BIOMATERIALS

Lecture 5: Carbon Biomaterials

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Last Lecture

- **Properties of ceramics**
- **Ceramics as biomaterials**

  Inert ceramics

  Porous ceramics

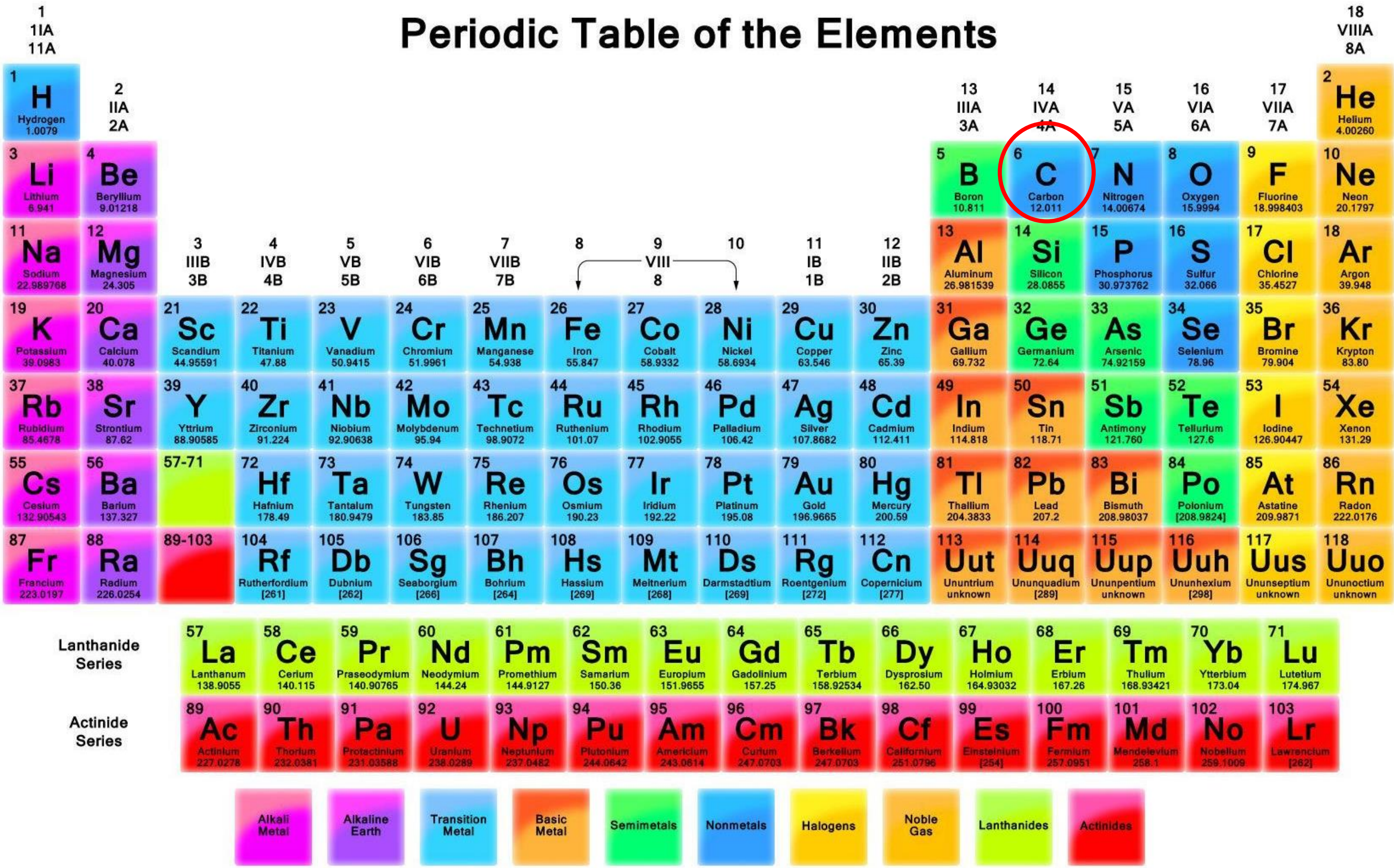
  Bioactive Ceramics, Active Glasses and Glass Ceramics

  Biodegradable ceramics

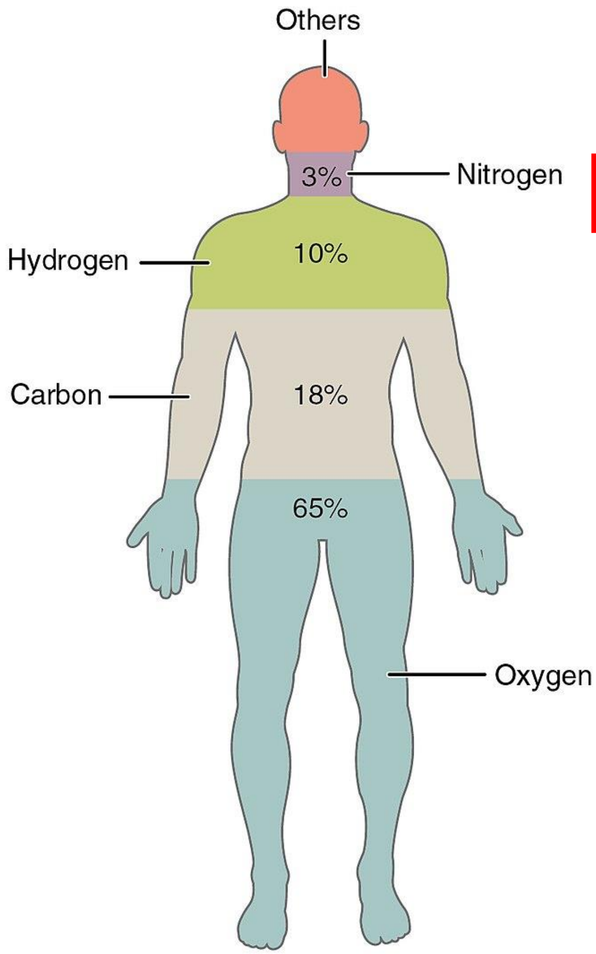
Contents

- **Introduction to Carbon and Carbon Materials**
- **Classification of Carbon Materials**
  1. Diamond
  2. Graphite
  3. Fullerene
  4. Pyrolytic carbon
  5. Graphene
  6. Carbon nanotubes
  7. Carbon dots and graphene dots
- **Raman spectrum of Carbon Materials**

1. Introduction to Carbon and Carbon Materials



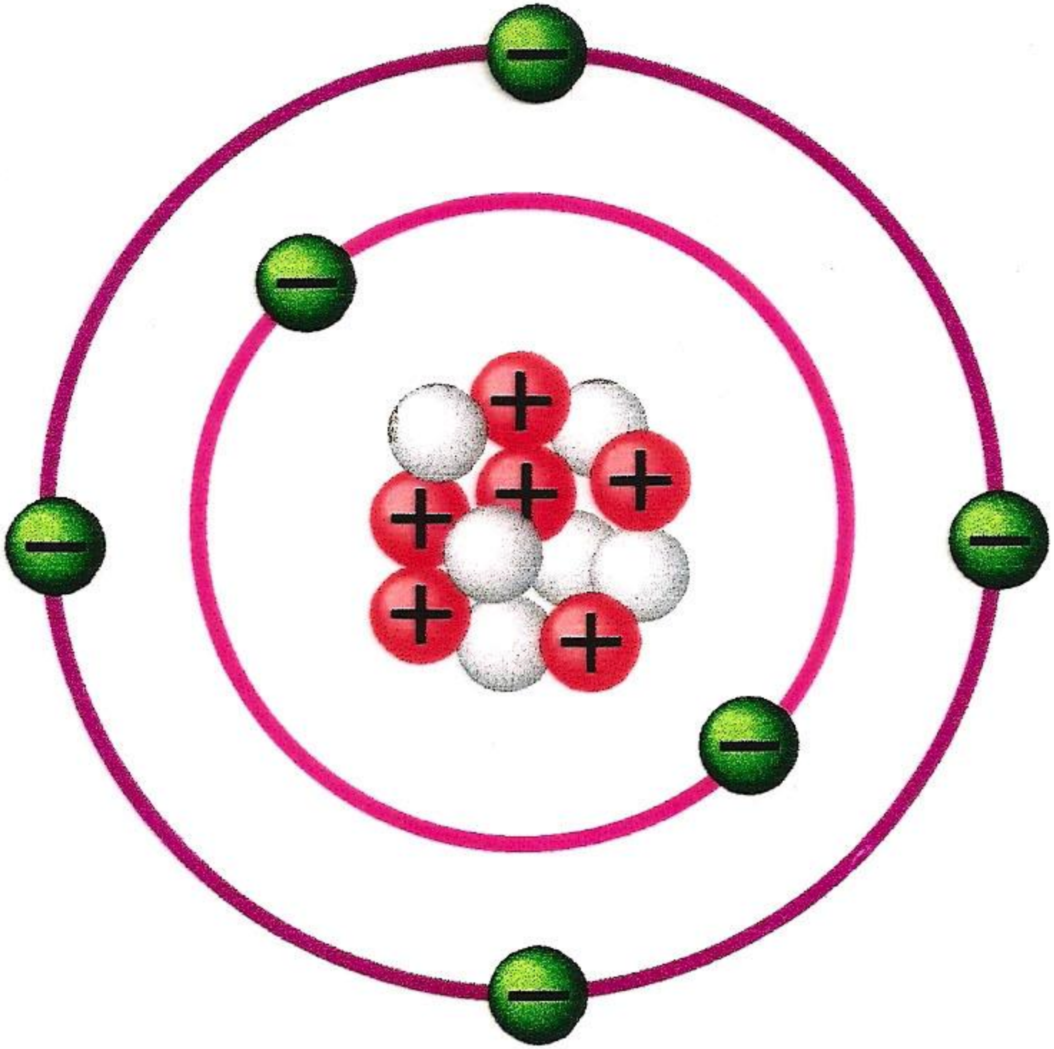
Composition of the human body



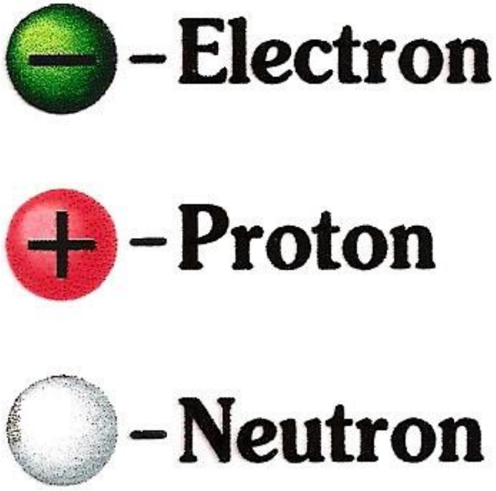
Weight percentage

Element	Symbol	Percentage in Body
Oxygen	O	65.0
Carbon	C	18.5
Hydrogen	H	9.5
Nitrogen	N	3.2
Calcium	Ca	1.5
Phosphorus	P	1.0
Potassium	K	0.4
Sulfur	S	0.3
Sodium	Na	0.2
Chlorine	Cl	0.2
Magnesium	Mg	0.1
Trace elements include boron (B), chromium (Cr), cobalt (Co), copper (Cu), fluorine (F), iodine (I), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se), silicon (Si), tin (Sn), vanadium (V), and zinc (Zn).		less than 1.0

Carbon atom

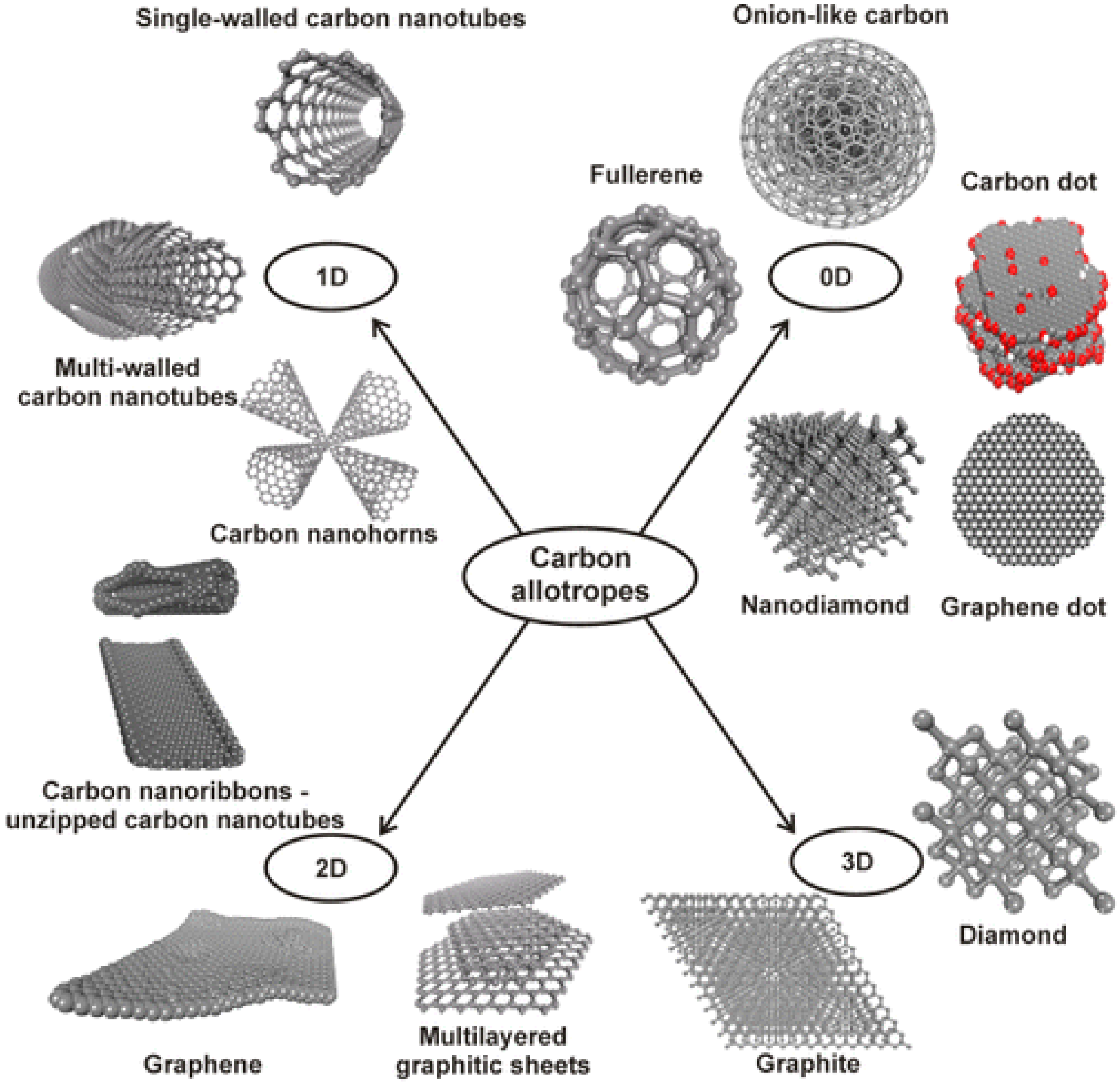


$C1s^2 2s^2\ 2p^2$



Structure of Carbon Materials

- Allotropic crystalline forms of carbon



- **Diamond:** tetrahedral sp^3 covalent bonding, one of the hardest materials known.
  covalent length:**1.54 Å**, tetrahedral unit repeats in 3D space.

- **Graphite**: anisotropic layered in-plane hexagonal covalent bonding, inter-layer van der Waals bonding structure.
  Within each planar layer, each carbon atom forms two single bonds and one double bond with its three nearest neighbors.
  In-plane atomic bond length: 1.42 Å
  Inter-layer van der Waals bond length: 3.4 Å

- **Fullerenes** have yet to be produced in bulk, Fullerenes and nanotubes consist of a graphene layer that is rolled up or folded to form a tube or ball.

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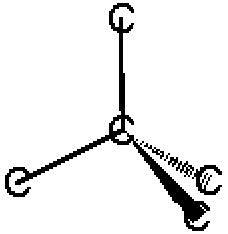
- Raman spectrum of Carbon Materials

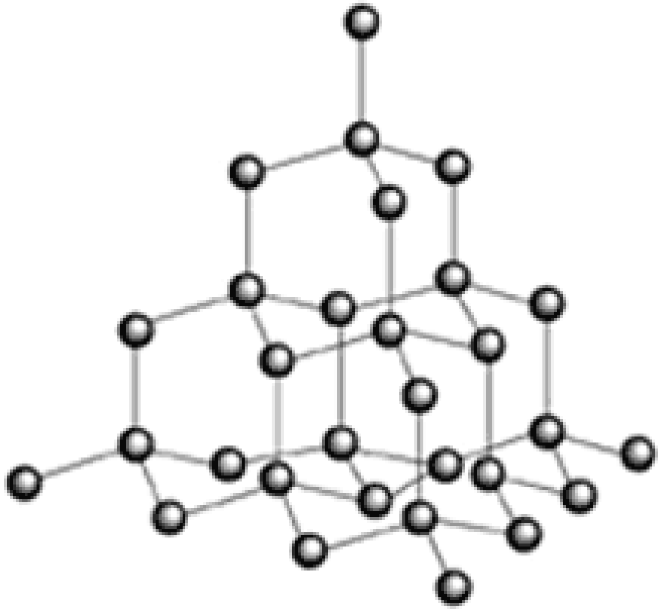
2. Classification of Carbon Materials

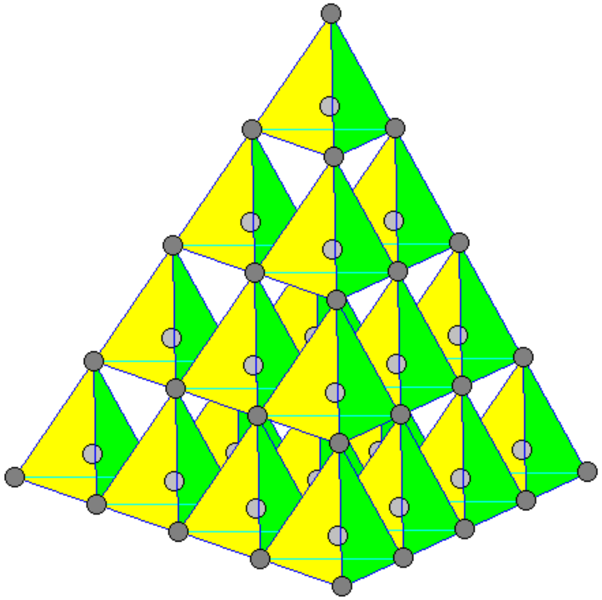
Diamond

sp^3



tetrahedral carbon in diamond



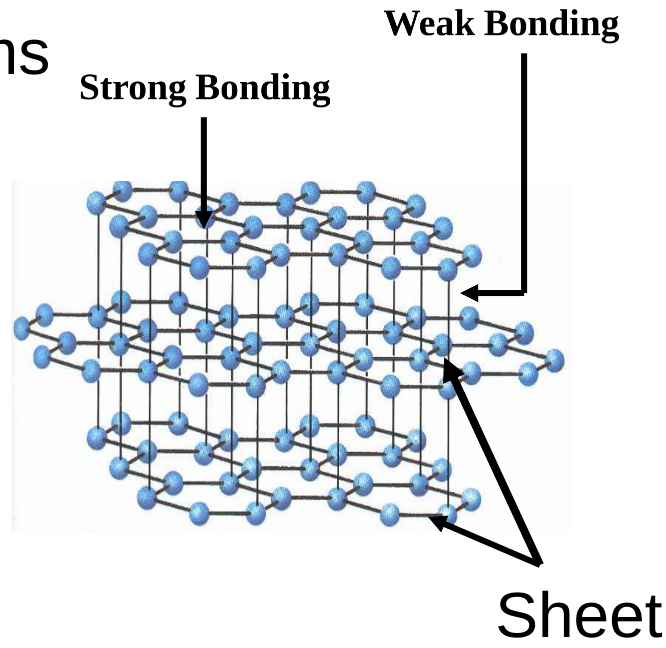


Diamond

- Diamond consists of a tetrahedral network of carbon atoms. Most stable atomic structure.
- Strength of bonding between carbon atoms are strong in all directions. No weak areas of bonding.
- Strong bonding and tetrahedral atomic arrangement allows diamond to be the hardest mineral with no apparent cleavage planes.

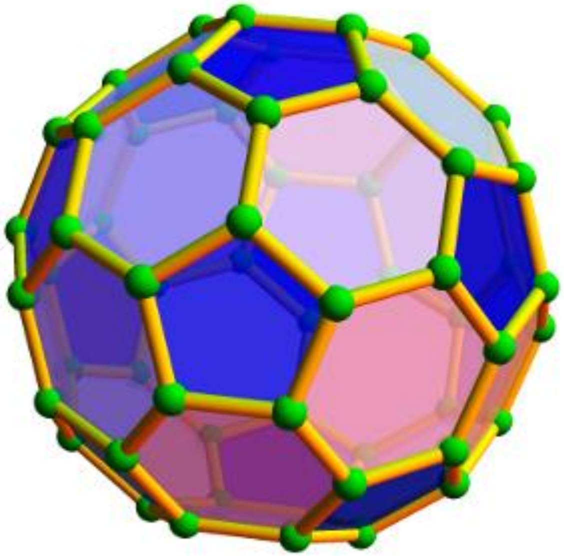
Graphite

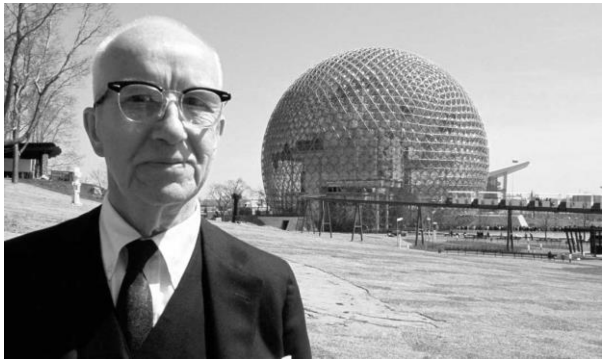
- Graphite consists of carbon atoms arranged in sheets or layers.
- Strength of bonding between carbon atoms within the layers are strong, while between the layers strength of bonding is weak.
- Weak bonding between the layers and a layered atomic arrangement causes graphite to be a soft mineral with basal cleavage (one cleavage plane).



Buckminsterfullerenes

Fullerene: C_{60}

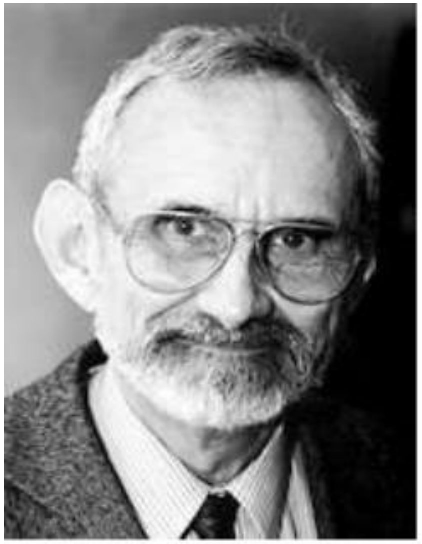




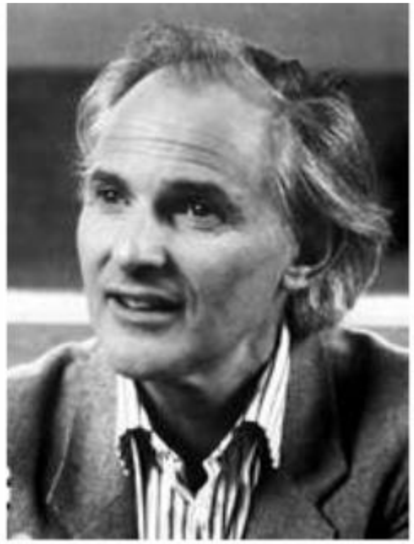
- Molecule consisting of 60 carbon atoms
- sp^2 hybridized bonds
- Has 20 hexagons, 12 pentagons
- Other related structures have 70 or 84 carbon atoms

named after **Richard Buckminster Fuller**

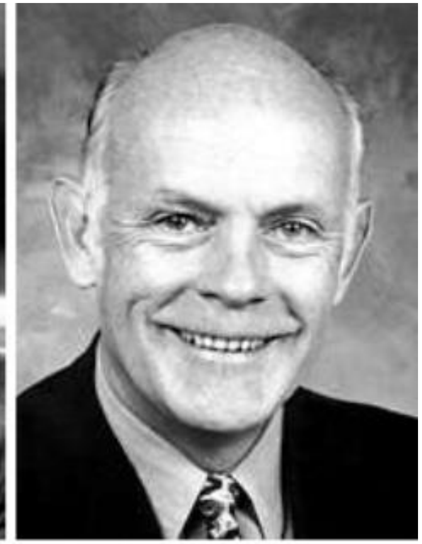
The 1996 Nobel Prize in Chemistry



Robert F. Curl Jr.



Sir Harold W. Kroto



Richard E. Smalley

Born: 23 August 1933, Alice, TX, USA
Rice University, Houston, TX, USA

Born: 7 October 1939, Wisbech, United Kingdom
Died: 30 April 2016, Lewes, East Sussex, United Kingdom
University of Sussex, Brighton, United Kingdom

Born: 6 June 1943, Akron, OH, USA
Died: 28 October 2005, Houston, TX, USA
Rice University, Houston, TX, USA

"for their discovery of fullerenes".

(1996)

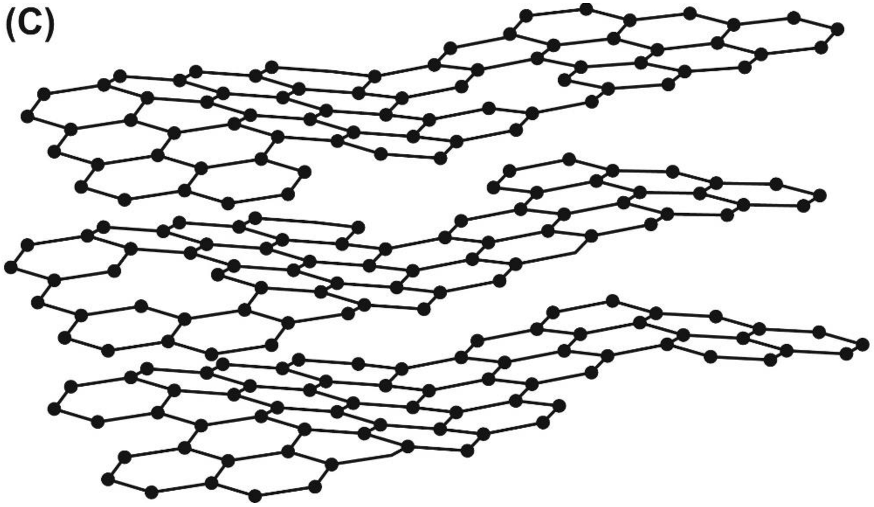
Pyrolytic carbon

- Pyrolytic carbon is a material similar to graphite, but with some covalent bonding between its graphene sheets as a result of imperfections in its production. Pyrolytic carbon is man-made and not found in nature.
- High temperature pyrolysis / thermal decomposition of hydrocarbons (e.g., propane, propylene, acetylene, and methane) in the absence of oxygen and subsequent recrystallization of elemental carbon
- Most successful and commonly used form

2. Classification of Carbon Materials

- Often used as a coating material
  - –machine preform, are coated, then machined and polished before assembly
  - –coat preform, diamond plated grinders and tools are needed because pyrolytic carbon is very hard
  - –polish, can be made very smooth

(C)



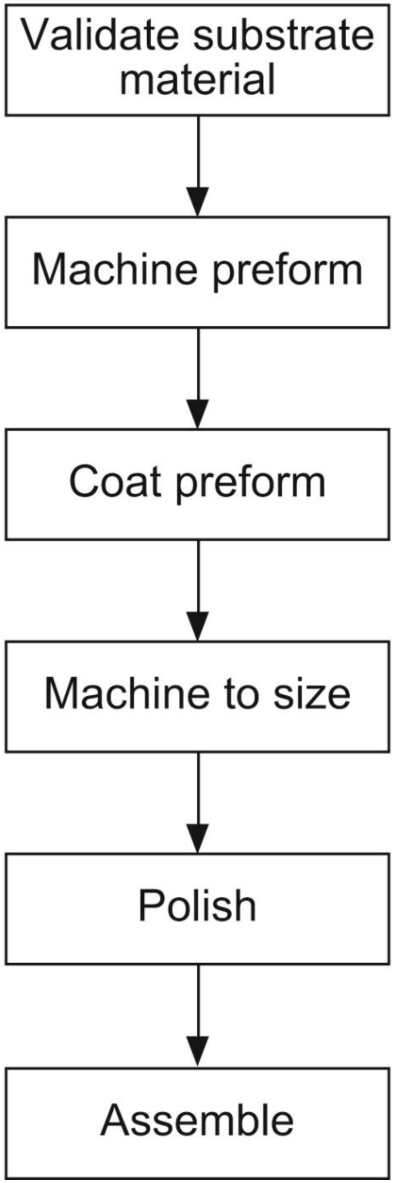
Turbostratic structure: order within carbon layer planes but no order between planes

Inter-layer spacing:
3.48 Å>3.4 Å (graphite)

Turbostratic pyrolytic carbon

2. Classification of Carbon Materials

Steps in the fabrication of pyrolytic carbon components



Mechanical Properties of Pyrolytic carbon

TABLE I.2.8.1 Mechanical Properties of Biomedical Carbons

Property	Pure PyC	Typical Si-alloyed PyC	Typical Glassy Carbon
Flexural strength (MPa)	493.7 ± 12	407.7 ± 14.1	175
Young's modulus (GPa)	29.4 ± 0.4	30.5 ± 0.65	21
Strain-to-failure (%)	1.58 ± 0.03	1.28 ± 0.03	-
Fracture toughness (MPa $\sqrt{m}$)	1.68 ± 0.05	1.17 ± 0.17	0.5–0.7
Hardness (DPH, 500 g load)	235.9 ± 3.3	287 ± 10	150
Density (g/cm^3)	1.93 ± 0.01	2.12 ± 0.01	<1.54
CTE (10^{-6} cm/cm°C)	6.5	6.1	-
Silicon content (%)	0	6.58 ± 0.32	0
Wear resistance	Excellent	Excellent	Poor

Applications of Pyrolytic carbon

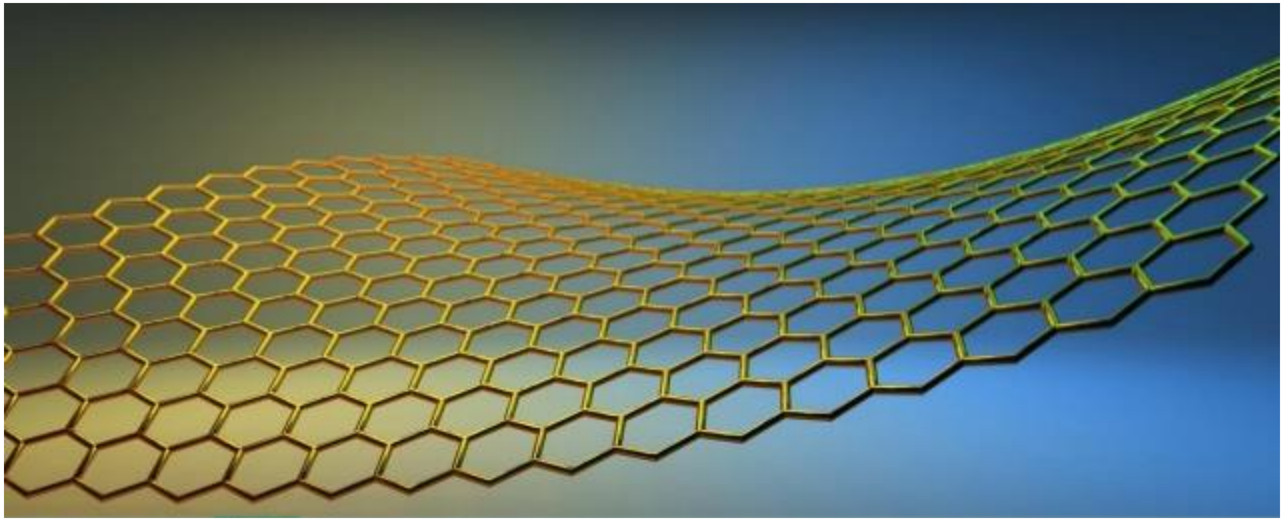
Components for On-X bileaflet heart valve

Applications of Pyrolytic Carbon

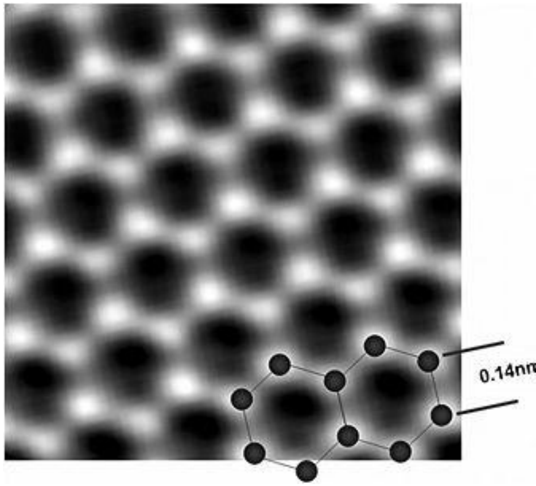
Replacement metacarpophalangeal total joint prosthesis components

Graphene

- ***Graphene*** *is a one-atom-thick planar sheet of* sp^2*-bonded carbon atoms that are densely packed in a honeycomb crystal lattice*
- *The name 'graphene' comes from graphite + -ene = graphene*



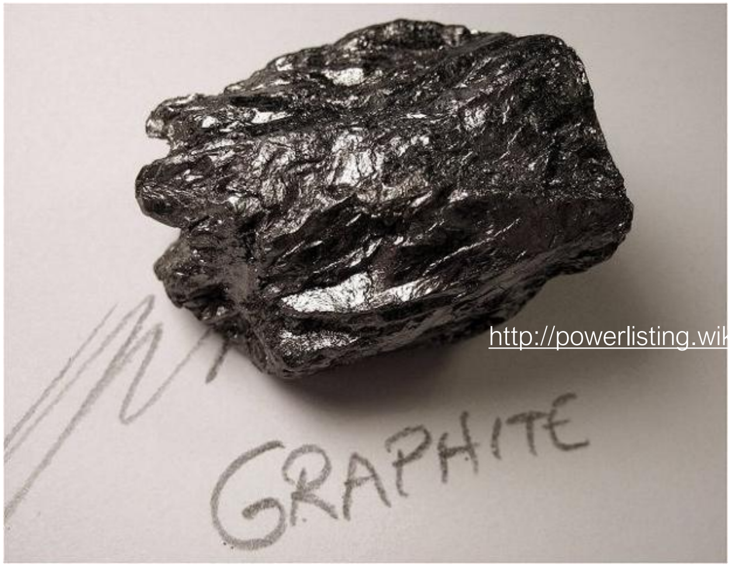
Molecular structure of graphene



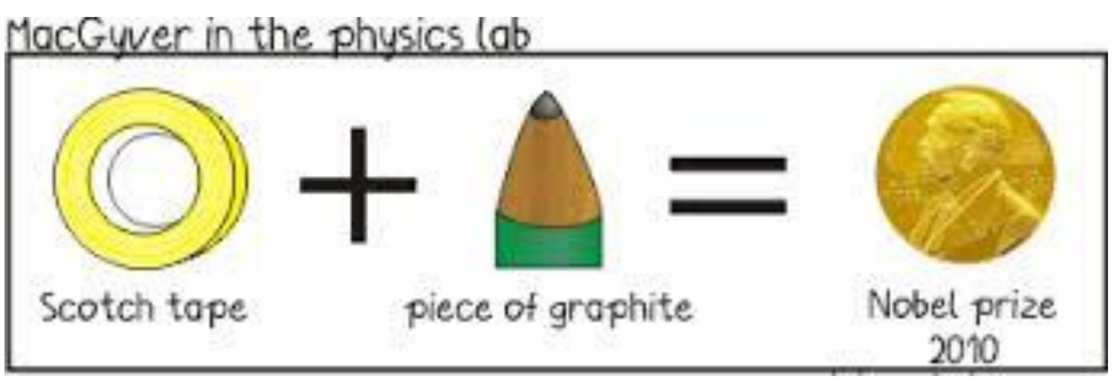
High resolution transmission electron microscope images (TEM) of graphene

History of graphene

- Studies on graphite layers for past hundred years
- Graphene theory first explored by P.R. Wallce (1947)
- Andre Geim & Kontantin Novoselov Nobel Peace Prize (2010)
- Physics observed using TEM

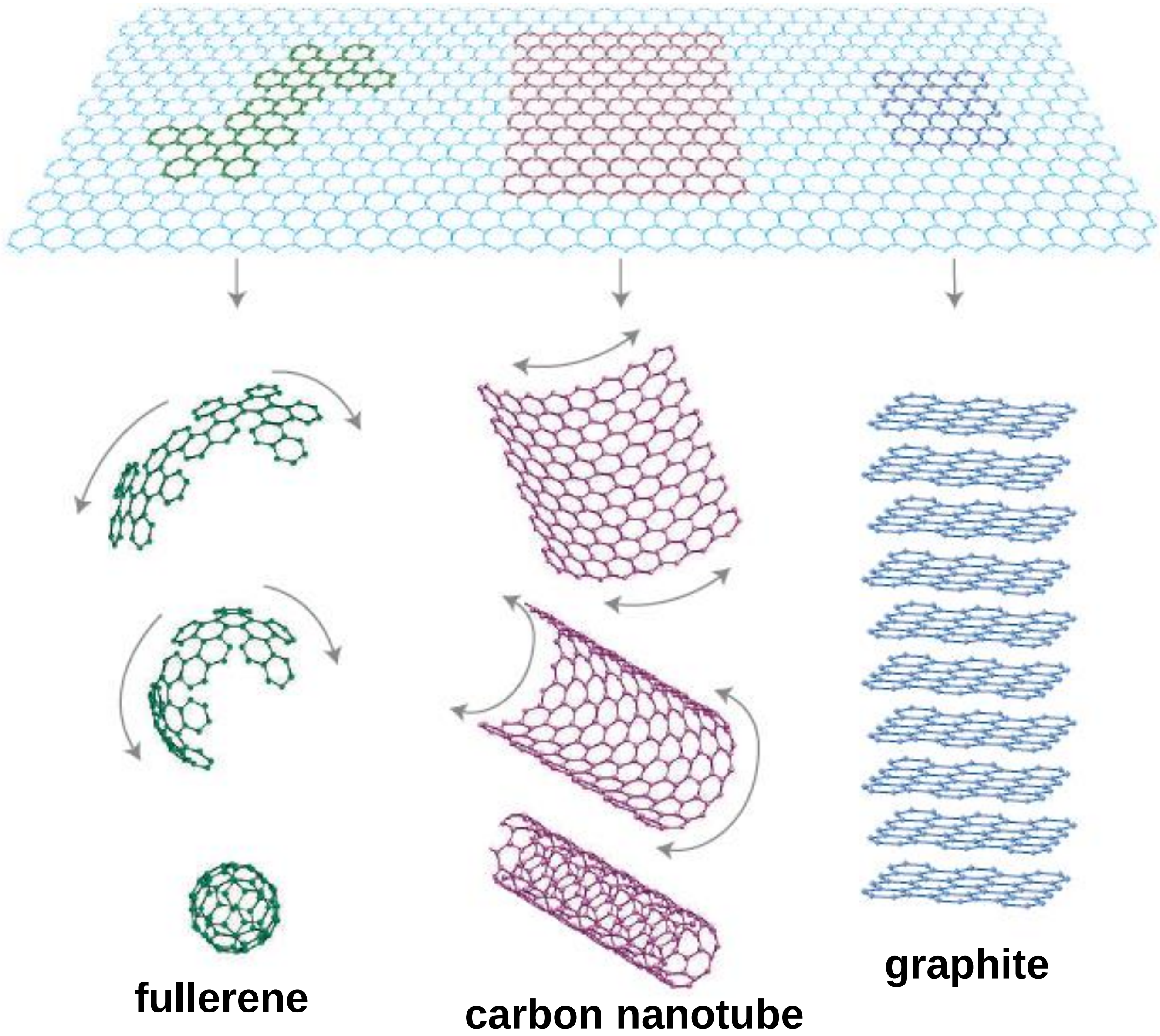


The 2010 Nobel Prize in Physics



2. Classification of Carbon Materials

Mother of all graphitic forms (fullerene, carbon nanotube, graphite)



Properties of graphene

- Electronic properties
- Thermal properties
- Mechanical properties
- Optical properties
- Relativistic charge carriers
- Anomalous quantum Hall effect

Electronic properties

- High electron mobility (at room temperature ~ 200,000 cm^2/(V·s),, ex. Si at RT~ 1400 cm^2/(V·s), carbon nanotube: ~ 100,000 cm^2/(V·s), organic semiconductors (polymer, oligomer): <10 cm^2/(V·s)

$$v_d = \mu E$$

Where u_d is the drift velocity in m/s (SI units)
E is the applied electric field in V/m (SI)
μ is the mobility in m^2/(V·s), in SI units.

- Resistivity of the graphene sheet ~10^{-6} Ω·cm, less than the resistivity of silver (Ag), the lowest resistivity substance known at room temperature (electrical resistivity is also as the inverse of the conductivity *σ* (*sigma*), of the material, or

$$\rho = \frac{1}{\sigma}$$

Materials	Electrical Conductivity ($S \cdot m^{-1}$)	Notes
Graphene	~ 10^8	
Silver	63.0×10^6	Best electrical conductor of any known metal
Copper	59.6×10^6	Commonly used in electrical wire applications due to very good conductivity and price compared to silver.
Annealed Copper	58.0×10^6	Referred to as 100% IACS or International Annealed Copper Standard. The unit for expressing the conductivity of nonmagnetic materials by testing using the eddy-current method. Generally used for temper and alloy verification of aluminum.
Gold	45.2×10^6	Gold is commonly used in electrical contacts because it does not easily corrode.
Aluminum	37.8×10^6	Commonly used for high voltage electricity distribution cables
Sea water	4.8	Corresponds to an average salinity of 35 g/kg at 20 °C.
Drinking water	0.0005 to 0.05	This value range is typical of high quality drinking water and not an indicator of water quality
Deionized water	5.5×10^{-6}	Conductivity is lowest with monoatomic gases present; changes to 1.2×10^{-4} upon complete de-gassing, or to 7.5×10^{-5} upon equilibration to the atmosphere due to dissolved CO_2
Jet A-1 Kerosene	50 to 450×10^{-12}	
n-hexane	100×10^{-12}	
Air	0.3 to 0.8×10^{-14}	

2. Classification of Carbon Materials

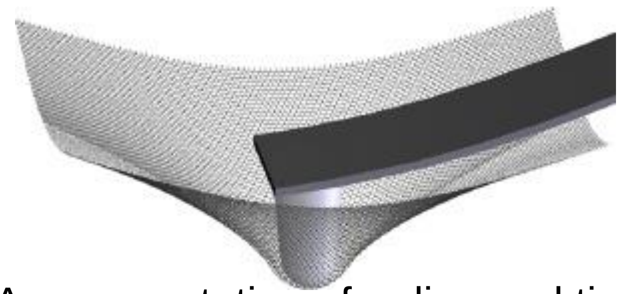
Thermal properties

Materials	Thermal conductivity W/(m·K)	Materials	Thermal conductivity W/(m·K)
Silica Aerogel	0.004 - 0.04	Ice	2
Air	0.025	Sandstone	2.4
Wood	0.04 - 0.4	Stainless steel	12.11 ~ 45.0
Hollow Fill Fibre Insulation Polartherm	0.042	Lead	35.3
Alcohols and oils	0.1 - 0.21	Aluminum	237 (pure) 120—180 (alloys)
Polypropylene	0.25	Gold	318
Mineral oil	0.138	Copper	401
Rubber	0.16	Silver	429
LPG	0.23 - 0.26	Diamond	900 - 2320
Cement, Portland	0.29	Graphene	(4840±440) - (5300±480)
Epoxy (silica-filled)	0.30		
Epoxy (unfilled)	0.59		
Water (liquid)	0.6		
Thermal grease	0.7 - 3		
Thermal epoxy	1 - 7		
Glass	1.1		
Soil	1.5		
Concrete, stone	1.7		

Mechanical properties

- High Young's modulus (~1,100 Gpa)
High fracture strength (125 Gpa)

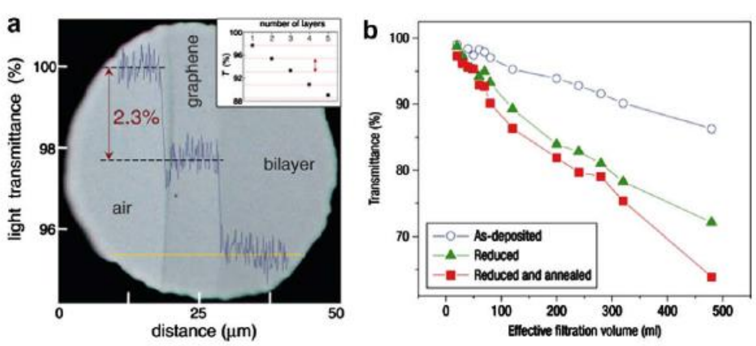
- Graphene is as the strongest material ever measured, some 200 times stronger than structural steel



A representation of a diamond tip with a two nanometer radius indenting into a single atomic sheet of graphene (*Science,* **321** (5887): 385)

Optical properties

- Monolayer graphene absorbs $\pi\alpha \approx 2.3\%$ of white light (97.7 % transmittance), where α is the fine-structure constant.



Preparation of Graphene

Top-down approach
(from graphite)

- **Scotch tape or peel-off method**: micromechanical exfoliation of graphite
- **Hummers method**: Creation of colloidal suspensions from graphite oxide or graphite intercalation compounds (GICs)

Bottom up approach
(from carbon precursors)

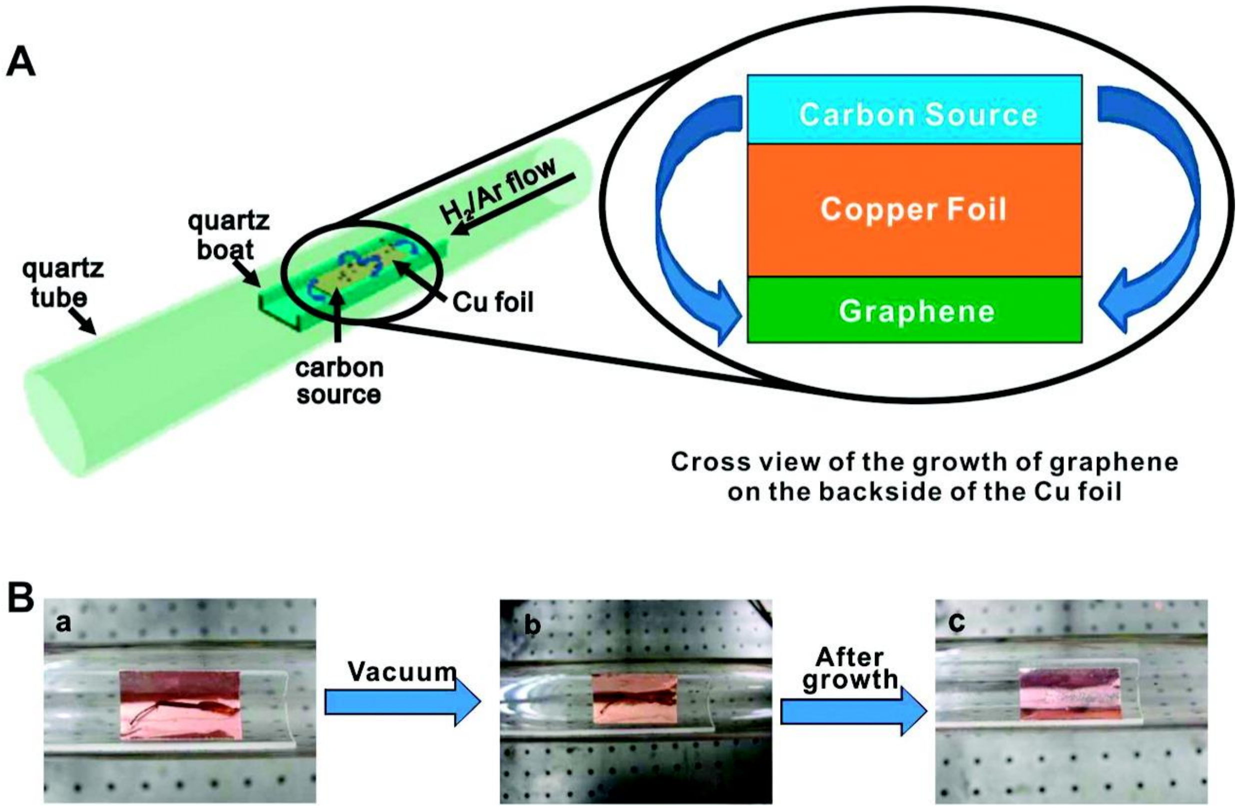
- **CVD**: from hydrocarbon

Table 1 – Advantages and disadvantages for techniques currently used to produce graphene.

	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed, SiO_2 thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (not suitable for large-scale production)
Epitaxial growth	Most even films (of any method) Large scale area	Difficult control of morphology and adsorption energy High-temperature process
Graphene oxide	Straightforward up-scaling Versatile handling of the suspension Rapid process	Fragile stability of the colloidal dispersion Reduction to graphene is only partial

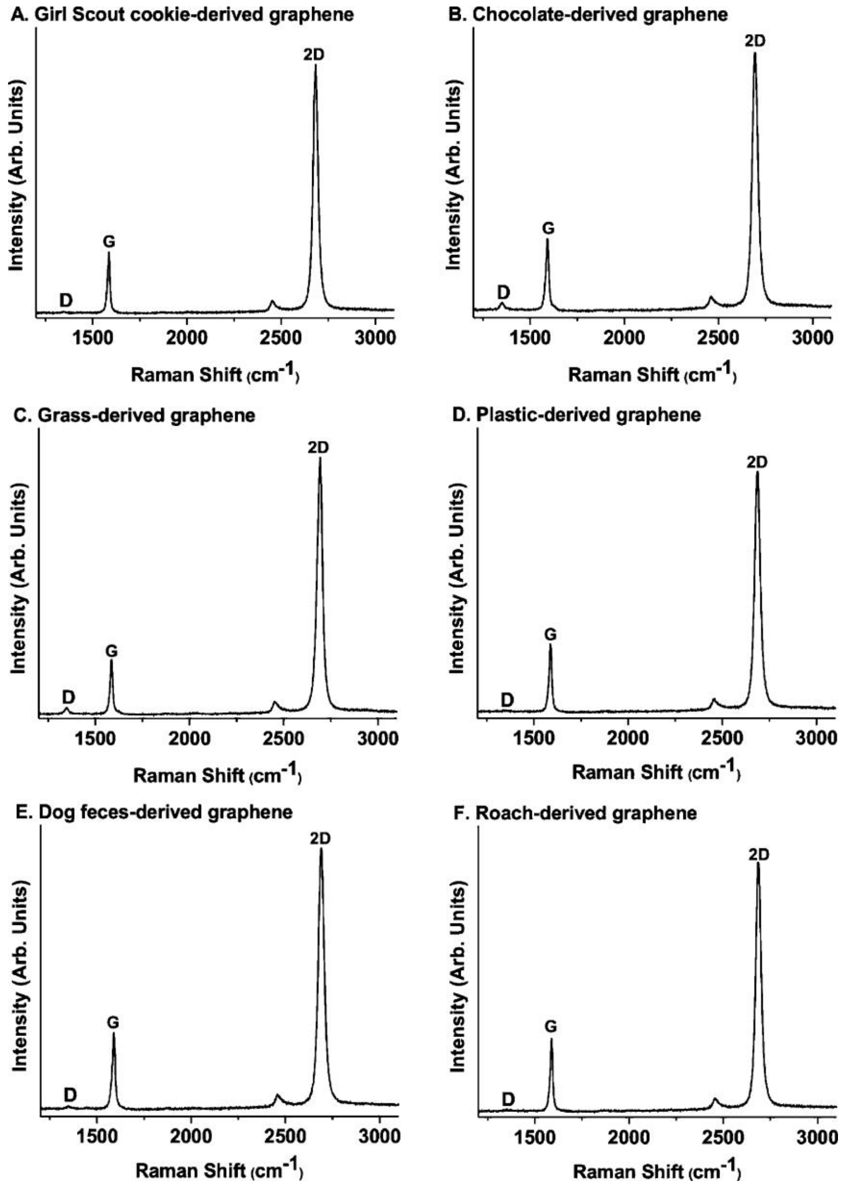
Preparation of Graphene

Growth of Graphene from Food, Insects, and Waste



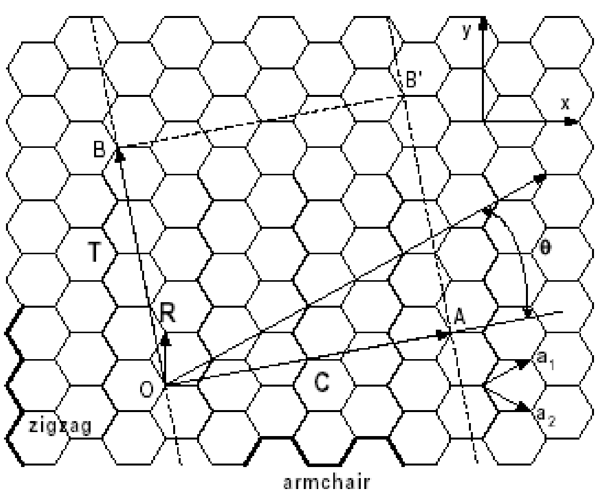
ACS Nano, **2011**, *5* (9), pp 7601–7607

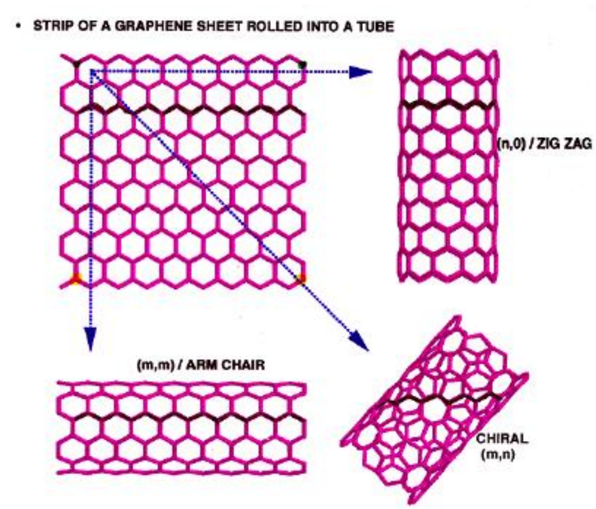
Raman spectra of monolayer graphene from six different carbon sources



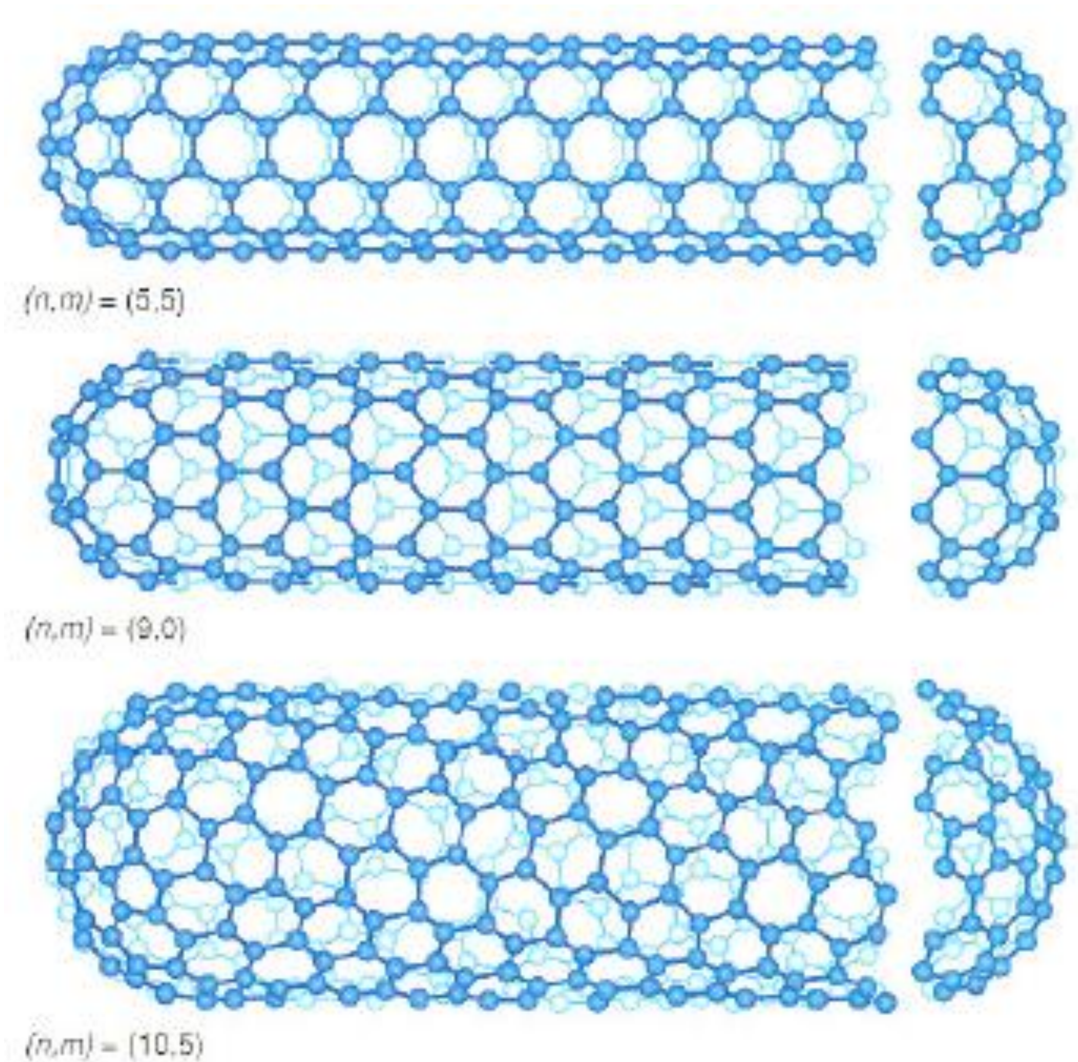
Carbon Nanotubes (CNTs)

- CNT is a tubular form of carbon with diameter as small as 1nm. Length: few nm to microns.
- CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.
- A CNT is characterized by its Chiral Vector: $\mathbf{C}_h = n\,\hat{a}_1 + m\,\hat{a}_2$, $\theta \rightarrow$ Chiral Angle with respect to the zigzag axis.





2. Classification of Carbon Materials



Armchair (n,m) = (5,5)
$\theta = 30°$

Zig Zag (n,m) = (9,0)
$\theta = 0°$

Chiral (n,m) = (10,5)
$0° < \theta < 30°$

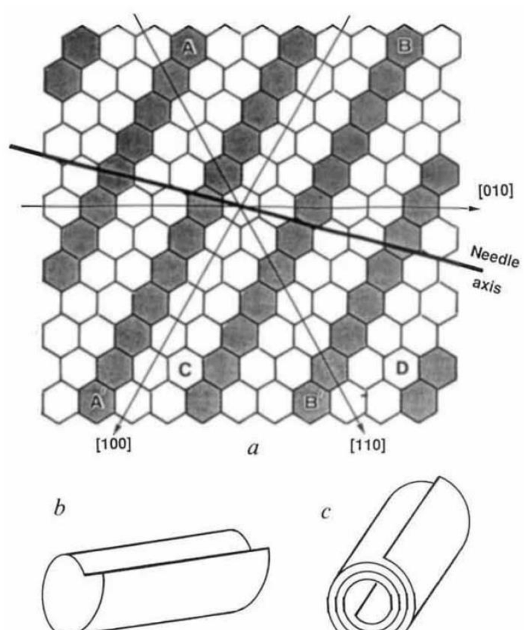
LETTERS TO NATURE

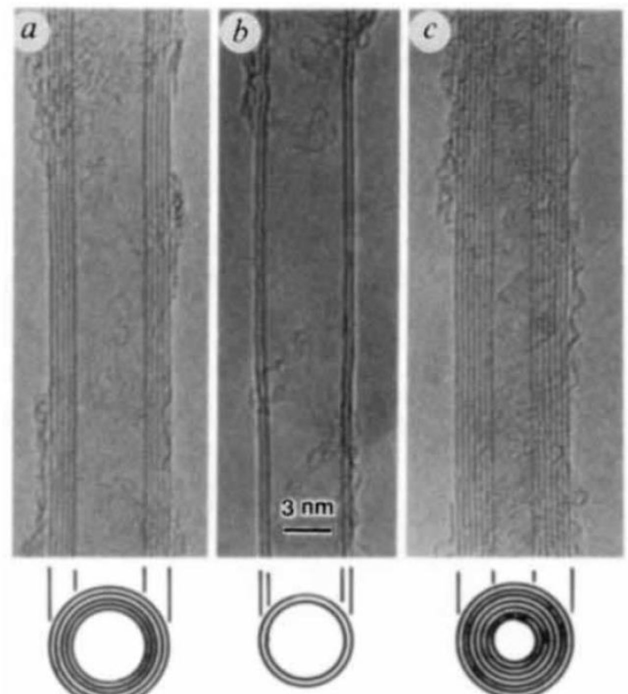
Nature **354**, 56-58 (7 November 1991) | doi:10.1038/354056a0; Accepted 21 October 1991

Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan



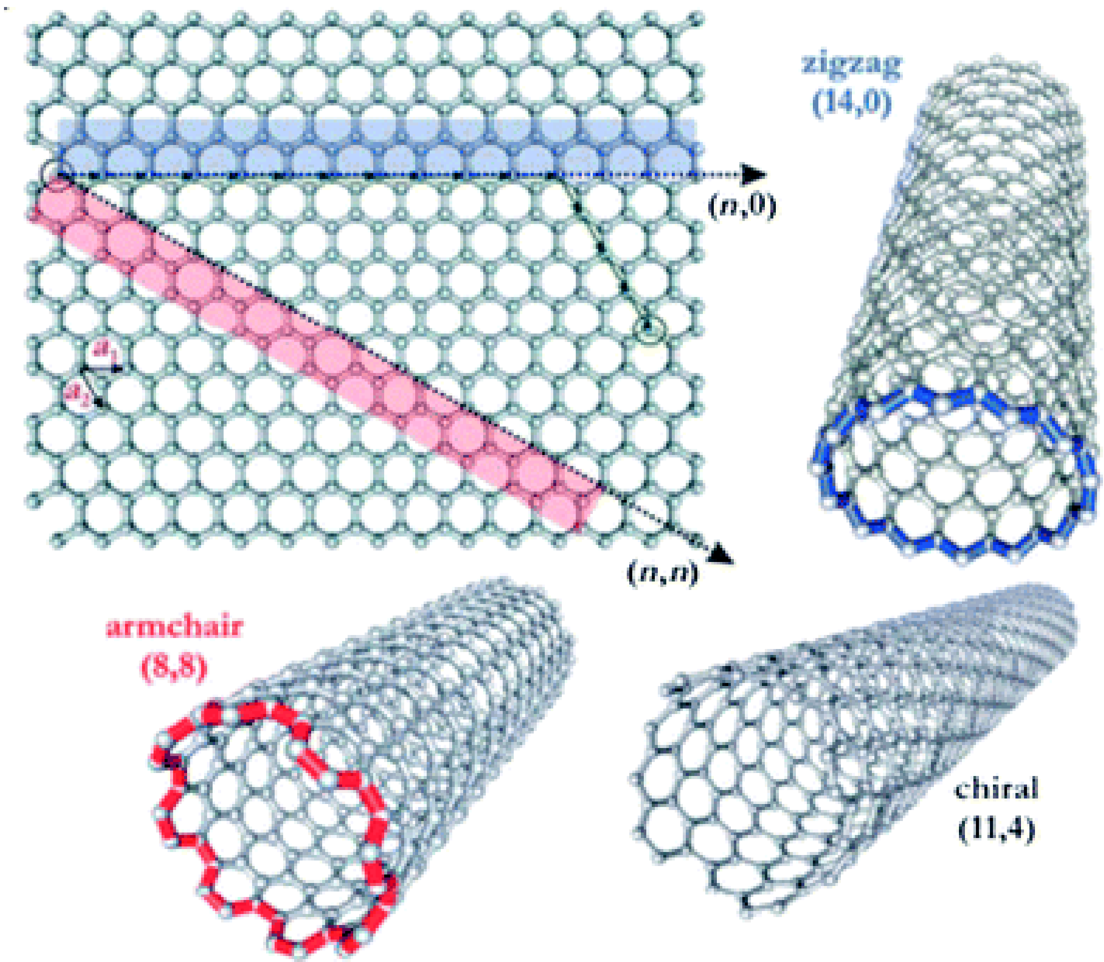


Types of CNTs

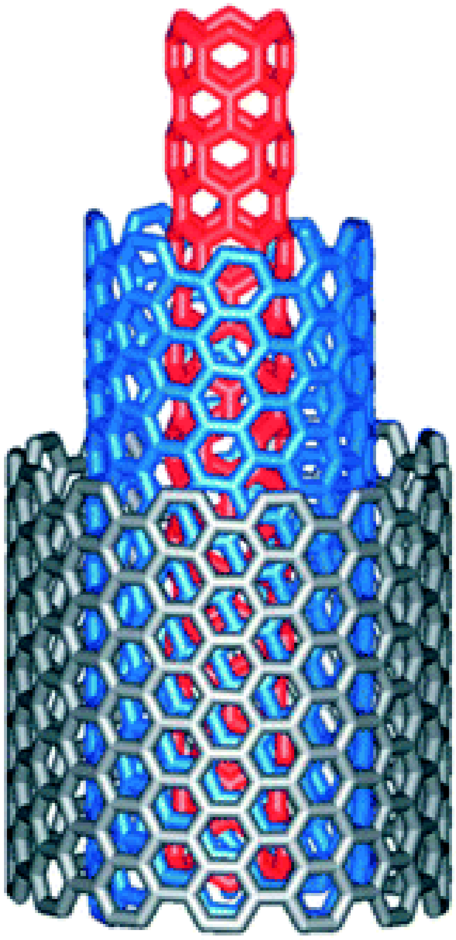
- Single Walled CNT (SWCNT)
- Multiple Walled CNT (MWCNT)
- Can be metallic or semiconducting depending on their geometry.

2. Classification of Carbon Materials

SWCNT



MWCNT



Advantages of CNTs

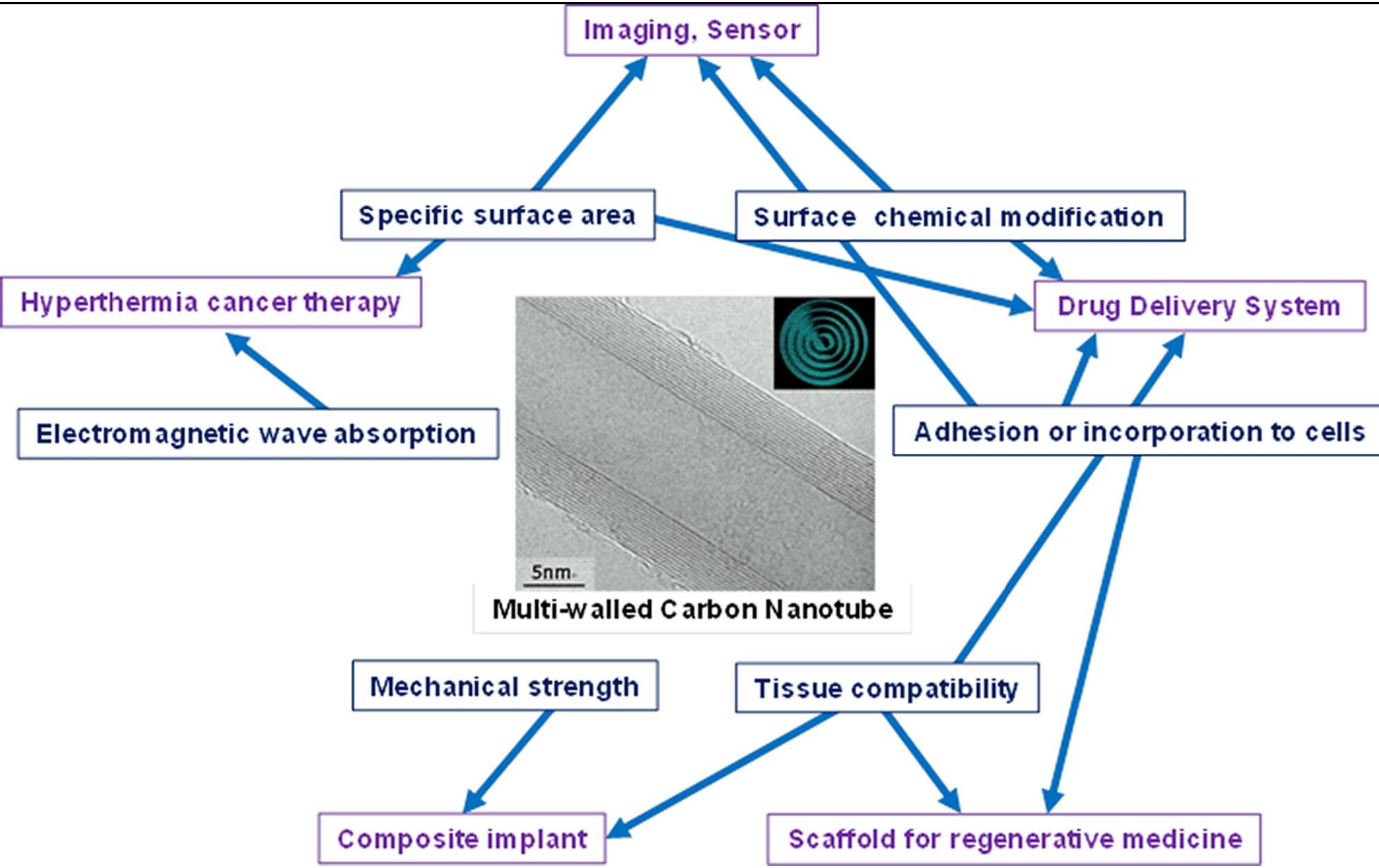
- High biocompatibility
- High strength-to-weight ratio
- High tensile strength
- Forming flexible nanofibers
- High chemical reactivity
- Conferring increased strength and other favorable characteristics to other substances when combined with them
- Inducing slow but significant biodegradation
- Colored in black that is easily distinguishable and detectable using a light microscope

Application of CNTs as Biomaterials

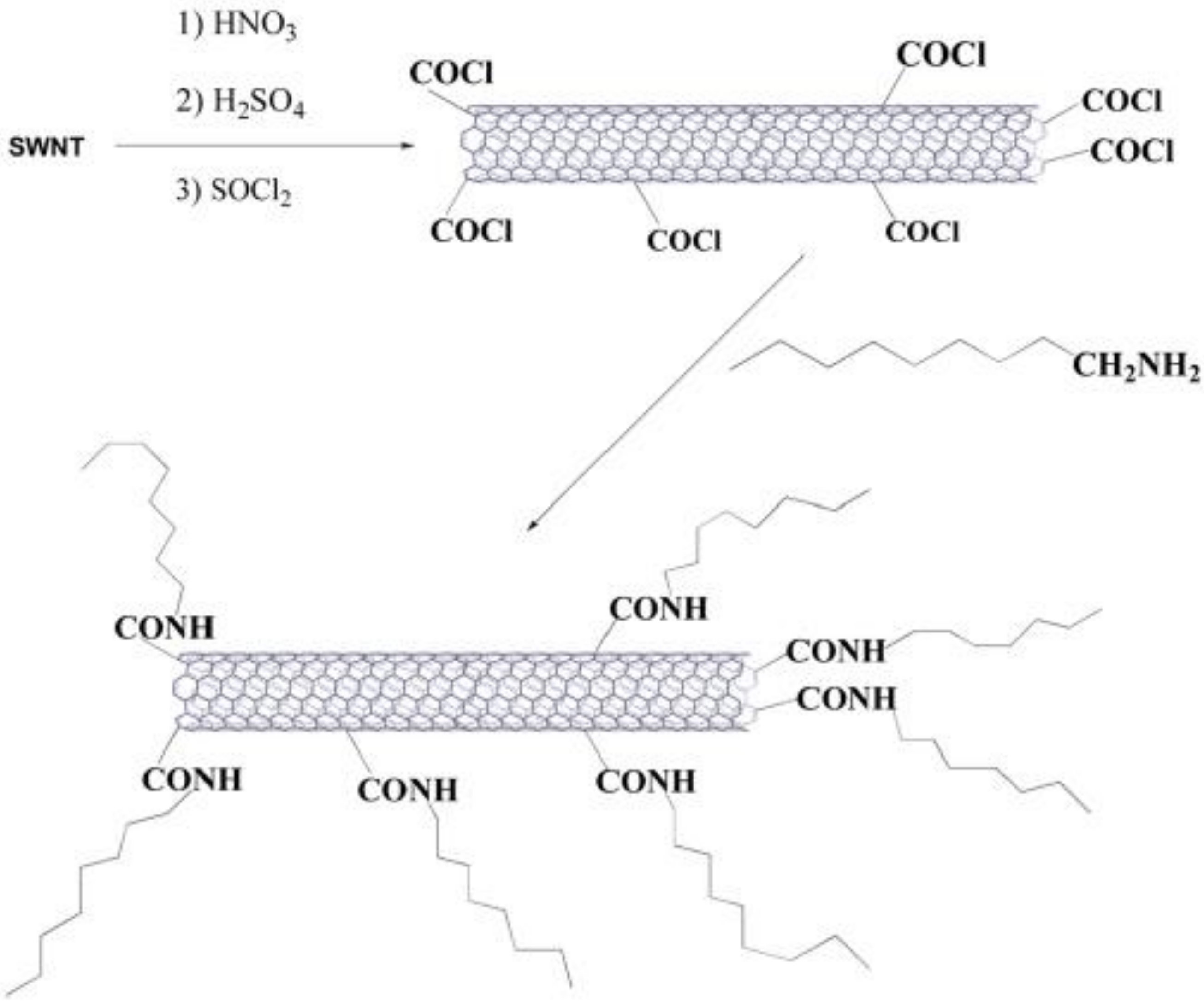
- Reacting with cells by entering the cells or adhering to cell surfaces
- Acting on biological macromolecules and cell organelles of similar size
- Acting on parts of the body with fine structures
- Distributed via the bloodstream after intravenous

  injection and the like; thus they may be used in targeted drug delivery systems and in vivo imaging
- Rapidly eliminated from the body
- Having effects when combined with other biomaterials, for example, on fine structures to increase their mechanical strength

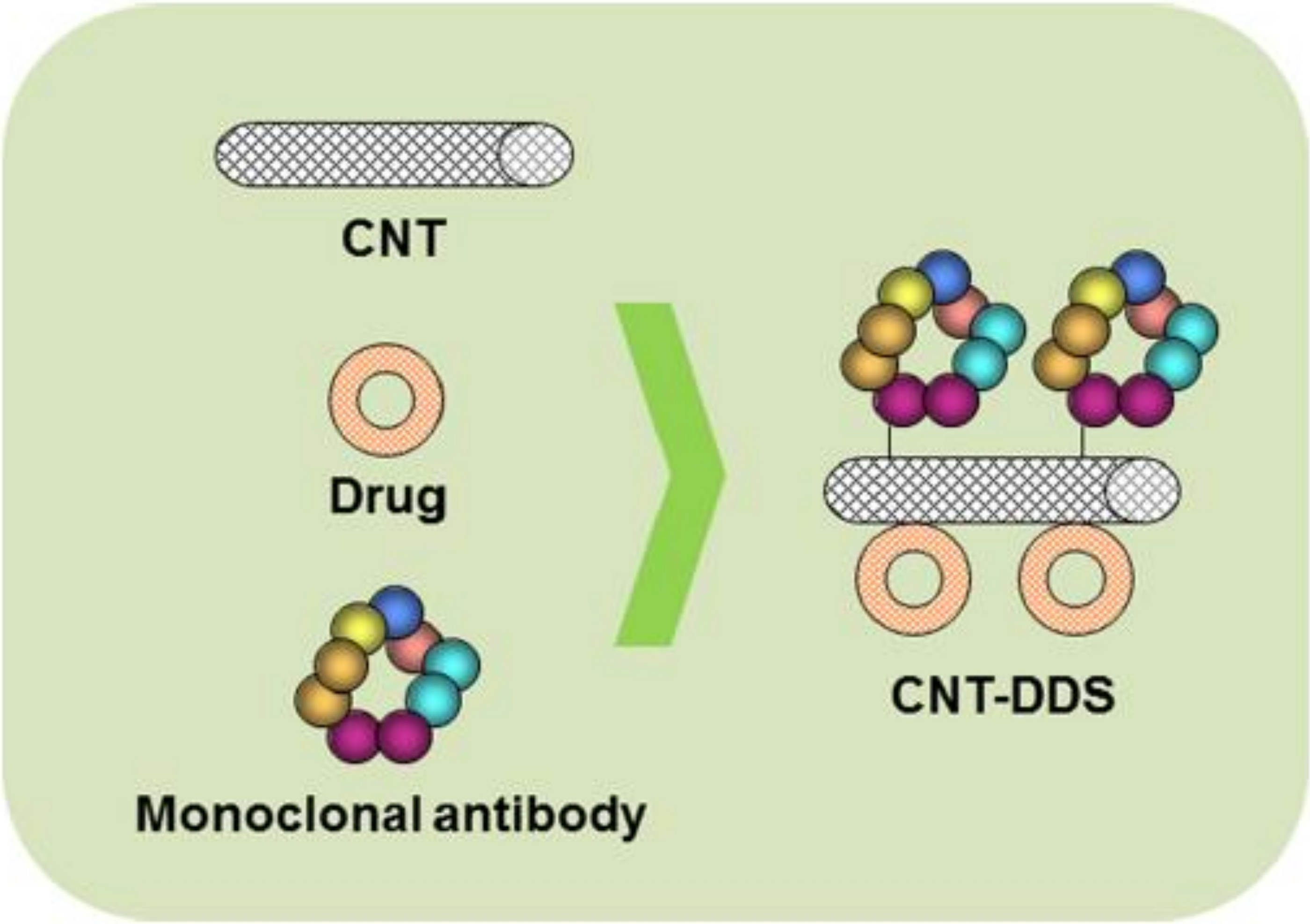
2. Classification of Carbon Materials



Functionalization of CNTs



2. Classification of Carbon Materials



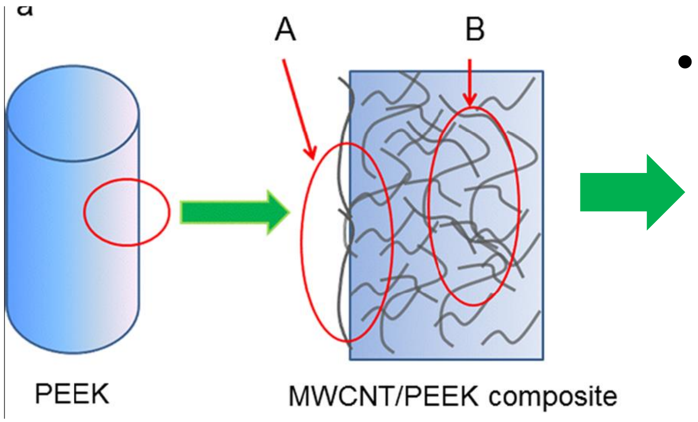
sliding parts of artificial joints, an ultrahigh molecular weight polyethylene (UHMWPE) conjugated with MWCNTs has been developed.

- A UHMWPE socket (left panel) and an MWCNT-conjugated UHMWP socket (right panel) for use in sliding parts of artificial joints.

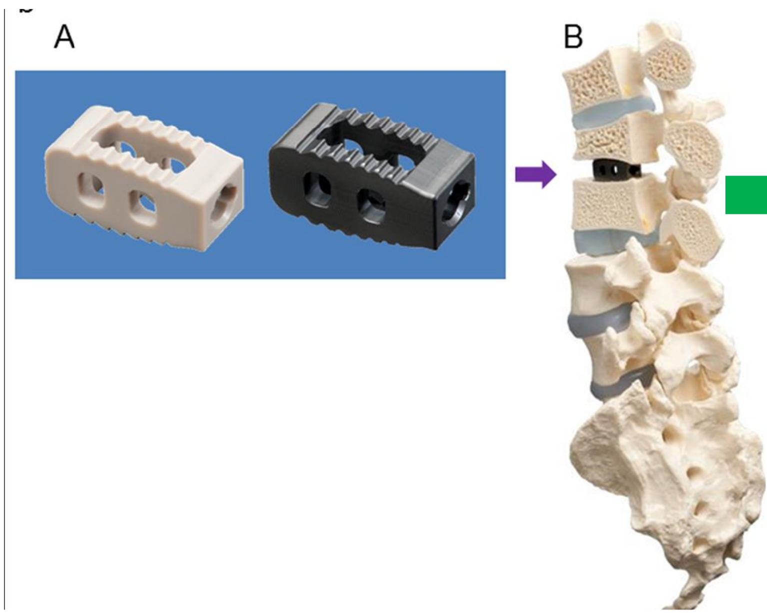
- A prototype artificial joint with a socket made of CNTs

MWCNT-conjugated UHMWPE is suitable as a sliding parts material for artificial joints, and having favorable characteristics that have not been achieved with conventional materials, that is, **high wear resistance and low breakability**.

Spine interbody fusion material, a polyetheretherketone (PEEK) composite with MWCNTs has been developed.



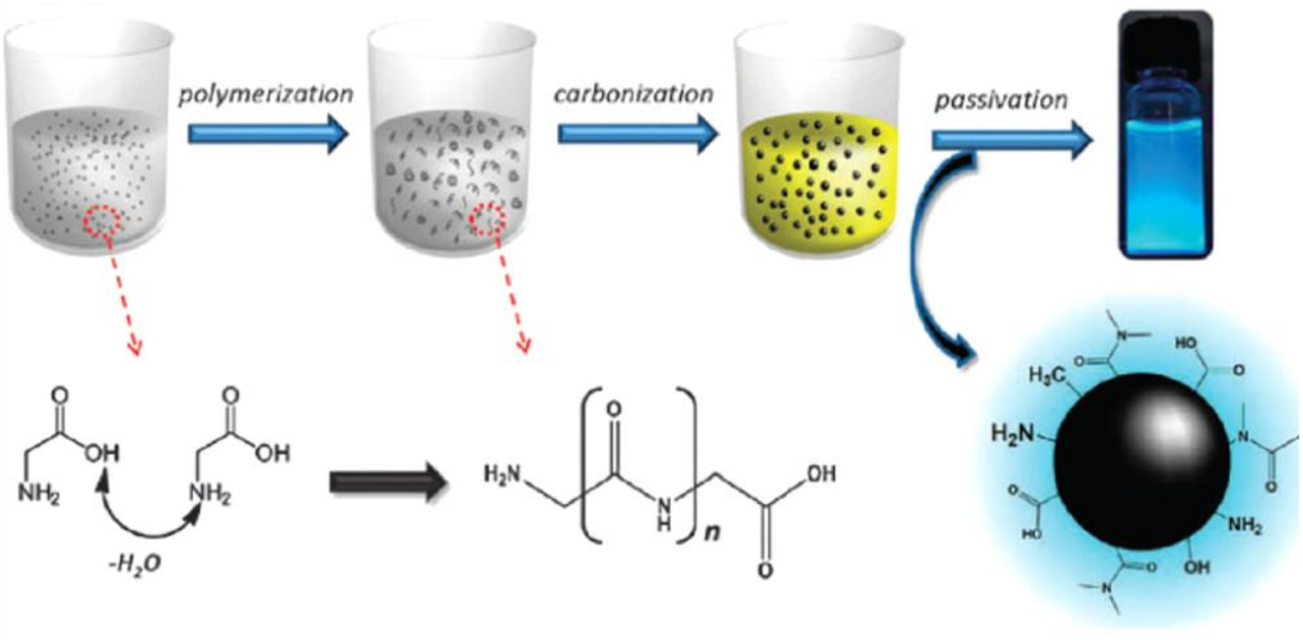
- A conceptual diagram showing that PEEK, when conjugated with MWCNTs, will become an innovative spine interbody fusion material possessing excellent mechanical characteristics and bone compatibility. (A) The MWCNTs on the surface confer bone compatibility. (B) The internally conjugated MWCNTs control the elastic modulus.



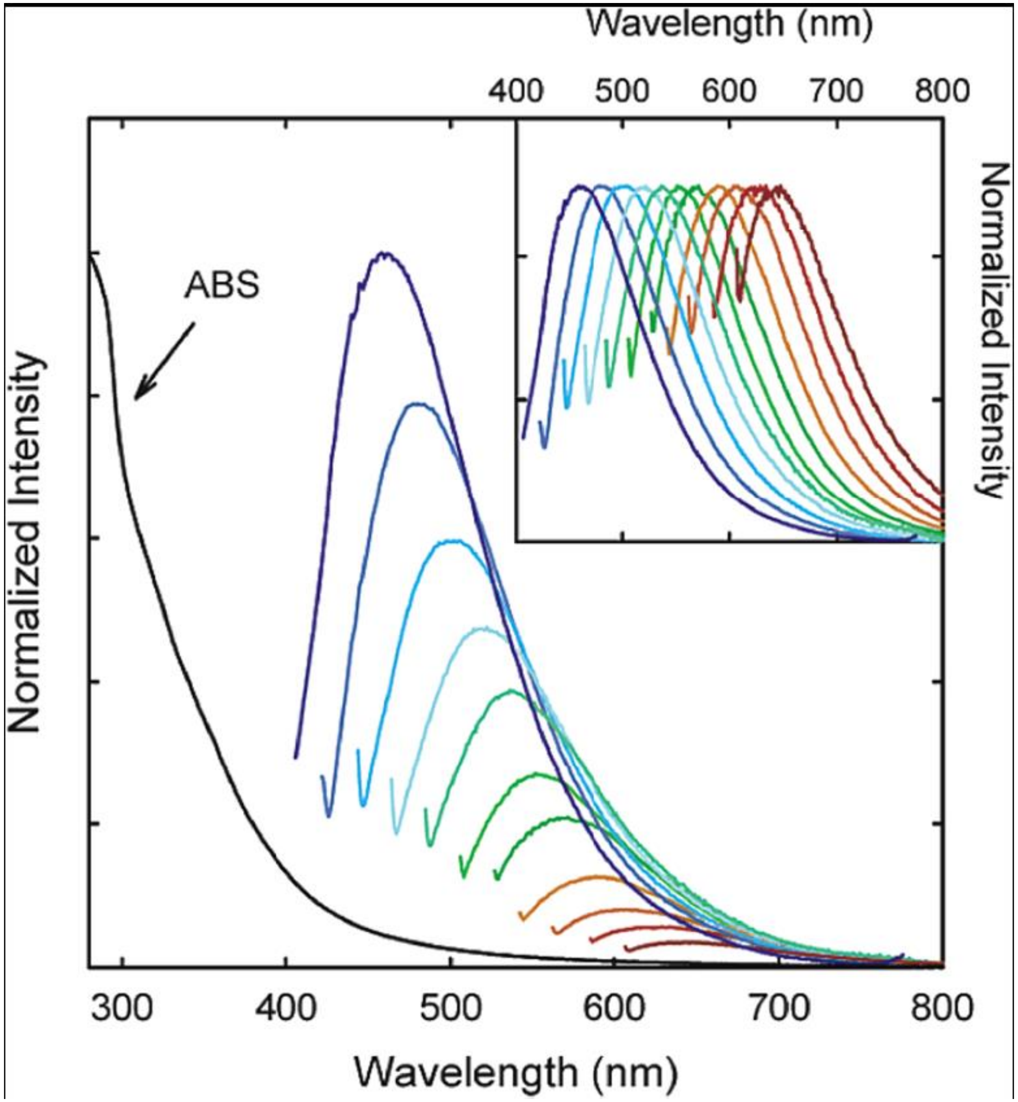
- (A) A PEEK spine interbody fusion cage (left panel) and an MWCNT-conjugated PEEK cage (right panel). (B) A prototype interbody fusion cage made of CNTs.

Conjugation with MWCNTs further improves the mechanical characteristics of PEEK and also induces osteogenesis

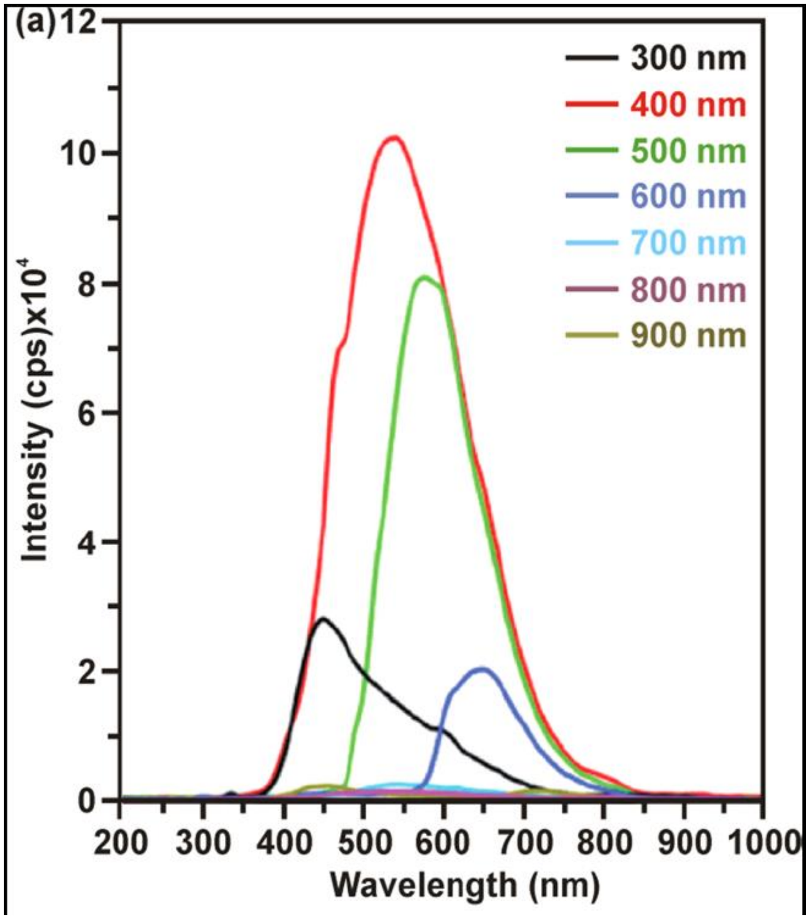
Carbon Dots

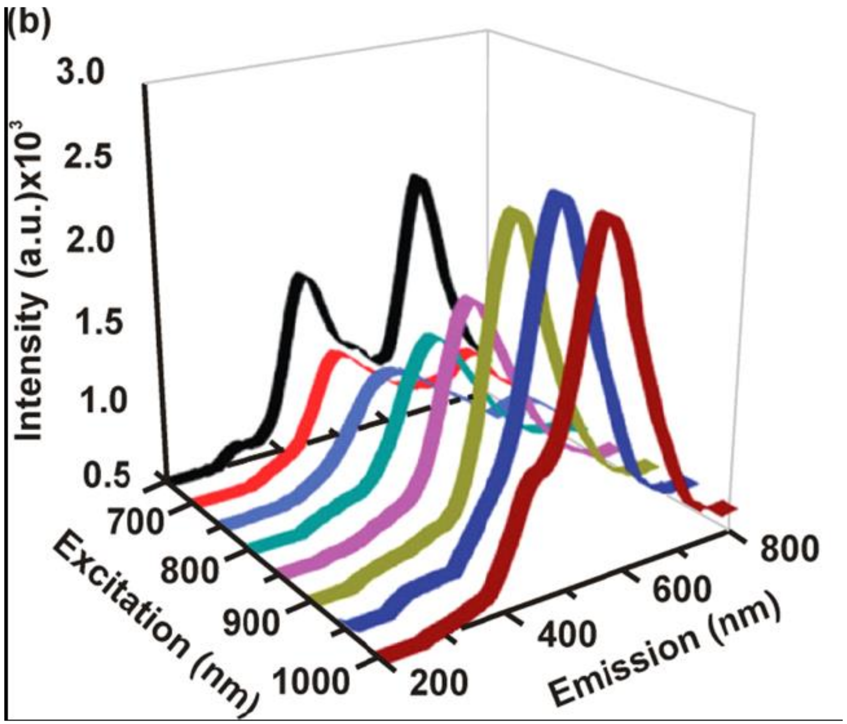


Photoluminescence of Carbon Dots



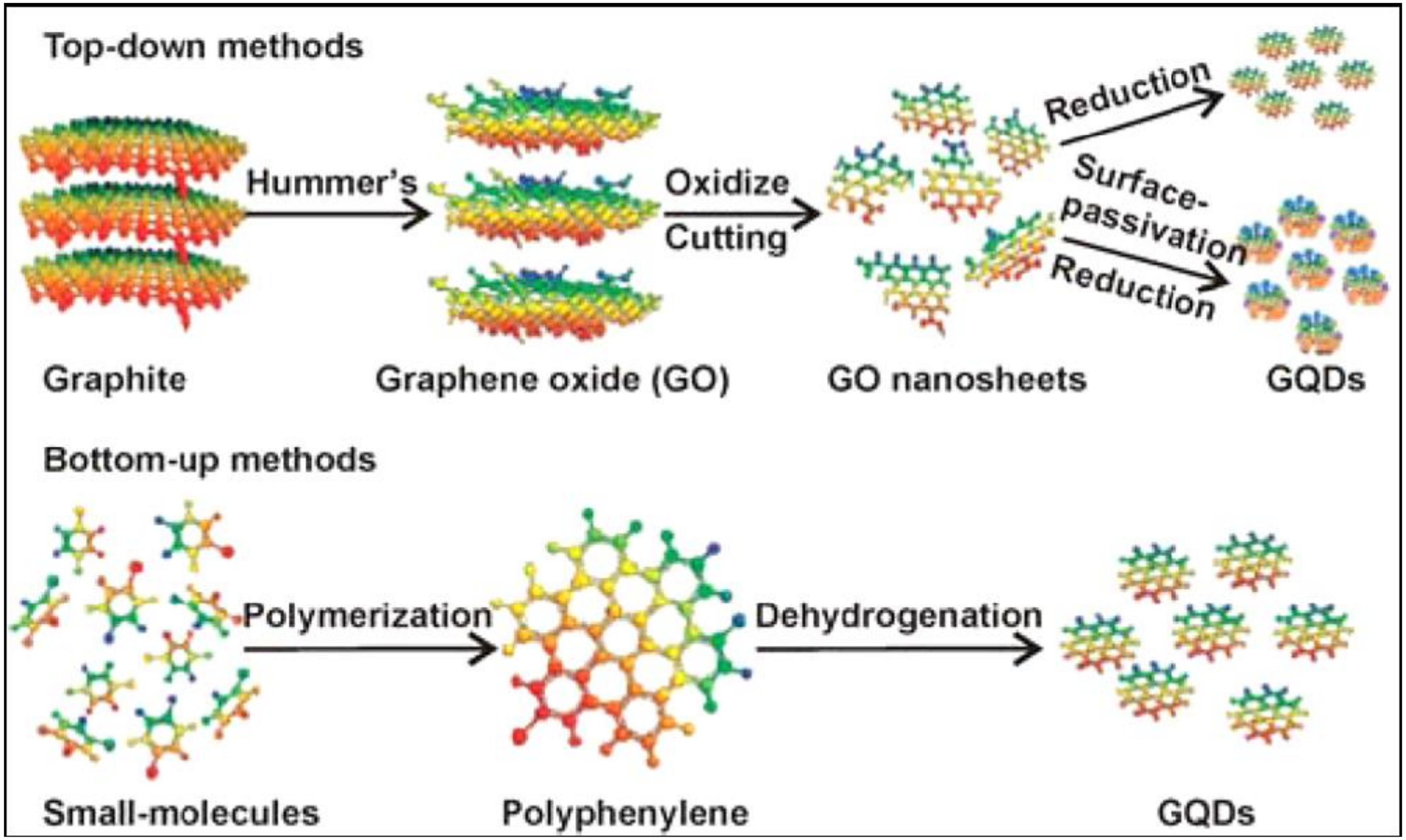
Carbon dots: excitation wavelength dependent photoluminescence



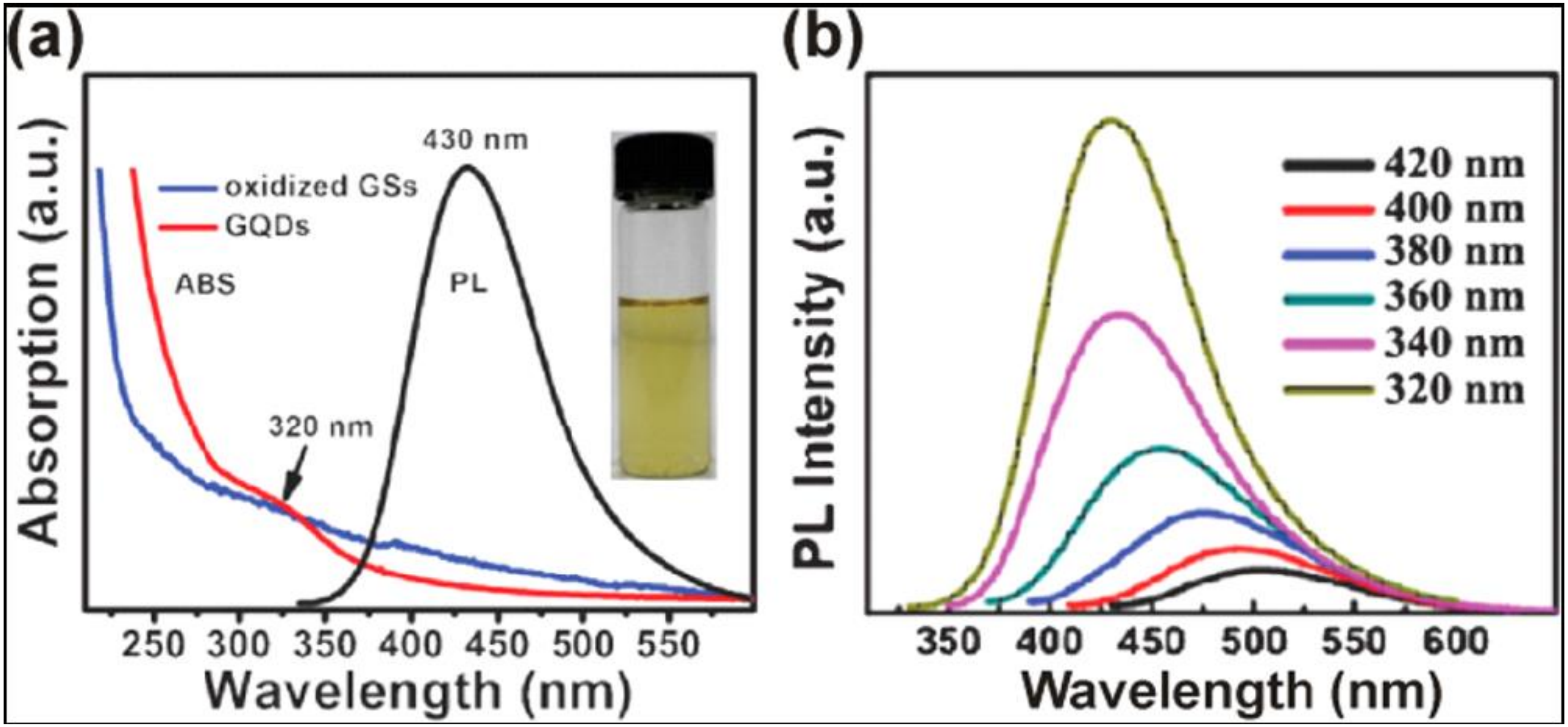


Graphene Dots

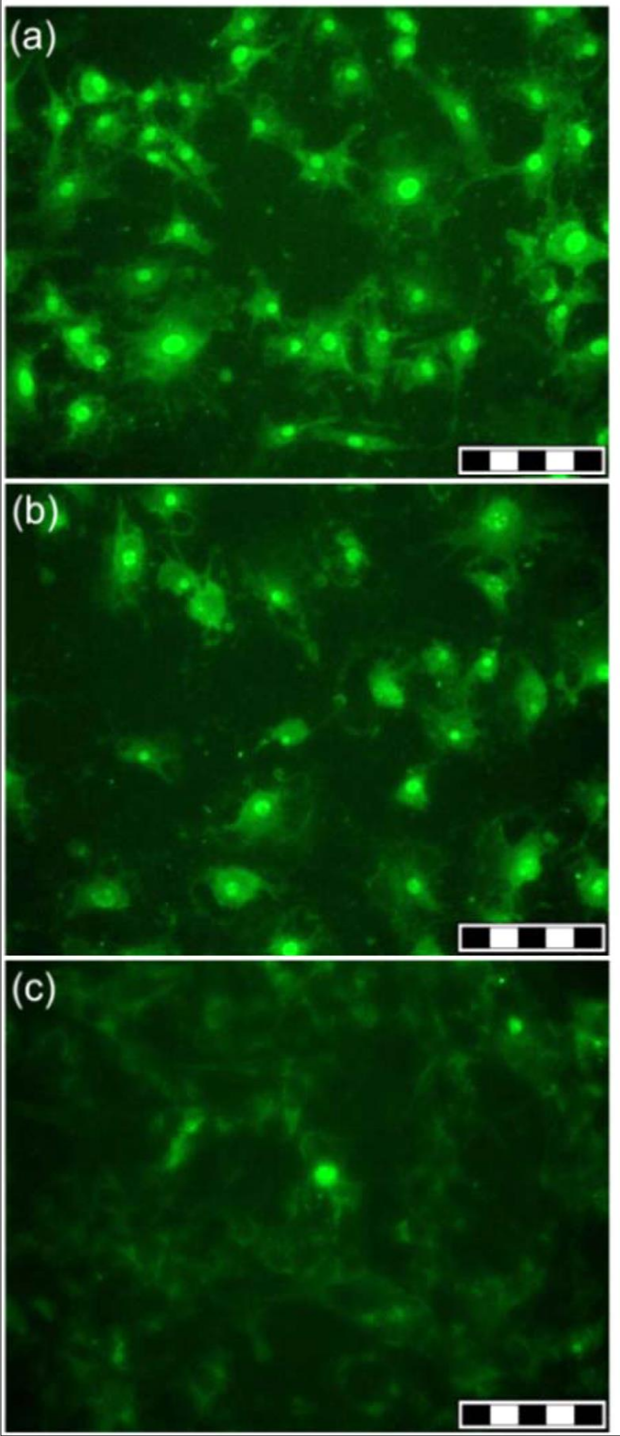
Schematic diagram of the top-down and bottom-up methods for the synthesis of GQDs.



Photoluminescence of graphene dots

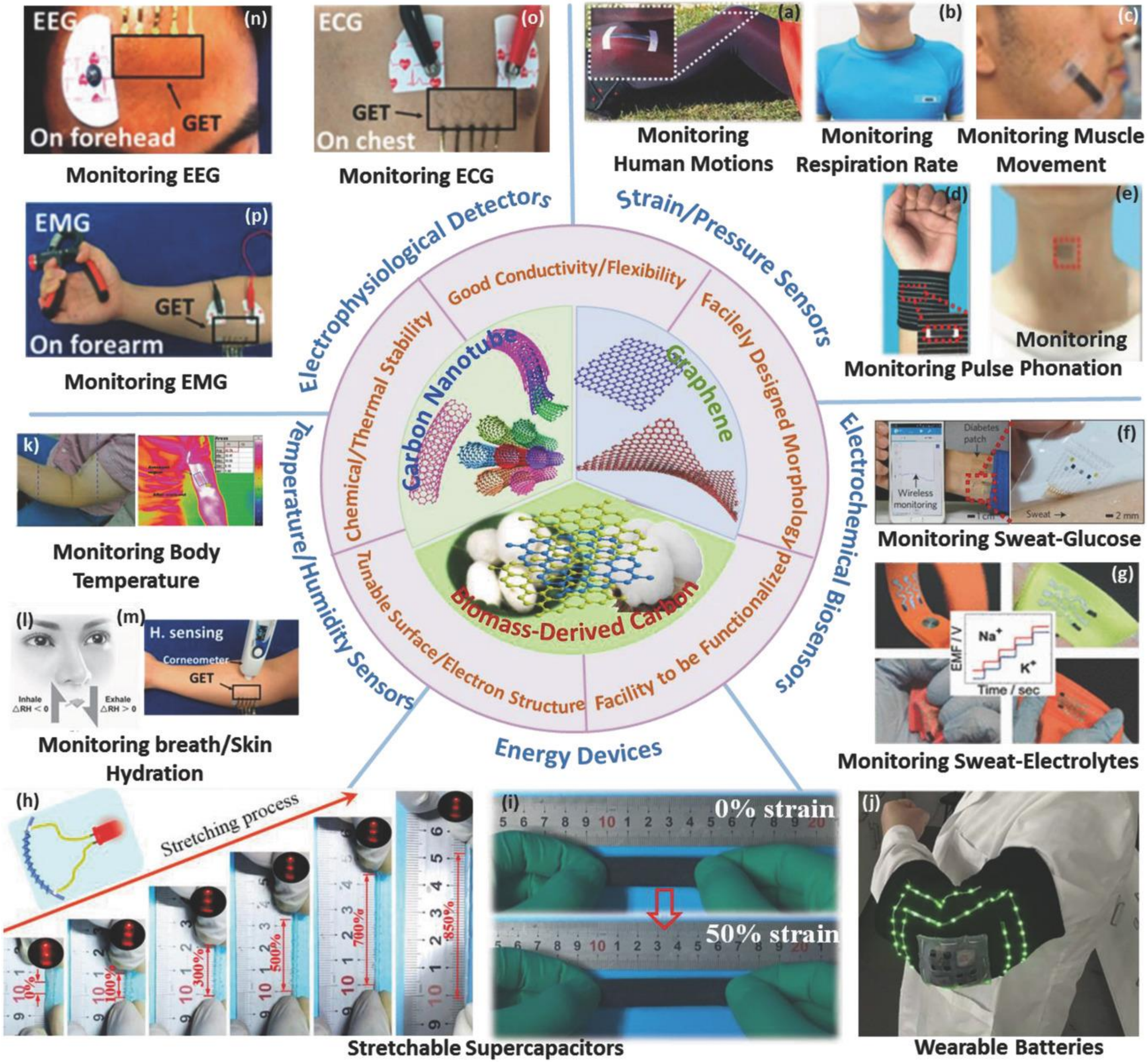


Carbon dots and graphene dots: applications



Fluorescence images of mouse fibroblast NIH/3T3 cells containing
(a) carbon dots
(b, c) carbon dot−graphene oxide hybrids

Applications of Carbon Materials



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Contents

- Introduction to Carbon and Carbon Materials
- Classification of Carbon Materials
  1. Diamond
  2. Graphite
  3. Fullerene
  4. Pyrolytic carbon
  5. Graphene
  6. Carbon nanotubes
  7. Carbon dots and graphene dots
- **Raman spectrum of Carbon Materials**

Queen of Carbon Science

Mildred (Millie) Dresselhaus

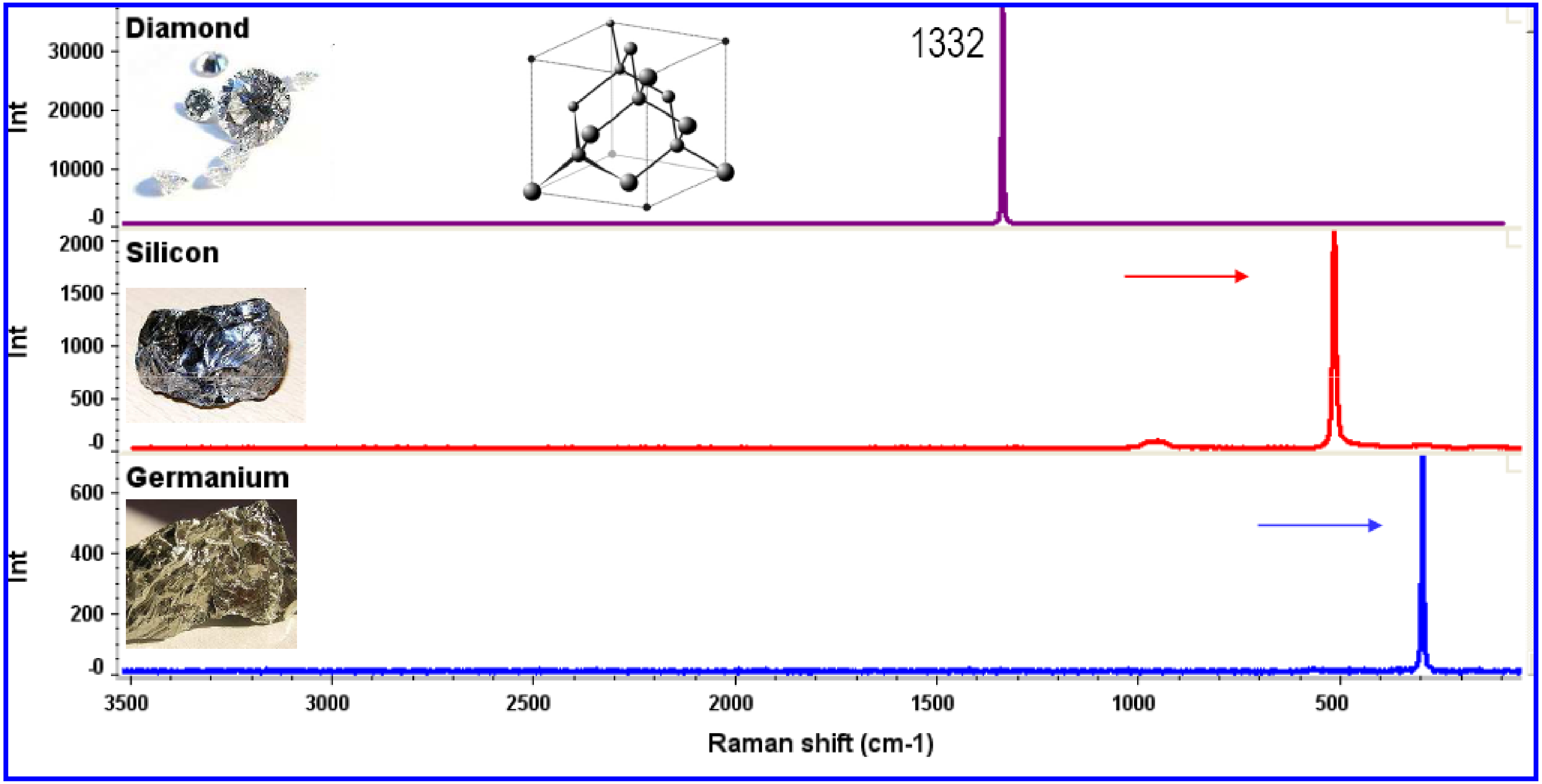
Dresselhaus was particularly noted for her work on graphite,graphite intercalation compounds, fullerenes, carbon nanotubes, spin-orbit coupling in semiconductors, and low-dimensional thermoelectrics. Her group made frequent use of electronic band structure, Raman scattering and the photophysics of carbon nanostructures. Her research helped develop technology based on thin graphite which allow electronics to be "everywhere," including clothing and smartphones.

Honors and awards [edit]

- Honorary Degree of Doctor of Science from the ETH Zurich, 2015[21]
- IEEE Medal of Honor, 2015 (first female recipient)
- National Inventors Hall of Fame induction 2014[22]
- Presidential Medal of Freedom, 2014[23]
- Honorary Degree of Doctor of Science, The Hong Kong Polytechnic University, Hong Kong, 2013[24]
- Von Hippel Award, Materials Research Society, 2013[25]
- Kavli Prize in Nanoscience, 2012
- Enrico Fermi Award (second female recipient), 2012
- Vannevar Bush Award (second female recipient), 2009
- ACS Award for Encouraging Women into Careers in the Chemical Sciences, 2009
- Oliver E. Buckley Condensed Matter Prize, American Physical Society, 2008
- Oersted Medal, 2007
- L'Oréal-UNESCO Awards for Women in Science, 2007
- Heinz Award for Technology, the Economy and Employment, 2005
- IEEE Founders Medal Recipients, 2004
- Karl Taylor Compton Medal for Leadership in Physics, American Institute of Physics, 2001
- Medal of Achievement in Carbon Science and Technology, American Carbon Society, 2001
- Honorary Member of the Ioffe Institute, Russian Academy of Sciences, St. Petersburg, Russia, 2000
- National Materials Advancement Award of the Federation of Materials Societies, 2000
- Honorary Doctorate from the Catholic University of Leuven, Belgium, February 2000
- Nicholson Medal, American Physical Society, March 2000
- Weizmann Institute's Millennial Lifetime Achievement Award, June 2000
- SGL Carbon Award, American Carbon Society, 1997
- National Medal of Science, 1990
- Society of Women Engineers Achievement Award, 1977

What can Raman tell us about carbon?

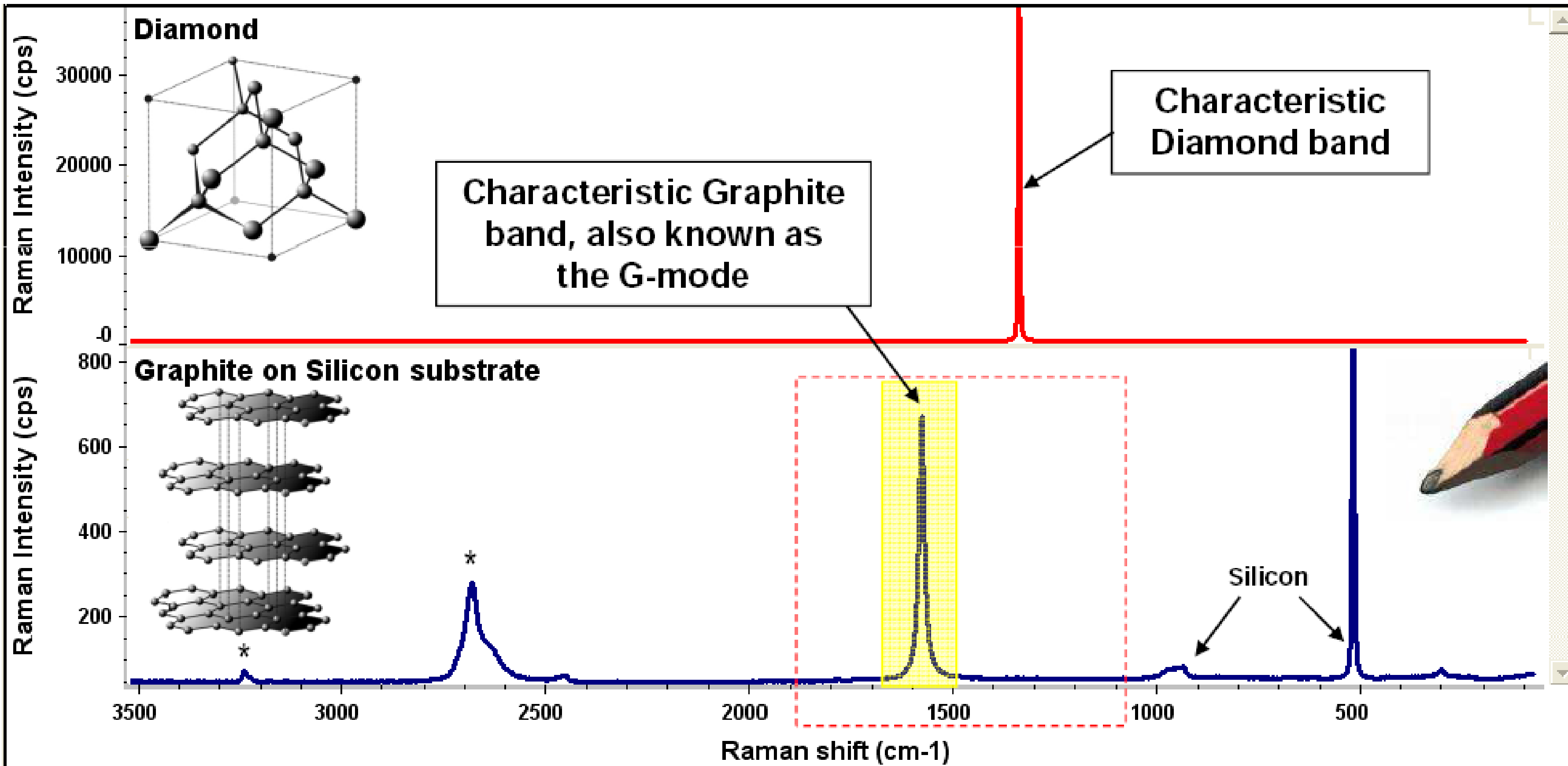
- **Raman can identify carbon and distinguish it from other materials**



The diamond spectrum is very similar to that of crystalline silicon and germanium except that the bonds with the lighter weight carbon atoms vibrate at higher frequency.

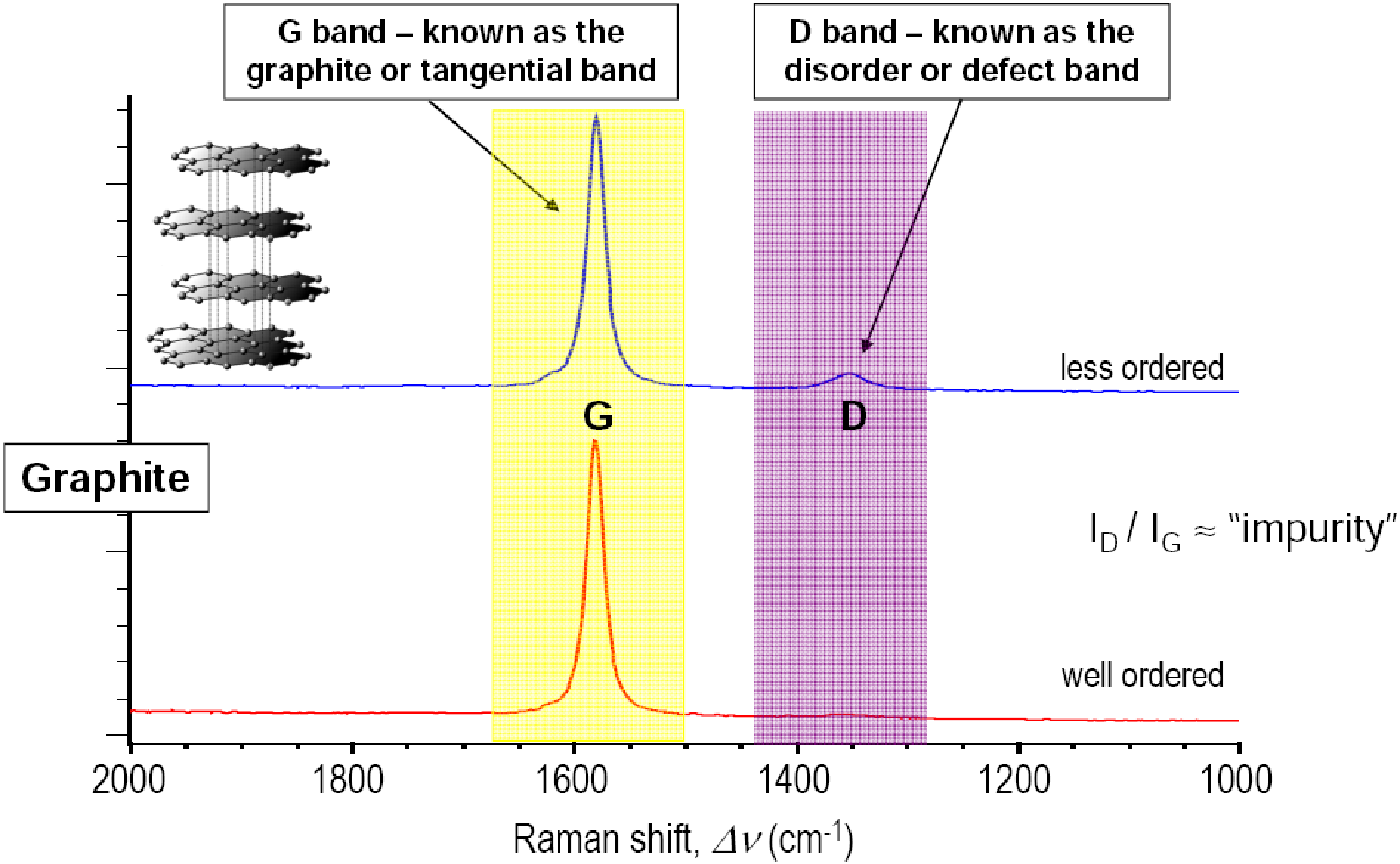
- **Raman easily differentiates different allotropes**

1) Characteristic Graphite band represents sp^2 bonds (planar configurations)
2) Characteristic Diamond band represents sp^3 bonds (tetrahedral configurations)
3) Bands here may also represent disorder in sp^2 bonds (graphene edge configurations)



3. Raman spectrum of Carbon Materials

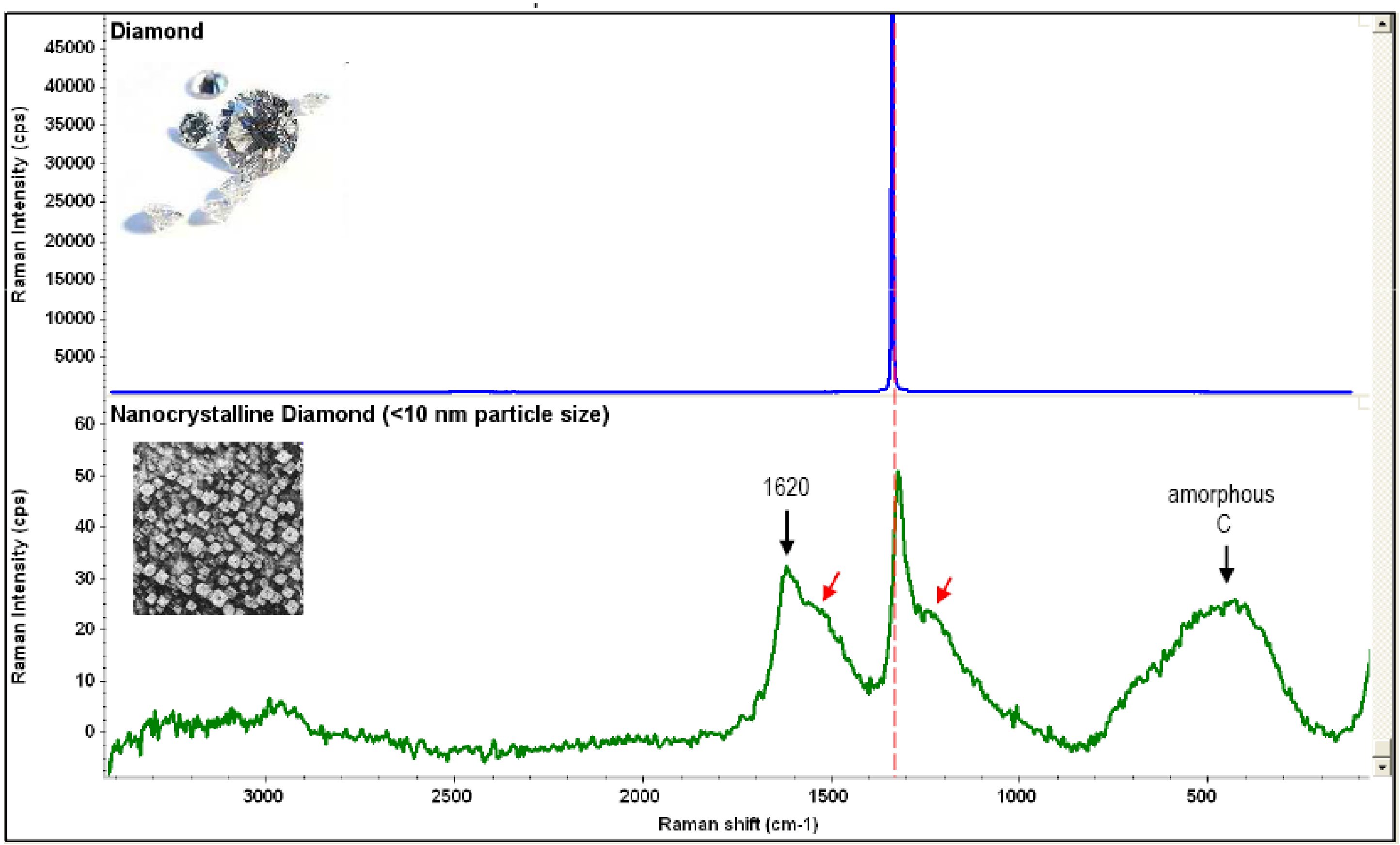
- **G and D modes are fundamental tools in the Raman spectra of carbon**



3. Raman spectrum of Carbon Materials

- **Raman is very sensitive to morphology differences**

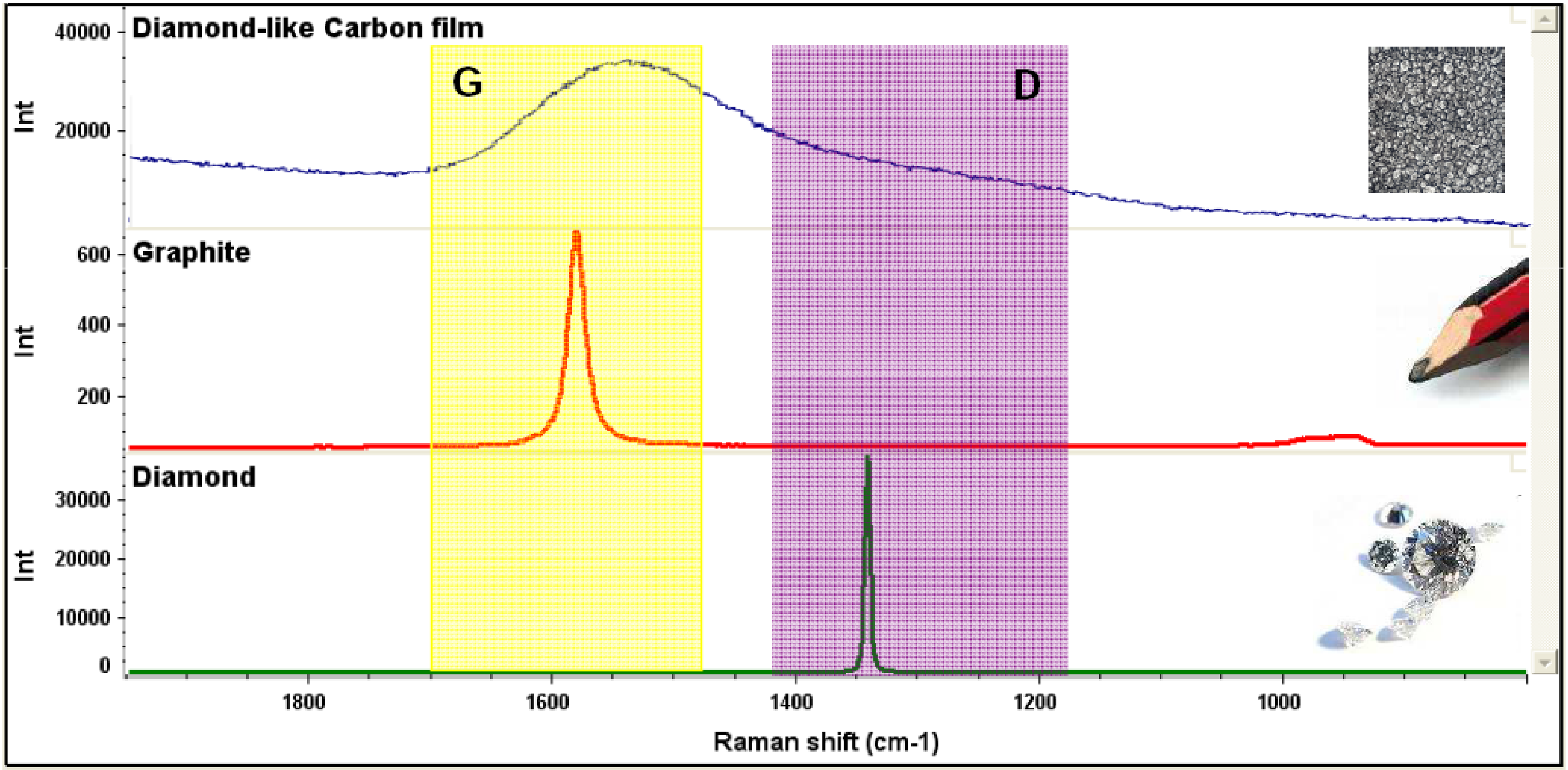
1) Nanocrystalline diamond has a different structure to bulk diamond due to the increased surface area of the nanocrystals
2) The effect on the Raman spectrum is dramatic



3. Raman spectrum of Carbon Materials

- **Diamond-like carbon film has both sp^2 and sp^3 carbon**

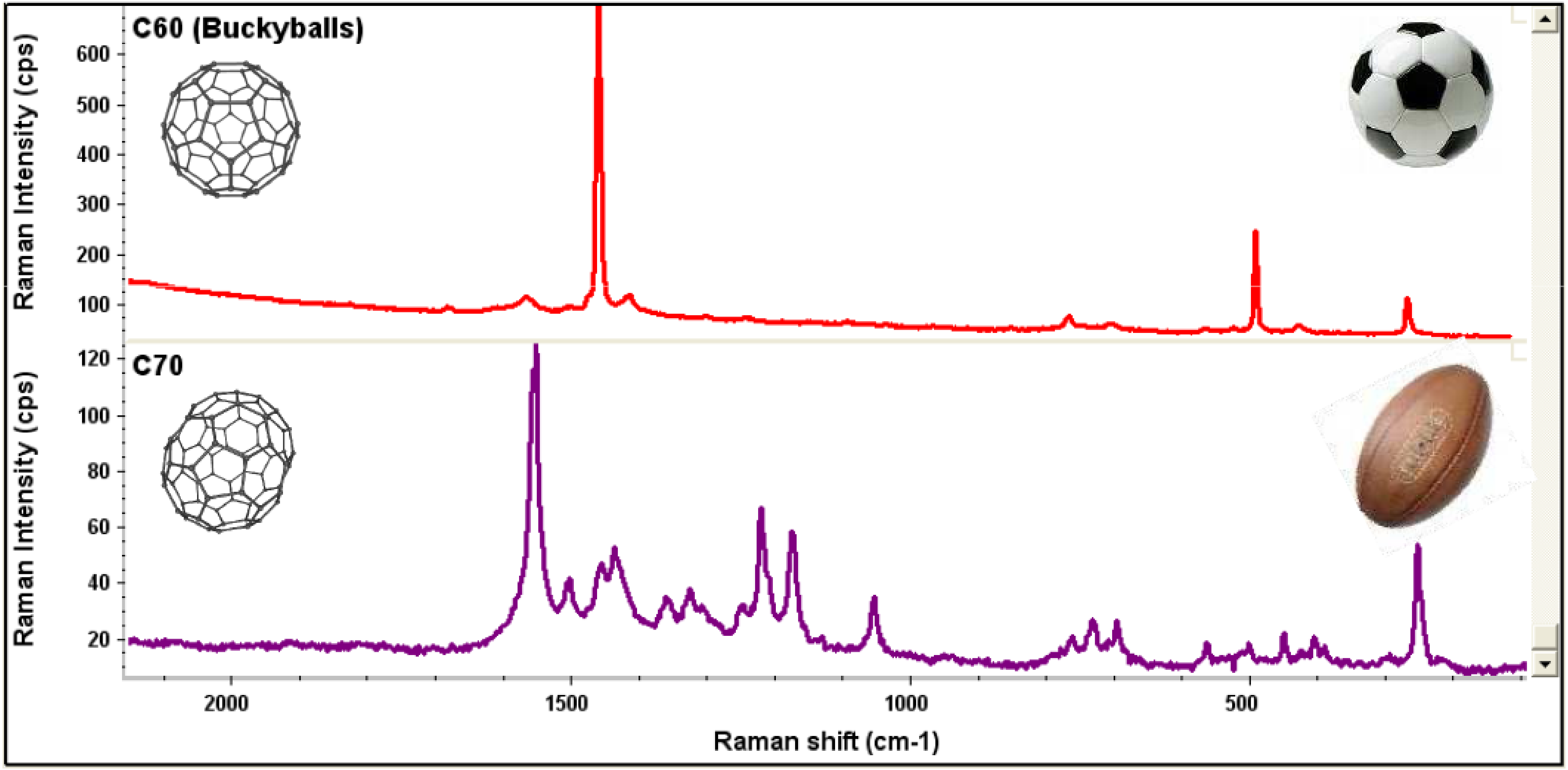
Raman spectroscopy can be used to non-destructively probe film quality and properties



3. Raman spectrum of Carbon Materials

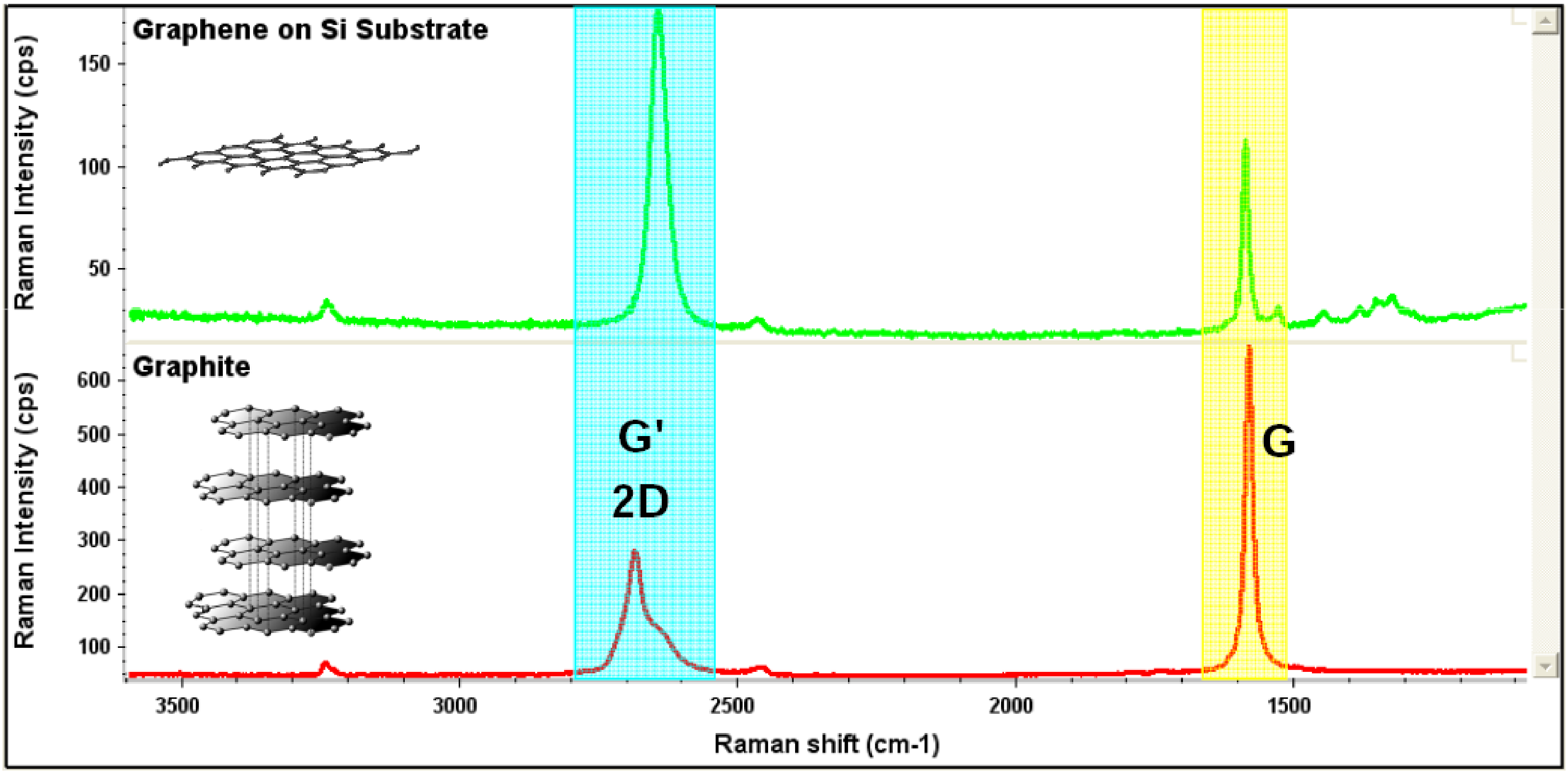
- **Raman tells us that C_{60} is much more symmetrical than C_{70}**

Raman can give us information on optical properties, doping and temperature and pressure response



3. Raman spectrum of Carbon Materials

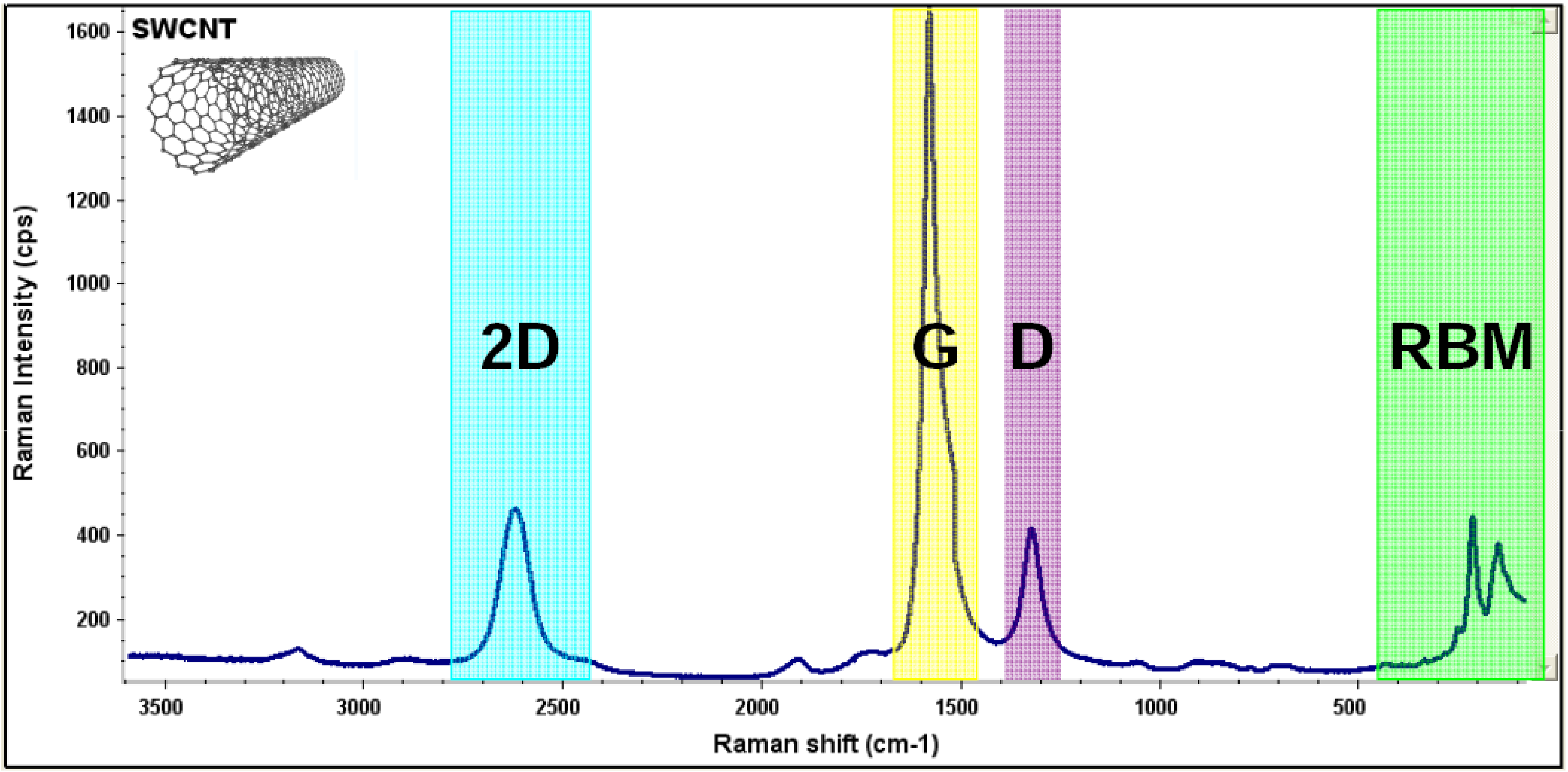
- **Graphene is the building block of important carbon materials and consists of the single layer units that make up graphite**



3. Raman spectrum of Carbon Materials

- **Single-Walled Carbon Nanotubes (SWCNT) - characteristic vibrational modes**

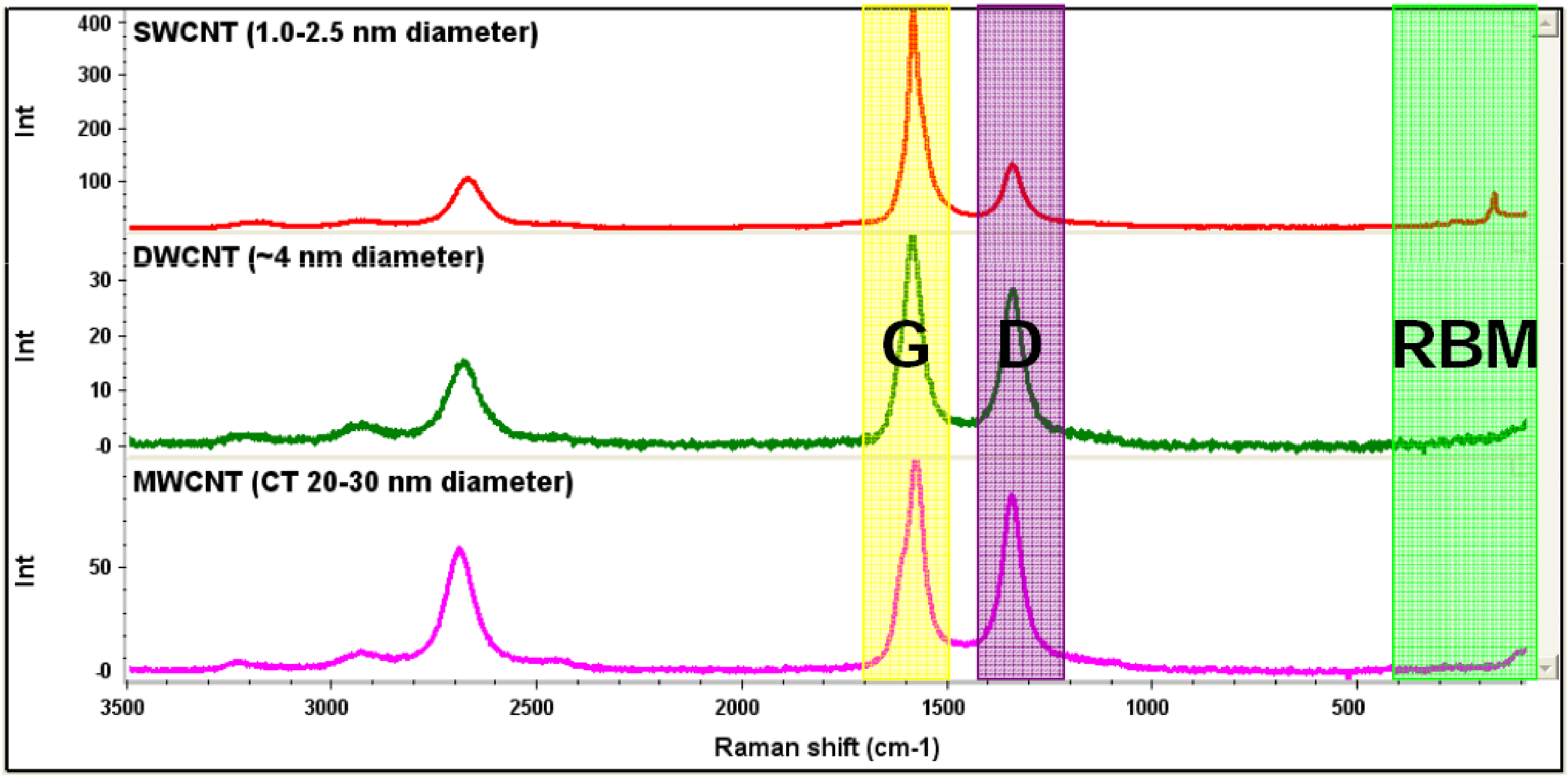
Radial Breathing Modes (RBM) – only in SWCNTs



3. Raman spectrum of Carbon Materials

- **Multiwall Carbon Nanotubes (MWCNT)**

1) Do not exhibit RBM modes
2) Typically have a higher D/G ratio than SWCNTs



Reading Materials:

Book: ***Biomaterials Science: An Introduction to Materials in Medicine*** (**3rd Edition**, **2013)**

- Pyrolytic carbon for long-term medical implants

Articles 1:Safe Clinical Use of Carbon Nanotubes as Innovative Biomaterials, *Chem. Rev.* 2014, 114, 6040−6079.

Article 2: Broad Family of Carbon Nanoallotropes: Classification, Chemistry, and Applications of Fullerenes, Carbon Dots, Nanotubes, Graphene, Nanodiamonds, and Combined Superstructures, *Chem. Rev.* 2015, 115, 4744−4822.

Next Lecture

Lecture 6: Microparticles and Nanoparticles-1

On Wednesday, September 25, 2019