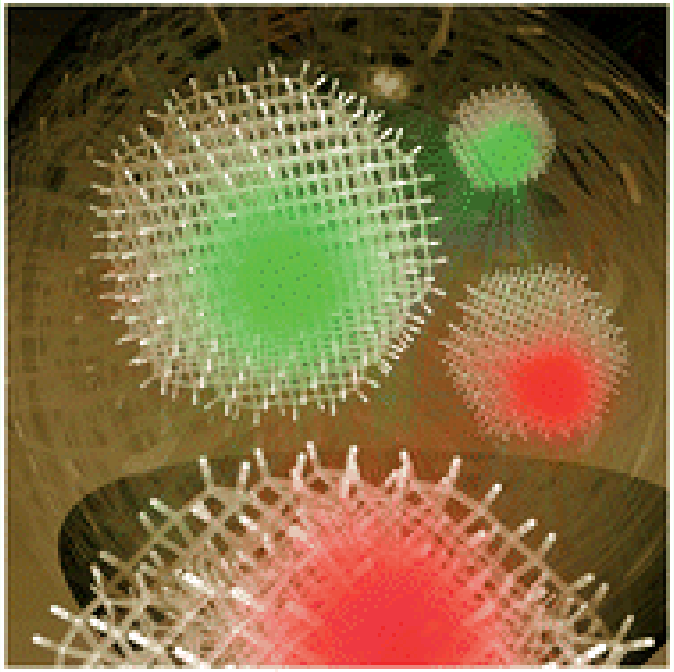
2) film growth:



The H_2 is critical to protect the unsaturated carbon atoms of deposited film in tetrahedral *sp*^{3} state.

Nanodiamonds, ultrafine diamonds, detonation diamonds

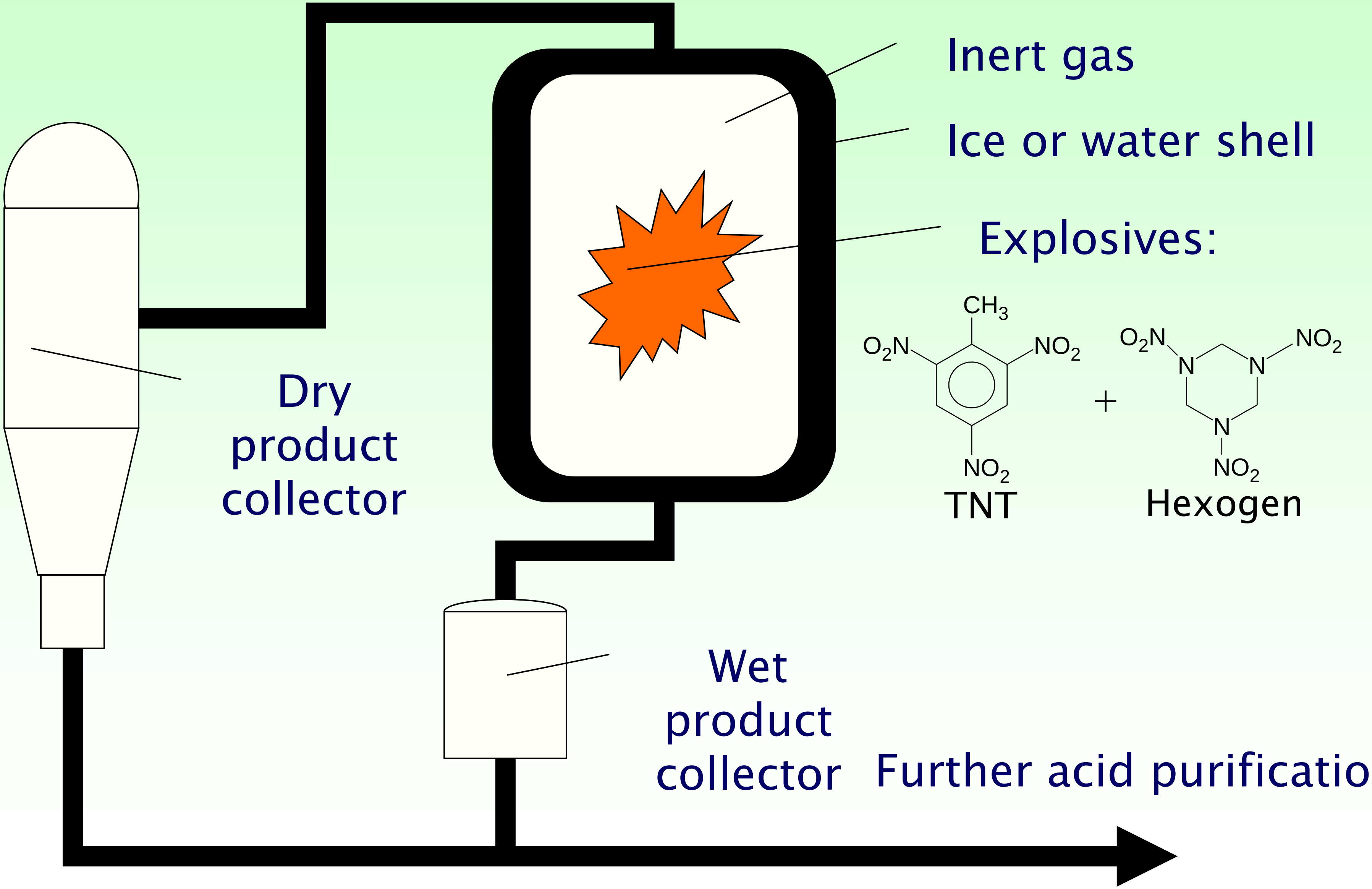
- **Formed in an oxygen-deficient explosive medium TNT / hexagen**
- **Particles with a diameter of 5 nm are formed in the front of a blast wave in a few microseconds.**



History

- The discovery of nanodiamond synthesis in 1963, followed by a prolonged suspension of active study.
- For several reasons, including the security measures in place in the USSR and a lack of industrial interest in nanotechnology at the time, them application of this nanodiamond (ND) remained unreported and under-exploited until very recently.
- Rediscovery of the synthesis in 1982–1993, with intensified study and production of nanodiamonds simultaneously at several research centers in the USSR. In this period, production potential exceeded the scale of application.
- Unprofitable production of small batches of nanodiamonds in 1993–2003, leading to the closure of a number of research centers and the termination of production.

Scheme of explosive technology



Inert gas

Ice or water shell

Explosives:

TNT

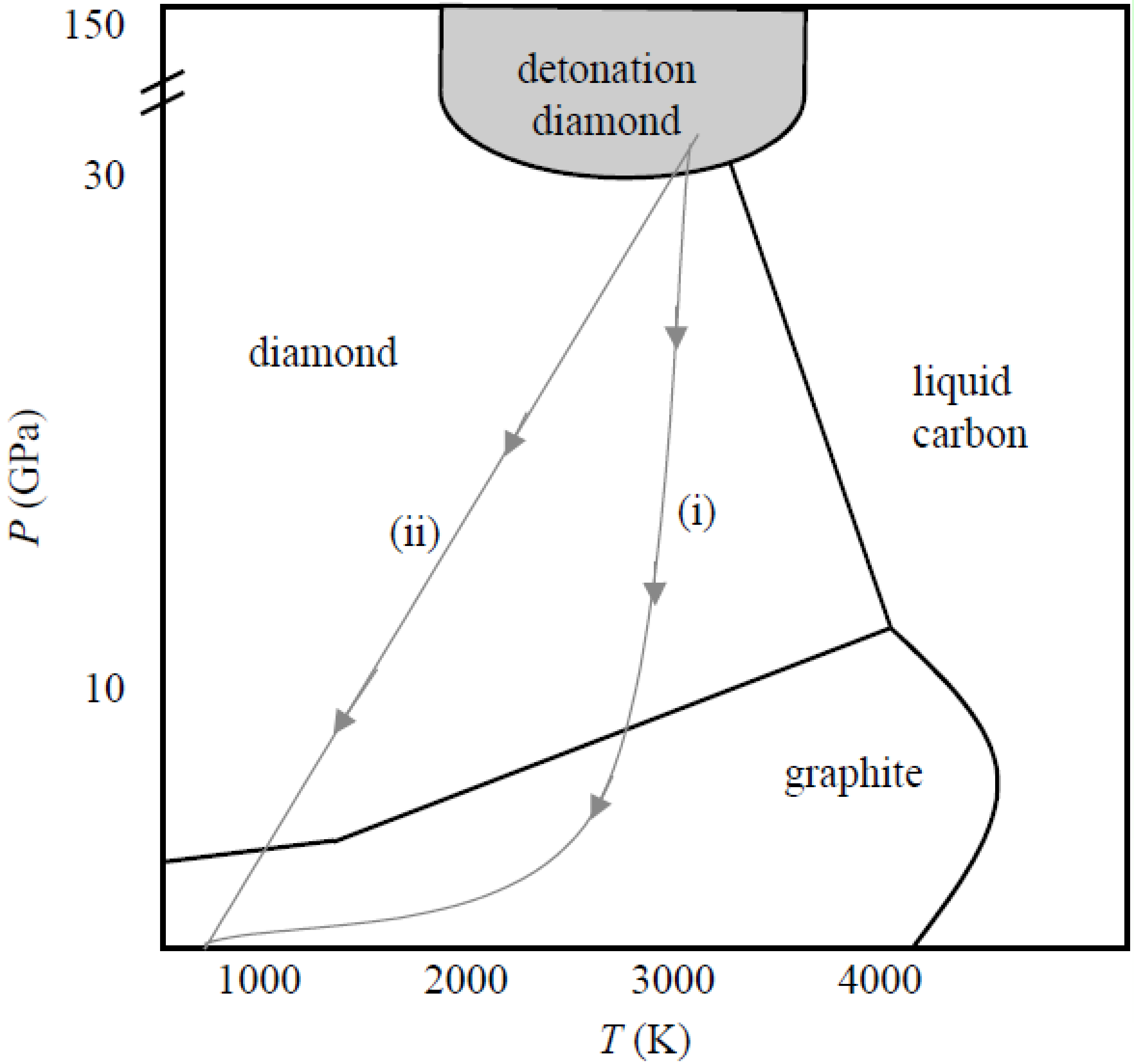
Hexogen

Dry product collector

Wet product collector

Further acid purification

Phase diagram for carbon



(i) Rapid decrease in pressure at high temperatures facilitates the diamond-to-graphite transition.

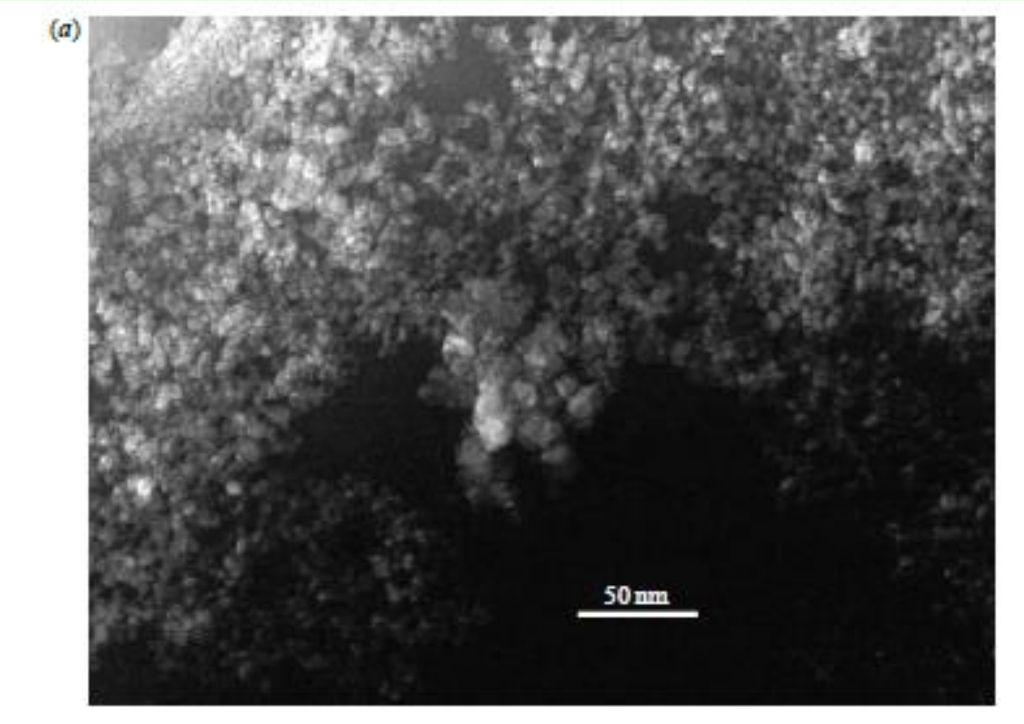
(ii) Rapid cooling ensures that diamond remains the most stable phase and results in higher yields of detonation ND.

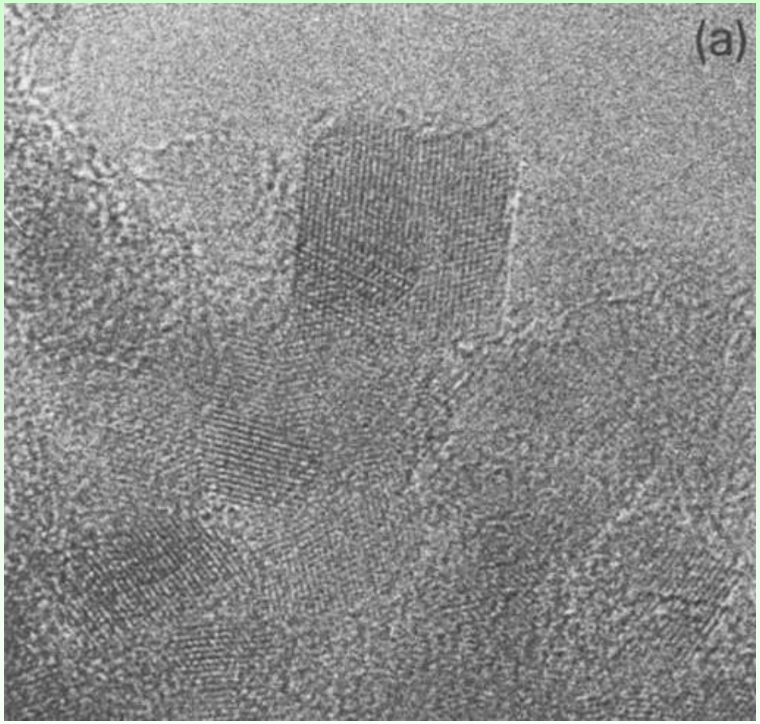
Phys. Sol. State, 2004 46, 611–615

ND FACTS

- The most commonly used explosives for the synthesis is a mixture of trinitrotoluene (TNT) and RDX or HMX. The explosions are carried out in a closed stainless steel chamber in the absence of oxygen.
- The yield of diamond grows in the presence of a coolant in argon, water, water foam and ice.
- Optimum cooling rates after the explosion of 3000-4000 K min-1. The detonation products are a complex mixture of ND particles with an average size of 5 nm and other graphite carbon forms.
- Cleaning methods typically include gaseous ozonation, oxidation in nitric acid solutions to remove sp2 carbon and metallic impurities.

TEM image ND





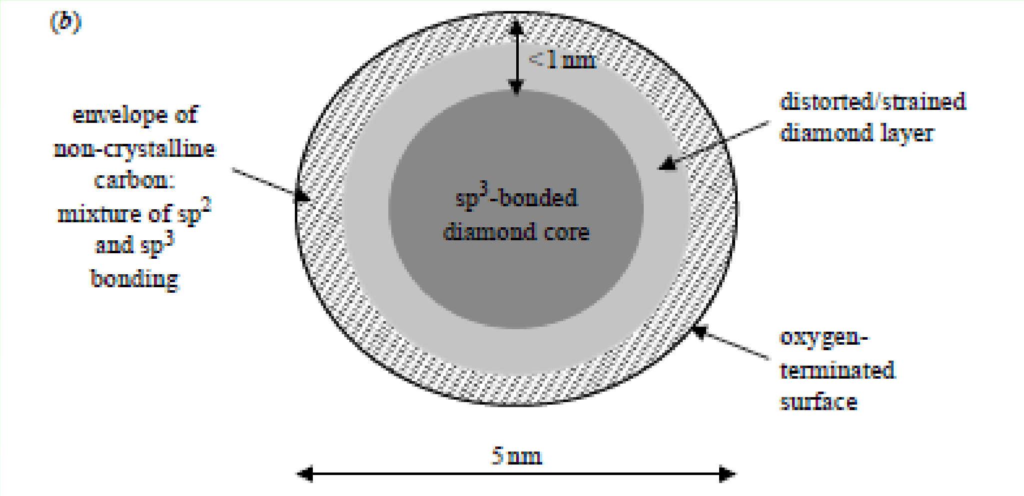
Kulakova, I. I. 2004 Surface chemistry of nanodiamonds. Phys. Solid State 46, 636–643.

NDs structure

- The exact nature of the outer layer remains unclear, but two general models have emerged:

(i) an amorphous shell with significant sp2 carbon content or

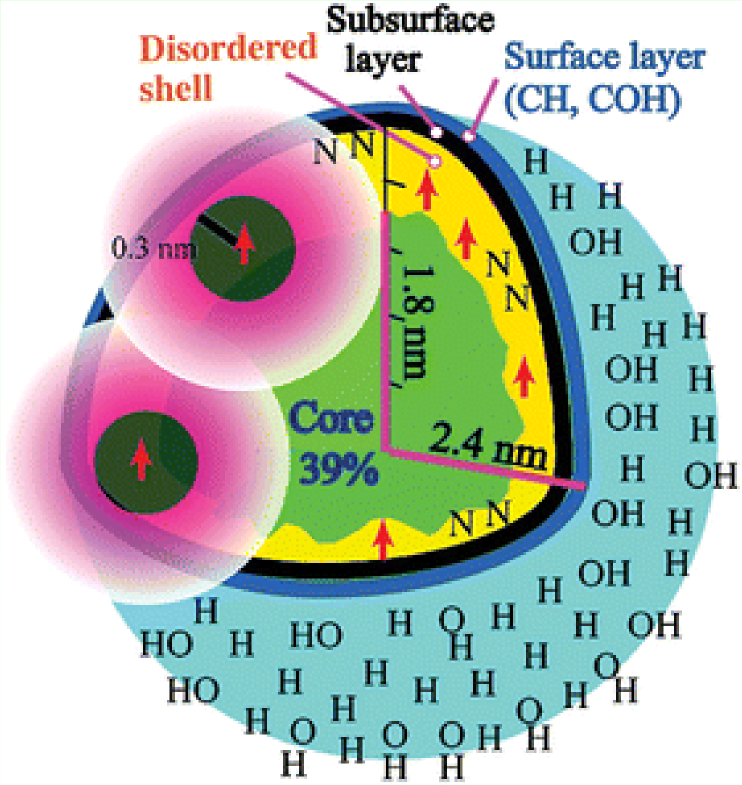
(ii) an sp2 graphene-type sheet, of a fullerene structure, giving rise to a structure described as ‘bucky-diamond’.



Heating ND particles to above 1000 K in vacuum does result in laminates of fullerene shells being formed around the diamond core and ultimately to the formation of ‘carbon onions’.

Schematic Model of NDs

- The hydrogenated surface is part of a 0.6 nm-thick shell of seven partially disordered carbon layers that contain 61% of all C and mostly produce higher-field ^{13}C NMR signals.

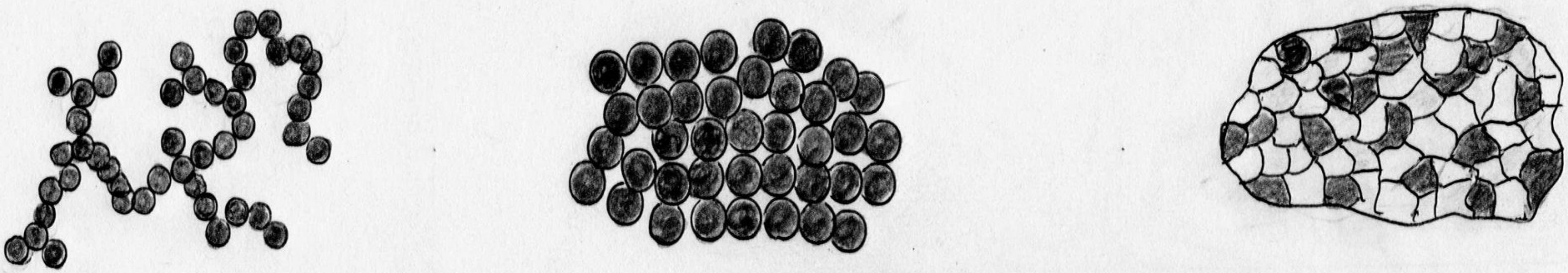


J. Am. Chem. Soc., 2009, **131**, 1426–1435

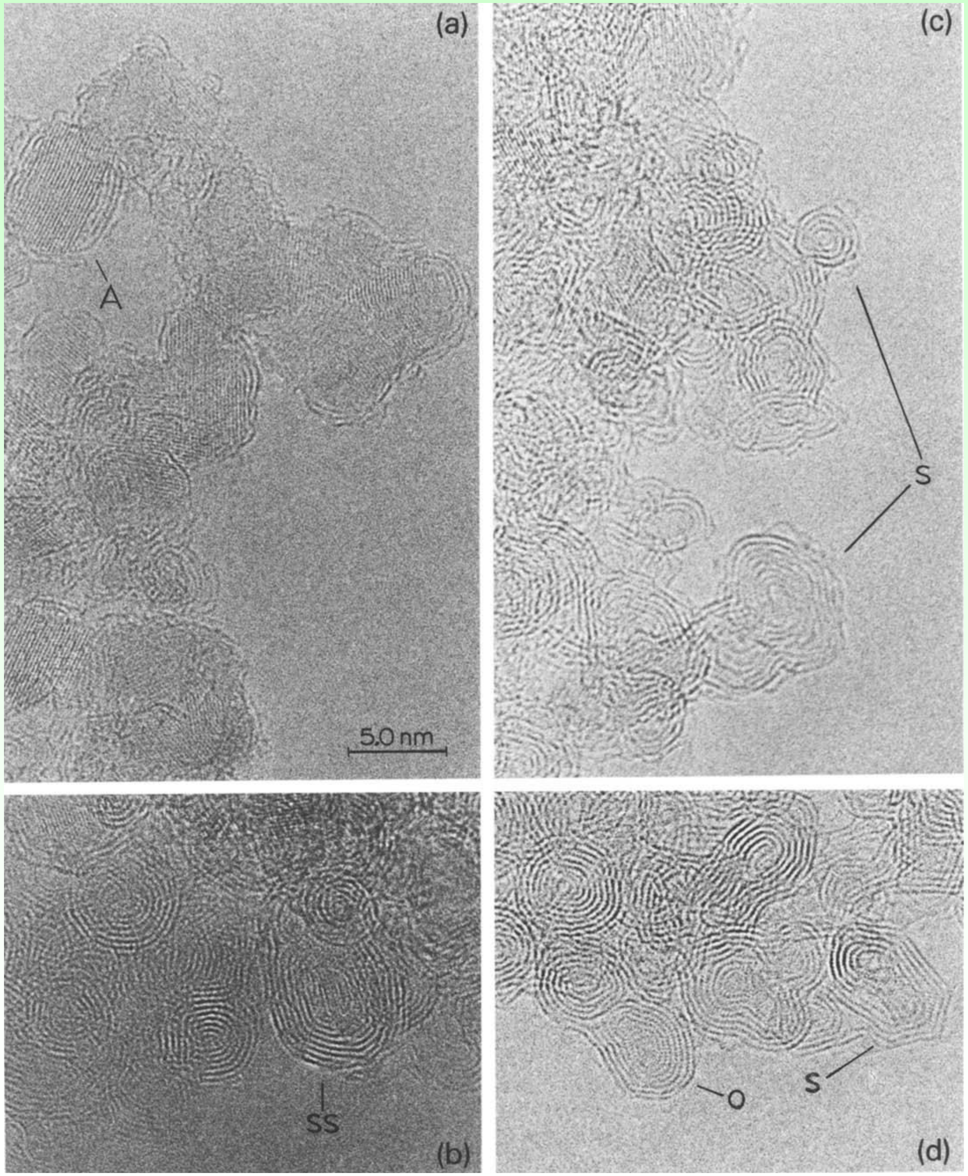
Influence of Detonation Conditions on the Quality of Nanodiamonds

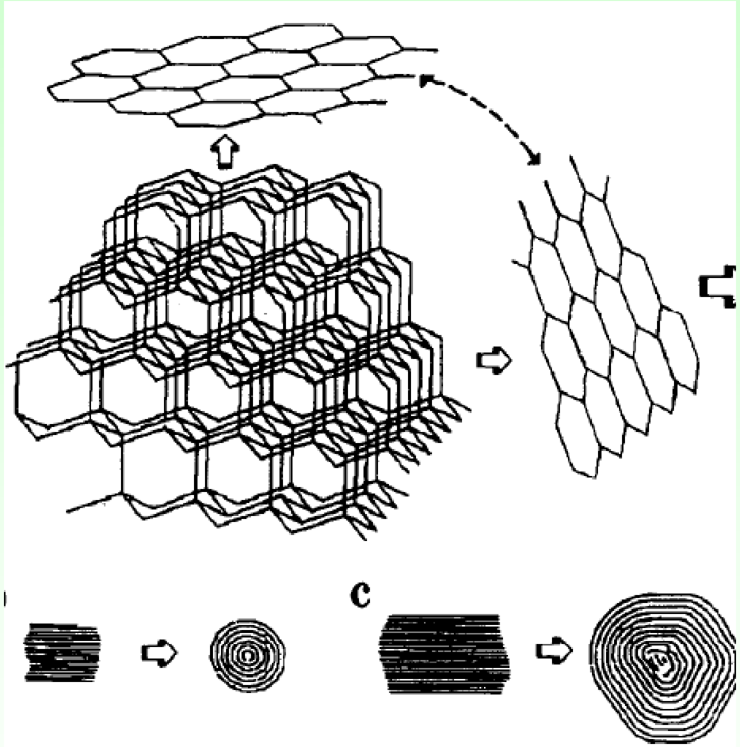
Increase in Temperature, pressure, time, carbon concentration →

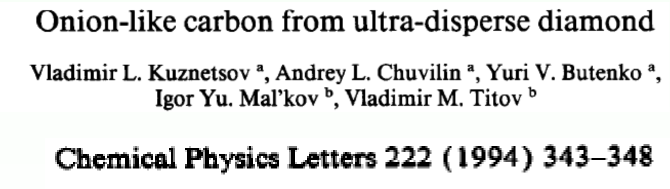
Fractal aggregates of monocrystalls	Porous polycrystalls	Polycrystalls
Single point binding	Multi point binding	Full binding
Nanoseconds	Microseconds	Milliseconds



Annealing of Nanodiamonds





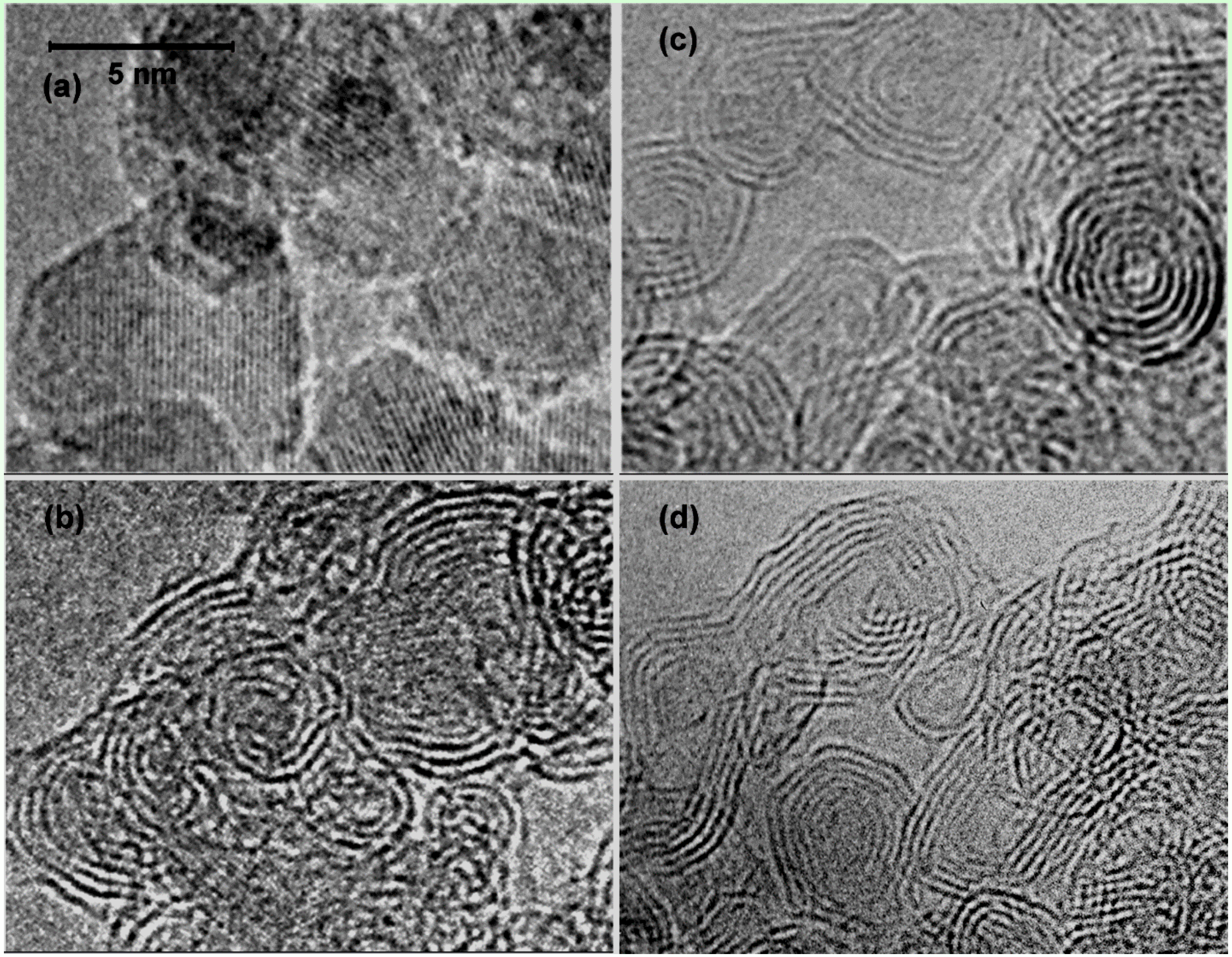


Onion-like carbon from ultra-disperse diamond

Vladimir L. Kuznetsov [a], Andrey L. Chuvilin [a], Yuri V. Butenko [a], Igor Yu. Mal'kov [b], Vladimir M. Titov [b]

Chemical Physics Letters 222 (1994) 343–348

HRTEM images of the products of nanodiamond annealed at 1150 K (a), 1600 K (b), 1900 K(c), and 2140 K (d)



DND Applications

- sp3/sp2:

  Nanodiamonds-graphite………. 20 – 75 %
  Pure DND…………………… ………. > 95%

- Optimal contents in materials – 0.5 – 5%
- Applications:

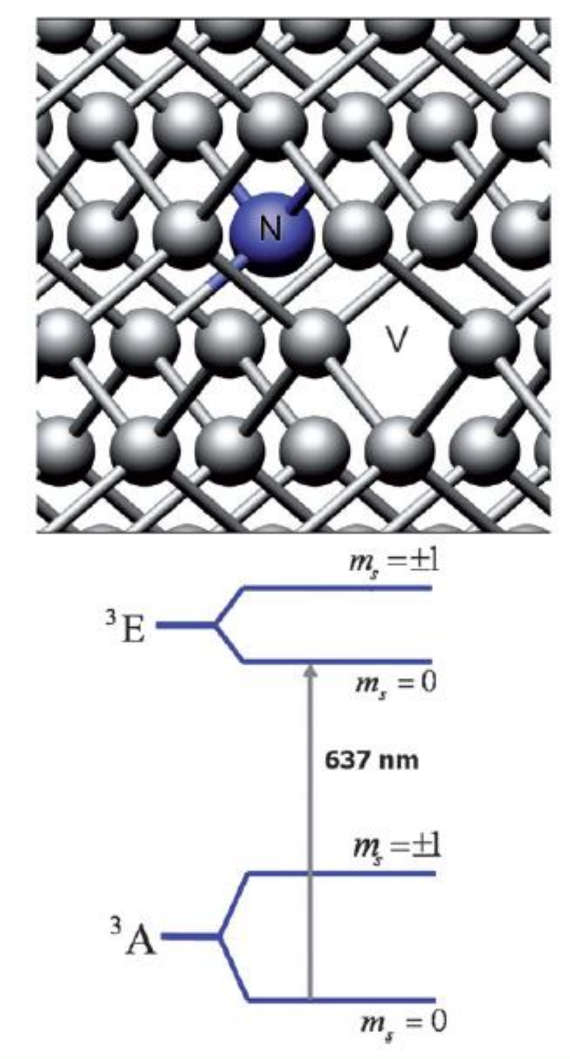
  Motor oil, lubricates, electroplates, resin, polymers, alloys, ceramics, polishing, biology, medicine…

Price for DND, $ / kg

Producer	NABOND China	Nanogroup Czech	ALIT Ukraine	In Europe
Detona - tion soot	550	550	550	800
DND	3000	1500	1600	2700
for small lots	>4000	2000	2000	6000

Nitrogen Defects

- NDs defect comprises of a single nitrogen impurity in a substitutional position directly adjacent to a lattice vacancy.
- This defect is of interest in the field of nanomedicine as it is fluorescent, with an unusually high quantum yield.
- The energy level structure of the N–V defect in diamond has a ground state and excited states forming an electron spin triplet with ^{3}A and ^{3}E, and due to the spin–spin interaction in the diamond crystal, the ground state is split into ($m_s = 0$) and ($m_s = \pm 1$) sub-levels. A transition between these states may be excited with light of ultraviolet wavelength (<400 nm).



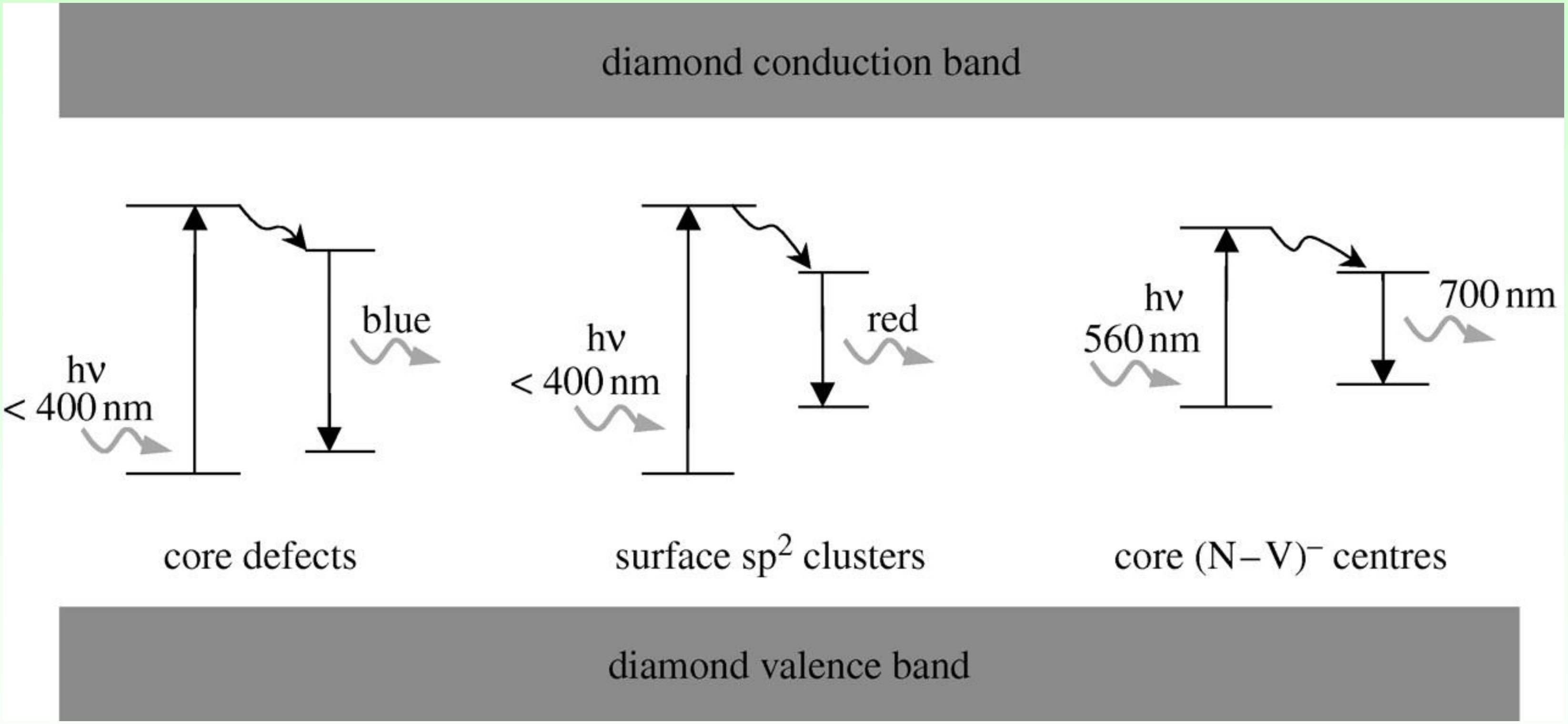
NDs Optical Properties

- One of the attractive properties of ND is its ability to fluoresce when excited with light of ultraviolet wavelength (<400 nm).

- The emission of 5 nm detonation diamond is dominated by a broad band in the visible region, from 390 to 650 nm.

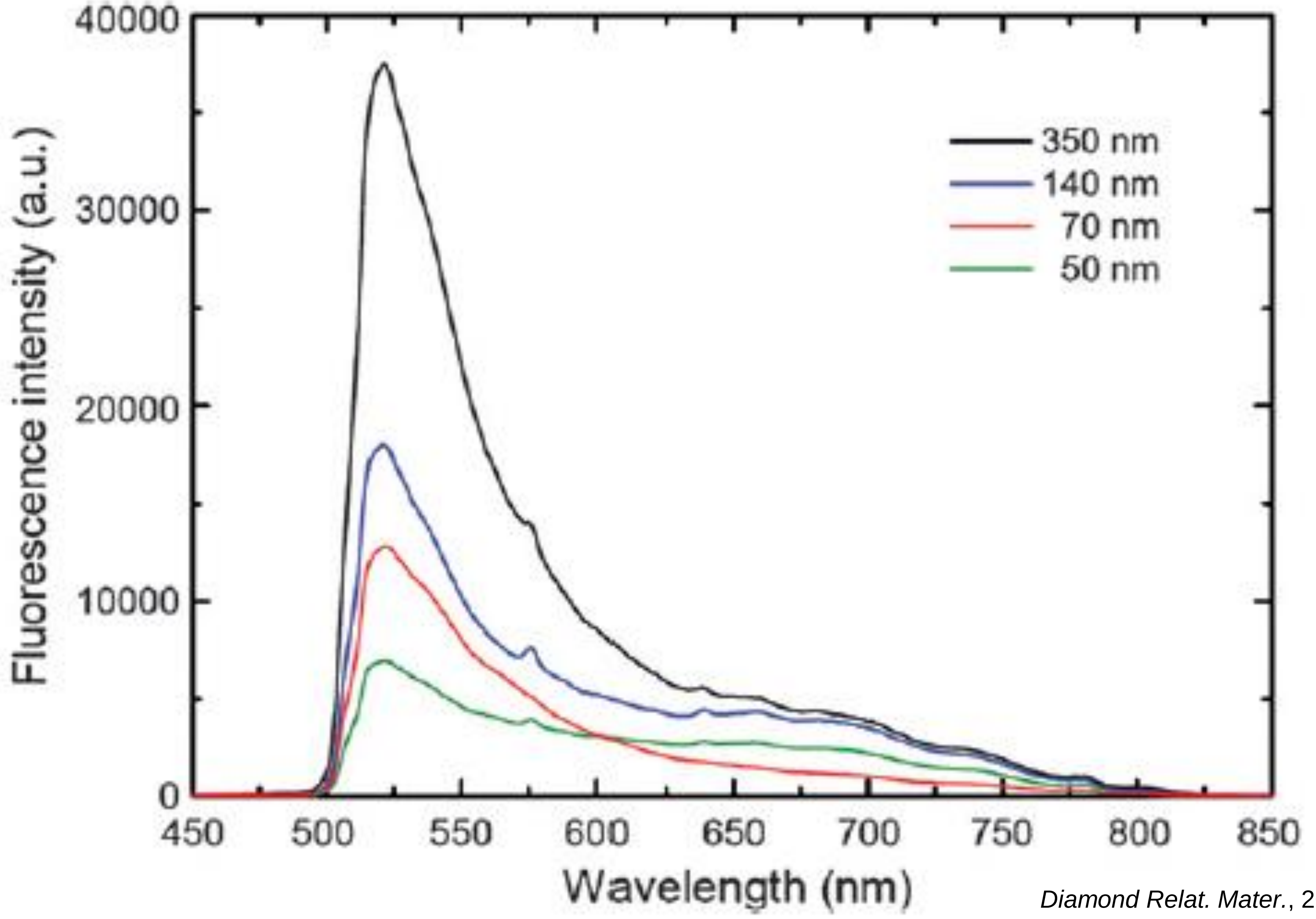
- The mechanism of photoluminescence has been assigned to the emission from impurity sites (e.g. dopants) within the core, defects in the diamond lattice or sp^2 clusters on the ND surface.

Schematic of available energy levels within the diamond band gap capable of undergoing excitation and photoluminescence.



Holt K B Phil. Trans. R. Soc. A 2007;365:2845-2861

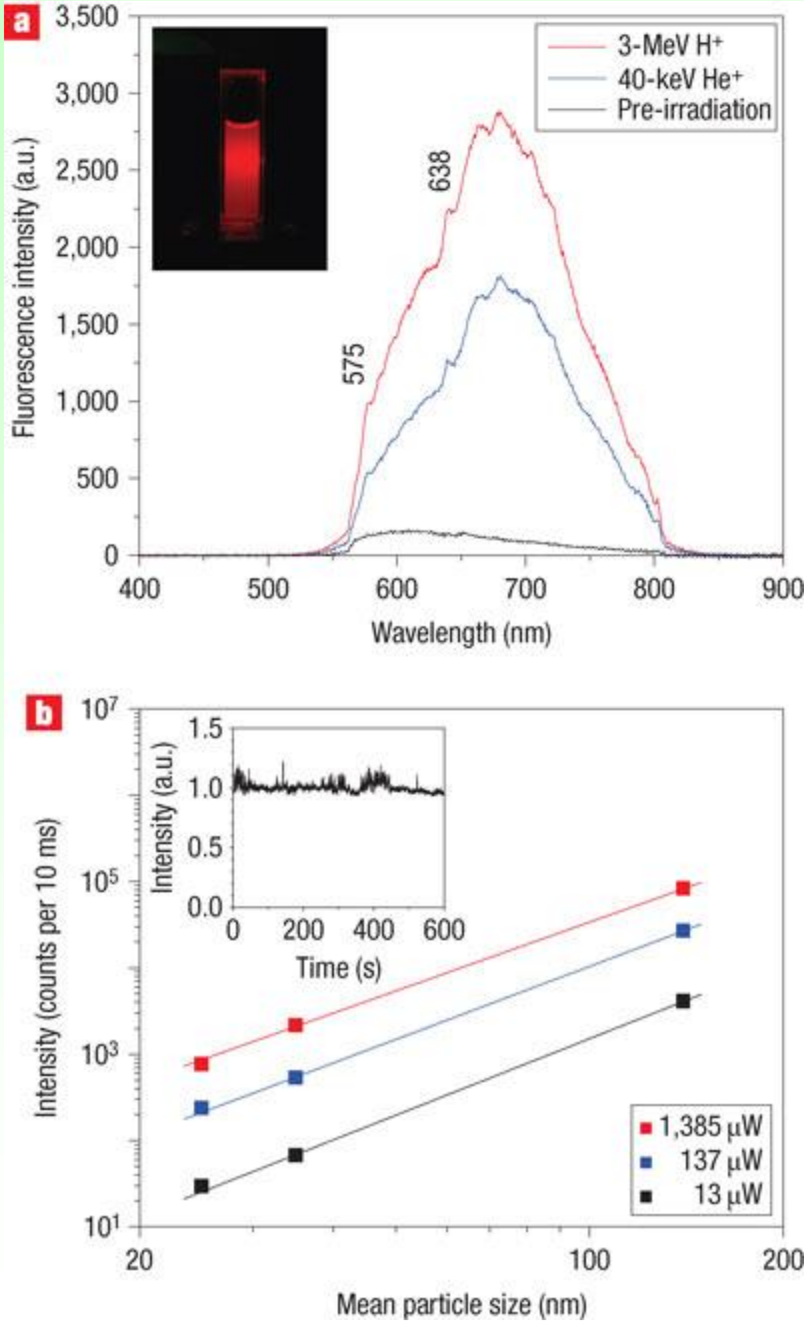
Size Dependent Fluorescence



Diamond Relat. Mater., 2009, **18**, 567–573

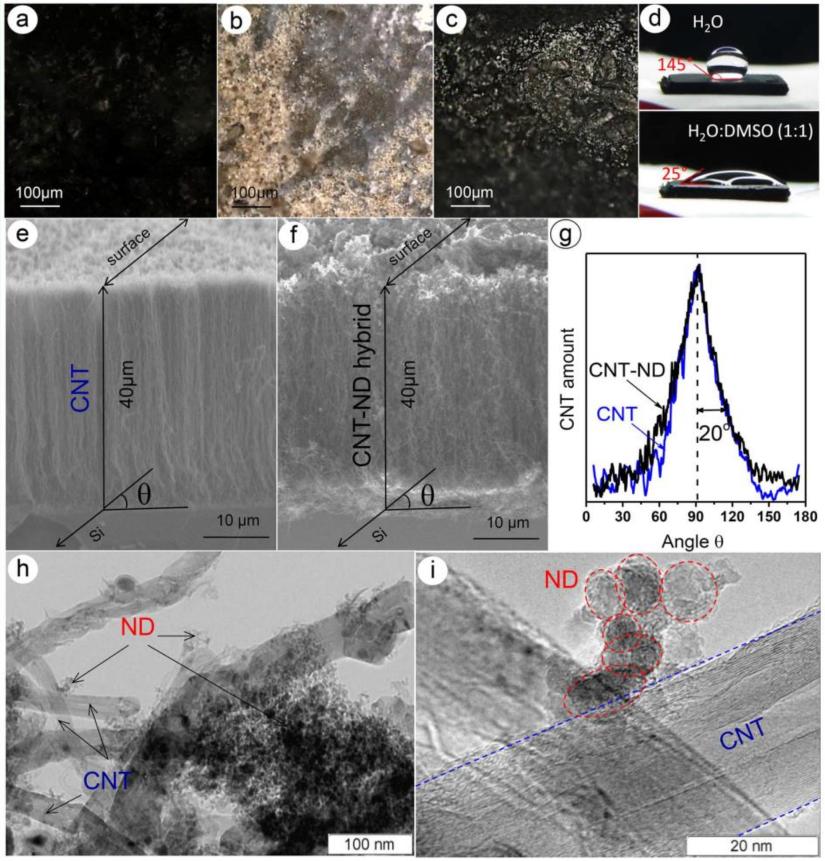
A. Fluorescence spectra of 35-nm FNDs suspended in water (1 mg ml^{-1} each), prepared with either 40-keV He^+ or 3-MeV H^+ irradiation. Inset: Fluorescence image of a 35-nm FND suspension excited by 532-nm laser light.

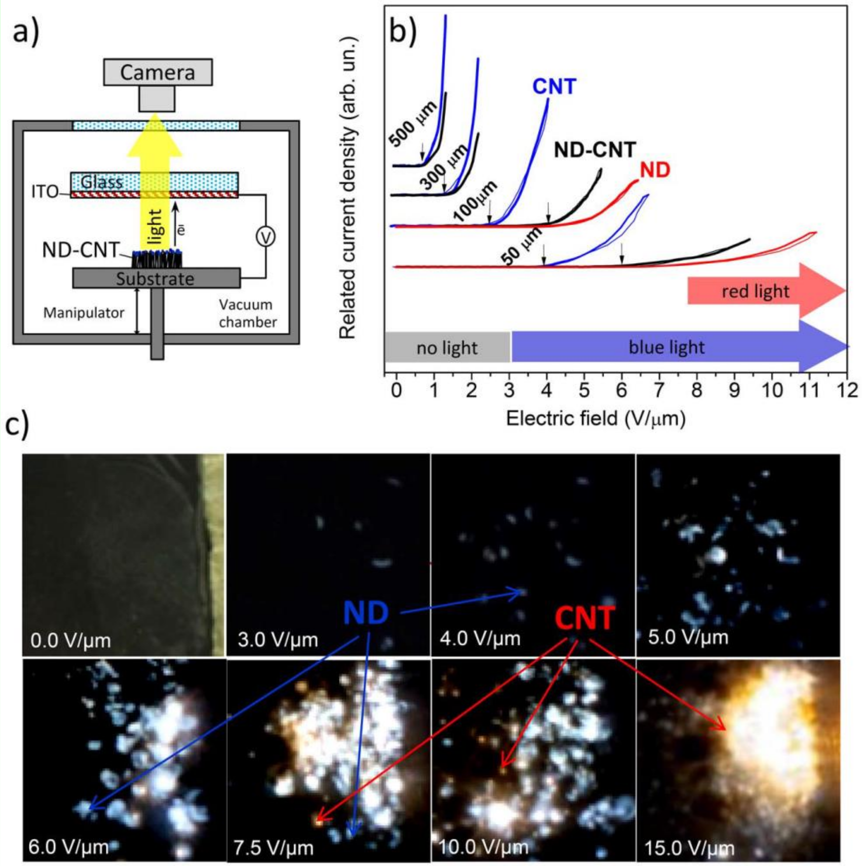
B. Fluorescence intensities of FNDs as a function of particle size at three different laser powers. Inset: Fluorescence time trace (intensity normalized) of a 25-nm FND.



Nat. Nanotechnol., 2008, 3, 284–288.

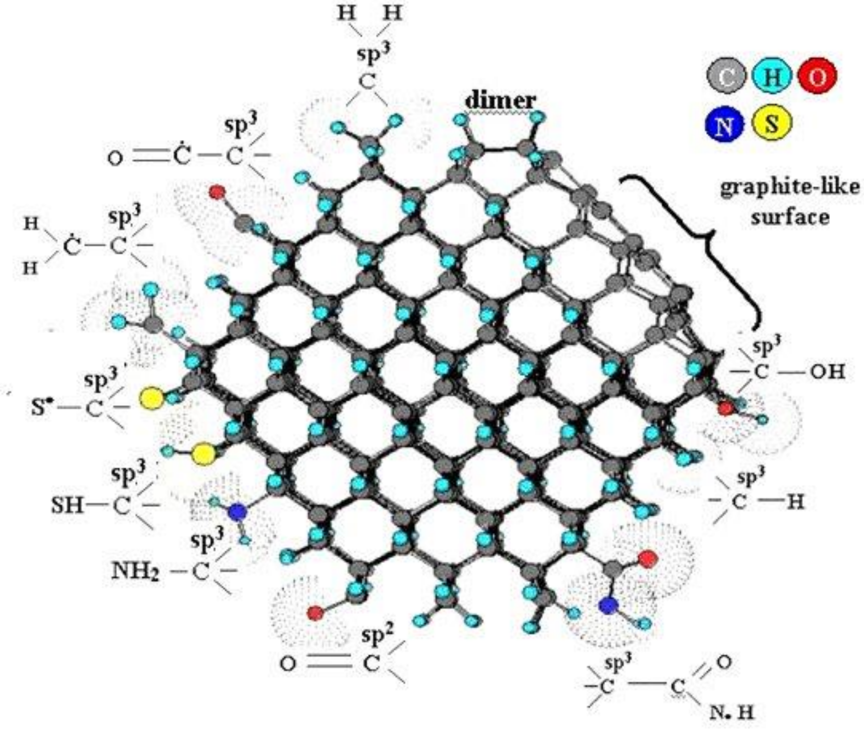
Field emission luminescence of ND deposited on the aligned carbon nanotube array





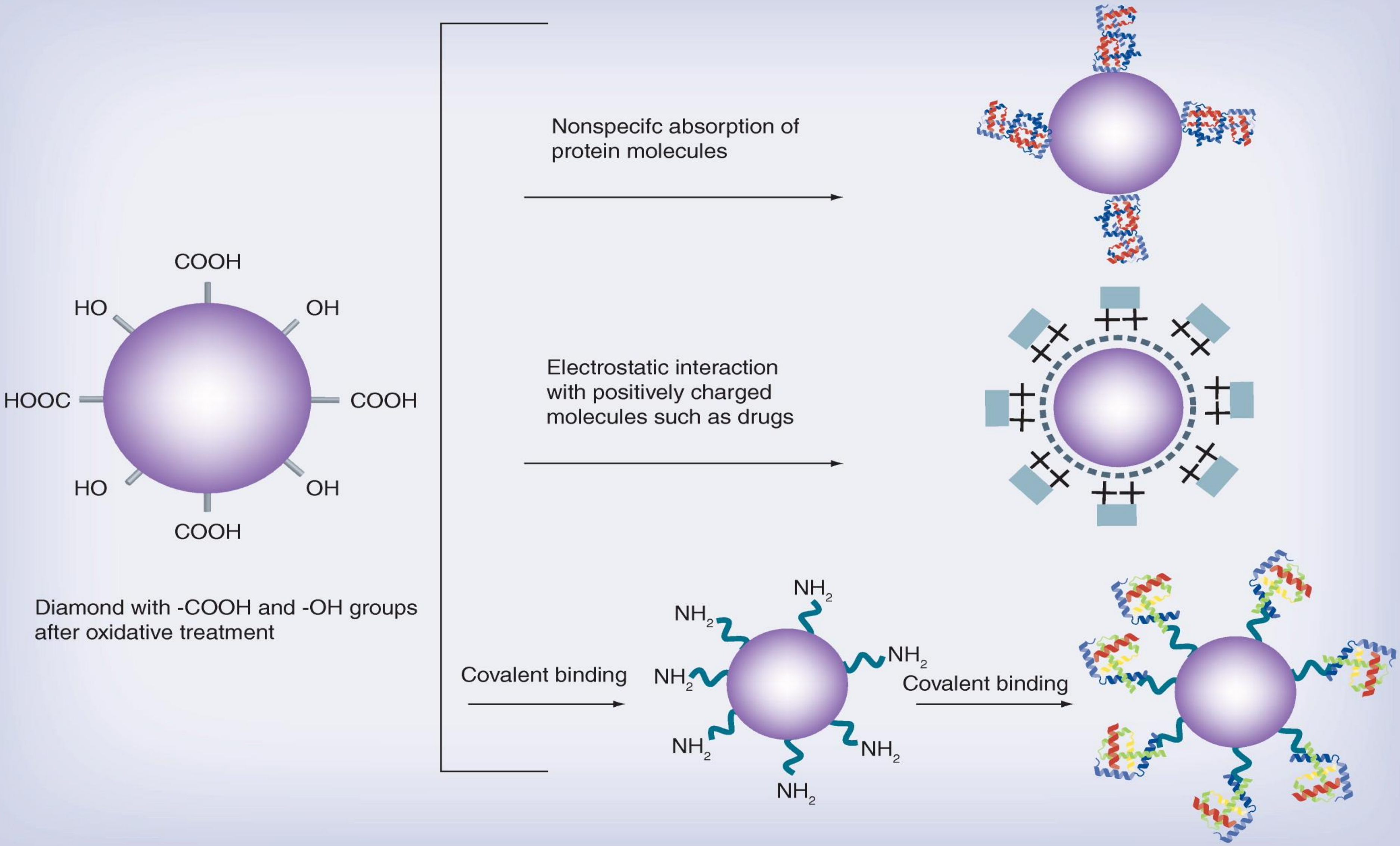
Nanodiamonds Chemotherapy

- Nanodiamonds are useful
  - Biocompatibility
  - Functional versatility
  - Unique surface electrostatics
- Drug delivery
  - Bypassing chemoresistance
  - Controlled delivery
  - Intracellular tracking (2)

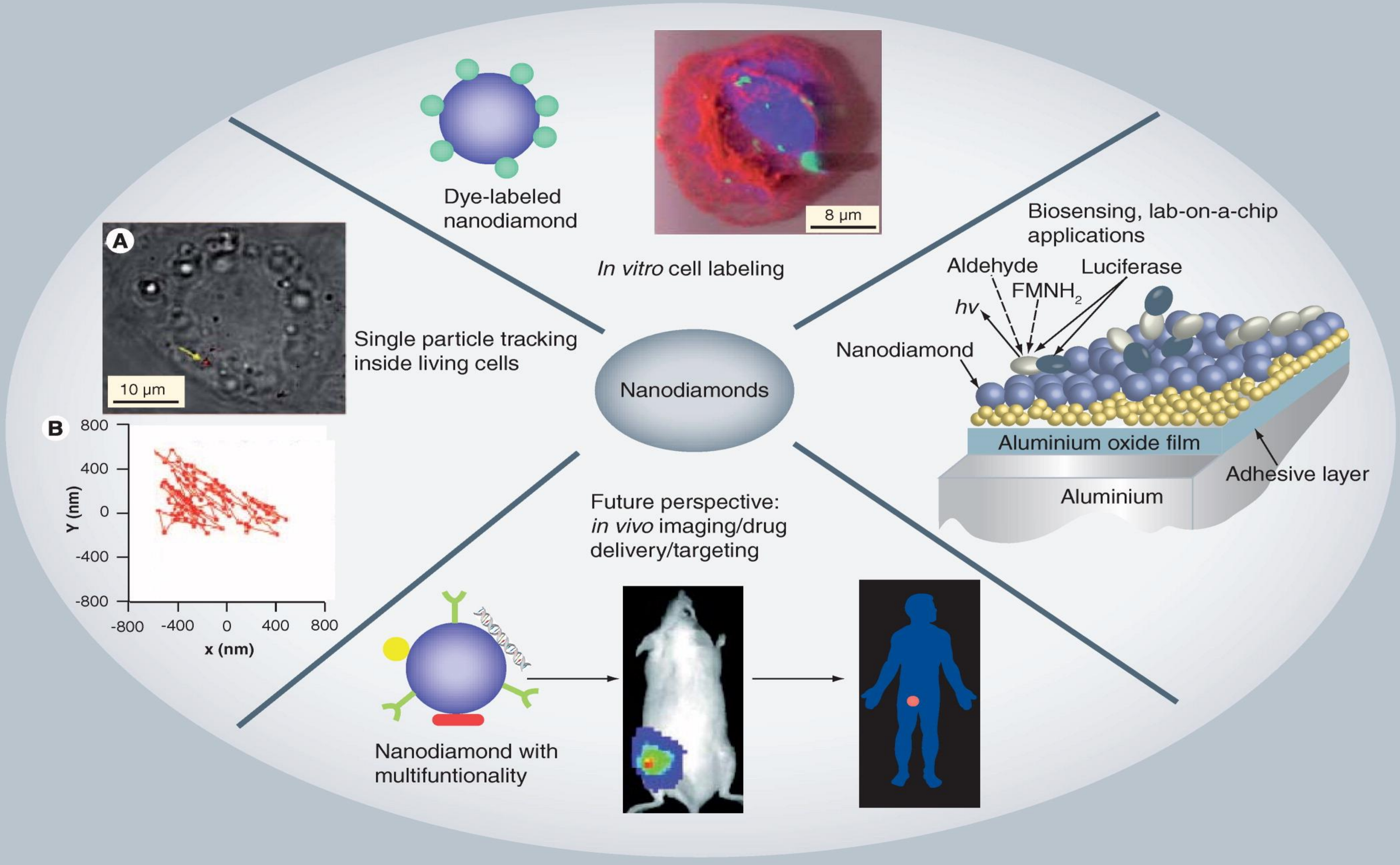


http://www.itc-inc.org/nanodiamond.html

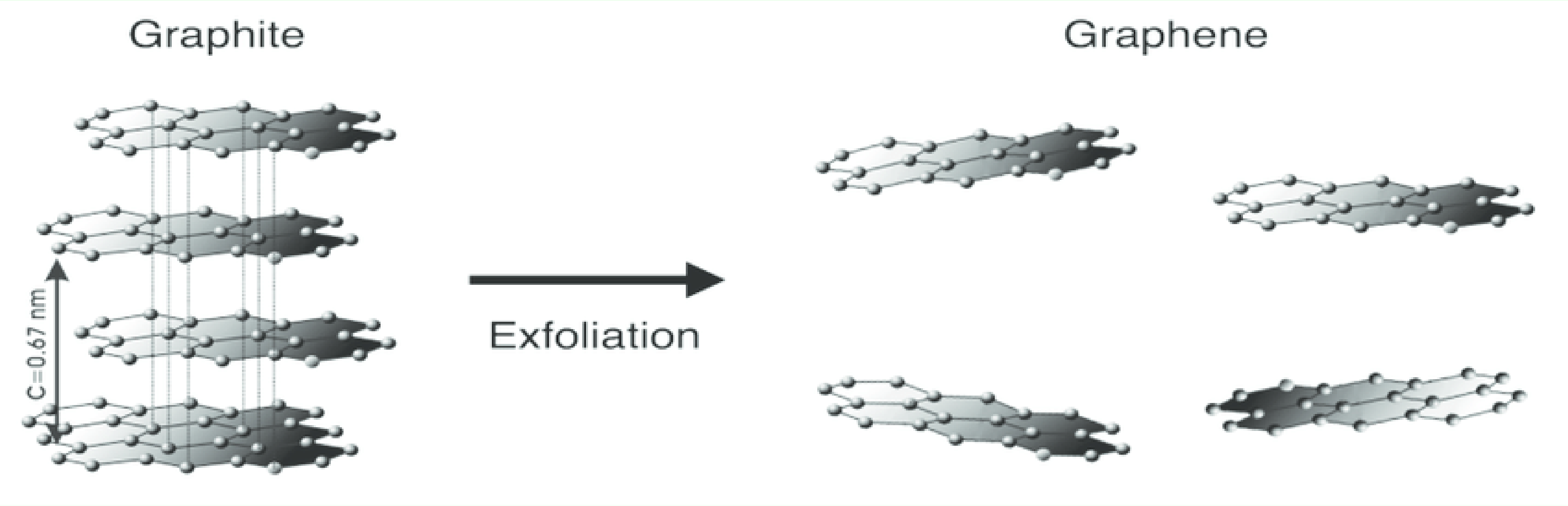
Bioconjugation Techniques with NDs



Ongoing and potential biological applications of nanodiamonds



Graphite and Graphene

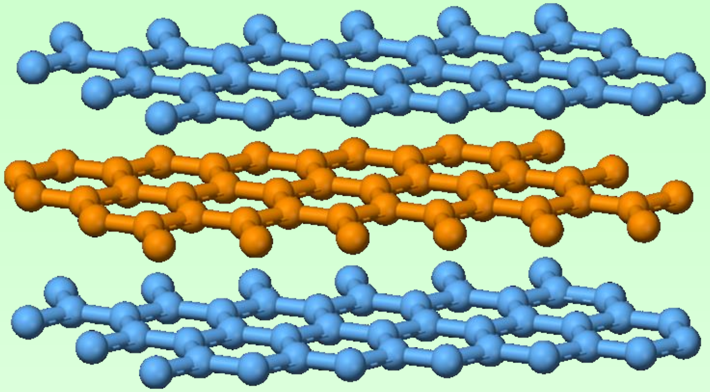


Graphite

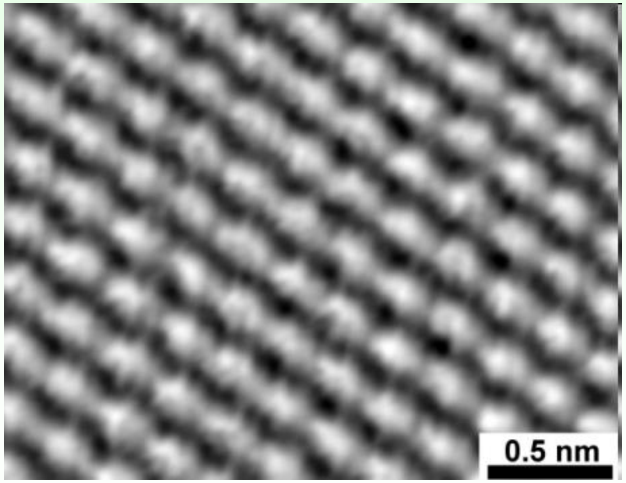
Graphite – carbon modification with triangular (sp^2) carbon atoms in the layered lattice

Properties of graphite:

- ■ Graphite structure is highly anisotropic: C–C distance 1.42 Å. Interlayer distance 3.35 Å, hence the anisotropic properties.
- ■ Dry lubricating properties, due to loose interlamellar coupling between graphene sheets and presence of intercalated fluids (absorbed air, water molecules) between the layers.
- ■ lustrous and conducting solid (typical metallic properties, resulting from the electronic structure)

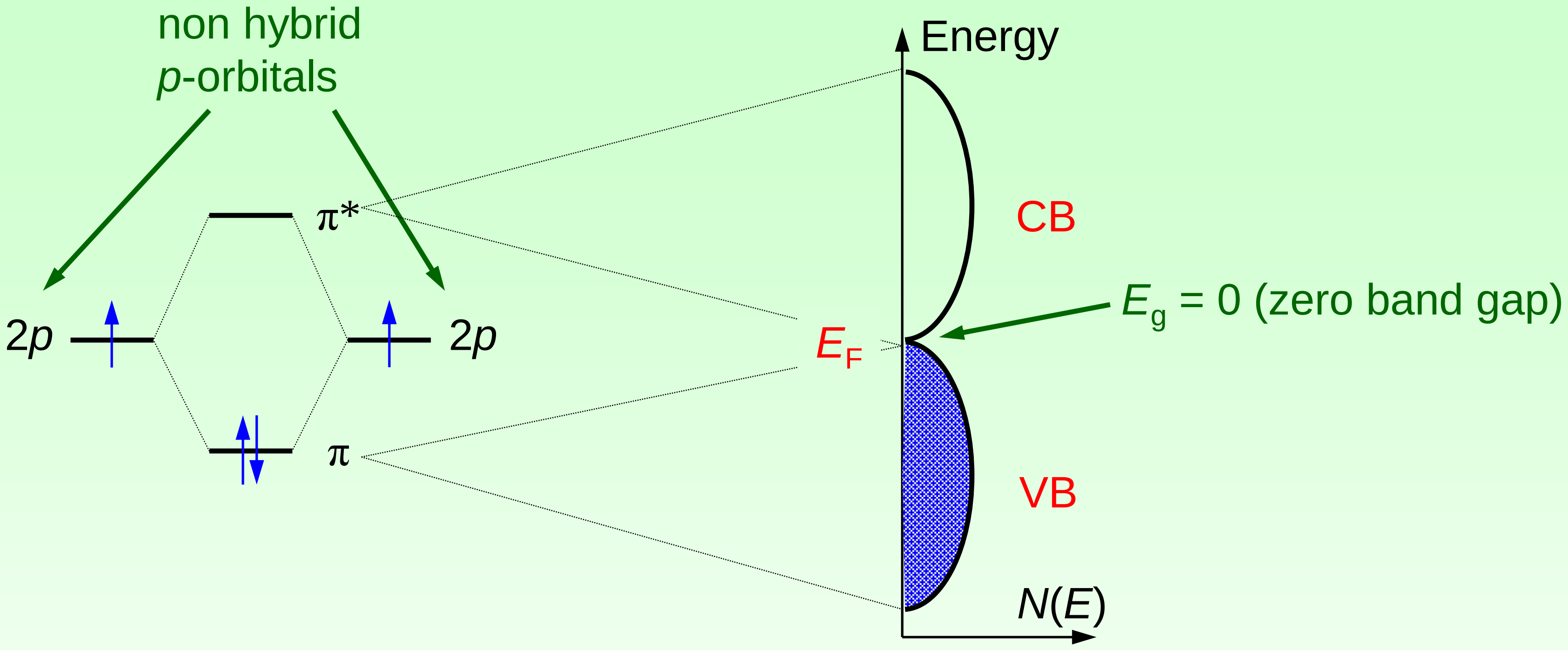


ABAB packing of graphene layers in α-graphite crystal structure

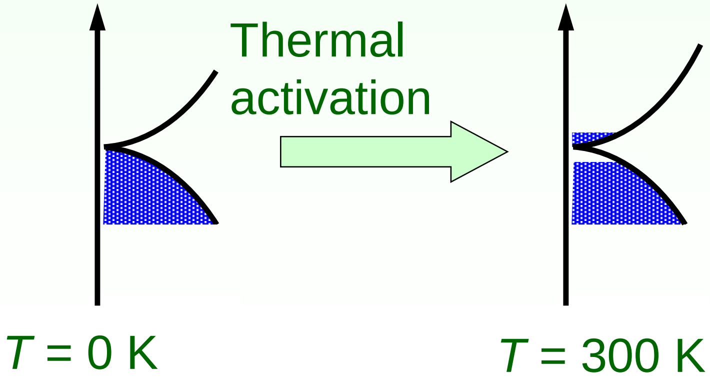


Scanning tunneling microscope image of graphite surface atoms

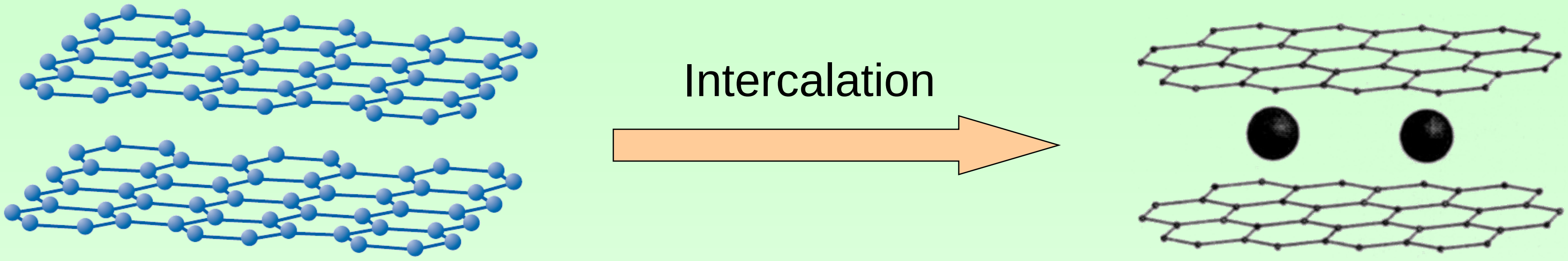
Band structure of the graphite



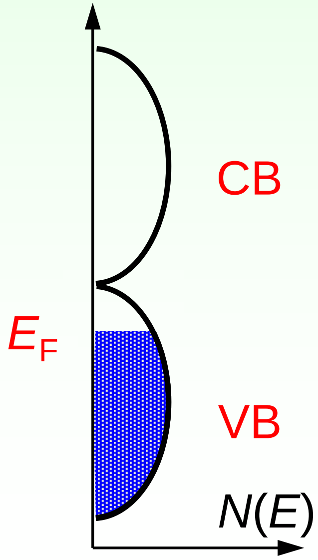
- Some notable electronic conductivity occurs along the graphene layers
- Despite the zero E_g, the actual number of delocalized electrons is small, due to low state density near the Fermi level. This makes graphite *semimetal*. The electrical conductivity is moderate, compared to typical metals, but increases with the temperature.



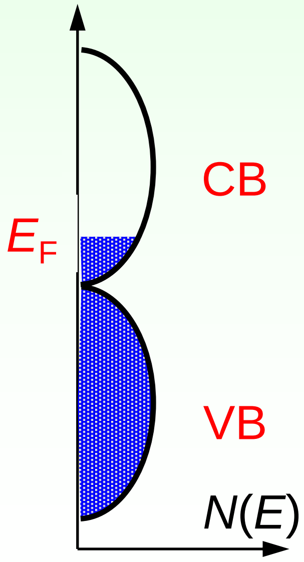
Band structure of the graphite intercalates



- $C + Br_2 \longrightarrow C_8^+ Br^-$
- $C + K \longrightarrow C_8^- K^+$

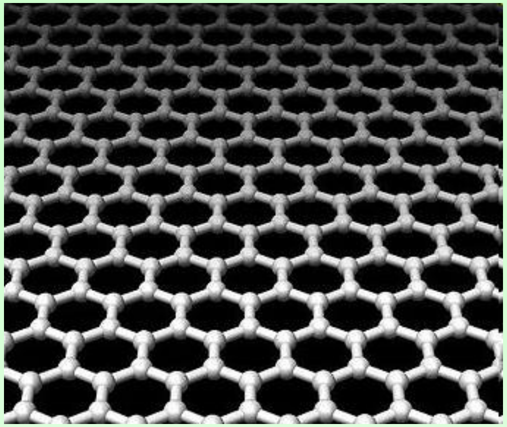


The graphite intercalation adds or removes electrons from the graphene layers and shifts the Fermi level up or down, to the higher density of states. Both C_8Br and C_8K therefore exhibit higher electrical conductivity, compared to pristine graphite

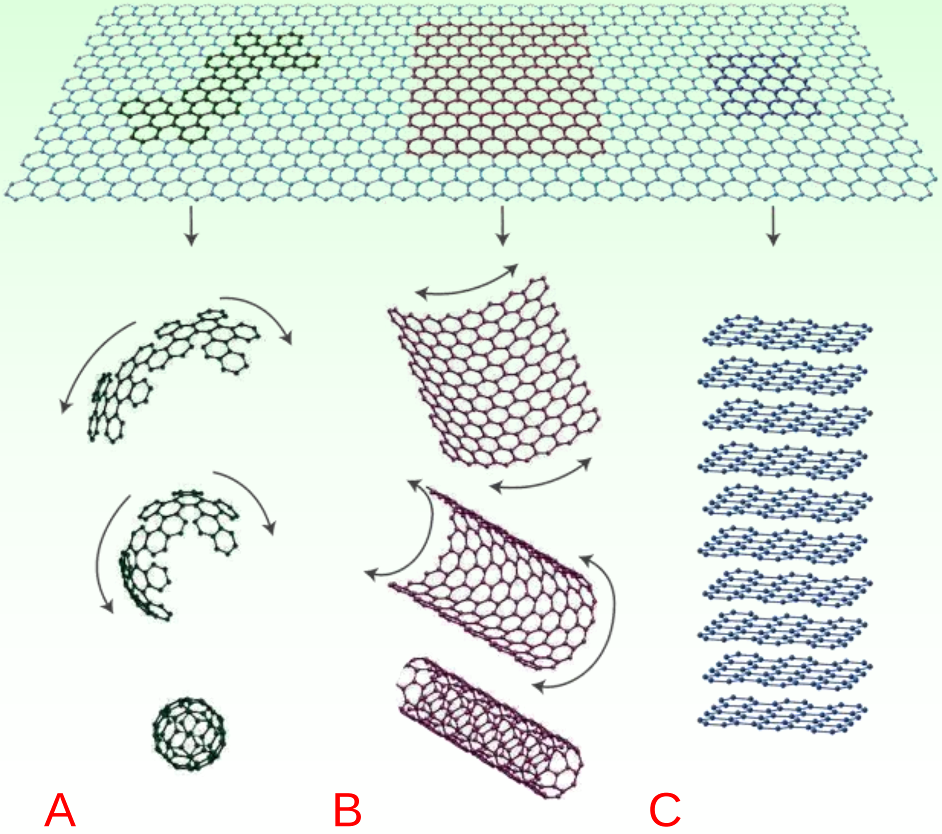


Graphene

Graphene – is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphite is composed of graphene layers



Structure of graphene layer

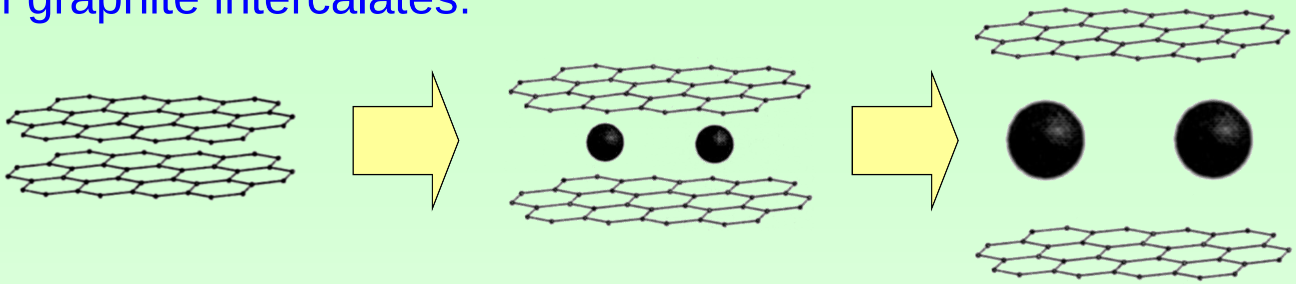


- Small single layers of graphene are thermodynamically unstable and should wrap into spheres (A), cylinders (B) or stack atop each other (C).
- According to quantum calculations, graphene sheet becomes thermodynamically stable if contains no less than 6000 atoms (~10 nm size)
- Graphene layers could be viewed as building material for fullerenes, nanotubes or graphite

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

Graphene synthesis

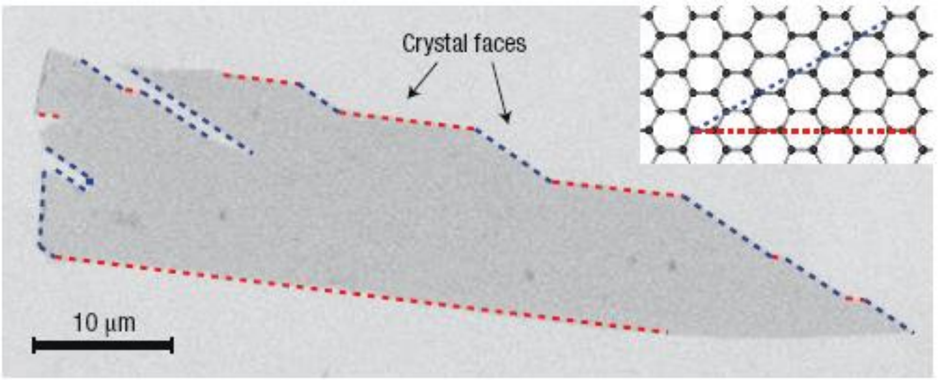
1) Exfoliation of graphite intercalates:



When graphite layers are significantly separated, the guest molecules are removed chemically (sometimes with ultrasonication), to obtain a sludge consisting of restacked and scrolled graphene sheets. Because of uncontrollable character, such material has attracted limited interest, however, considerable developments of this method has been achieving recently.

2) Exfoliation of graphite layers by scotch film.

Sticky scotch film was repeatedly used to split graphite crystal into smatter flake pieces. The organic film then was dissolved, thin graphite flakes precipitated onto amorphous Si support and was investigated by AFM. Some macroscopic isolated single layered graphene sheets were found and characterized.



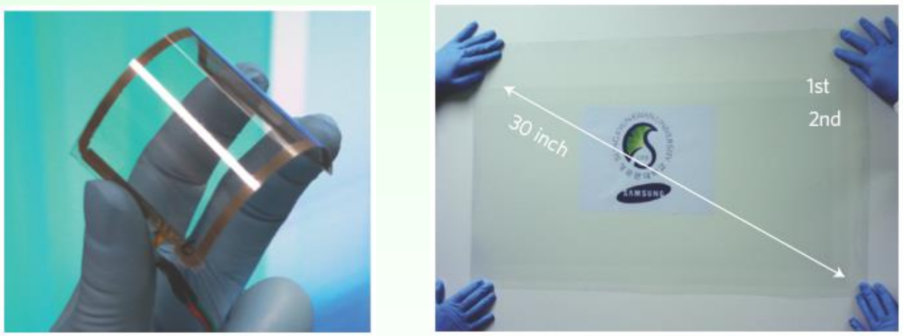
Graphene synthesis

3) Epitaxial growth on SiC surface:

3.1) The growth of graphene on insulating silicon carbide (SiC) surfaces by high-temperature annealing in vacuum (Si atoms sublimes from the structure) yielding graphene layers with small grains (30–200 nm).

3.2) Large (same as the substrate wafer size) and homogeneous layers of graphene are obtained by the epitaxial growth on hexagonal SiC wafer (0001 surface), annealed in a Ar atmosphere (pressure ~1 bar, T = 1500 – 2000 °C). The face of the SiC used for graphene creation, the silicon-terminated or carbon-terminated surface highly influences the thickness and carrier density of the graphene.

4) Epitaxial growth on metal (Ir, Ru, Ni, Cu) substrates by CVD.

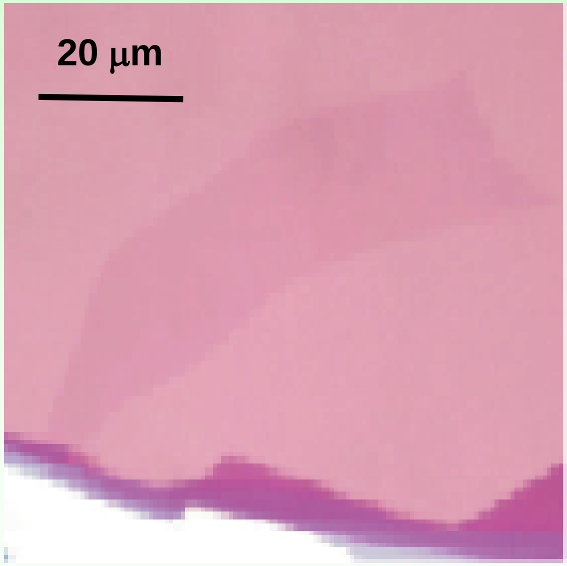


30-inch graphene films grown by chemical vapour deposition onto flexible copper substrate.

5) Reduction of graphene oxide paper in pure hydrazine H_4N_2

Exfoliated Graphene Monolayers and Bilayers

Reflecting microscope images.



Monolayer

Bilayer

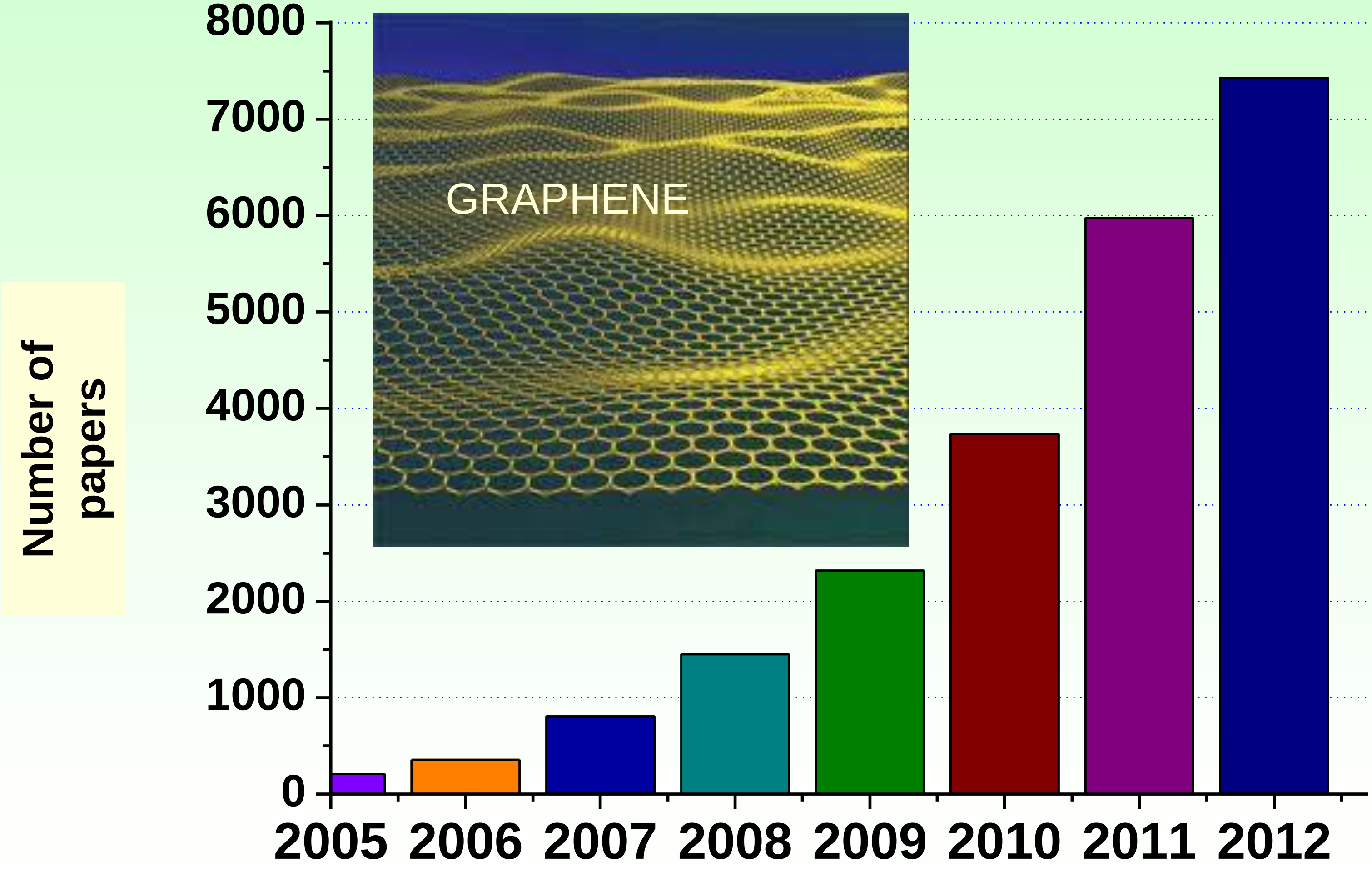
K. S. Novoselov *et al.*, *Science* **306**, 666 (2004).

Graphene properties

It was shown that the electronic structure of multilayered graphene rapidly evolves with the number of layers, approaching the 3D limit of graphite at 10 layers. Therefore, single- or double layered graphenes possess unique properties, such as:

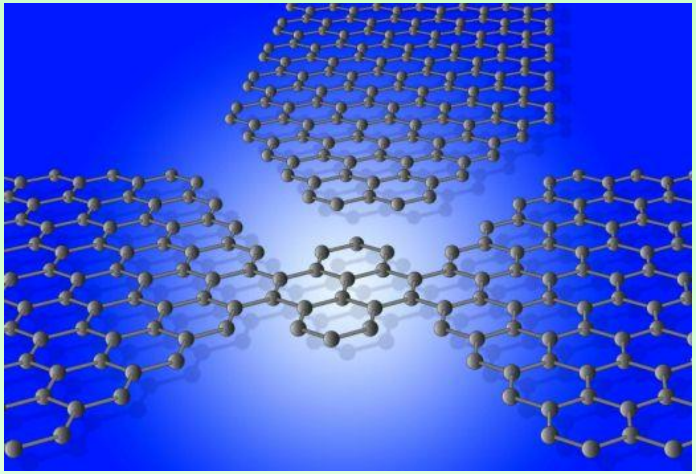
- novel magneto-transport properties
- high carrier (electron) mobility and ballistic transport up to room temperature. The corresponding resistivity of the graphene sheet could be 10^{-6} Ω·cm, less than the resistivity of silver!
- potential for technological applications as a successor of silicon in the post Moore's law era, as field-effect transistor effect for double layered graphene was demonstrated (E_g tuning from 0 to 0.25 *e*V by applying voltage)
- a single-molecule gas sensor
- in spintronics
- quantum computing
- terahertz oscillator
- in composite materials to improve its conductive or/and mechanical properties (requires cheap, large scale synthesis)

Dynamics of research development in the field of graphene

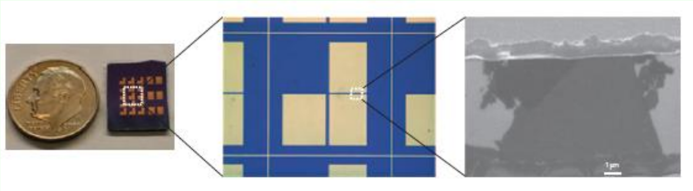


Graphene materials

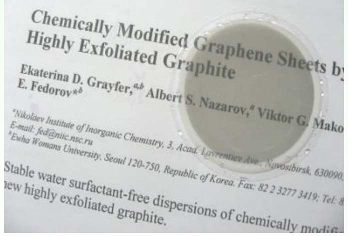
- High electrical conductivity
- High thermal conductivity
- High mechanical strength
- High specific surfaceи др.



Potential applications :



Integrated Circuits



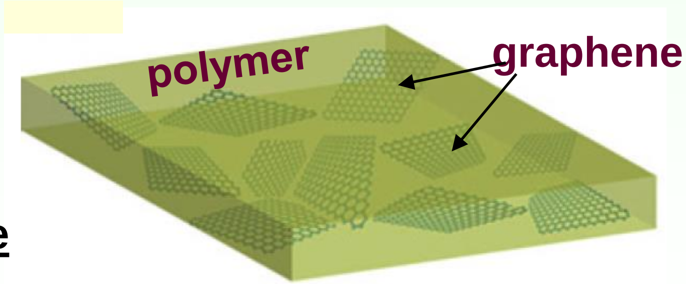
Chemically Modified Graphene Sheets by
Highly Exfoliated Graphite

Ekaterina D. Grayfer,[a,b] Albert S. Nazarov,[a] Viktor G. Mako
E. Fedorov*[a,b]

[a]Nikolaev Institute of Inorganic Chemistry, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090,
E-mail: fed@niic.nsc.ru
[b]Ewha Womans University, Seoul 120-750, Republic of Korea. Fax: 82 2 3277 3419; Tel: 8

Stable water surfactant-free dispersions of chemically modi
ew highly exfoliated graphite.

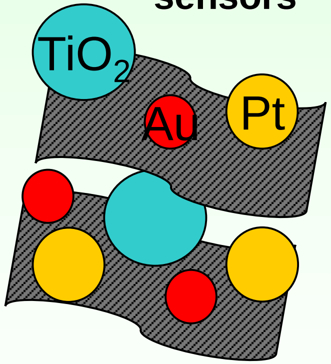
Transparent conductive flexible films



catalysis

sensors

energy conversion



composites

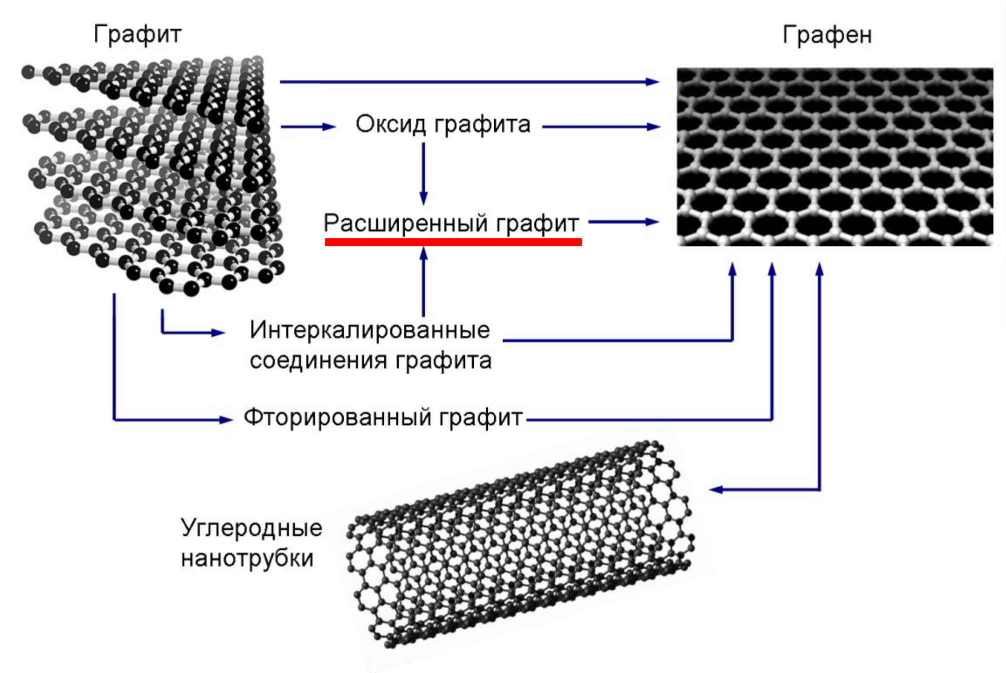
Synthesis

- **Mechanical cleavage**
- **Growing on a substrate**
- **Organic synthesis**

1 layer - "graphene"
Up to 10 layers - “low layer graphene”

Chemical cleavage of compounds containing graphene layers

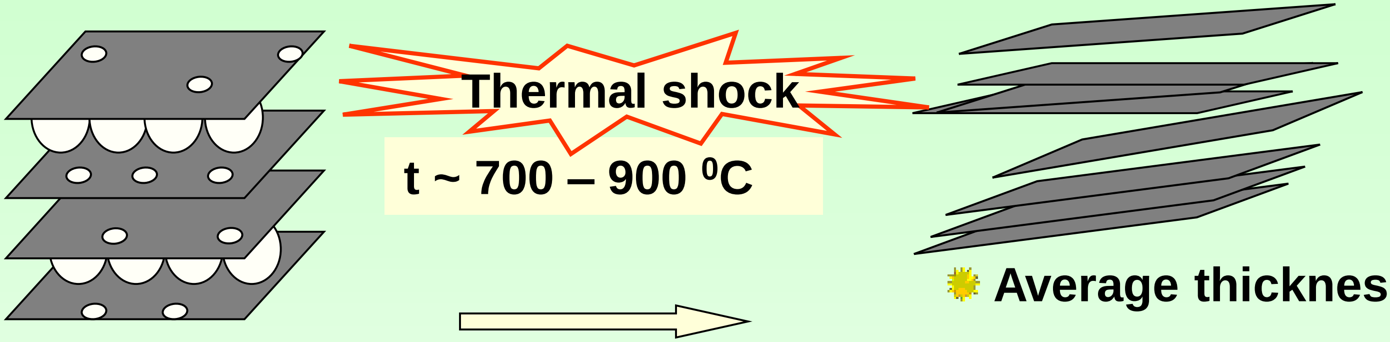
- **production of large quantities**
- **wide possibilities for modifying properties**
- **convenience of many technological operations (mixing, application, impregnation, etc.)**



Scheme for highly exfoliated graphite (HEG)

Intercalate $C_2F{\bullet}xR$

$C_2F{\bullet}xClF_3$



Thermal shock

t ~ 700 – 900 ^{0}C

○ = F

Ⓡ = ClF_3,
$(CH_3)_2CO$,
CCl_4, C_6H_6,
CH_3CN и т.д.

- **Average thickness :**
  3 – 4 nm
- **Bulk density :**
  0,4-1,0 g/l
- **Volume increase:**
  up to 2500 times

$C_2F{\bullet}x(CH_3)_2CO$

$C_2F{\cdot}xClF_3 \rightarrow$ HEG $+ CF_4 + C_xF_y + C_xF_yCl_z$

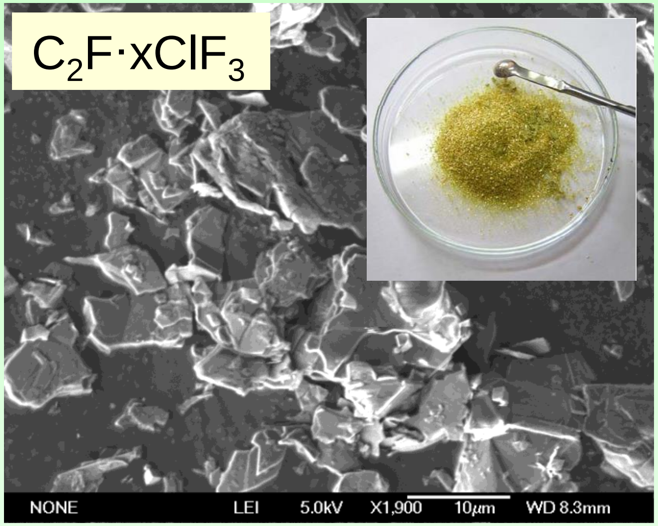
$C_2F{\cdot}xCCl_4 \rightarrow$ HEG $+ CF_4 + C_xF_y + CCl_4$

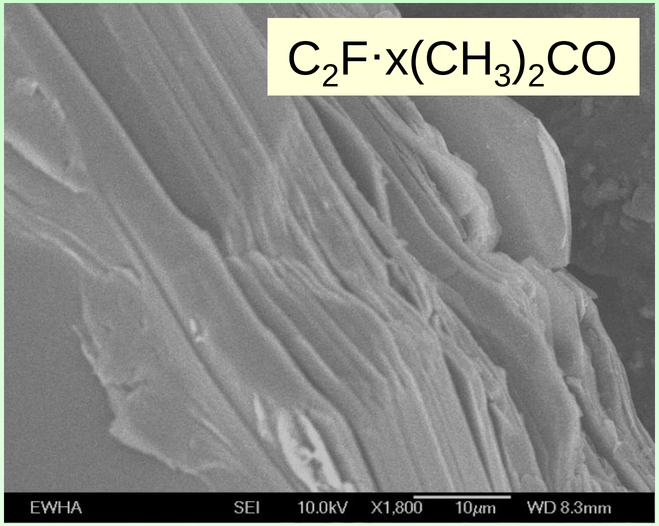
$C_2F{\cdot}x(CH_3)_2CO \rightarrow$ HEG $+ CF_4 + C_xF_y + (CH_3)_2CO + HF + \ldots..$

- **Yield: 35 – 60 %**

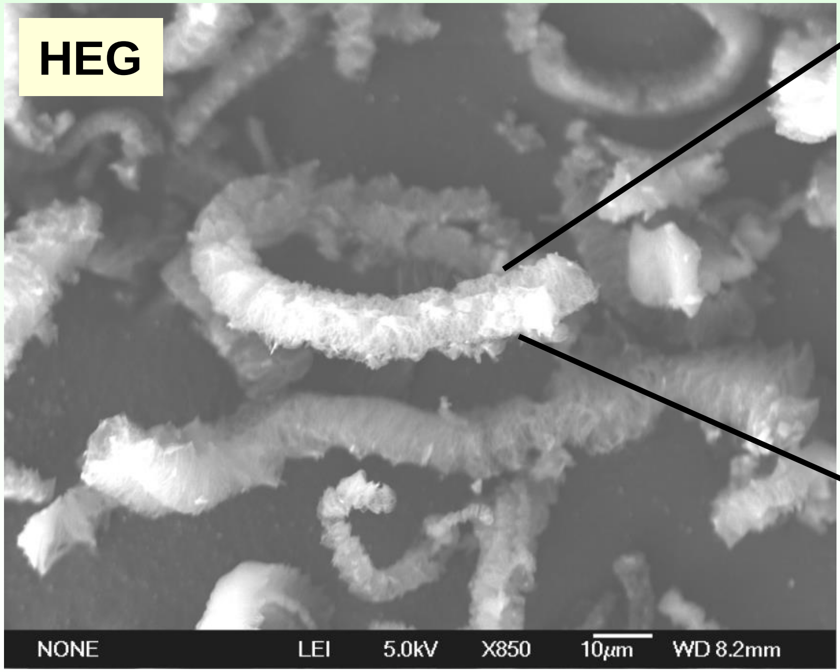
V.G. Makotchenko, E.D. Grayfer, A.S. Nazarov, S.-J. Kim, V.E. Fedorov, *Carbon*, 49(10), 3233-3241 (2011)

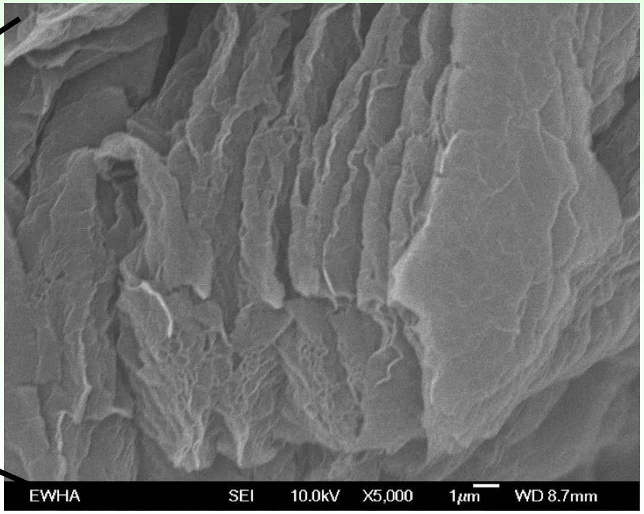
Characterization of highly exfoliated graphites: **SEM**





Layered morphology of the precursors

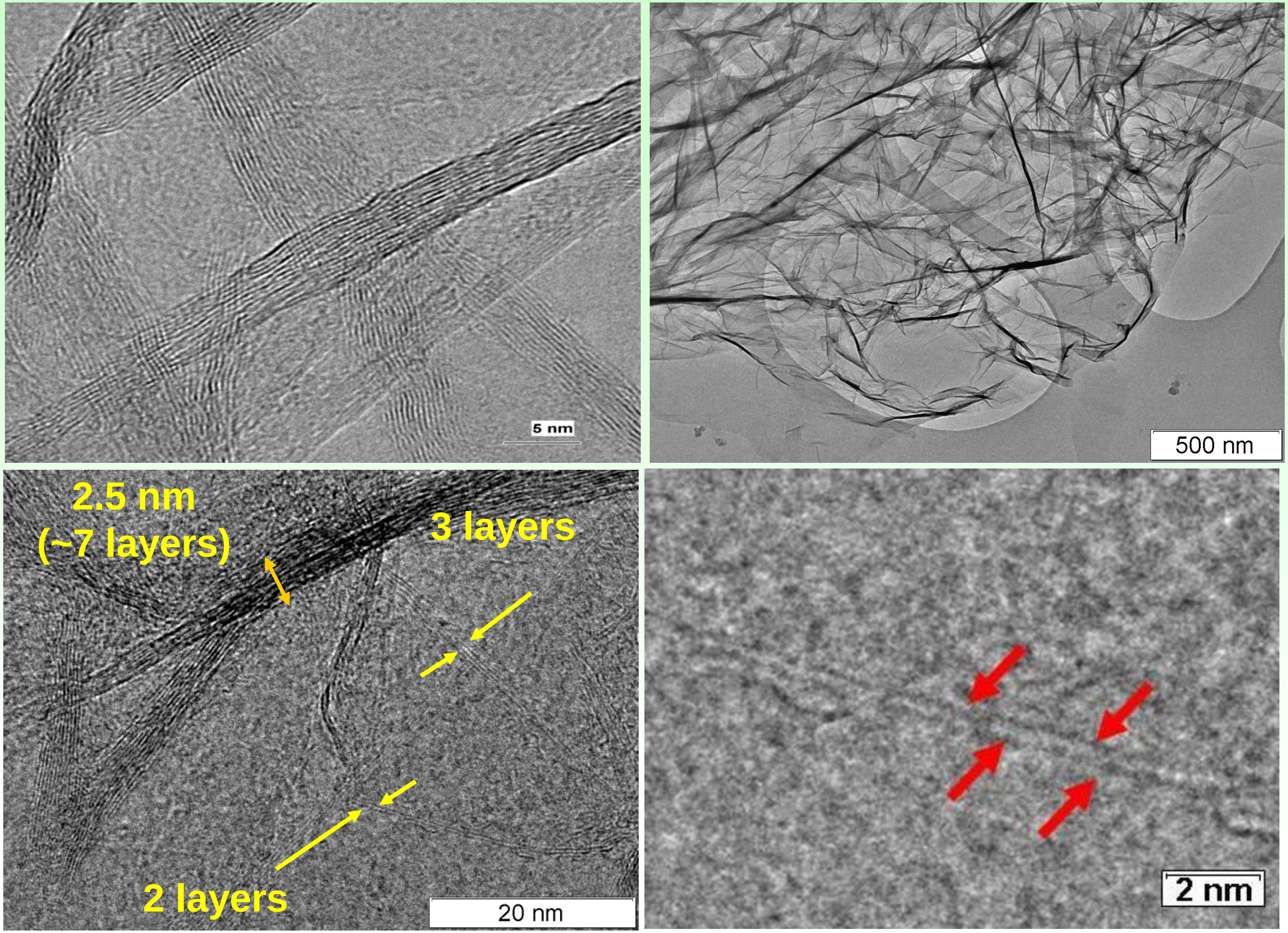




"Worm-like" morphology of HEG

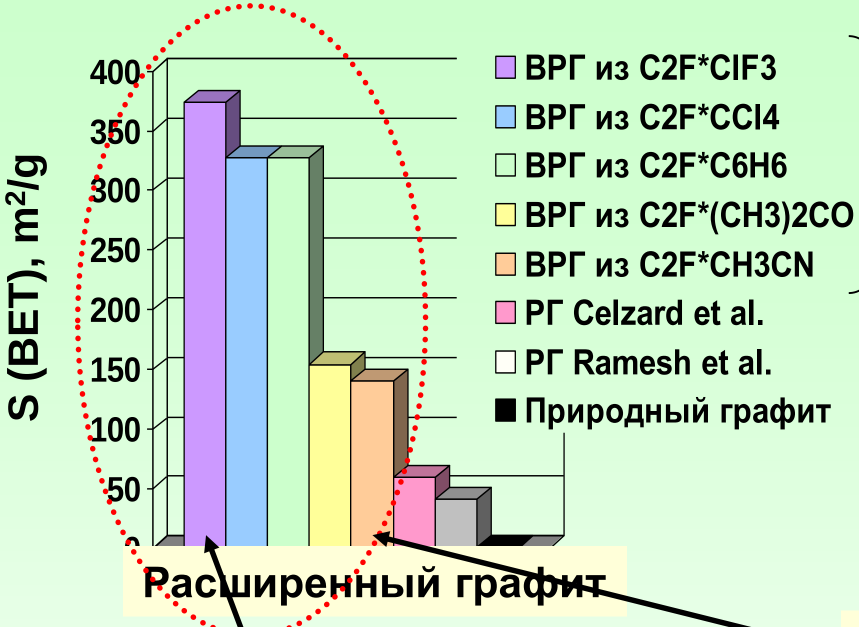
V.G. Makotchenko, E.D. Grayfer, A.S. Nazarov, S.-J. Kim, V.E. Fedorov, *Carbon*, 49(10), 3233-3241 (2011)

Characterization of highly exfoliated graphites: TEM

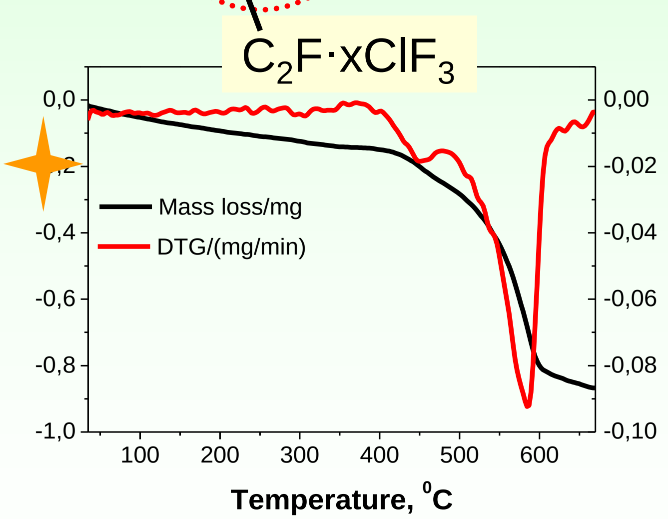


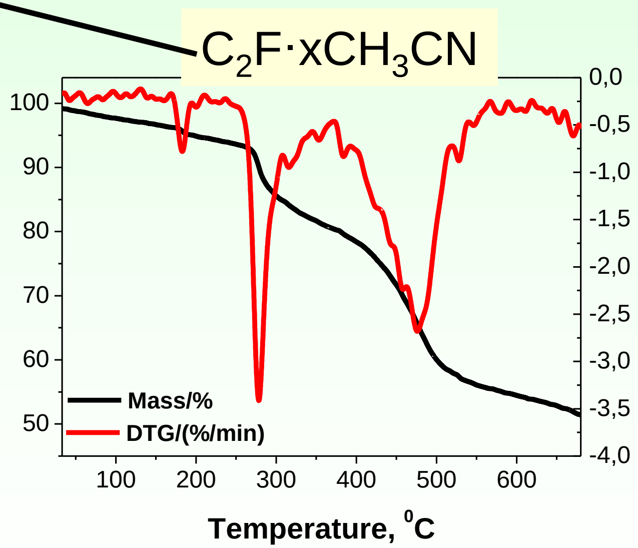
V.G. Makotchenko, E.D. Grayfer, A.S. Nazarov, S.-J. Kim, V.E. Fedorov, *Carbon*, 49(10), 3233-3241 (2011)

Characterization of highly exfoliated graphites: BET, TG



All HEGs surpass the well-known materials in their characteristics. However, the degree of exfoliation from different precursors is somewhat different.





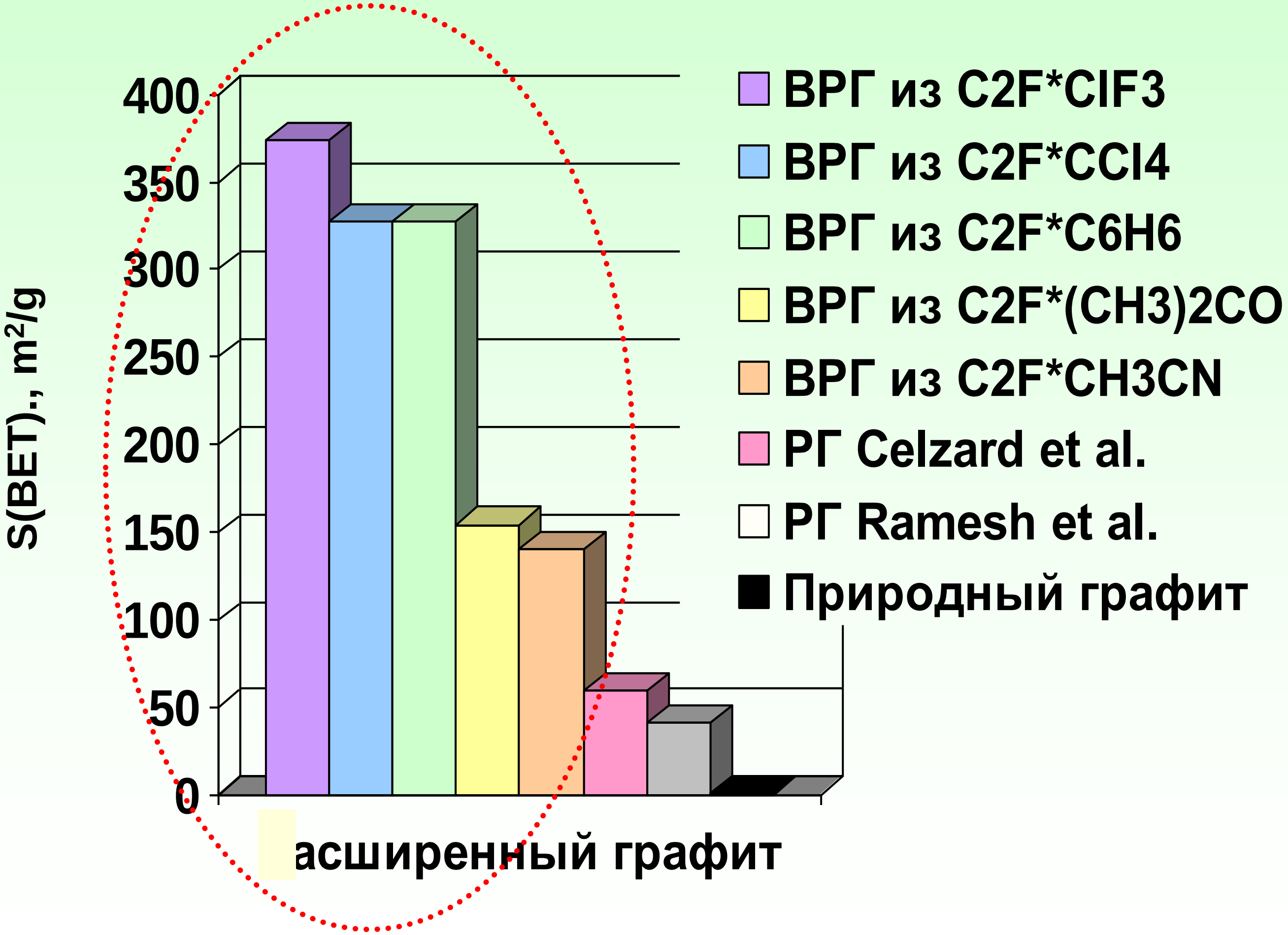
- The most highly exfoliated sample is obtained by decomposition of the intercalate with chlorine trifluoride.
- The use of other intercalate allows to increase the yield.

Only one decomposition stage: more efficient exfoliation

Several stages

V.G. Makotchenko, E.D. Grayfer, A.S. Nazarov, S.-J. Kim, V.E. Fedorov, *Carbon*, 49(10), 3233-3241 (2011)

Comparison of Specific Surfaces of Expanded Graphite (EG) and Highly Exfoliated Graphite (HEG)



Removal of volatile organic compounds (VOCs) has attracted much attention recently because VOCs have caused environmental and health problems, such as urban smog, destruction of ozone layer, infection to eyes, nose and even cancer. Now many technologies have been developed to remove VOCs, including condensation, catalytic oxidations, biological treatments, adsorption and absorption. Among them, the **absorption is a simple and effective technology**.

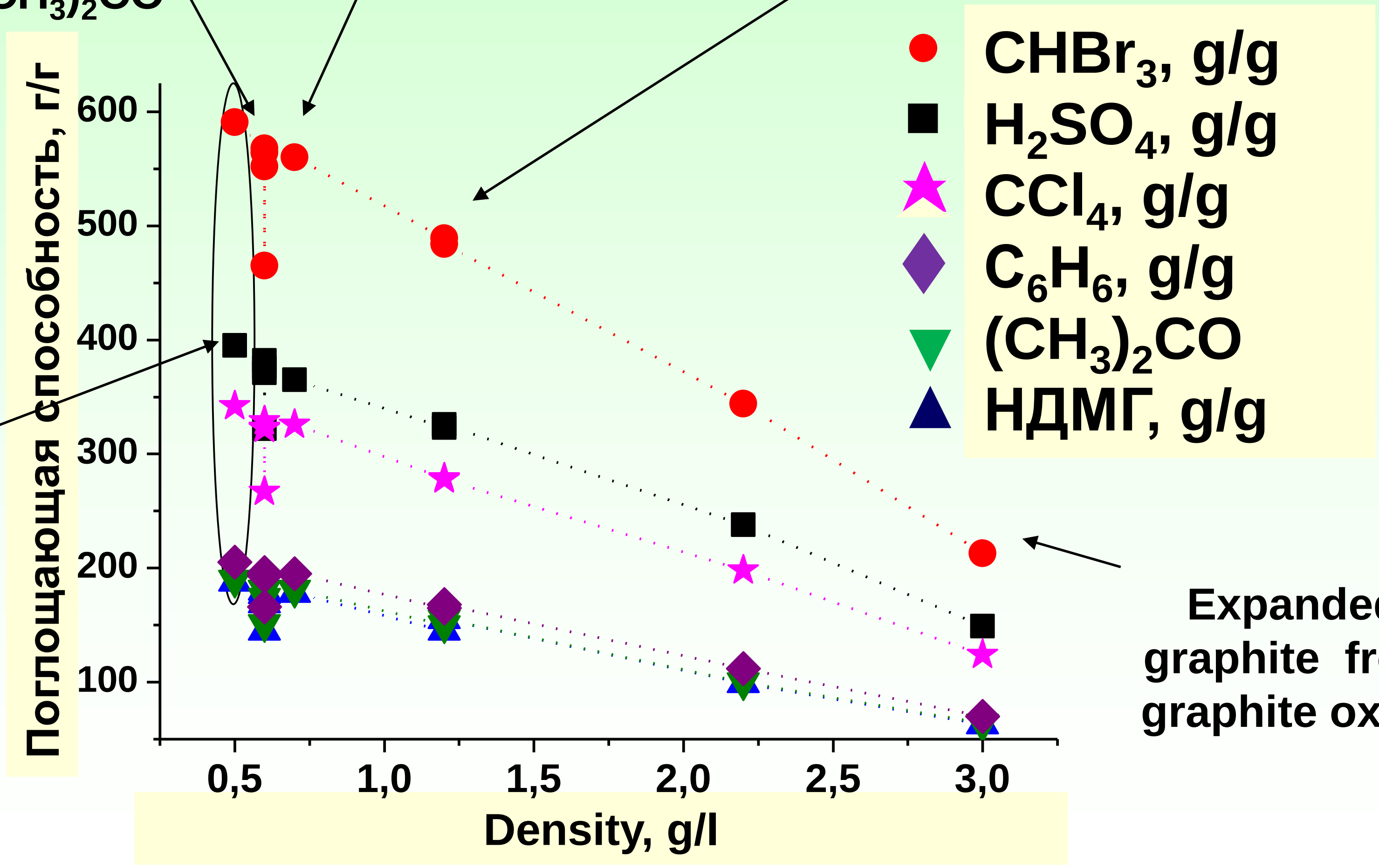
Expanded graphite (EG) prepared from graphite intercalated compounds is a kind of hydrophobic carbon material and has varied macro- and mesopores. As a new carbon material, EG has been proposed as an adsorbent for oil because of its surprising sorption capacity. It was reported that 1 g of EG could adsorb 86 g of A-grade heavy oil or 76 g of crude oil.

Absorbency of Highly Exfoliated Graphite (HEG)

HEG from $C_2F{\cdot}xCH_3CN$, $C_2F{\cdot}x(CH_3)_2CO$

HEG from $C_2F{\cdot}xCCl_4$

HEG from $C_2F{\cdot}xC_6H_6$



HEG from $C_2F{\cdot}xClF_3$

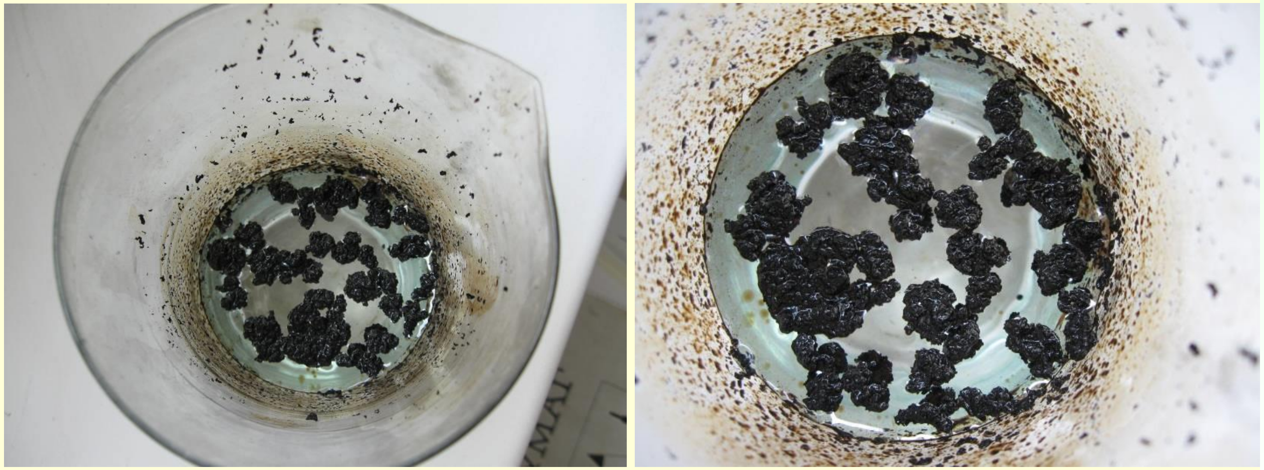
Expanded graphite from graphite oxide

Oil absorption by highly exfoliated graphite (HEG)

Oil on the
surface of the
water

Oil + HEG

Oil + HEG (5 min) – total absorption:



~ 180 ml of
oil for
1 g HEG

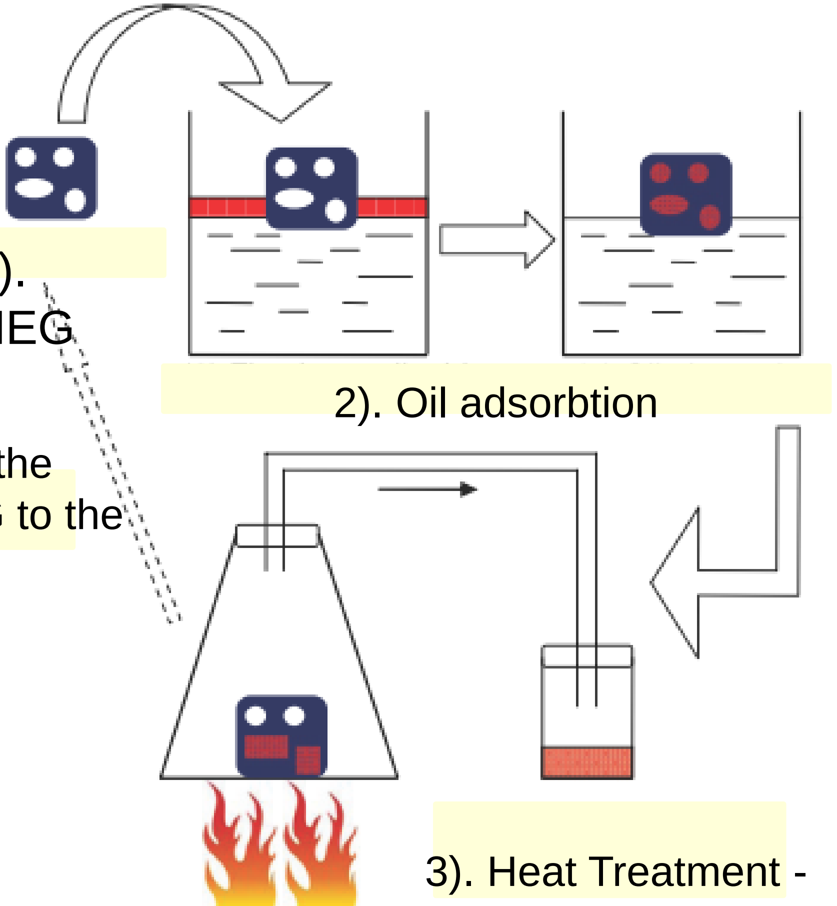
Inagaki et al:
40-80 g for 1 g EG

The high absorption capacity of
HEG in relation
to a number of liquids

⇨

Perspective sorbent for the elimination of
spills of oil and other applications (sterile
cotton wool in medicine, etc.)

Recycling Highly Exfoliated Graphite in the process of oil sorption



1). HEG

2). Oil adsorbtion

3). Heat Treatment - Petroleum Distillation

4). Return of the restored HEG to the process

From HEG, which absorbed oil, it is possible to distillate easily boiling fractions of oil when heated.

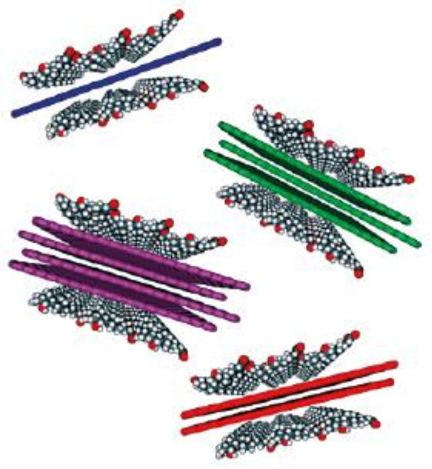
Such regeneration of the sorbent can be carried out several times without significant loss of sorption capacity.

H. C. Bi, et al.,
Adv. Funct. Mater. 2012, 22, 4421–4425

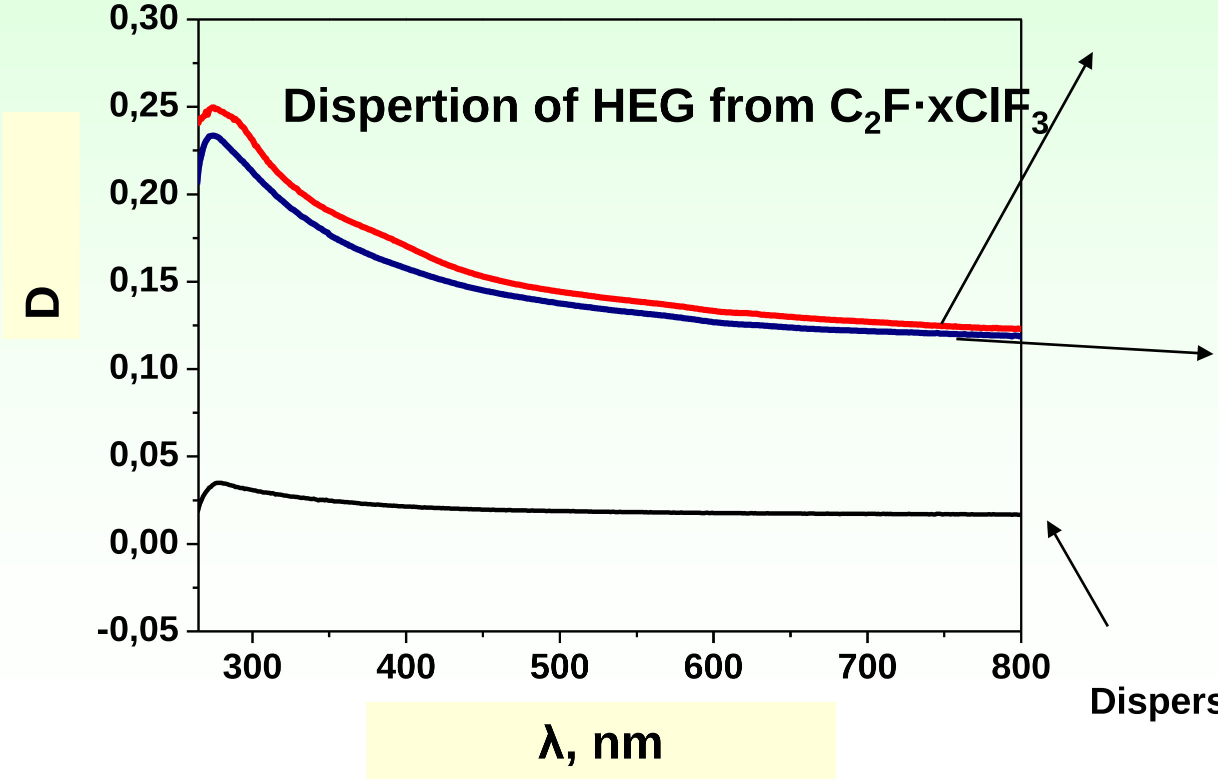
Dispersing of Highly Exfoliated Graphite

Non-covalent functionalization :

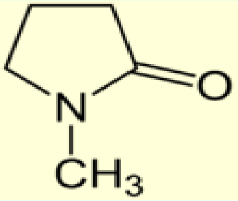
Sonication in DMF or NMP



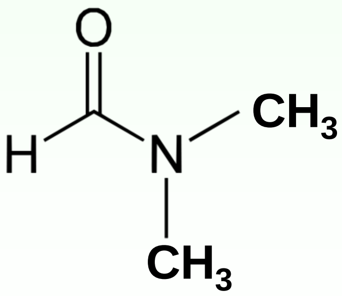
The dispersion concentration of HEG in DMF:
~ 18 ± 3 mg/l for 1 hour of sonication
(for natural graphite ~ 4 ± 2 mg/l for 24 hours sonication)



NMP

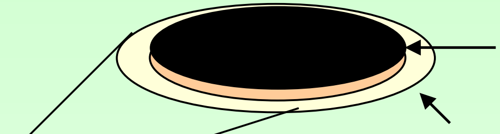


DMF



Dispersion of natural graphite in DMF or NMP

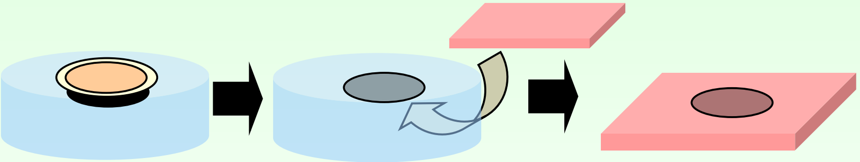
Production of graphene films and graphene "paper" from colloidal dispersions by filtration

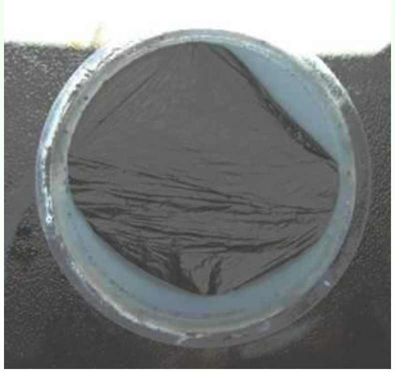


graphene material

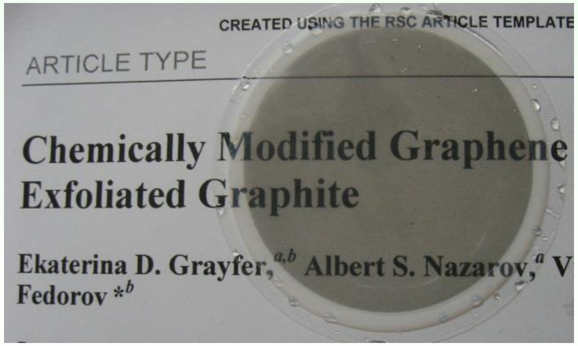
filter

Filter Dissolution and Transfer graphene film





"Graphene paper" (thickness 1-10 microns)



CREATED USING THE RSC ARTICLE TEMPLATE

ARTICLE TYPE

Chemically Modified Graphene Exfoliated Graphite

Ekaterina D. Grayfer,[a,b] Albert S. Nazarov,[a] V
Fedorov *[b]

A thin graphene film on the filter Anodisc 0.02 microns

[a] Nikolaev Institute
40 Novosibirsk, 6300
3309253; E-mail: f
[b] Ewha Womans U
3277 3419; Tel: 82

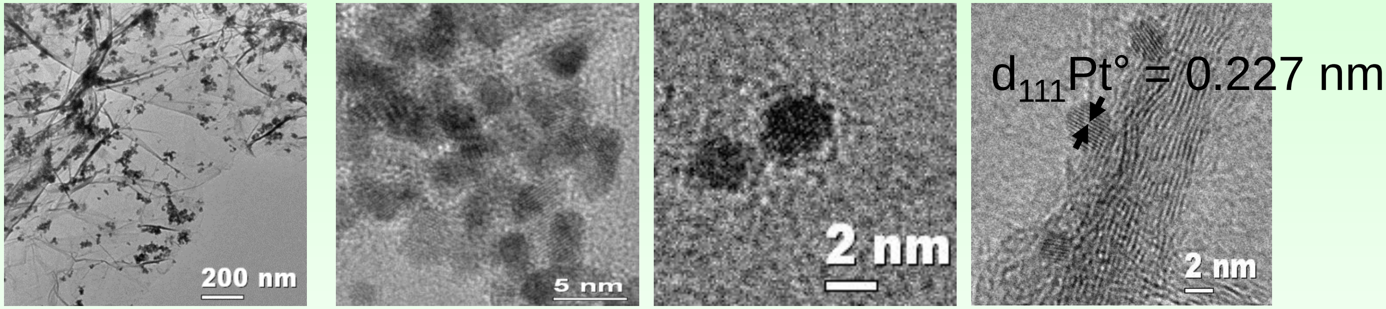
Thin graphene film on quartz

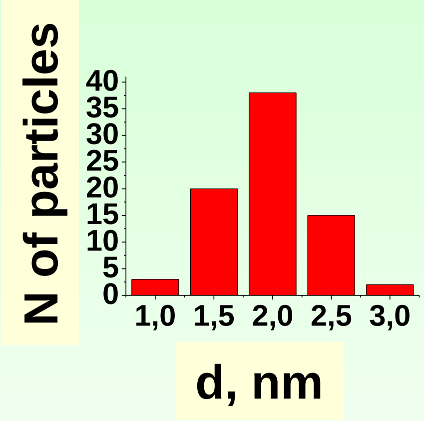
Pt nanoparticle deposition on Highly Exfoliated Graphite (HEG) and catalysis

HEG $\xrightarrow[\text{2) heating with } K_2PtCl_4 \text{ in atm. } N_2]{\text{1) Ultrasonic treatment in } H_2O \text{ / ethylene glycol}}$ **Pt/HEG**

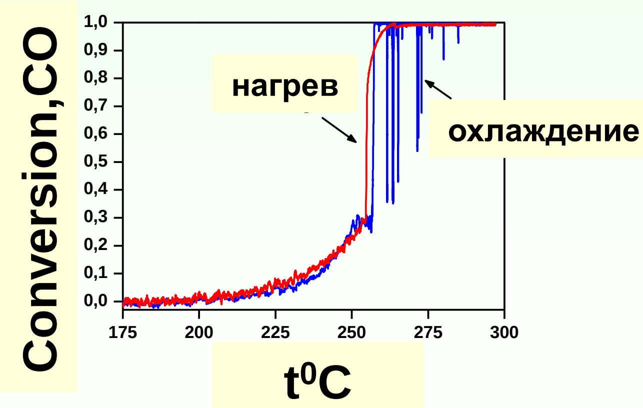
Upto 20 % of Pt.

TEM

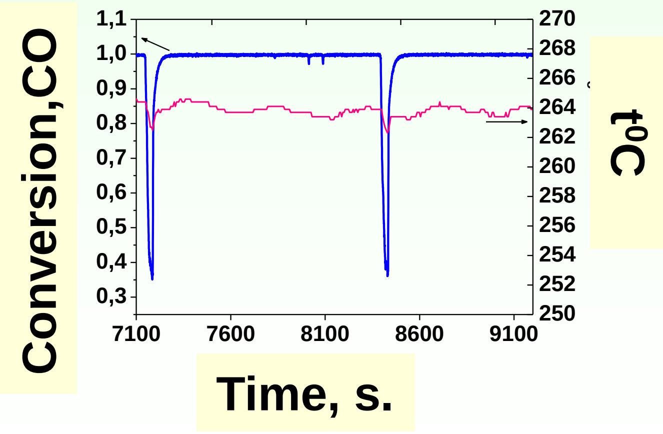




Catalytic test for CO oxidation: oscillation mode!



CO conversion versus T



Dependence of CO conversion on time at constant T

Modification of Highly Exfoliated Graphite

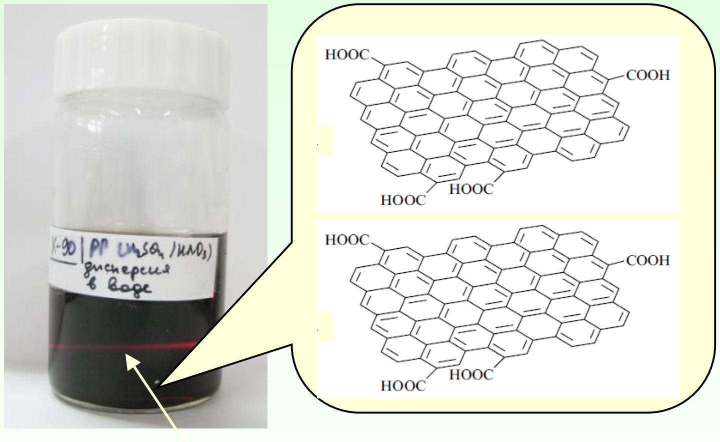
Known Hammers method of obtaining graphite oxide($H_2SO_4/NaNO_3/KMnO_4$):

- the introduction of O groups leading to exfoliation and solubility
- poorly controlled process, contamination by-products, high O content

Goal: the introduction of a small amount of O-groups, sufficient to achieve delamination and dissolution, not bringing to the graphite oxide

HEG

1. **Reaction with acids H_2SO_4/HNO_3 at T**
2. **Separation of the product, washing**
3. **Dispersion in water**

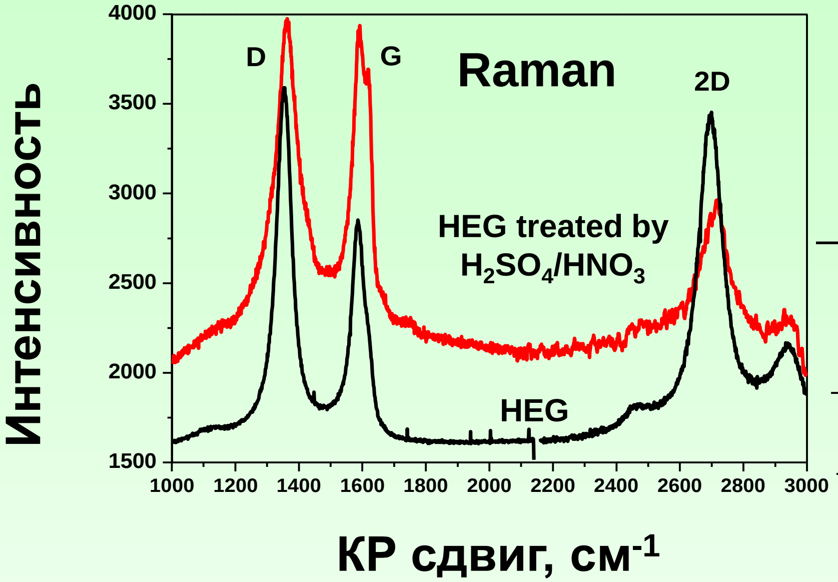


Tyndall effect

Modified Graphene Aqueous Dispersion

E.D. Grayfer, A.S. Nazarov, V.G. Makotchenko, S.-J. Kim, V.E. Fedorov,
J. Mater. Chem., 21(10), 3410-3414 (2011)

Characterization of HEG modified by oxygen



Elemental analysis of HEG before and after acid treatment:

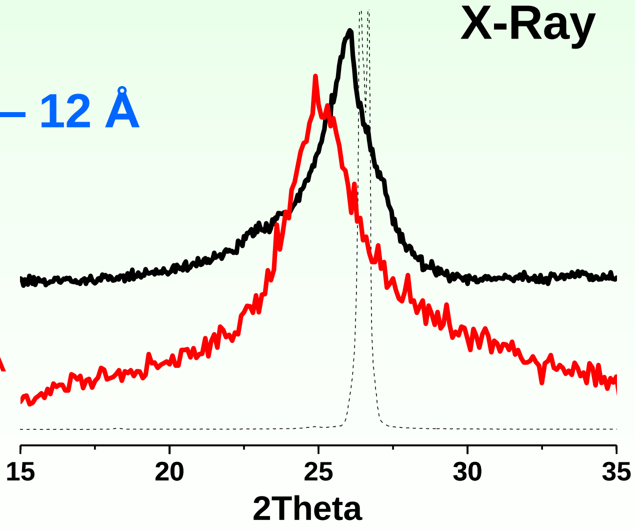
	C	F	Cl	H	O
до	94.06	2.95	1.86	0.46	0.67
после	85.04	2.11	1.16	1.11	10.58
GO	~ 56-59	-	-	~ 1-2	~ 40-43

Graphite oxide (GO): d_{002} ~ 6 – 12 Å

HEG: d_{002} ~ 3.50 Å

HEG after oxidation: d_{002} ~ 3.58 Å

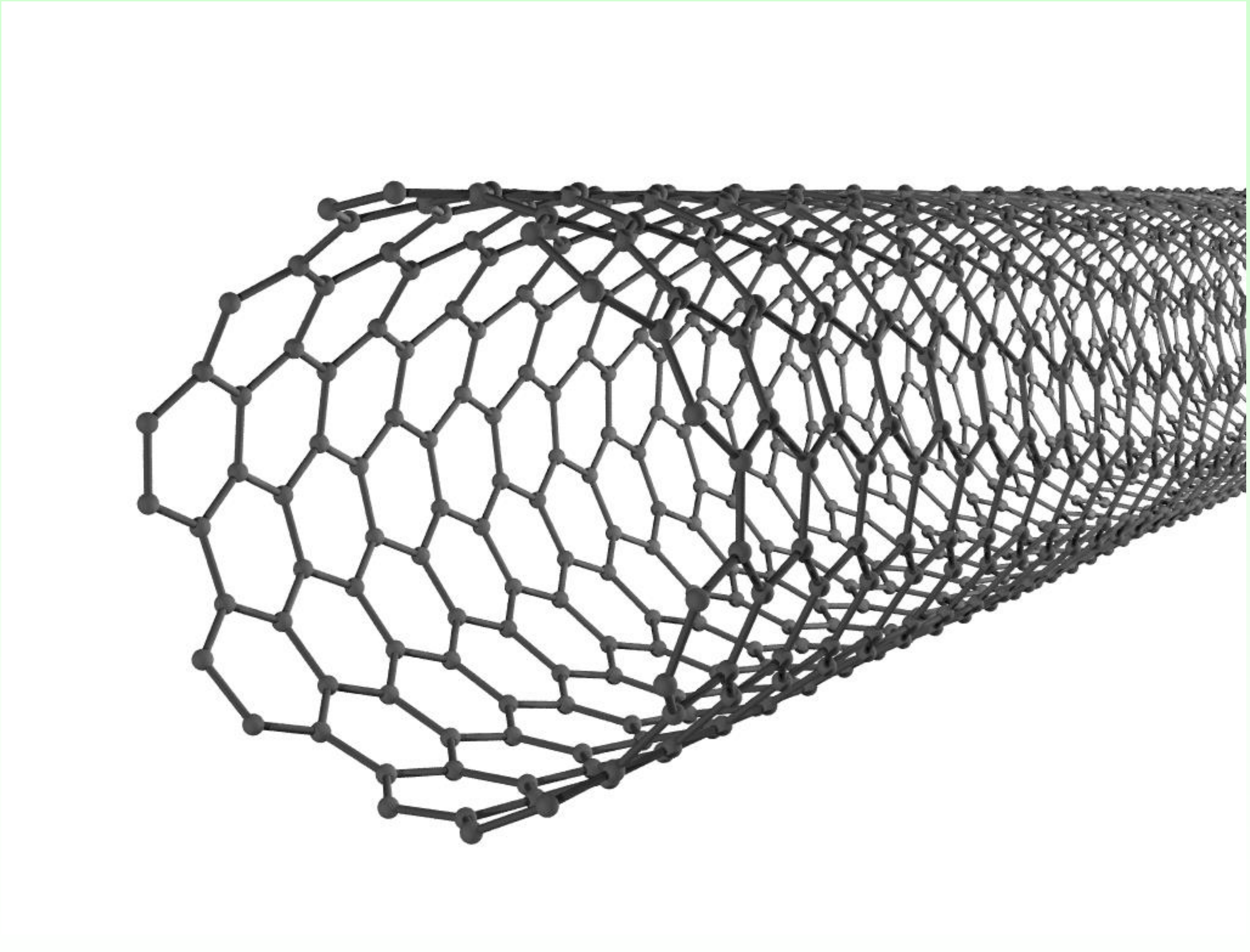
Graphite: d_{002} ~ 3.35 Å



- **introduction of O-groups, but no GO phase**
- **preservation of the structure of the graphene layer after modification**

E.D. Grayfer, A.S. Nazarov, V.G. Makotchenko, S.-J. Kim, V.E. Fedorov, *J. Mater. Chem.*, 21(10), 3410-3414 (2011)

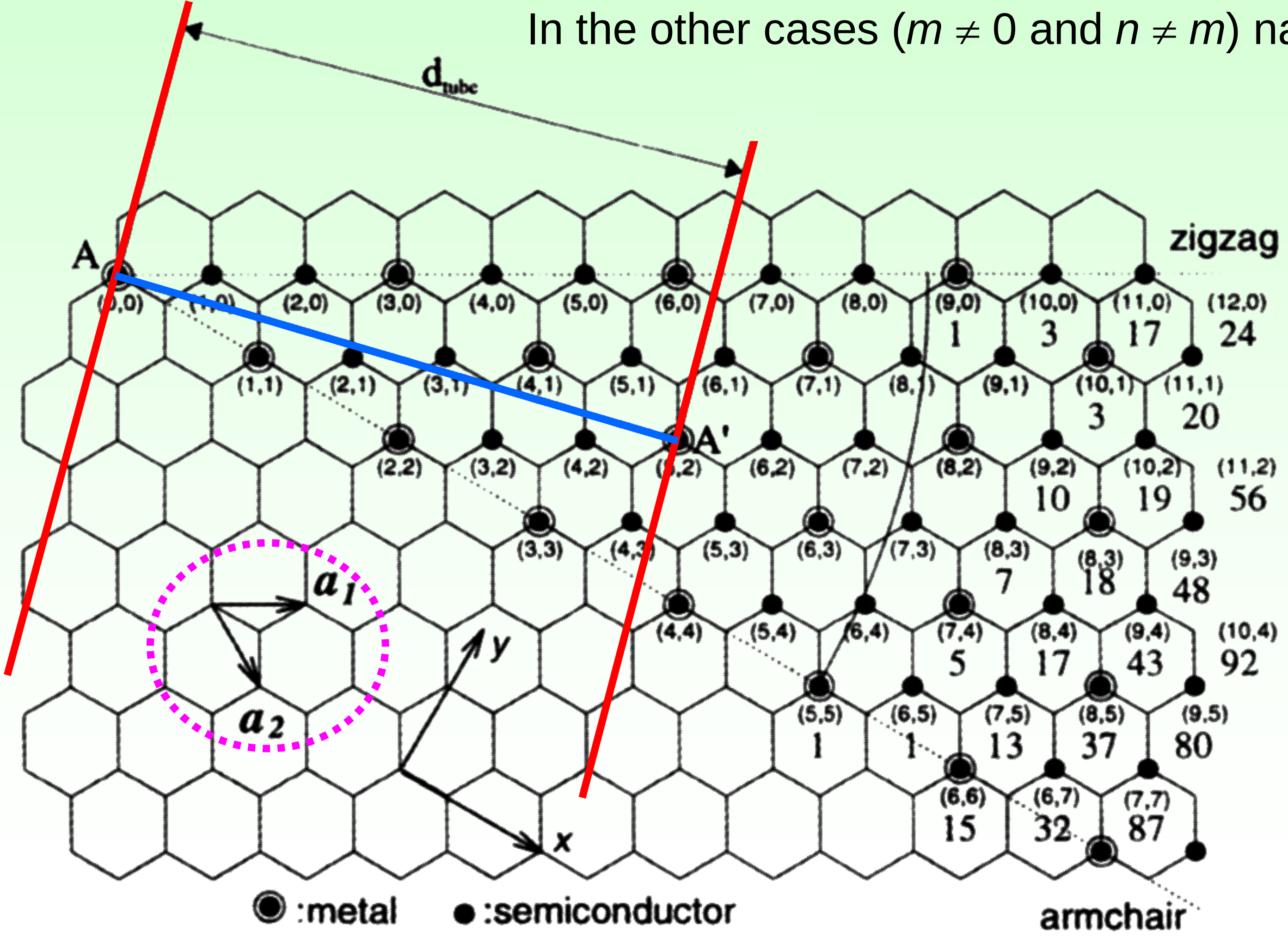
Carbon nanotubes



Single-walled carbon nanotubes (SWNT)

Carbon nanotubes are produced by wrapping of the monolayered graphene ribbon. That ribbon could be defined by single vector (Hamada vector, HV), which connect crystallographically equivalent graphene lattice sites. HV could be written as combination of indexes (***n***,***m***): HV = $\boldsymbol{n}a_1 + \boldsymbol{m}a_2$ (where a_1 and a_2 are graphene unit cell vectors). There are two extreme cases for HV: zigzag (m = 0) and armchair (n = m).

In the other cases ($m \neq 0$ and $n \neq m$) nanotubes are chiral.



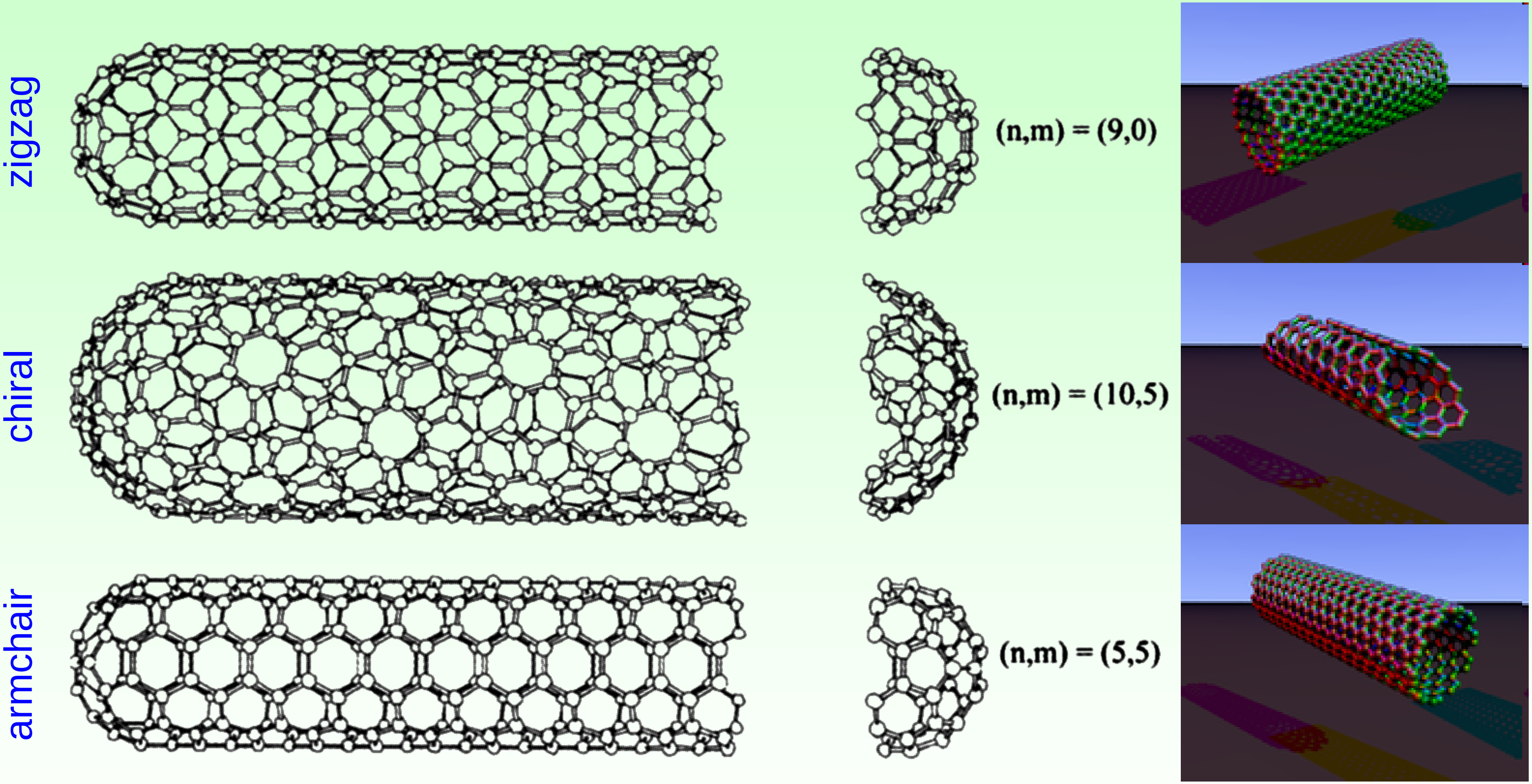
|| graphene ribbon

| Hamada vector

○ graphene unit cell vectors

Nanotube diameter:
Ø = HV / π

Example of carbon nanotubes



Examples of zigzag, armchair and chiral nanotubes

Single-walled carbon nanotubes (SWNT)

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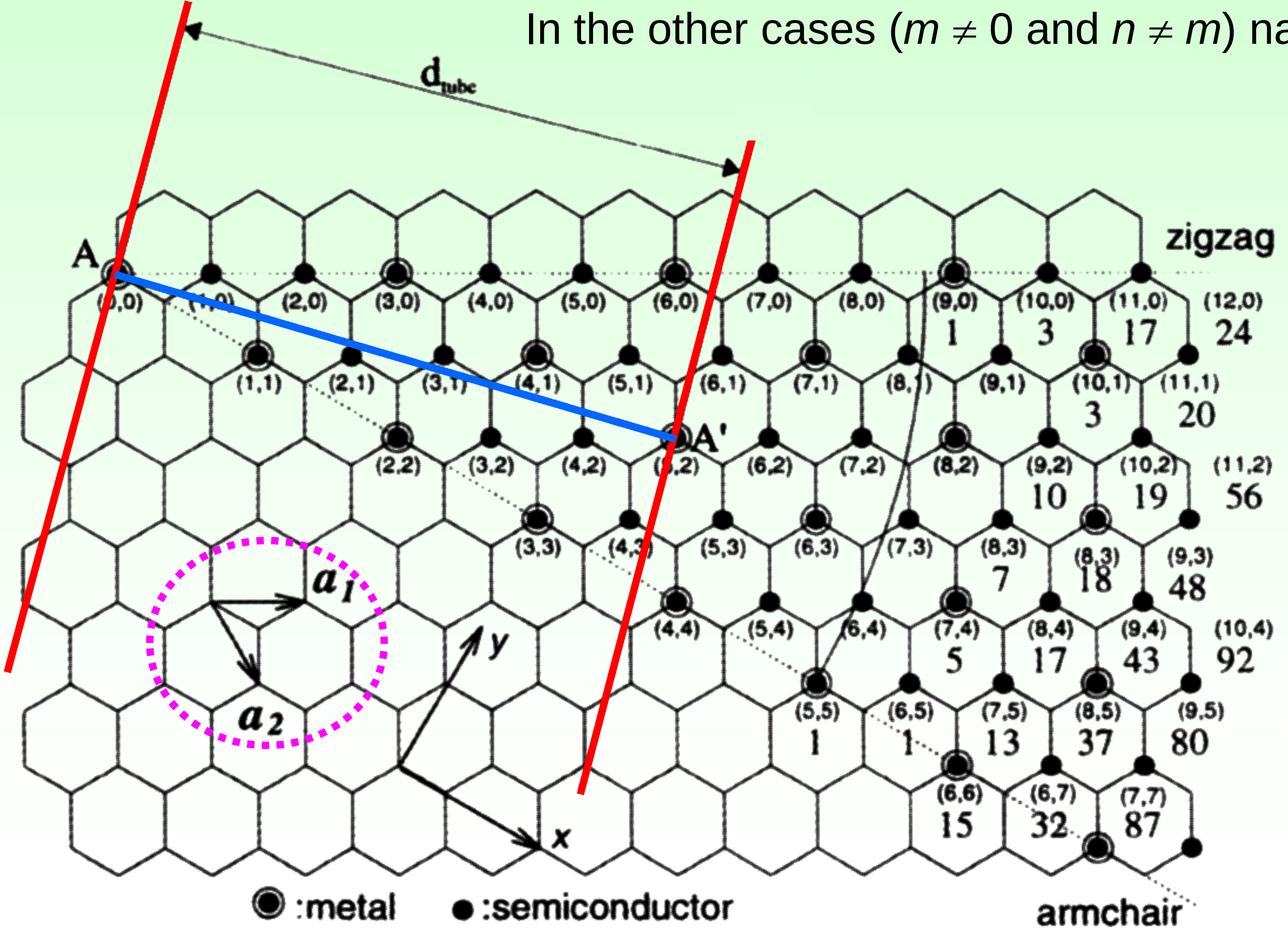


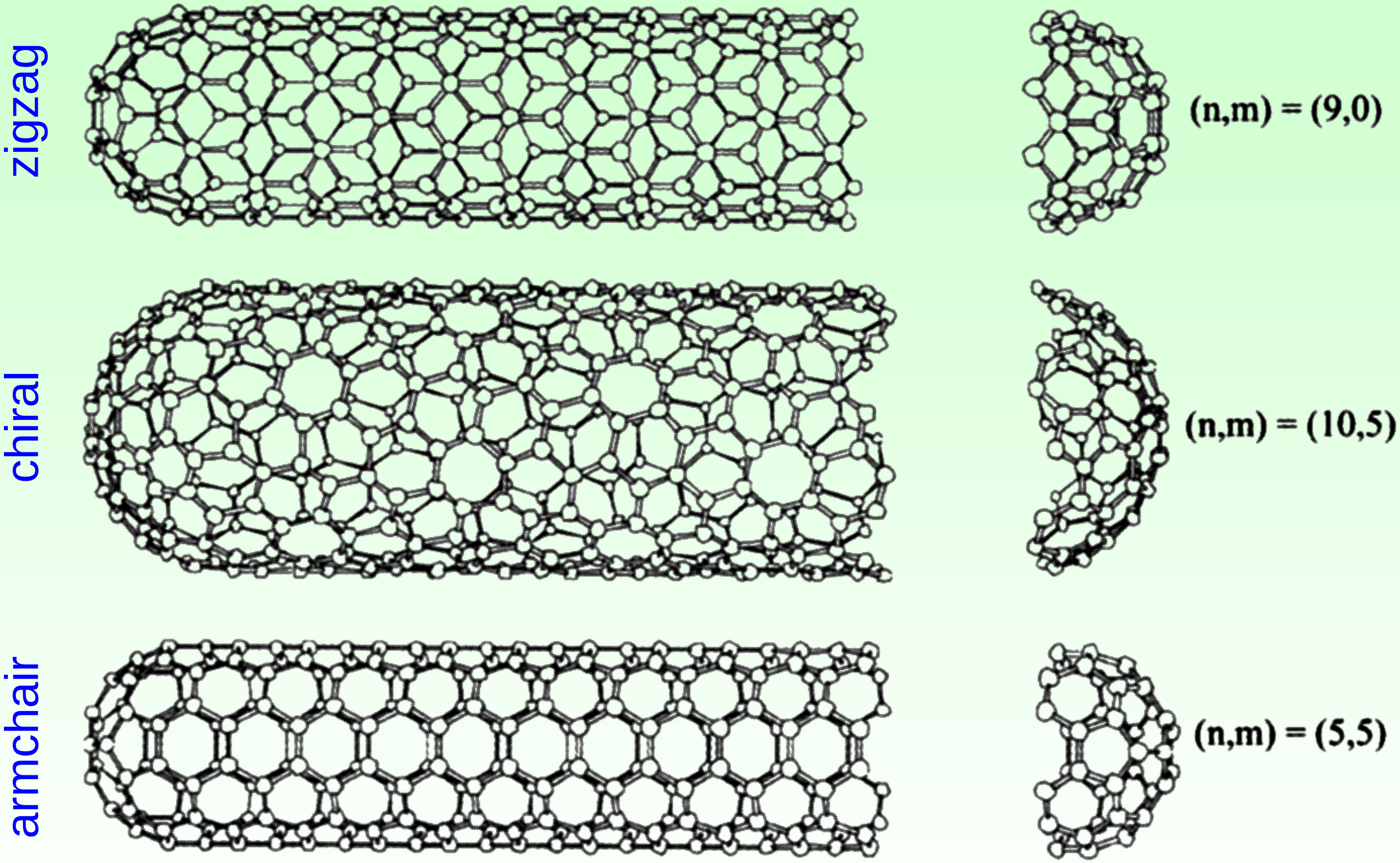
‖ graphene ribbon

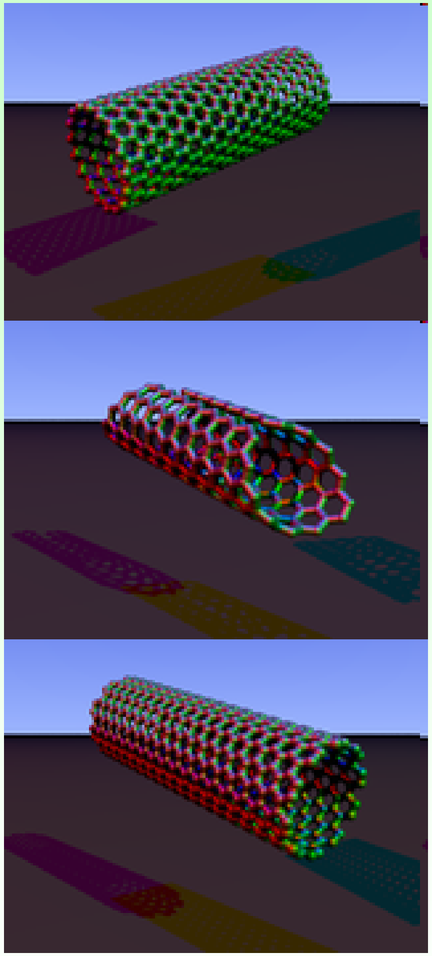
| Hamada vector

◌ graphene unit cell vectors

Nanotube diameter:
Ø = HV / π

Example of carbon nanotubes





Examples of zigzag, armchair and chiral nanotubes

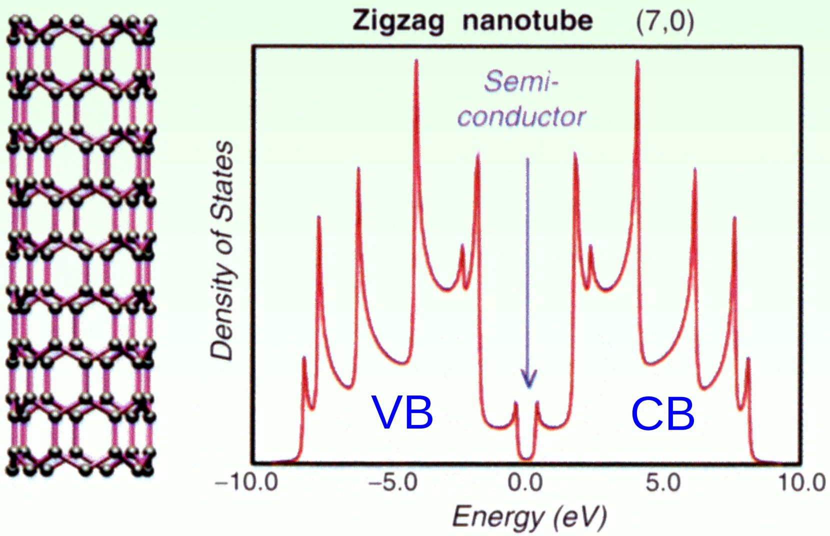
Electronic structure of carbon nanotubes

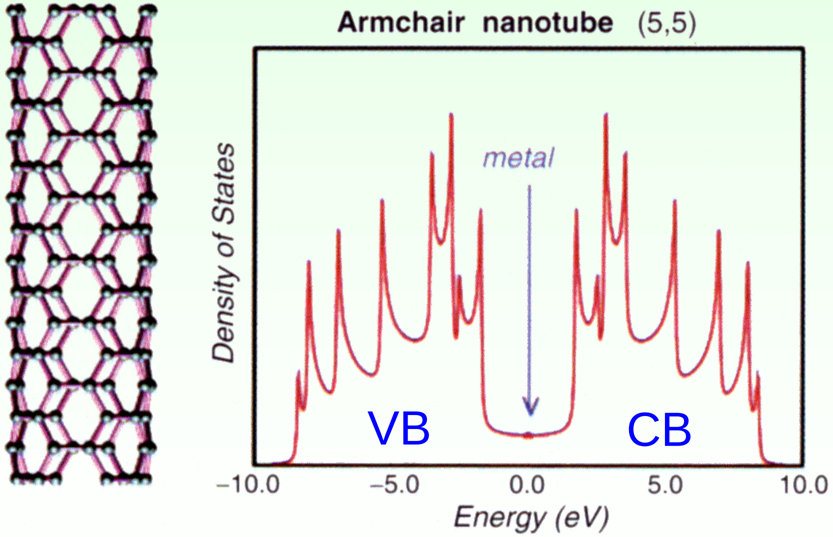
The electronic structure of the nanotubes (metallic or semiconducting) turns out to depend on the (***n***,***m***) indexes (there are, however, some exceptions):

■ Nanotubes (***n***,***m***), where (2***n*** + ***m***)/3 is integer are metallic. Otherwise – semiconductors.

- The armchair nanotubes are metallic.
- The zigzag nanotubes (***n***,**0**), where ***n*/3** is integer are metallic. Otherwise – semiconductors.

■ For the series of semiconducting nanotubes with the same chirality, the band gap E_g is inversely proportional to the tube diameter: *e.g*. E_g (7,0) > E_g (10,0).



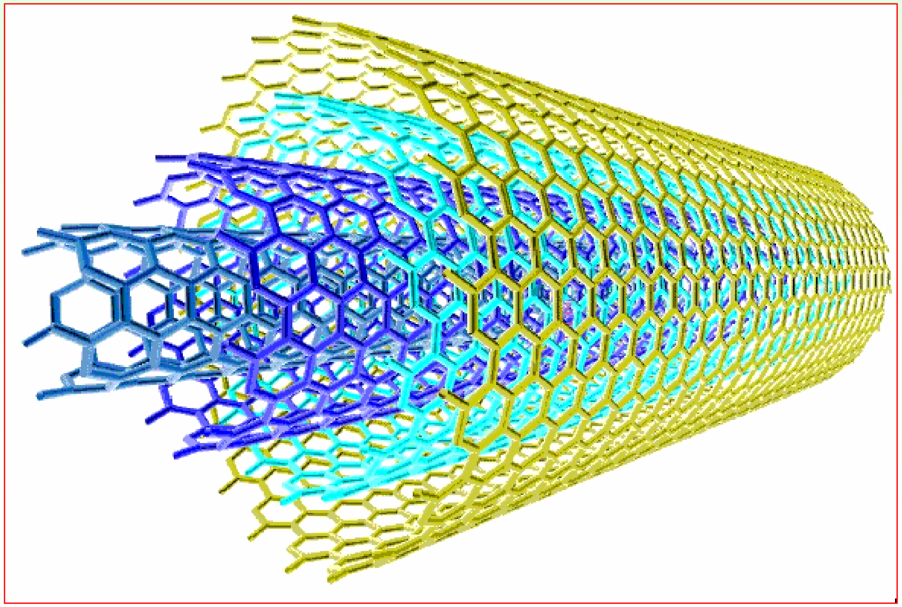


The band gap E_g could be tuned from ~ 10 meV to 1 eV, without any dopant, simply by changing the ribbon geometry!

Multiwalled carbon nanotubes (MWNT)

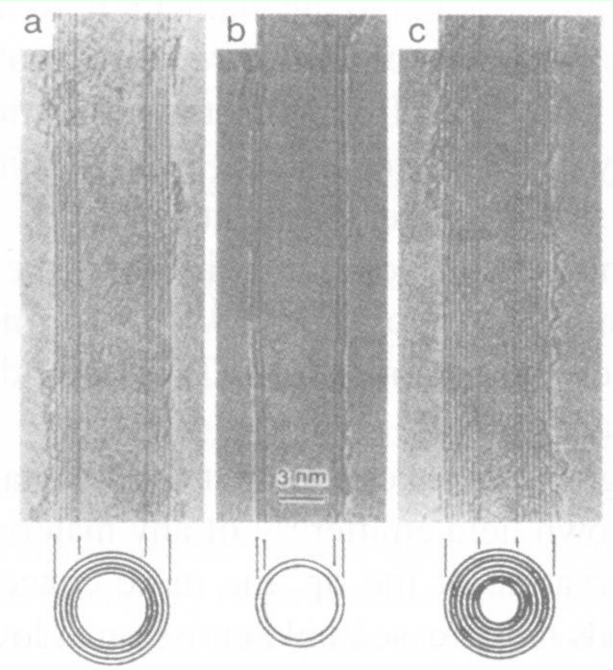
Multi-walled nanotubes consist of multiple rolled layers of graphite. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, *ca*. 3.4 Å. There are two models which can be used to describe the structures of multi-walled nanotubes:

- The Russian Doll model: sheets of graphite are arranged in concentric cylinders, *e.g*. a (8,0) single-walled nanotube within a larger (16,1) single-walled nanotube.
- Parchment model: a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper.



The Russian Doll model of MWNT

TEM images of MWNTs



Synthetic methods for carbon nanotubes

- Laser evaporation (ablation) of graphitic targets
- Arc discharge methods
- Chemical vapor deposition (CVD)

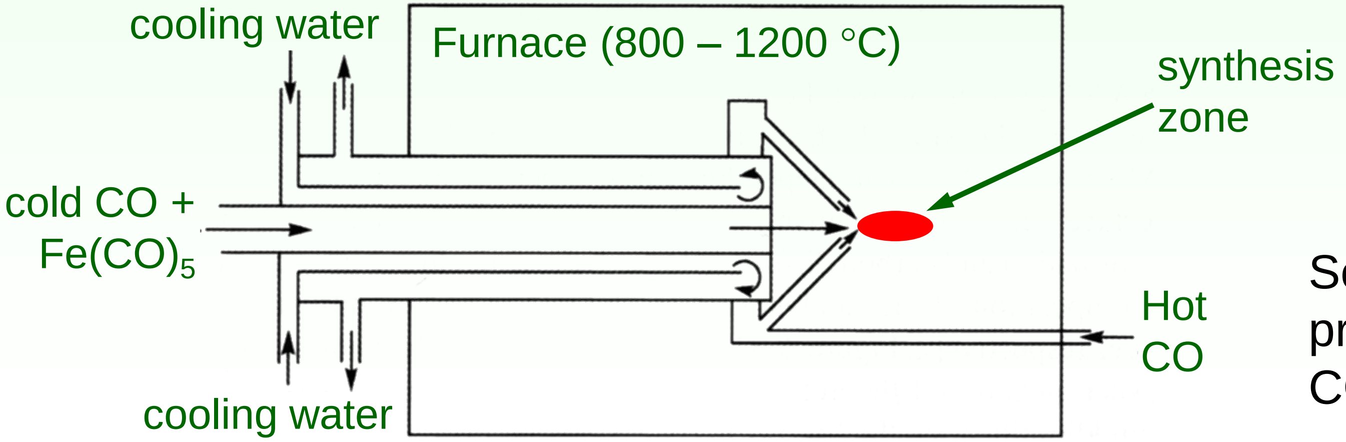
Carbon nanotubes, obtained by laser evaporation and arc discharge methods usually contain a number of products and impurities (fullerenes, amorphous soot, different MWNTs, SWNTs, etc.)

CVD methods require metal catalyst, but usually provide uniform products and could be used for large scale nanotube synthesis.

Lately, carbon nanotubes are mainly synthesized by CVD methods.

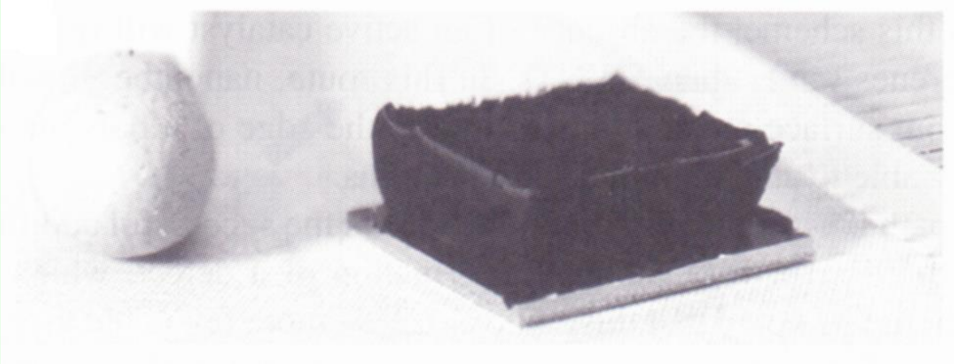
CVD methods the carbon nanotube synthesis

- Carbon source: CH_4, C_2H_2, C_2H_4, CO, MeOH, EtOH.
- Process gas (ammonia, nitrogen or hydrogen)
- Metallic catalyst nanoparticles (Ni, Mo, Co, Fe or corresponding alloys) on a hot support. For the synthesis of free-standing CNs a volatile catalytic precursor (such as $Fe(CO_5)$)) could be transferred into CVD furnace together with carbon source. The size of metallic nanoparticle catalyst governs the diameter of carbon nanotubes. After the synthesis the catalytic nanoparticles are removed (*e.g*. by acid treatment).
- Co-reactant (*e.g*. water) greatly improves the catalytic performance and uniformity of the product.
- *T* ~ 700 ÷ 1200 °C; moderate pressures (*ca*. 1 – 10 bar)

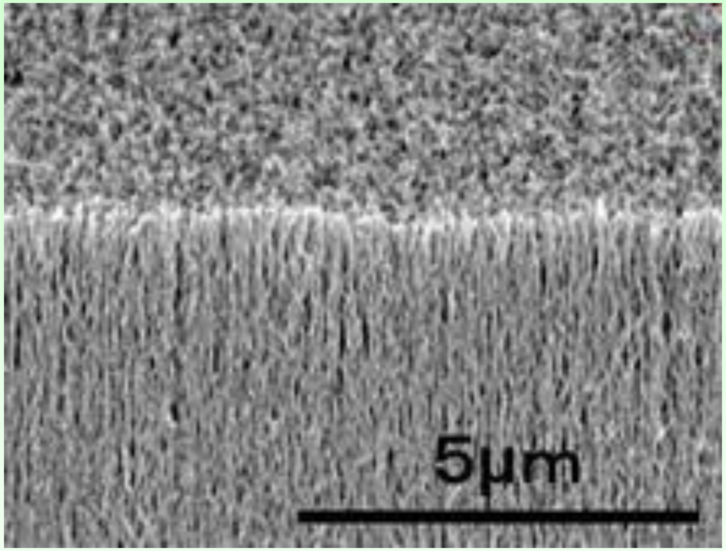


Scheme of HiPco CVD process (High pressure CO CVD)

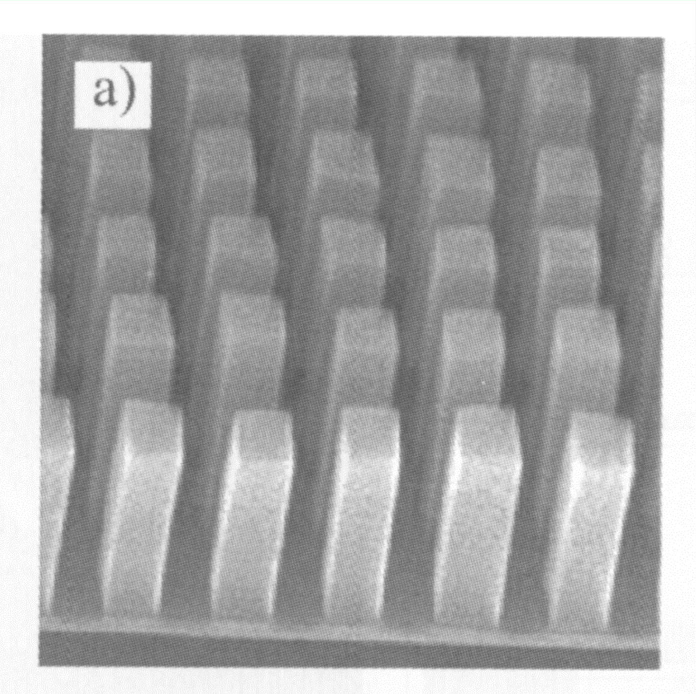
Examples of carbon nanotubes obtained in CVD process



A cm-scale SWNT forests, grown on metal support and matchstick to compare the size



SEM image of SWNT forests, produced in HiPco process



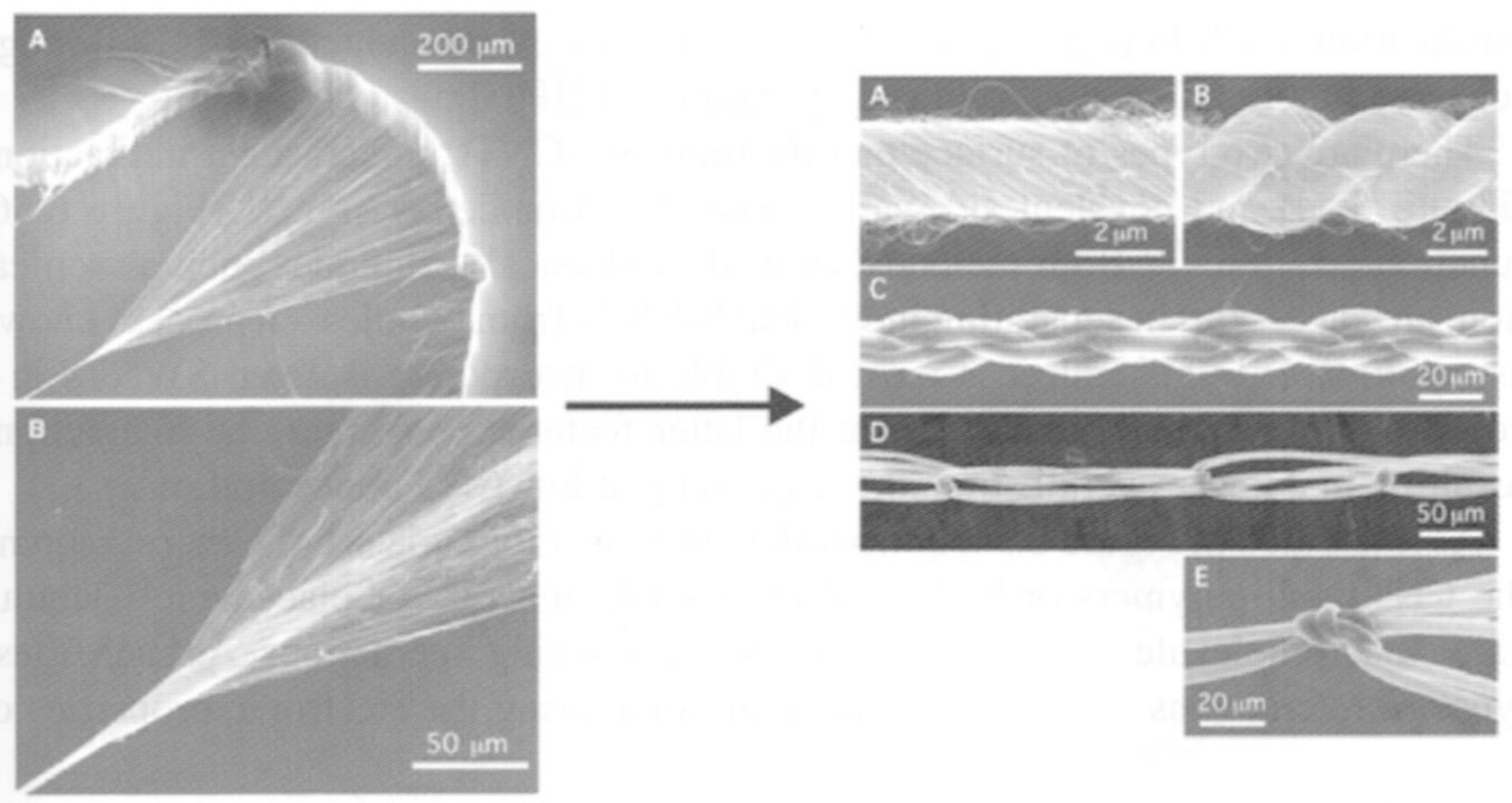
Ordered growth of carbon nanotubes on patterned support

Specific tensile strength of various materials

Material	Tensile strength (MPa)	Density (kg / L)	Specific strength (kN·m / kg)
Concrete	10	2.30	4.34
Rubber	15	0.92	16.3
Brass	580	8.55	67.8
Nylon	75	1.15	97.3
Polypropylene	80	0.90	88.9
Aluminum	600	2.70	222
Steel	2000	7.86	254
Titanium	1300	4.51	288
Silicon carbide	3400	3.16	1088
Glass fiber	3400	2.60	1307
Graphite	4300	1.75	2457
Kevlar	3620	1.44	5246
CNTs	62000	1.34	46270

Carbon nanotubes are the strongest and the stiffest materials known to date

Applications for carbon nanotubes

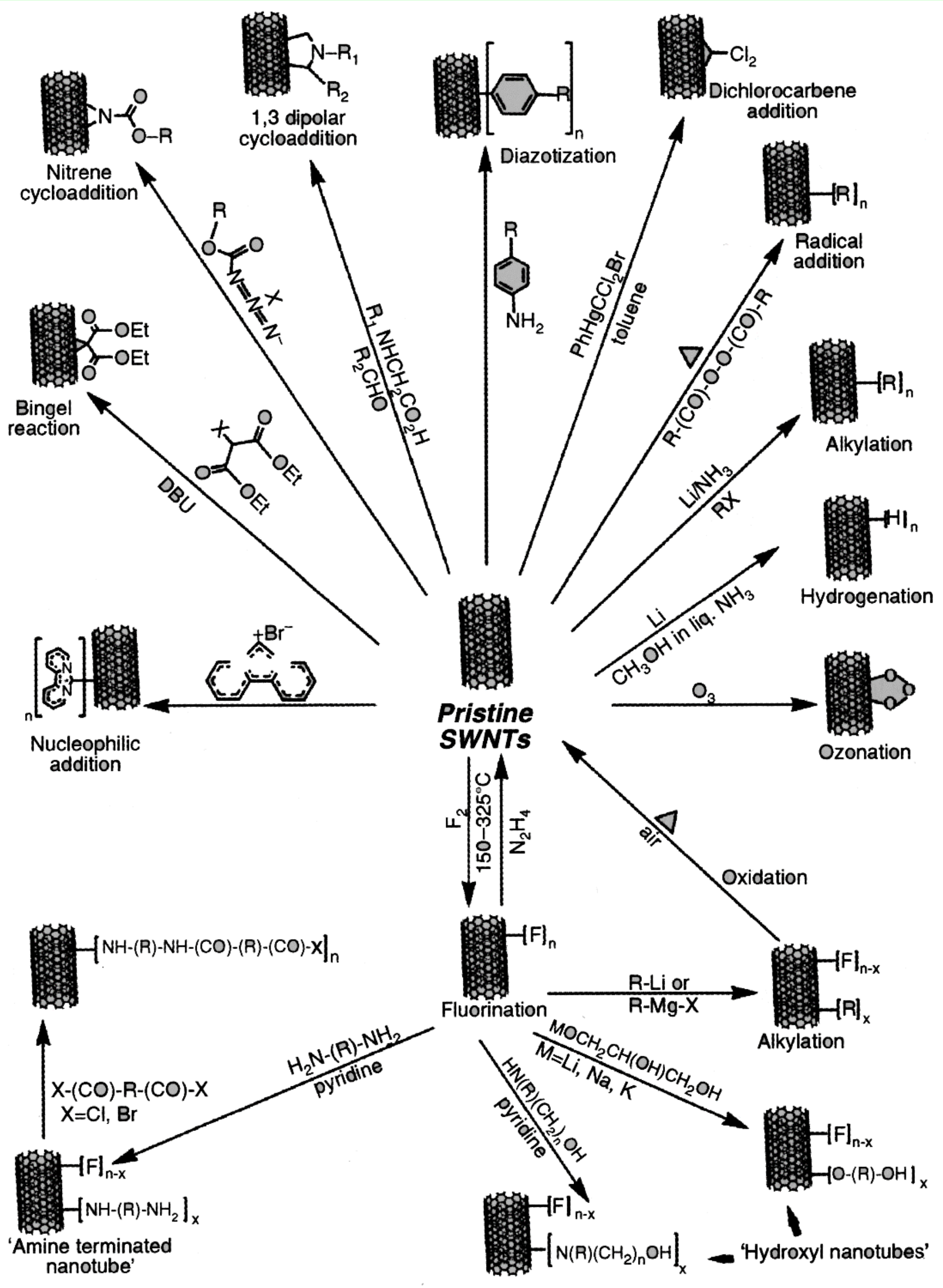


Spinning of MWNT forests into a fibers (left), weaved into nanotextile yarns (right), both flexible and very strong

Properties of carbon nanotubes

- ■ Unique electrical conductivity, depending on the structure. Could vary from metallic to semiconducting with tunable band gap energy E_g.
- ■ Possess high conductivity and sharp tip, therefore carbon nanotubes are best known electric field emitters with the highest field density near the tip. Nanotubes could be used to generate higher field emissions at lower voltage with prospective applications in plasma displays.
- ■ Design of next-generation field-effect transistors (FETs), outperforming currently used Si-based FETs.
- ■ Due to its unbeatable mechanical properties, carbon nanotubes are widely used to improve properties of composite materials, resulting in new high-strength and lightweight materials (carbon fiber composites).
- ■ MWNTs are good example of low-friction nanorotors. Such property has been utilized to create the world's smallest rotational motor with possible future applications such as a gigahertz mechanical oscillator devices
- ■ Carbon nanotubes are hollow, therefore could be used for molecular transport and/or storage of some important molecules (volatile gases, drugs, etc.)

Various methods for sidewall fictionalization of SWNTs



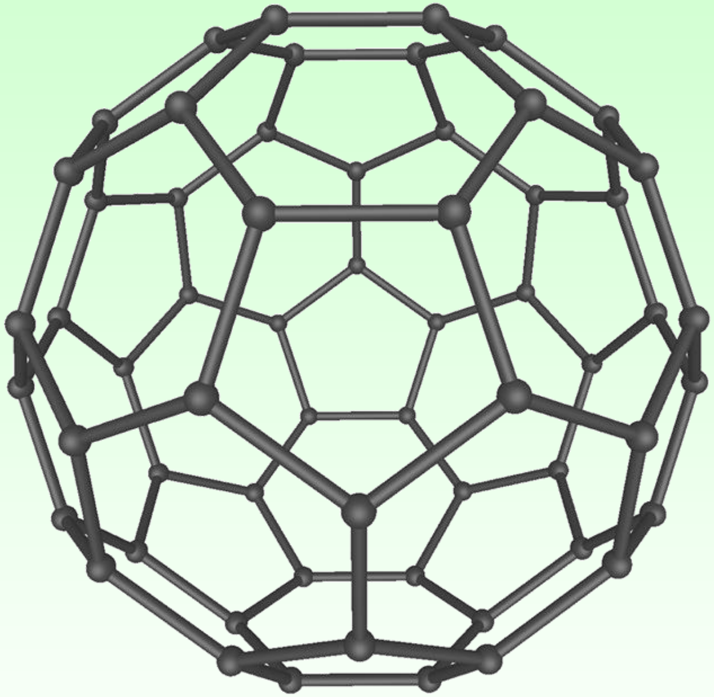
Chemical modification of carbon nanotubes allows:

1) tuning physical properties

2) to improve interactions with surrounding functional molecules in complex devices and composites.

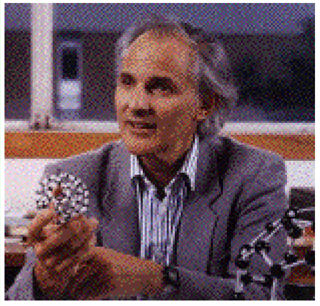
3) to separate different nanotubes from the mixtures *via* selective modification

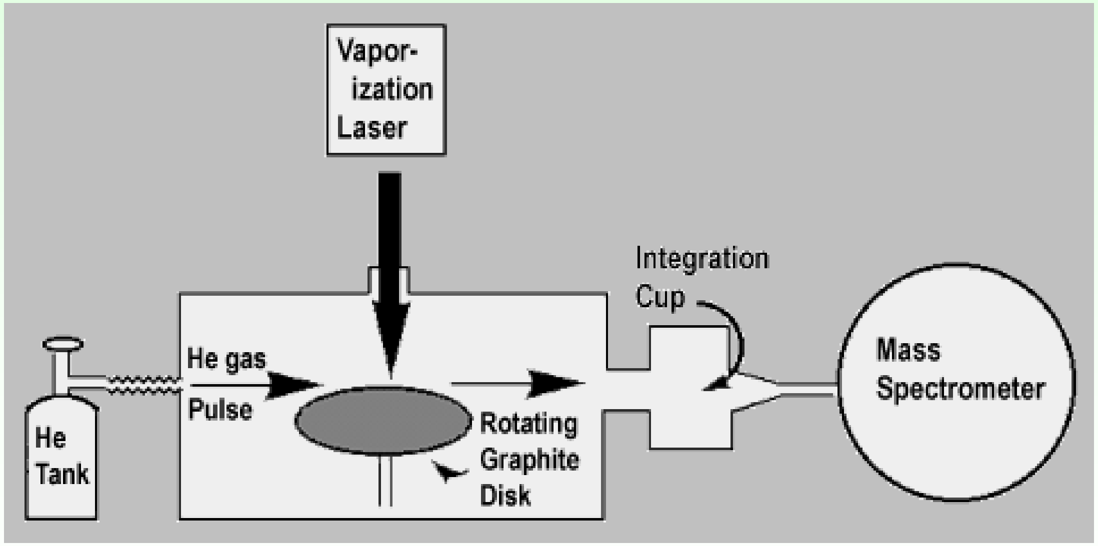
Fullerenes

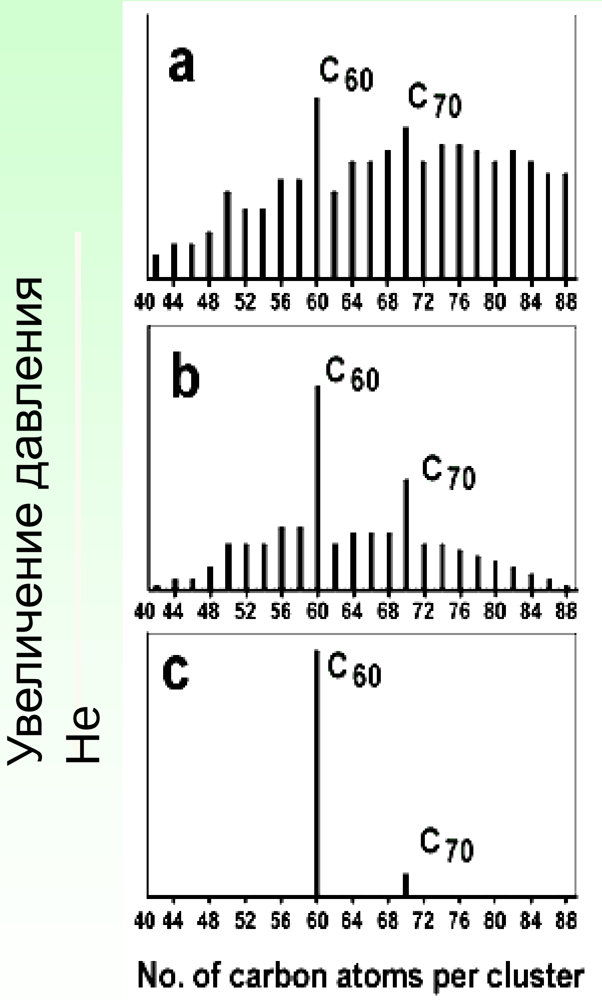


Discovery of fullerenes

In 1985



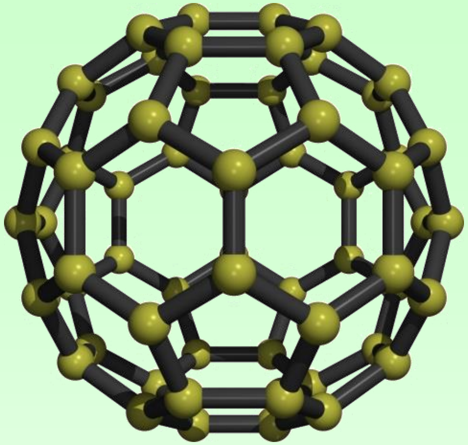




Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry
In 1992, fullerenes were found in a family of minerals known as shungites in Karelia, Russia.

Fullerenes

Fullerenes – spherical carbon nanoparticles, composed of adjacent hexagonal and pentagonal carbon rings.

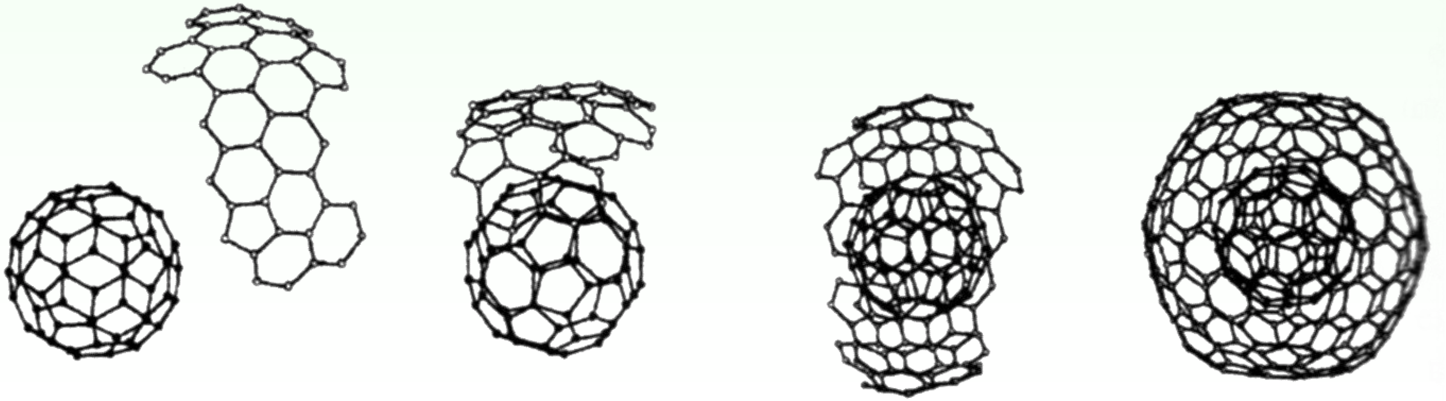


Fullerene C_{60}
(Buckminsterfullerene)

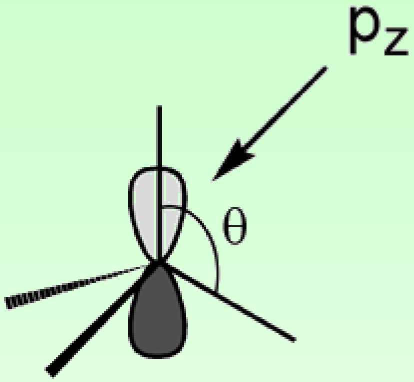
■ There are a number of fullerenes obtained (C_{60}, C_{70}, C_{76}, C_{78}, C_{80}, C_{84}, etc.), and much more are predicted.

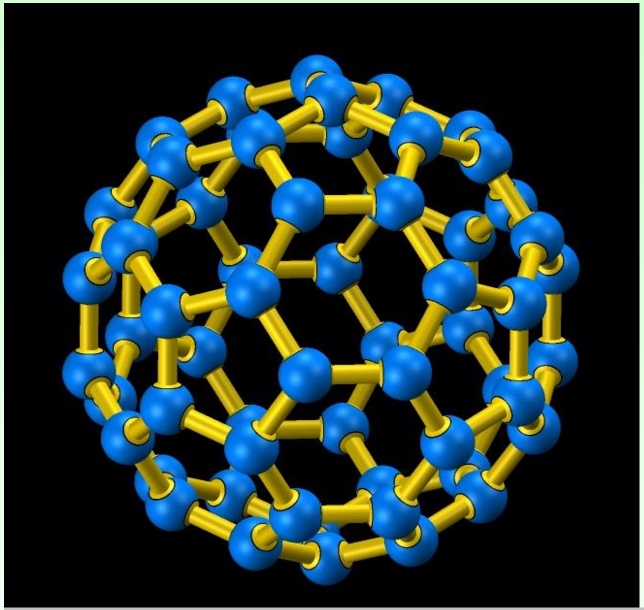
■ Some fullerenes are inherently chiral (*e.g.* C_{76}, C_{78}, C_{80}, C_{84}) because they have D_2-symmetric group and have been successfully resolved.

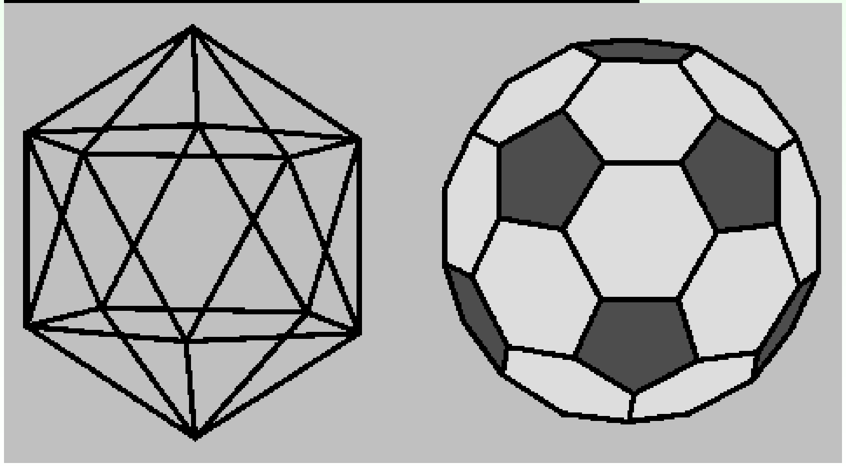
■ Similar to multi-walled nanotubes, there are multishell fullerenes (C_{60}@C_{240} or even C_{60}@C_{240}@C_{560}), where the smaller core sphere templates the outer shell:



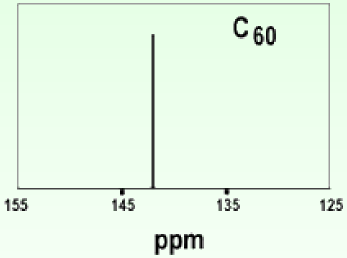
Structure of C_{60}

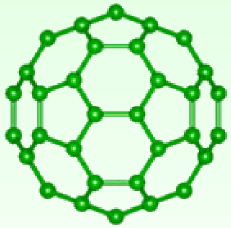


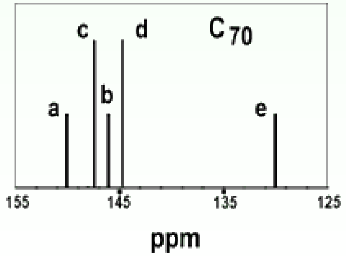


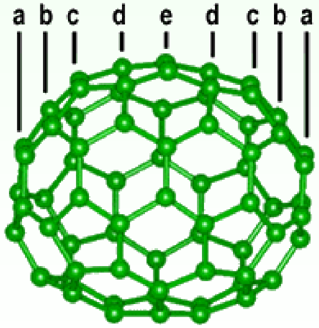


NMR

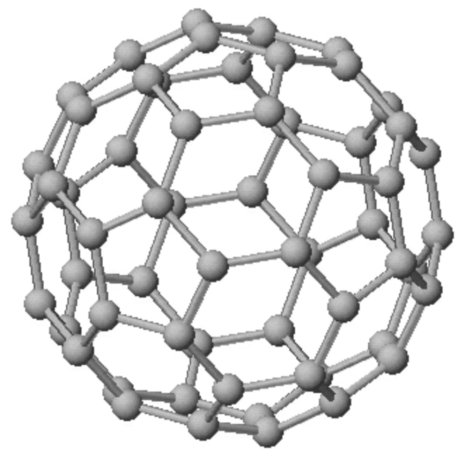






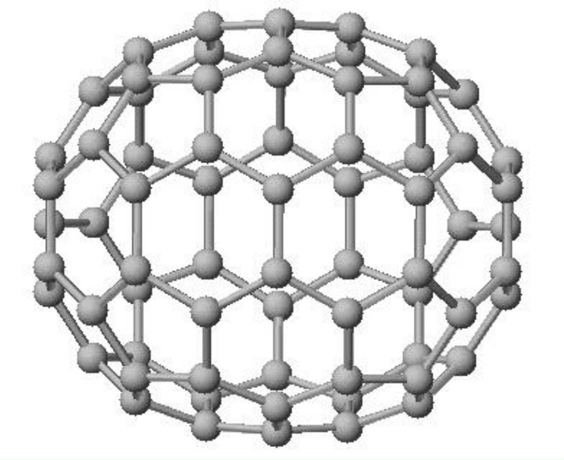


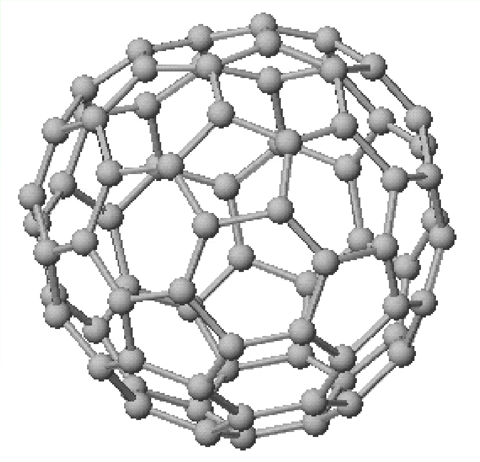
Fullerenes



C_{60}

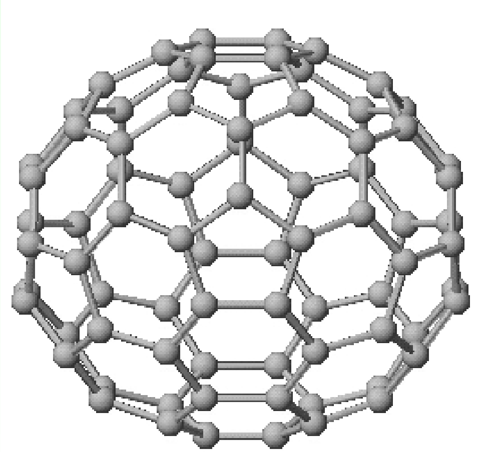
C_{70}





C_{76}

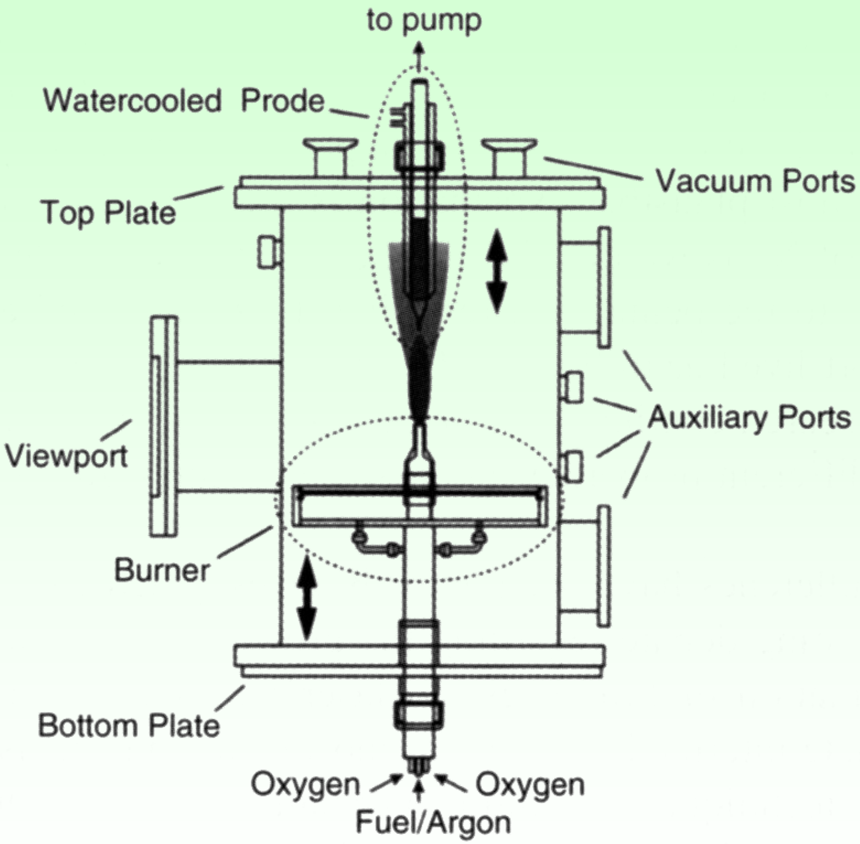
C_{80}



Synthesis of fullerenes

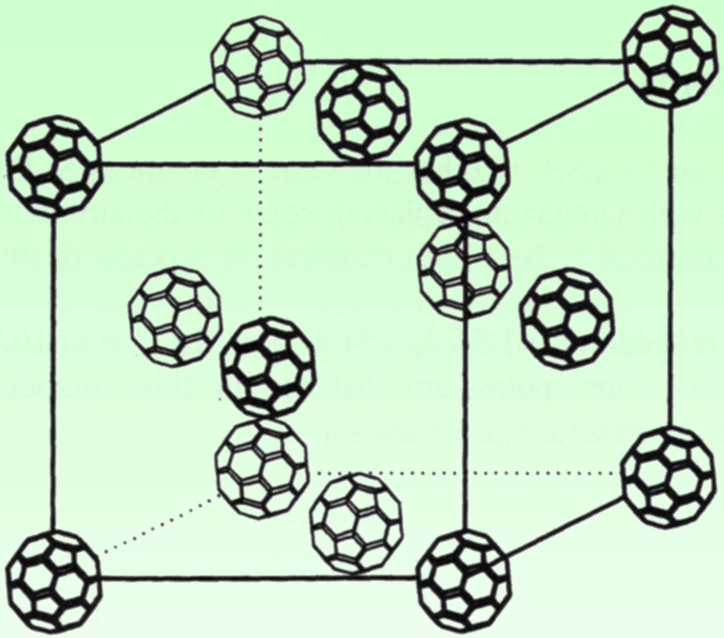
Typically, “brute-force” methods are used to obtain mixture of fullerenes (as well as other carbon materials). The desired products could be extracted and separated further.

- ■ Laser-assisted high temperature pyrolysis of some carbon source (*e.g*. graphite).
- ■ Electric arc-discharge evaporation method.
- ■ High temperature combustion of benzene.



Reduced-pressure fuel-rich pyrolytic chamber for the combustion fullerene synthesis

The crystal structure of hexecontacarbon (C_{60}) molecules

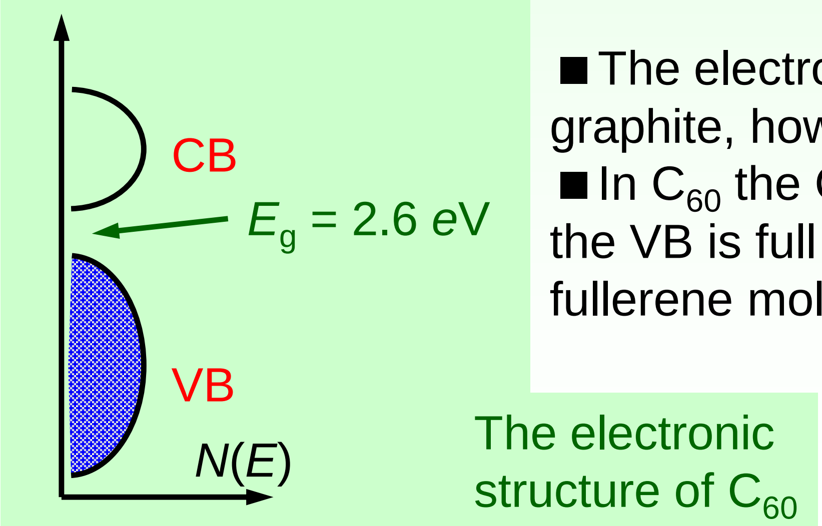


The C_{60} packing obeys dense packing of spheres, which is very well expected:

■ The covalent diameter of each C_{60} = 7.06 Å.

■ The lattice parameter *a* = 14.17 Å.

■ Therefore, the van-der-Waals contact between C_{60} spheres is 2.96 Å, slightly shorter than in graphite layers (3.35 Å).



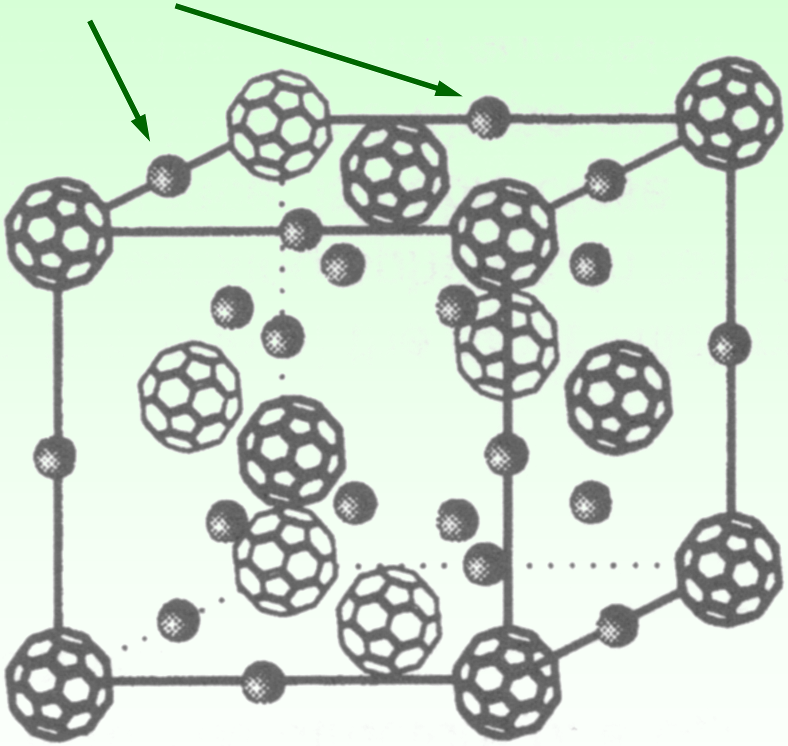
The electronic structure of C_{60}

■ The electronic band structure of solid C_{60} is similar to graphite, however the band gap is larger (E_g = 2.6 eV)

■ In C_{60} the CB is empty and contains 3 orbitals (*max* 6 e^-); the VB is full and contains 6 orbitals (*max* 12 e^-) per one fullerene molecule.

The intercalation compounds of fullerene

Fullerides are obtained by alkali metals incorporation into the fullerene close packing structure, similarly to graphite intercalation.



Guest cations in *ccp* C_{60} lattice

Typically, the guest cations occupy all tetrahedral and octahedral cages in *ccp*. The ratio is therefore G_3C_{60}.

Alkali metal dopped fullerene M_3C_{60} demonstrates metallic behavior, since $3e^-$ from alkali metals fill half of CB. Moreover, it was shown that these compounds becomes <u>superconducting</u> at low temperatures:

$T_c(K_3C_{60}) = 18$ K;

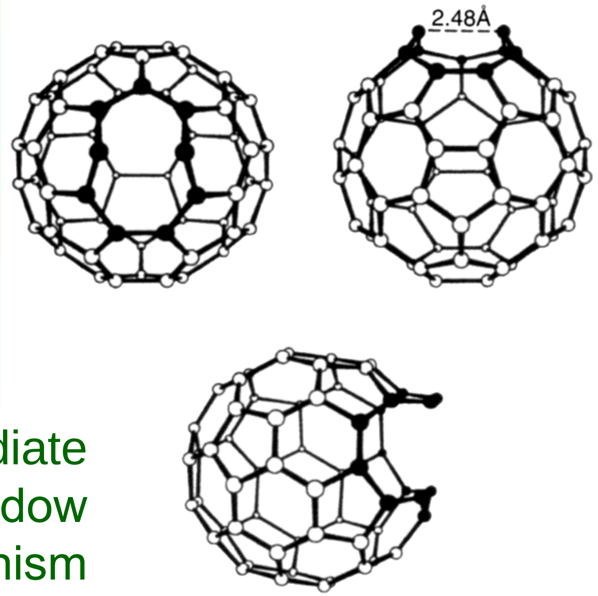
$T_c(Cs_3C_{60}) = 38$ K;

$T_c(Cs_2RbC_{60}) = 33$ K;

Endohedral fullerenes

- Endohedral fullerenes, where heteroatoms (heteroions) are trapped inside the fullerene shell. Such inclusion compounds are prepared *in situ*, e.g. from the metal-dopped graphite source using arc discharge or laser ablation method.

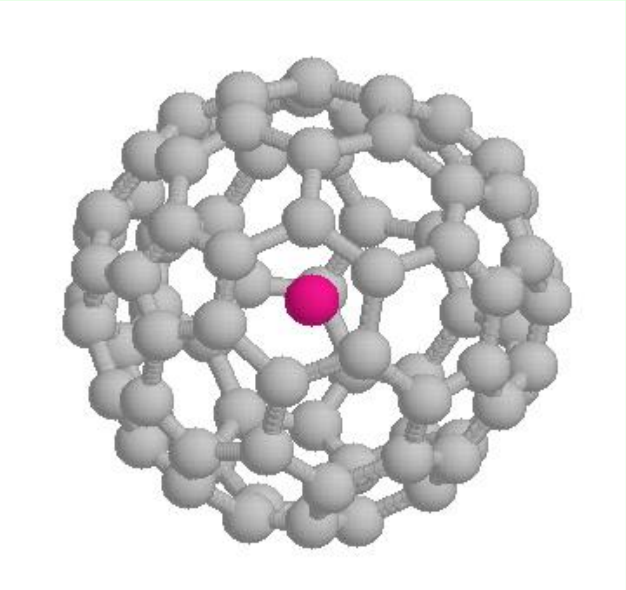
Very small molecules (H, H^+, He) can penetrate through C_5 or C_6 rings. For larger species theoretically predicted mechanism propose “window opening” due to some C—C bond cleavage. The window is closed back after the atom incorporation

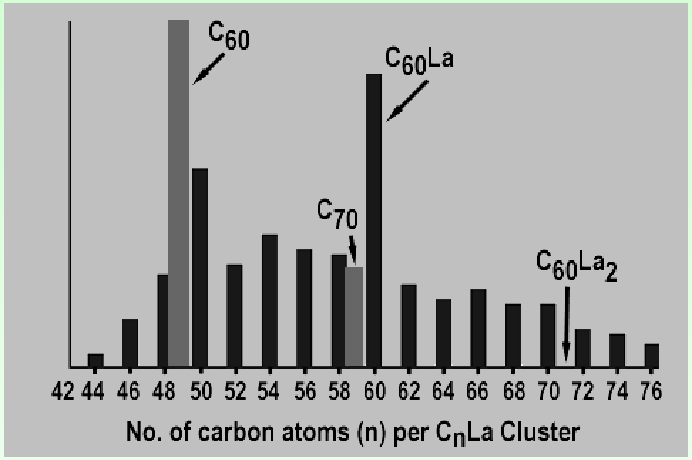


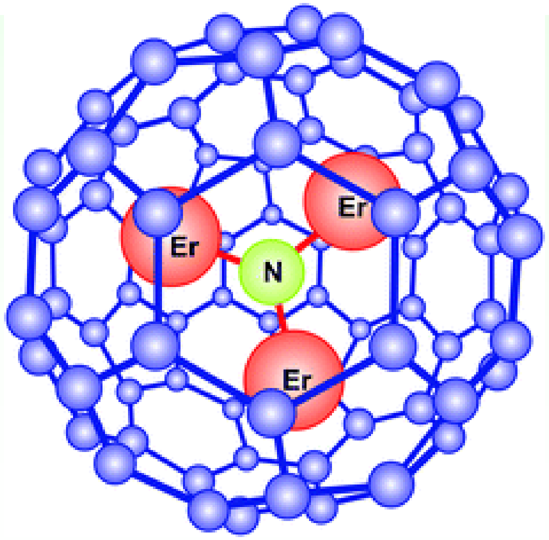
proposed intermediate structures for “window opening” mechanism

Small guest species stabilize the fullerene structure (noble gases, Li^+, $F^–$,$Cl^–$, etc.). Larger ions destabilize the cage (Rb^+, $Br^–$,$I^–$) and are unlikely formed by the “window opening” mechanism (more than one C—C bond needs to be cleaved). Instead, such species are trapped inside the fullerene core during the carbon shell formation.

Endohedral fullerenes







Семейство $M@C_{82}$, $M@C_{84}$ и др.

M = Sc, Y, La, Ce, ….

ScN_3 и др.

$Li@C_{60}$, $He^3@C_{60}$

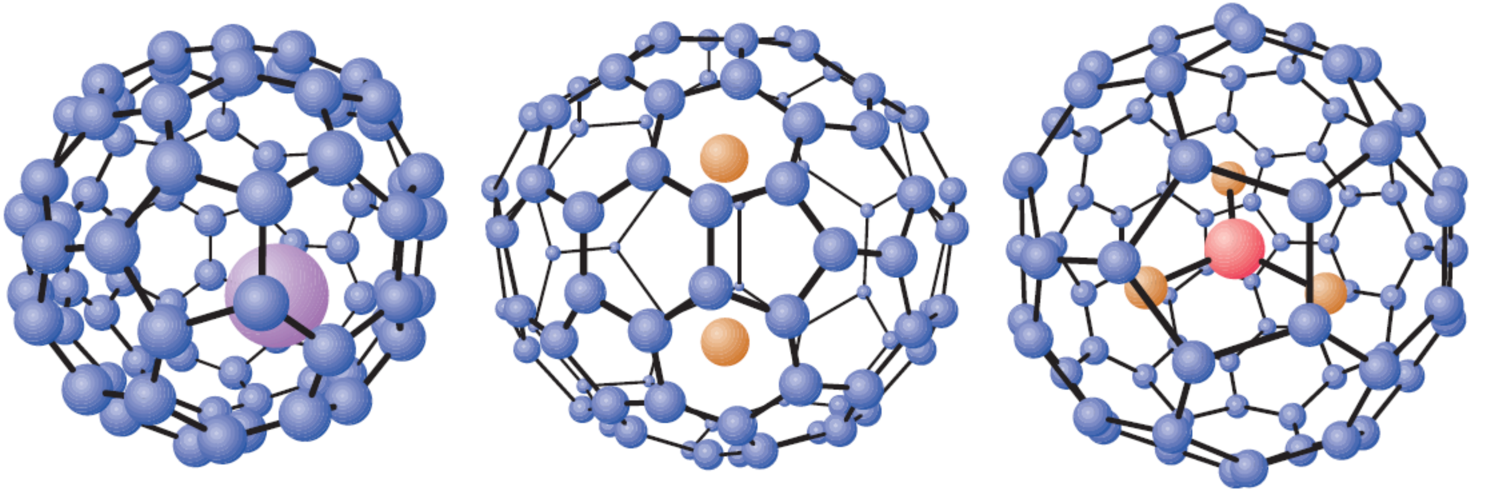
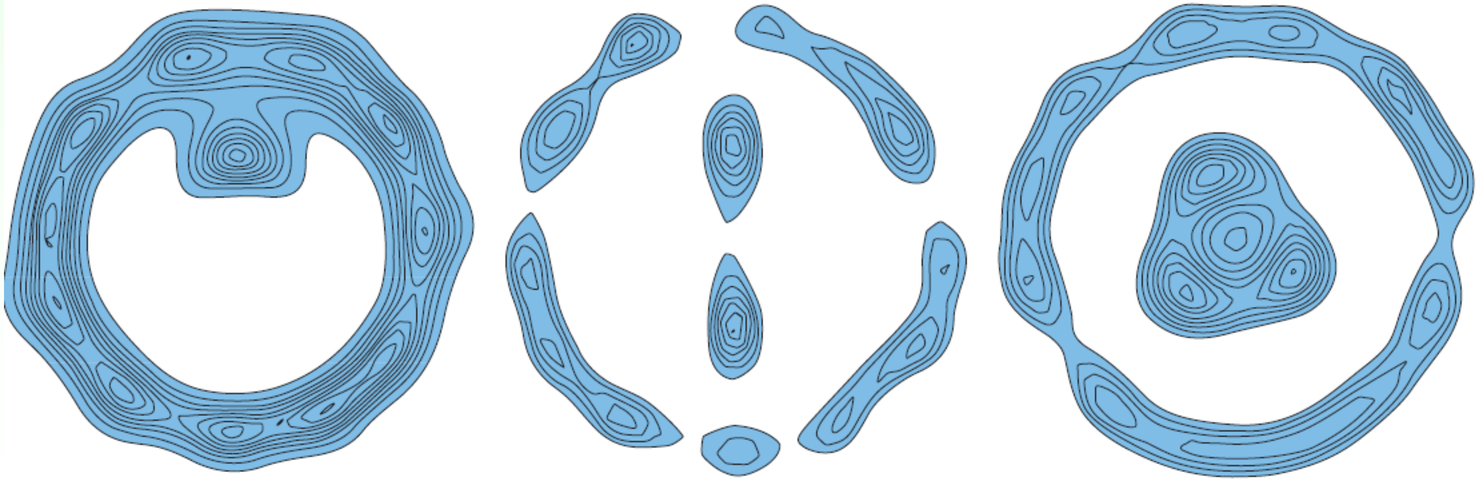
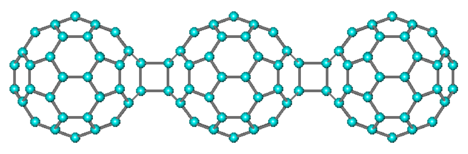
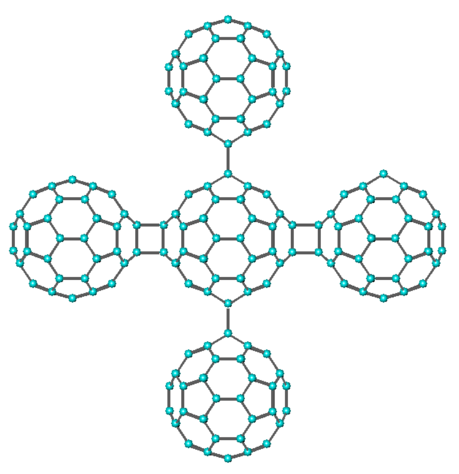


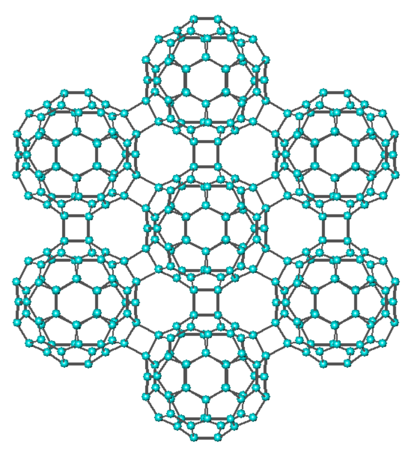
Рис. 1. Структуры соединений La@C$_{82}$, Sc$_2$@C$_{82}$ и Sc$_3$N@C$_{80}$ (последний приведен с разрешения журнала “Nature” (www.nature.com))

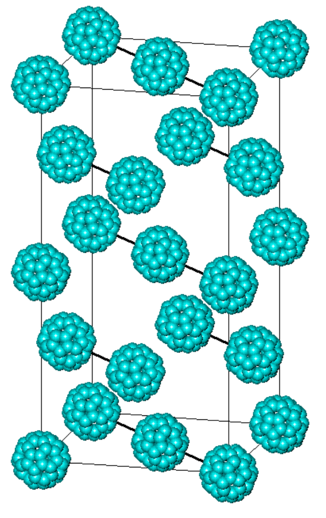


C_{60} polymerization

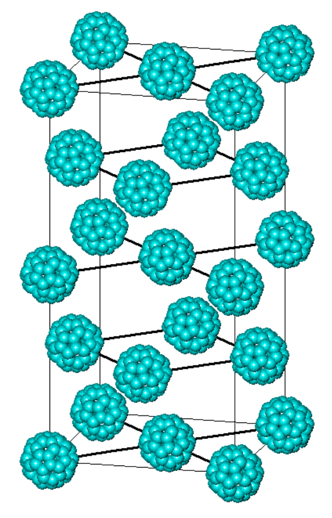




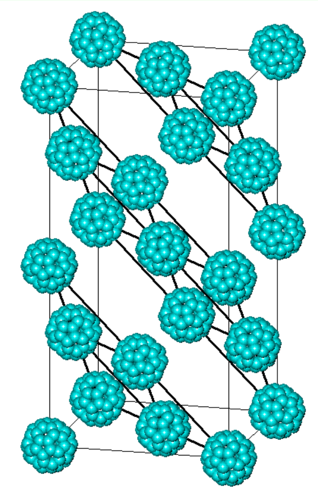




Orthorhombic

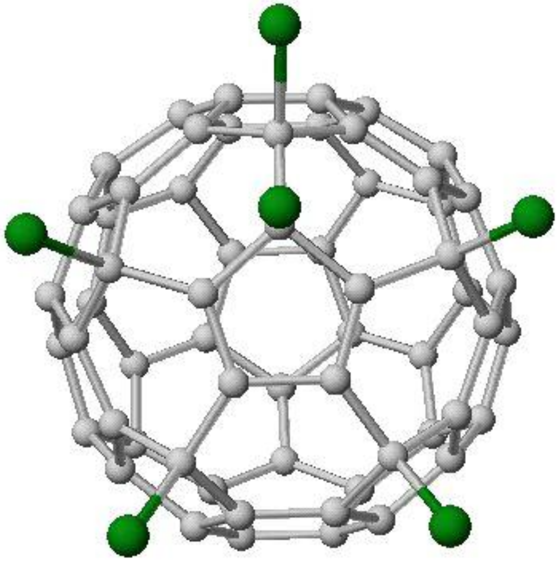


Tetragonal

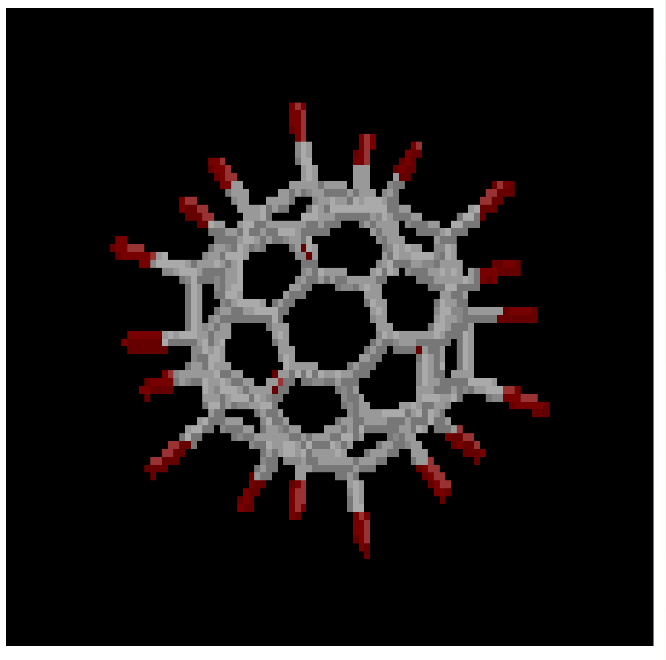


Hexagonal

Fullerene compounds with halogens

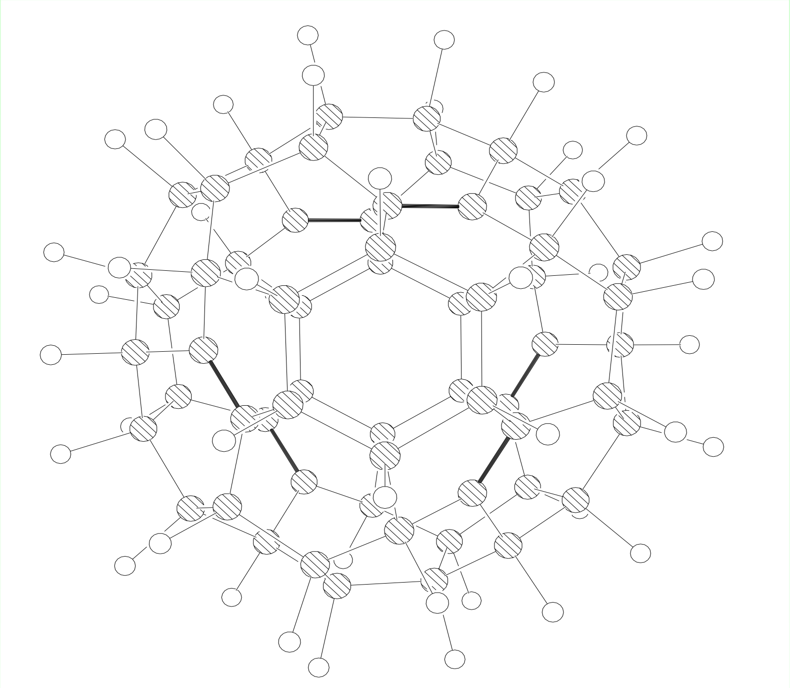


$C_{60}Cl_6$

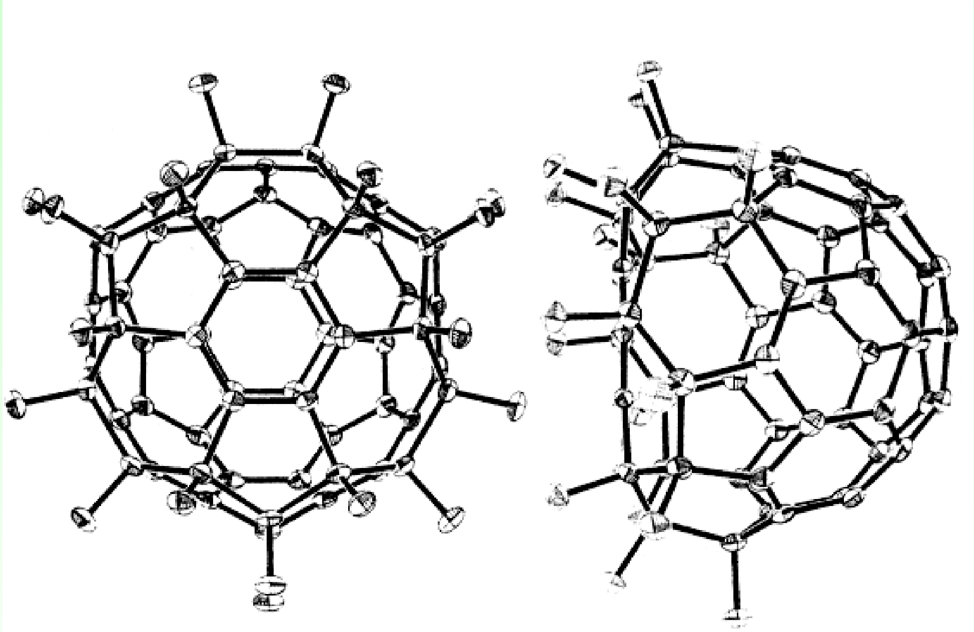


$C_{60}Br_{24}$

Fluorofullerenes

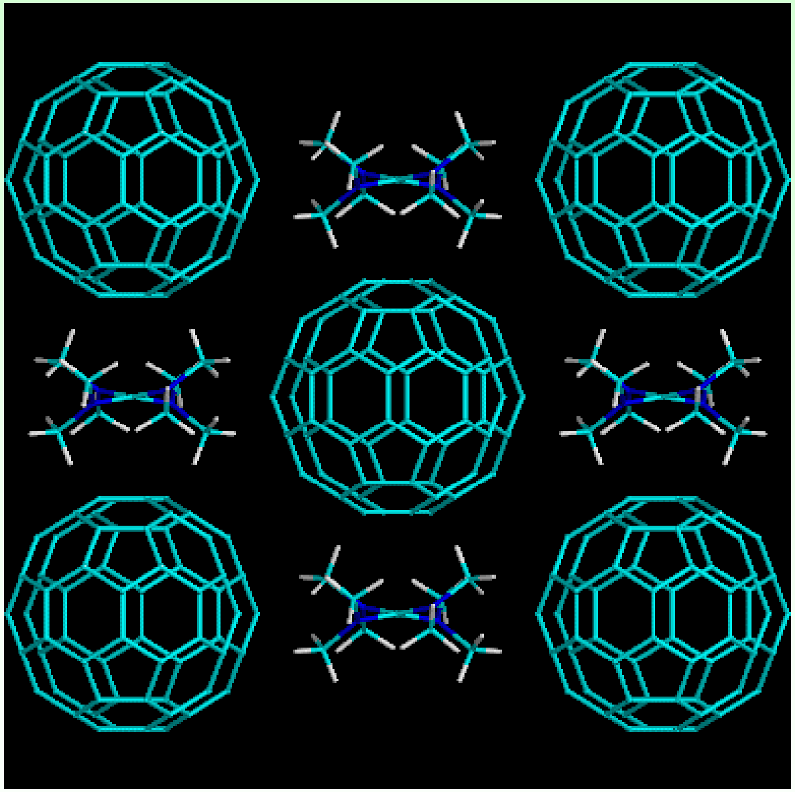


$C_{60}F_{48}$

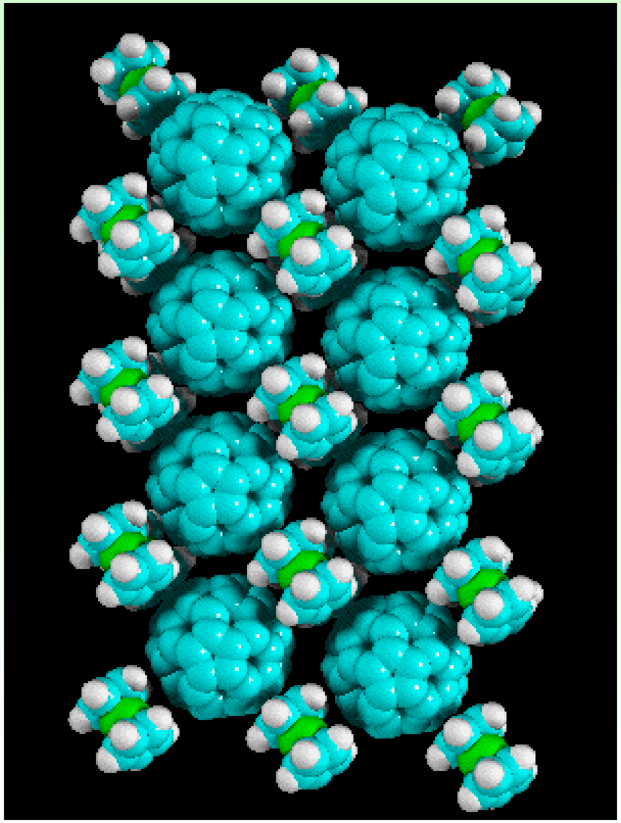


$C_{60}F_{18}$

Donor-acceptor complexes of fullerenes



$TDAE \cdot C_{60}$



$C_{60} \cdot Fe(C_5H_5)_2$

Tetrakis(dimethylamino)ethylene Electron donors