Graphene: The Wonder 2D-material of the 21st century

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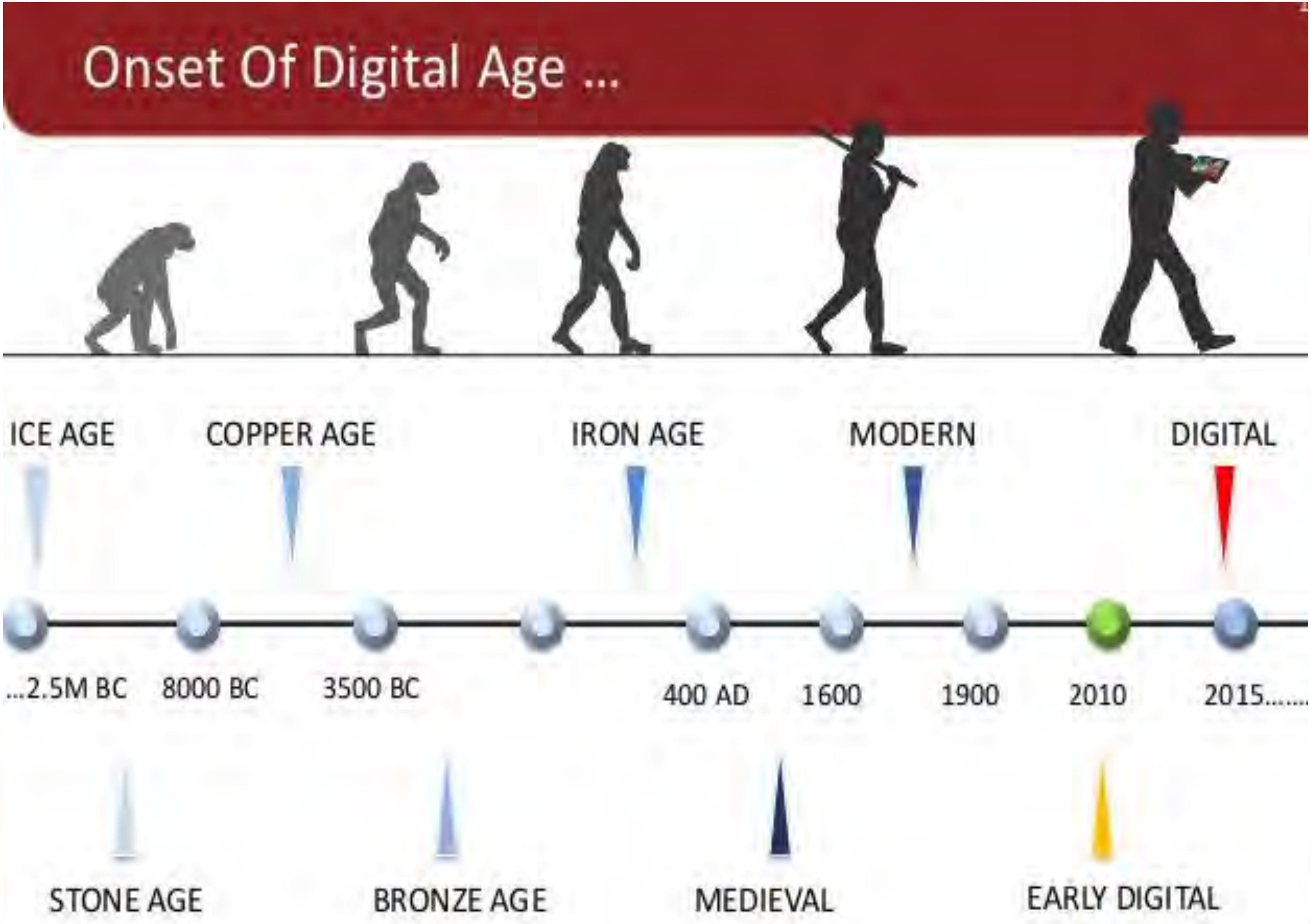

Onset Of Digital Age ...
ICE AGE
COPPER AGE
IRON AGE
MODERN
DIGITAL
...2.5M BC
8000 BC
3500 BC
400 AD
1600
1900
2010
2015.......
STONE AGE
BRONZE AGE
MEDIEVAL
EARLY DIGITAL

⇒ **Each age is levelled by the Material**

⇒ **that bearing the new technology**

⇒ **that makes the new society**

What will be the next age??

What will be next material??

CARBON AGE

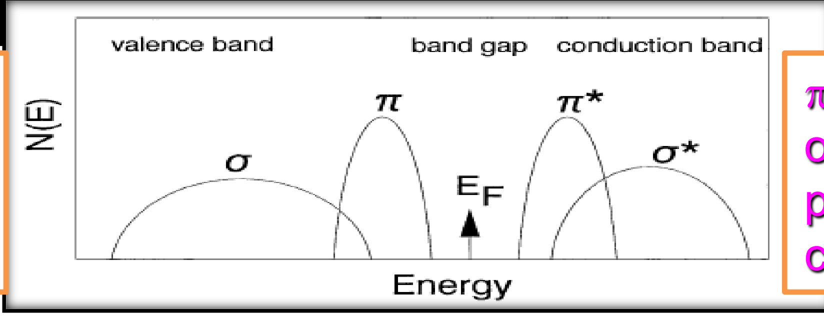
or

GRAPHENE AGE !!

Electronic distribution of carbon

sp^3 configuration sp^2 configuration sp^1 configuration

π /σ is bonding state originated from the in-plane, bonds of *sp*^{2} -/*sp*^{3} -configuration



π*/σ* is anti-bonding state originated from the out-of-plane, bonds of *sp*^{2} - /*sp*^{3} -configuration

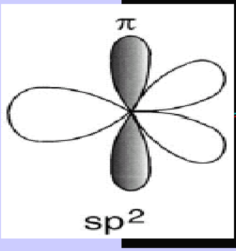
Electronic distribution of Carbon

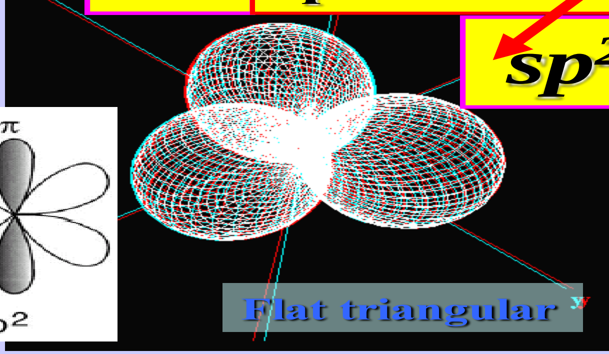
1s^2 2s^2 2p^2

Hybridization of Carbon atoms

2s^1 2p^2 +

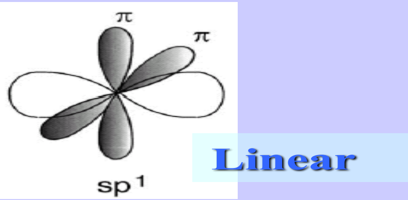
sp^2

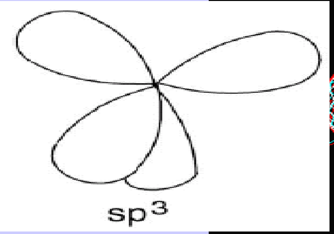




sp^1

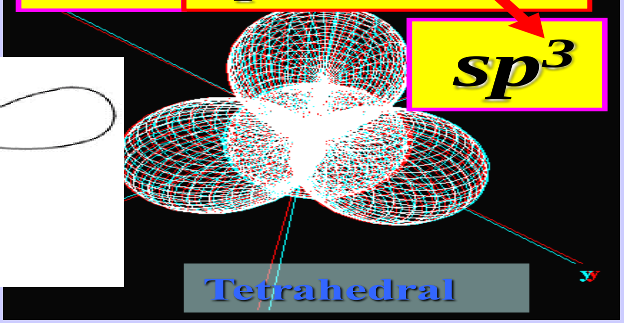
2s^1 2p^1 +





2s^1 2p^3

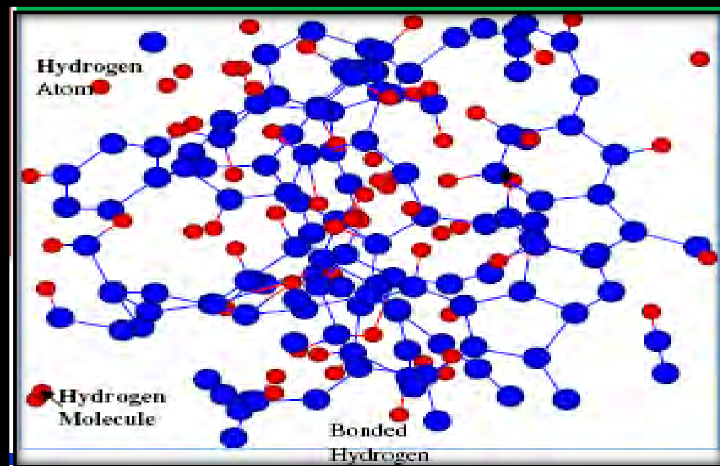
sp^3

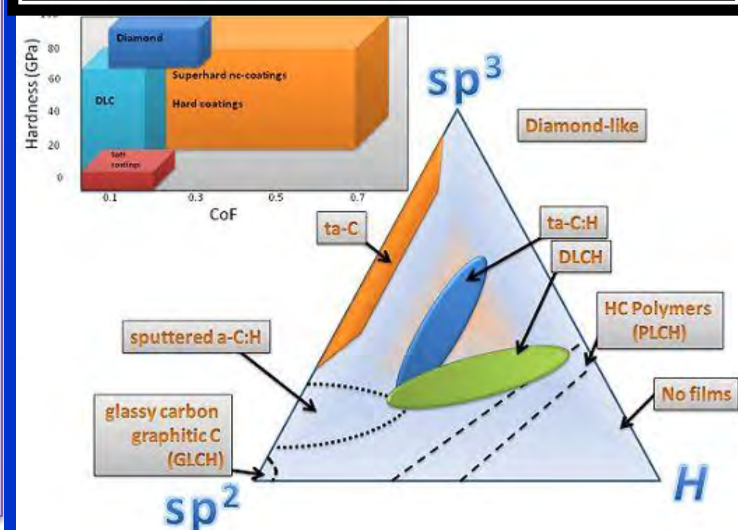


Graphite
$(100\%sp^2)$

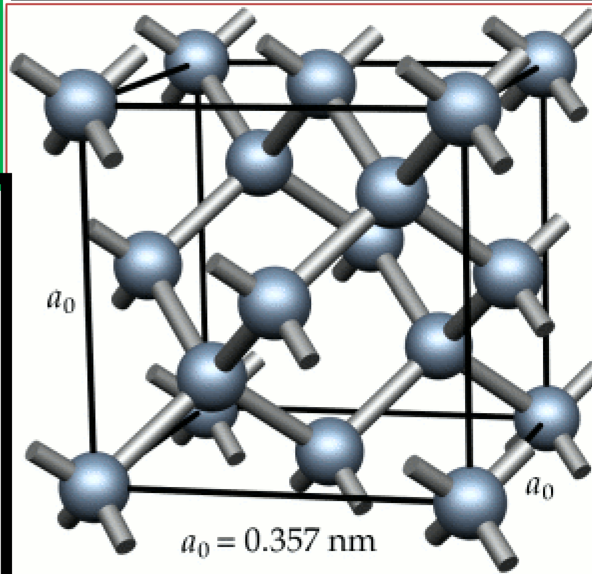
Amorphous Carbon or Diamond like carbon

$(\text{Mixture of } sp^2 \text{ \& } sp^3)$





Diamond
$(100\%sp^3)$



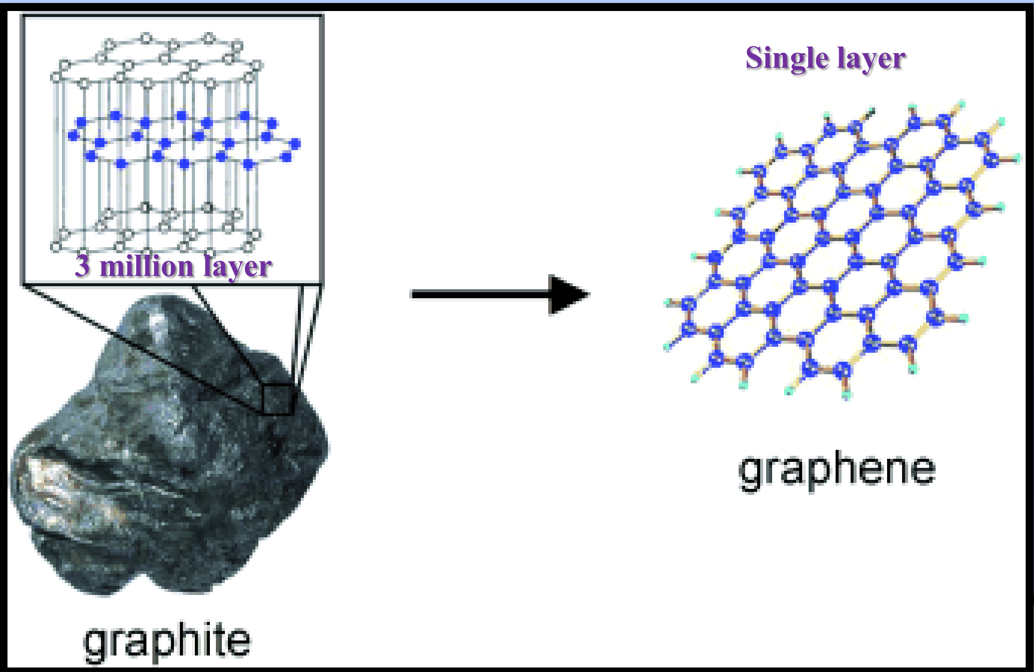
Properties of graphite:

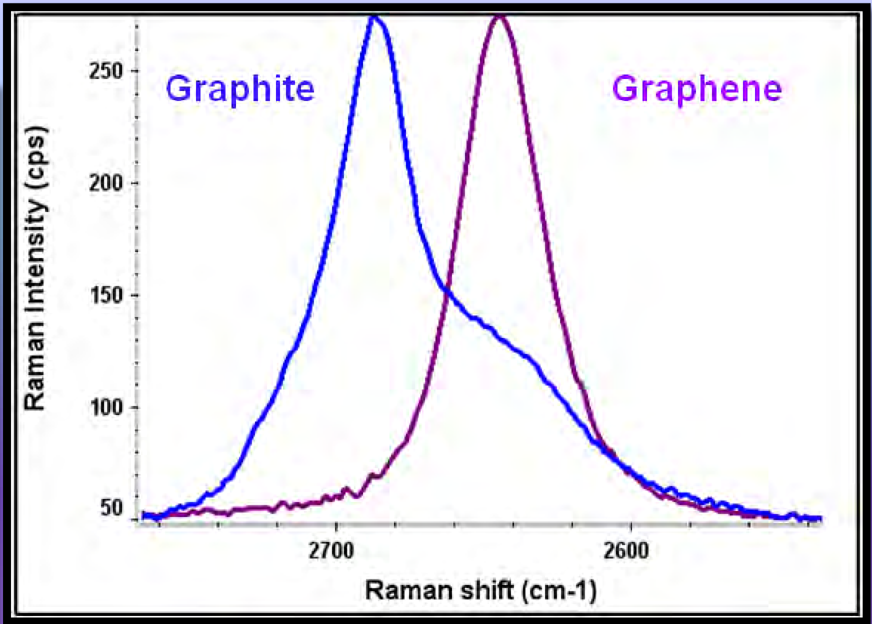
1. Graphite is a soft, slippery, grayish-black substance. It is metallic luster and is opaque
2. Specific gravity is 2.3.
3. Graphite is a good conductor of heat and electricity.
4. Although graphite is a very stable allotrope of carbon but at a very high temperature it can be transformed into artificial diamond.
5. Chemically, graphite is slightly more reactive than diamond.

Properties of diamond:

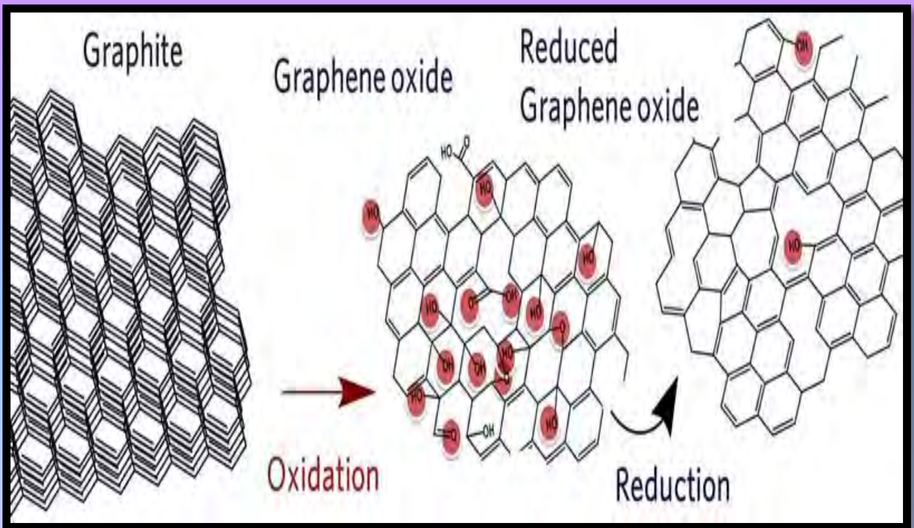
1. It is the hardest substance known.
2. It has a high refractive index and gives an extraordinary brilliance.
3. The specific gravity of diamond is 3.52.
4. Diamond is a bad conductor of heat and electricity because it lacks free electrons.
5. Chemically, diamonds are un-reactive under ordinary conditions.

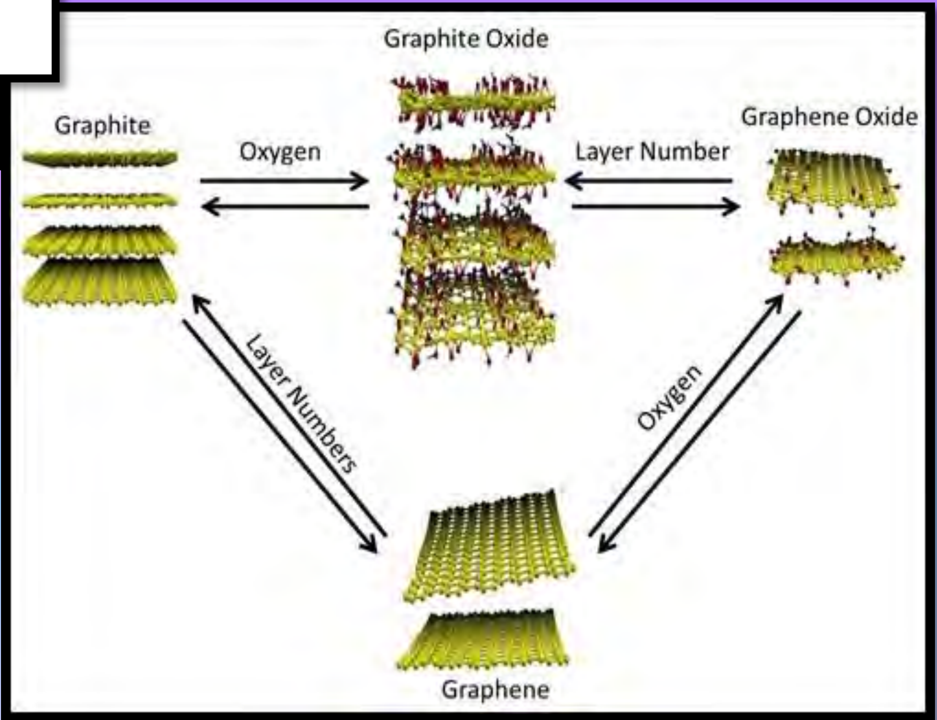
Graphite ⇒ Graphene



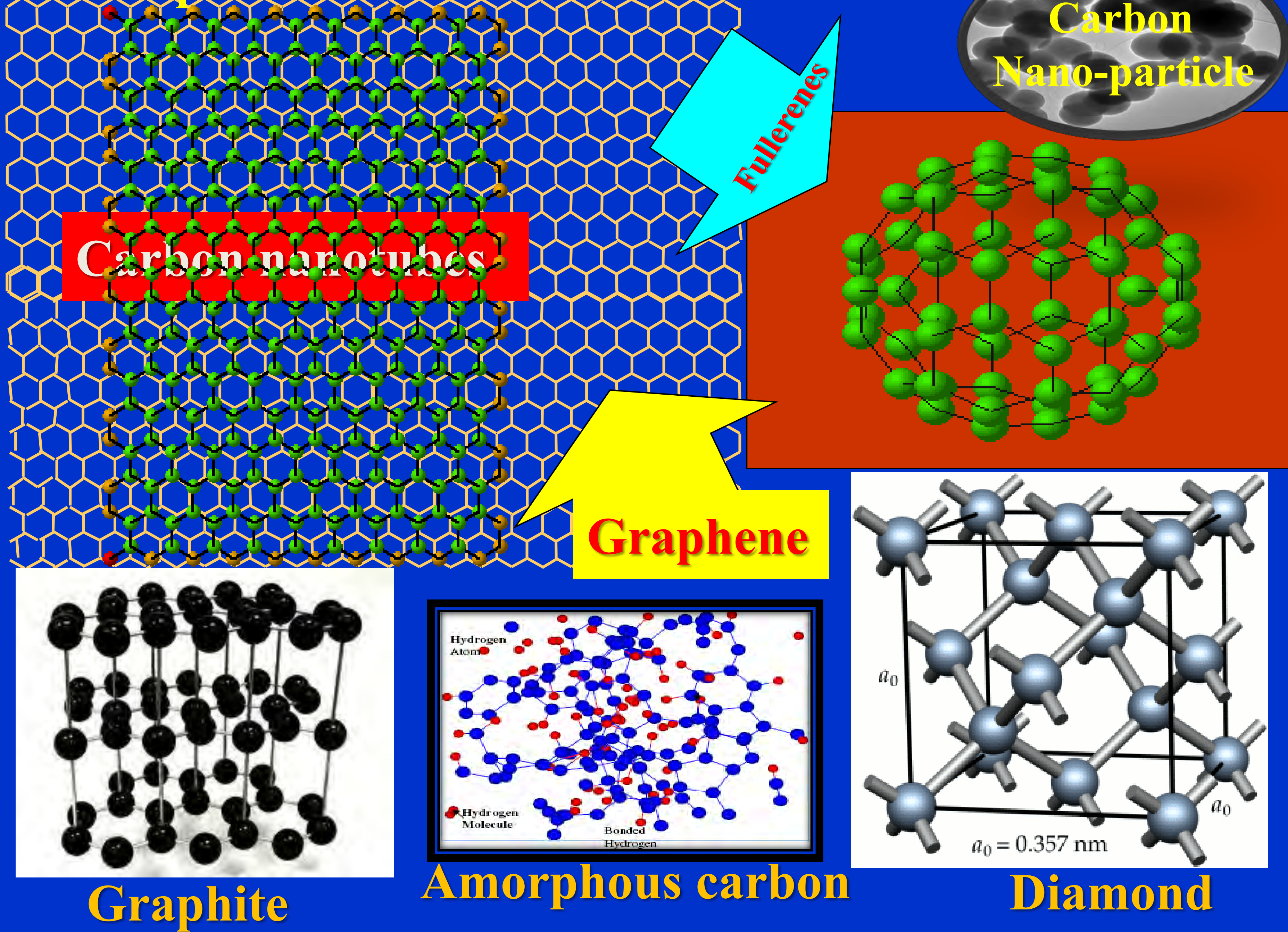


Graphite ⇒ Graphene Oxide

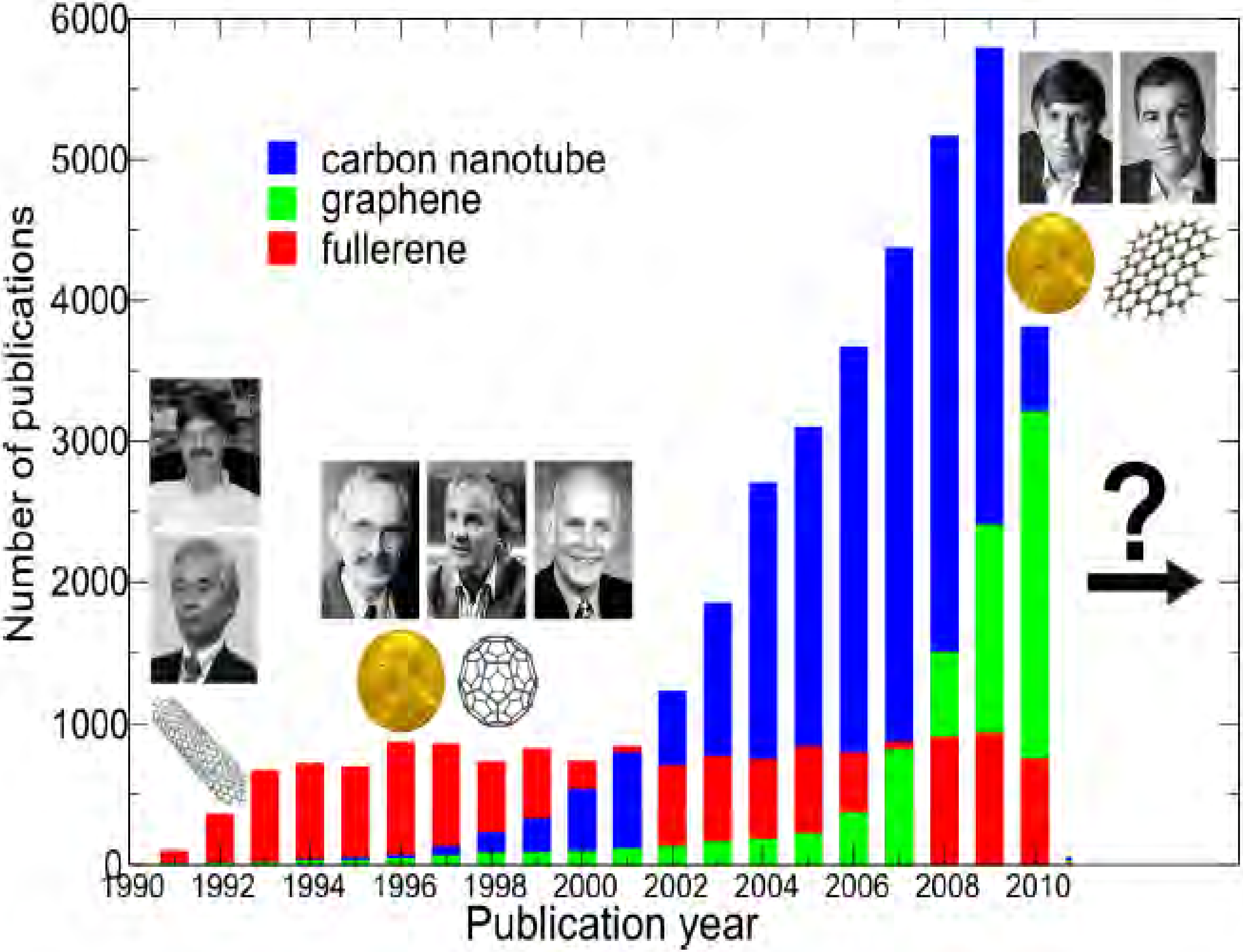




Allotropes of Carbon Materials

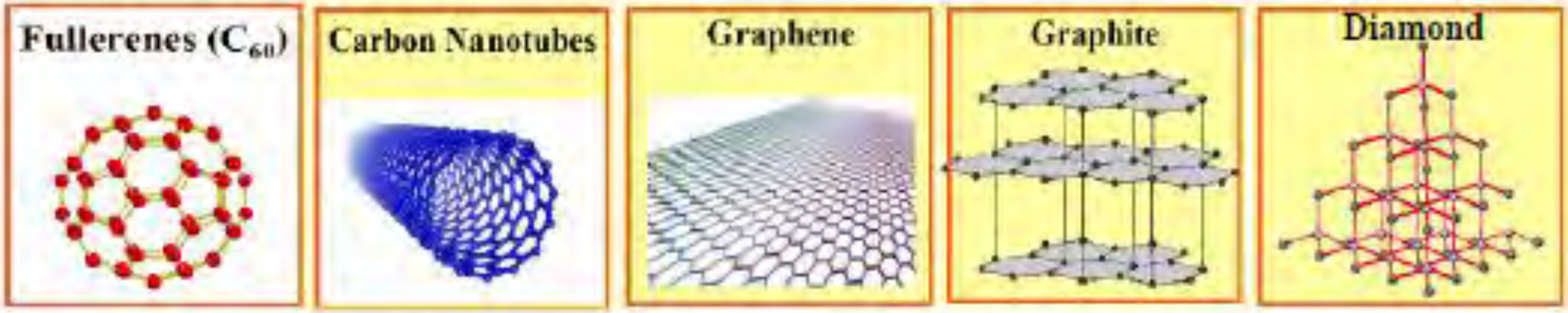


Six Giant on carbon materials



Allotropes of Carbon

Carbon can form structures from zero to three-dimensions



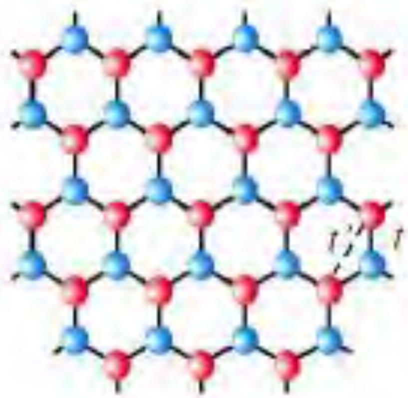
0D (1997) | 1D (1991) | 2D (2004) | 3D | 3D

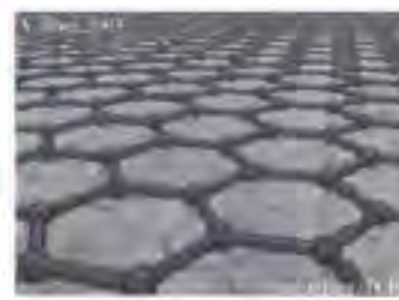
Dimensionality is one of the most defining material parameters. The various structural forms of carbon (polymorphism) give carbon a unique variety of properties and applications.

Graphene

⇒ **Graphene is a one-atom-thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.**

⇒ **It can be viewed as an atomic-scale chicken wire made of carbon atoms and their bonds.**





Characteristics of Graphene

→World's first 2D-Materials

→World's strongest material

(100-300 times stronger than steel: 1 TPa)

→World's lightest/ultra-light material

(Density 4 times lower than copper)

→World's thinnest/ultra-thin material

(0.34 nm ≅ One million times thinner than a human hair)

→ Smallest molecule

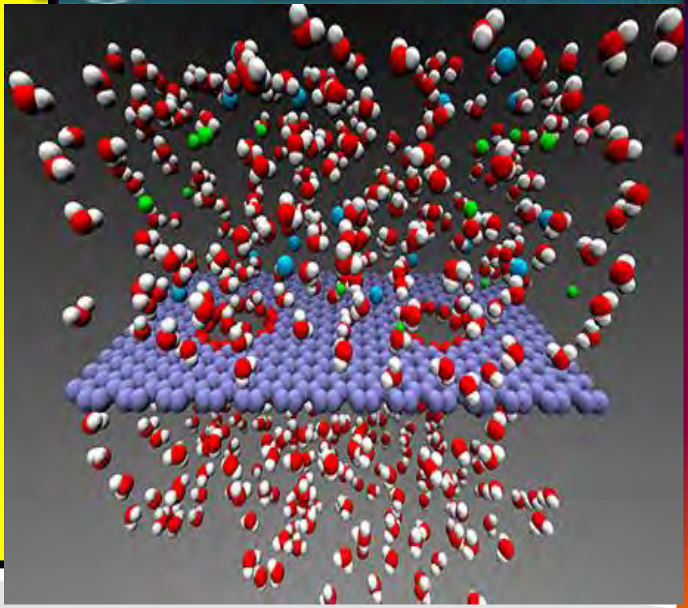
→High surface area of ~2500m²/g

→ World's incredibly flexible material

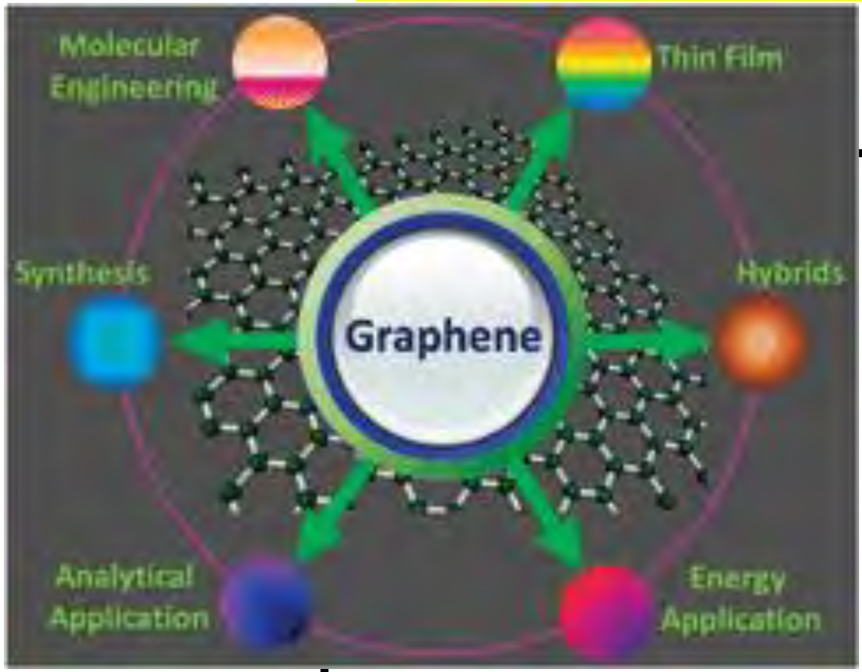
(highly stretchable, transparent and impermeable)

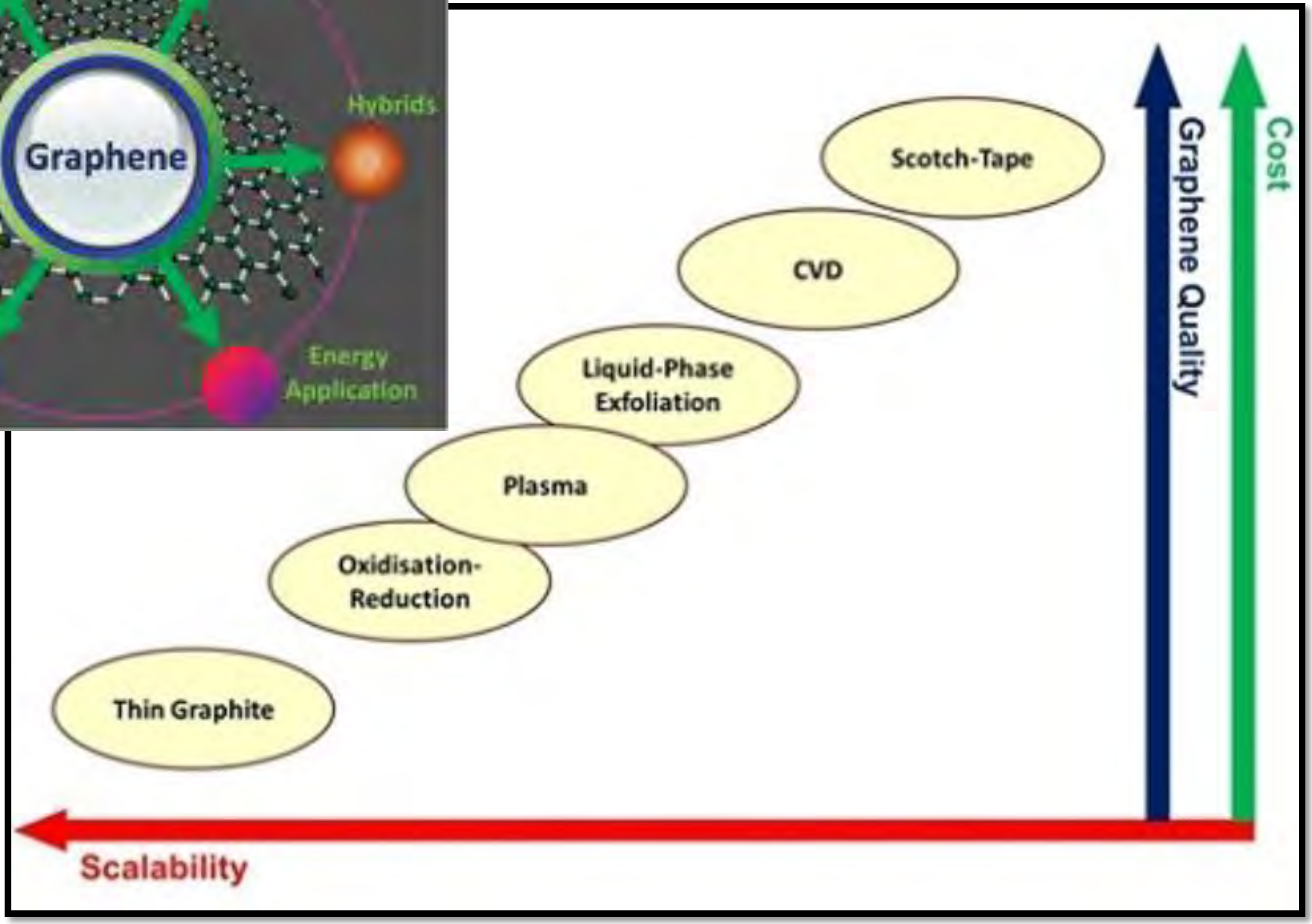
→World's superb transparent conducting material (5-order times that of copper)

→Able to filter harmful organic materials

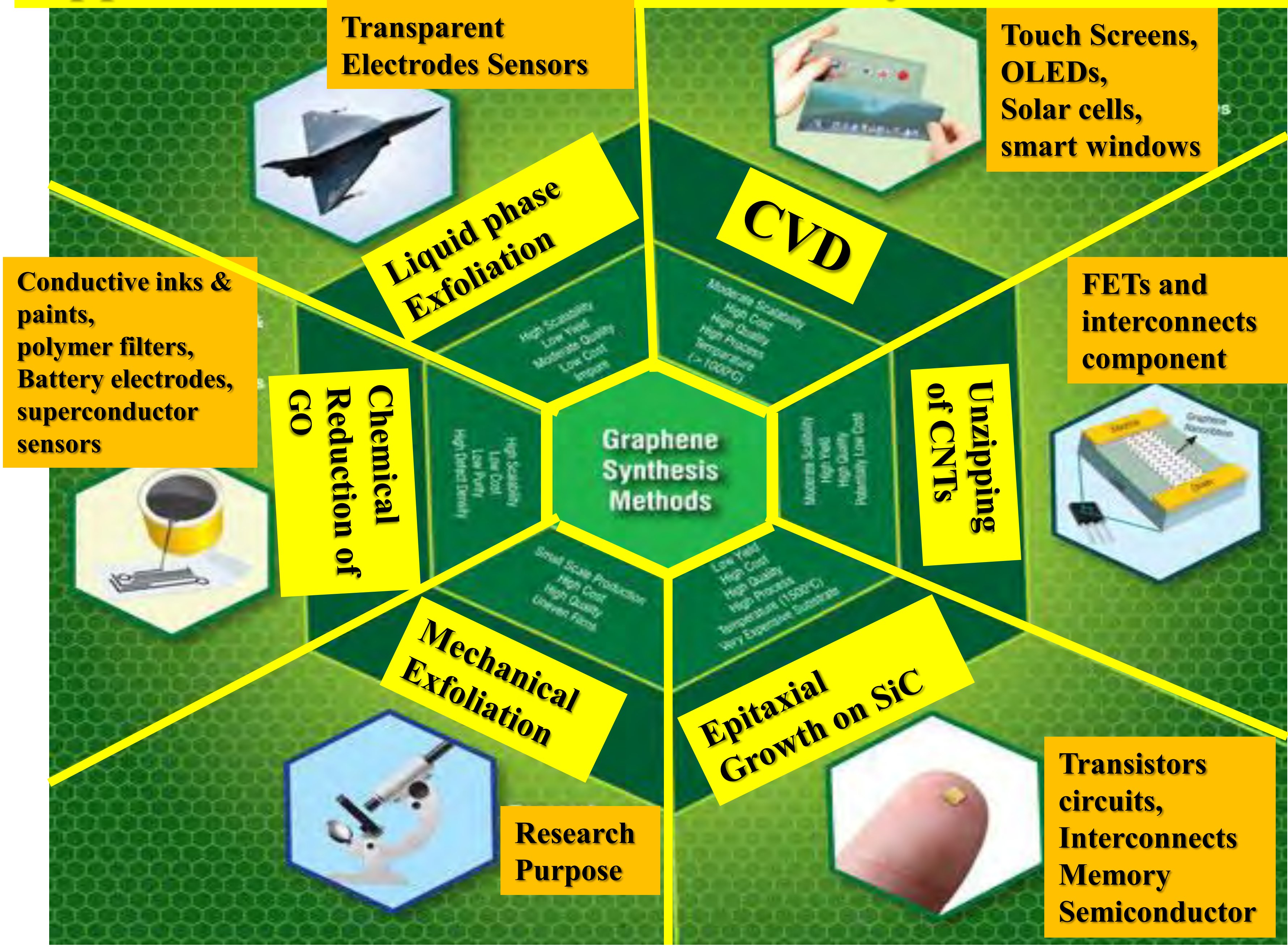


Synthesis Process of Graphene

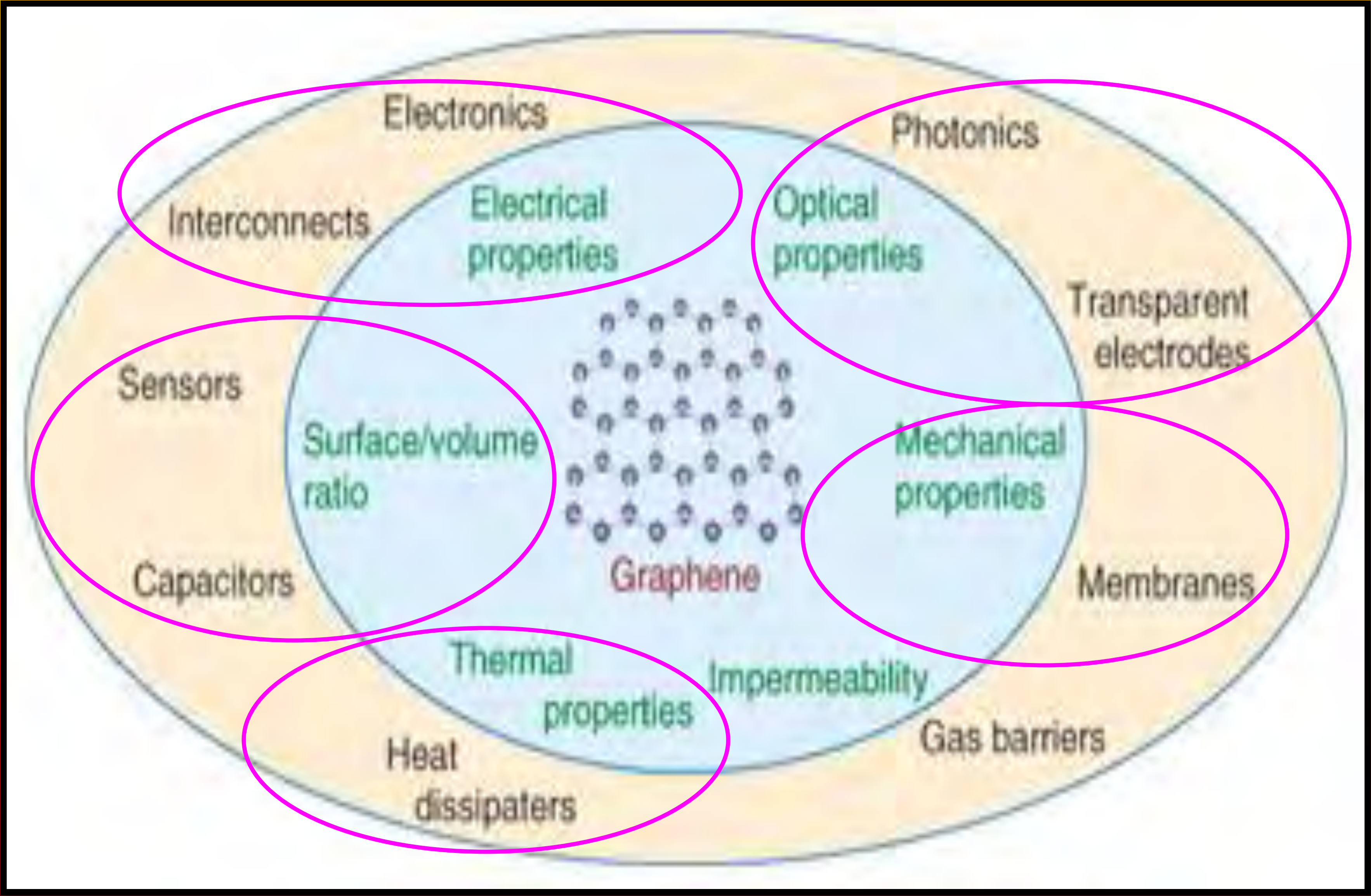


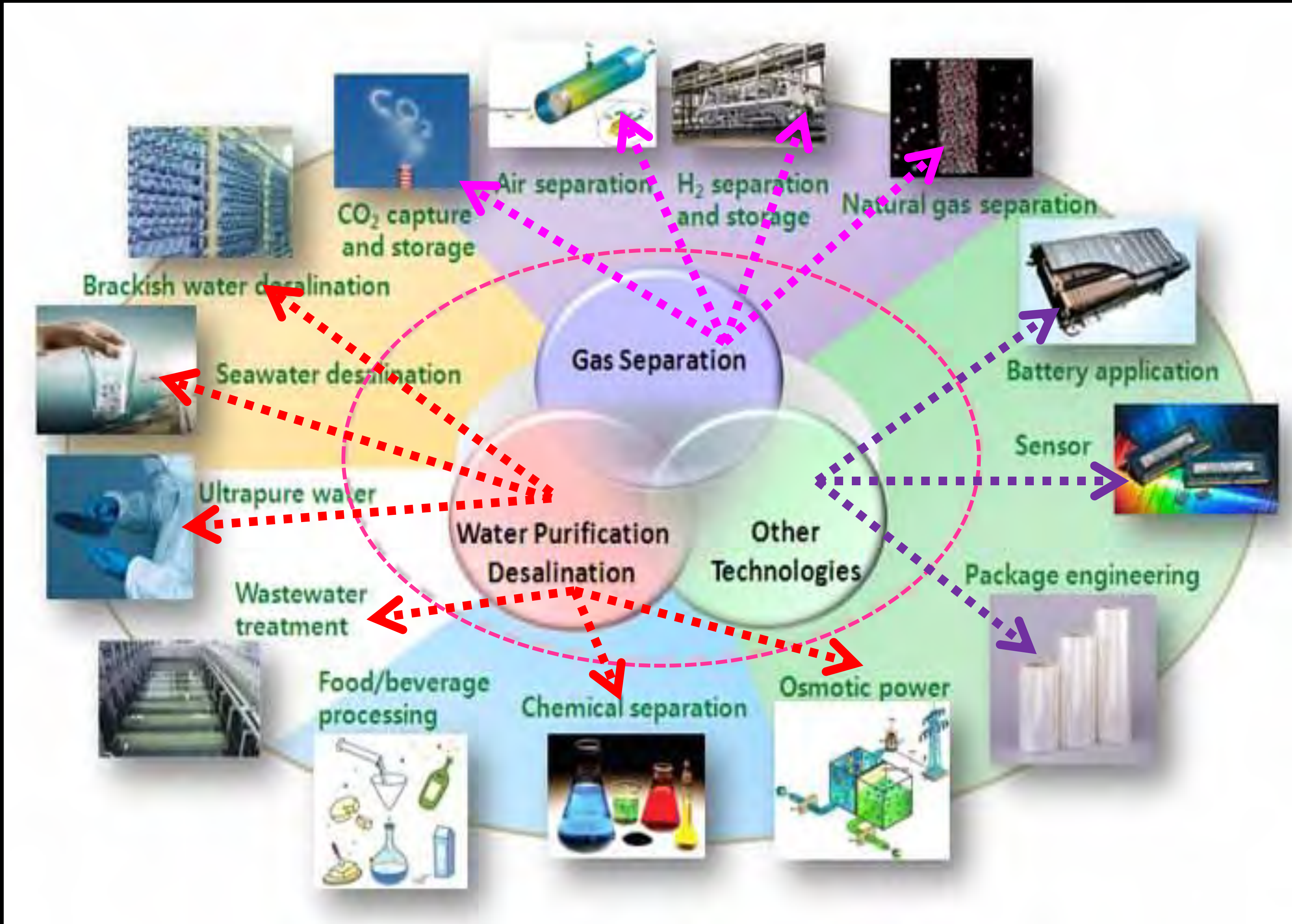


Applications of Graphene based on Synthesis Process

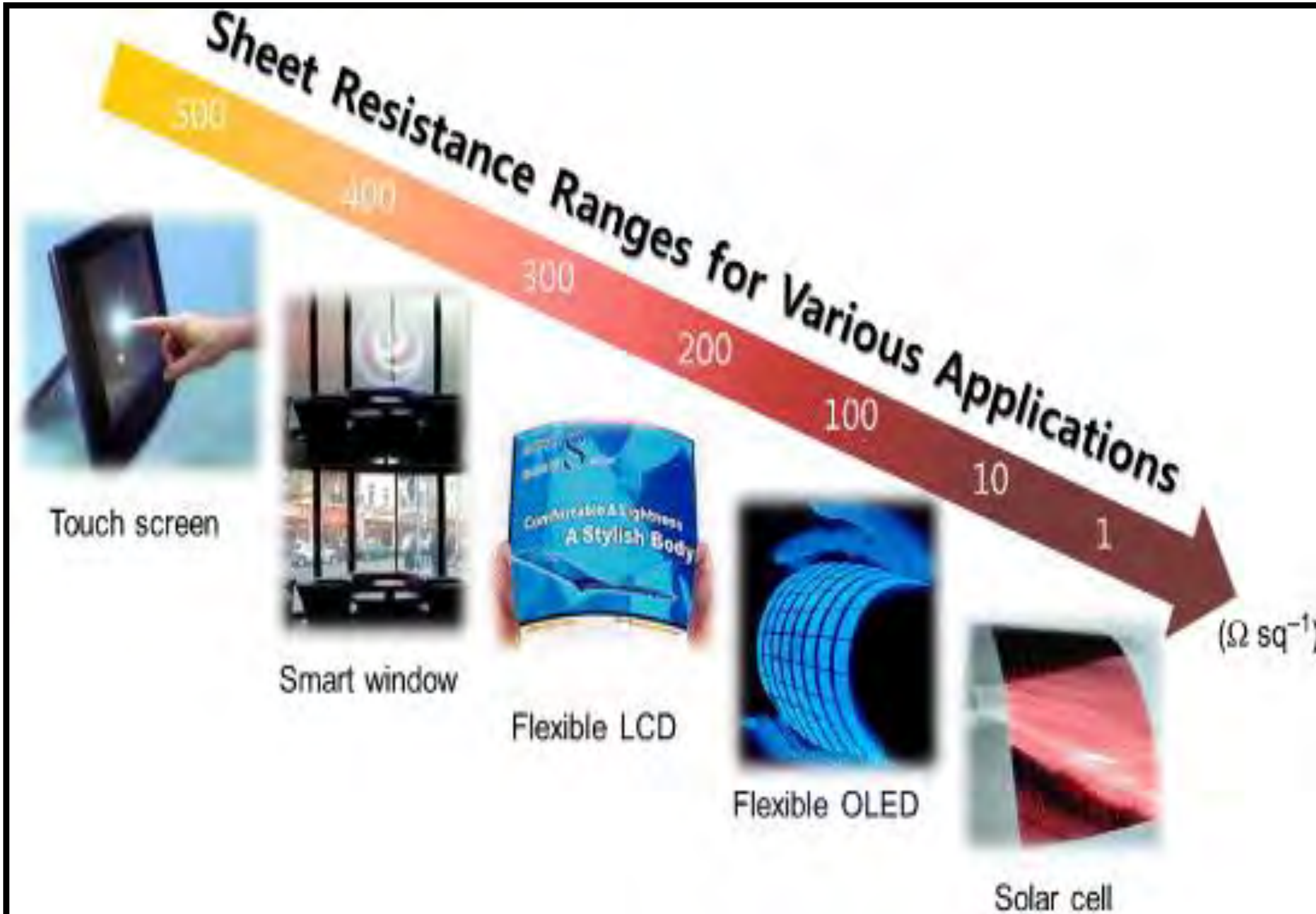


Applications of Graphene based on Properties





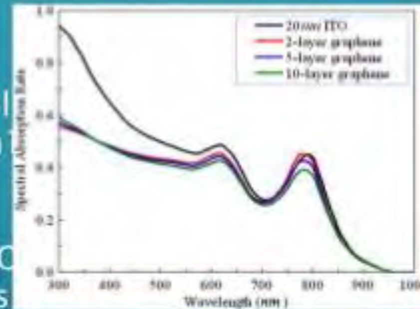
Air separation
H_2 separation and storage
Natural gas separation
CO_2 capture and storage
Brackish water desalination
Seawater desalination
Ultrapure water
Wastewater treatment
Food/beverage processing
Chemical separation
Osmotic power
Package engineering
Sensor
Battery application
Gas Separation
Water Purification Desalination
Other Technologies


Sheet Resistance Ranges for Various Applications
500
400
300
200
100
10
1
(Ω sq⁻¹)
Touch screen
Smart window
Flexible LCD
A Stylish Body
Flexible OLED
Solar cell

OPTICAL ELECTRONICS

Graphene Advantages

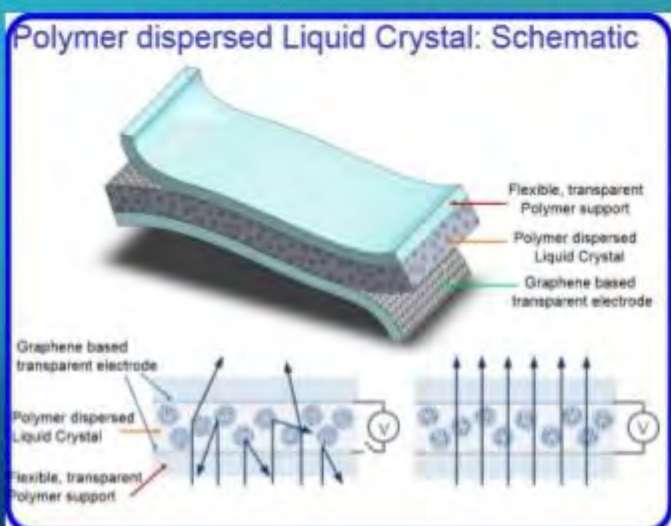
* Optically transmit more than 90% of l
* Conductivity more than 1x 106 Ω1m
* Completely Transparent material
* High Tensile strength and Flexible
* Able to replace Indium Tin Oxide (ITO due to less cost and better properties

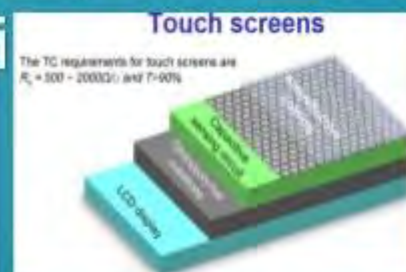


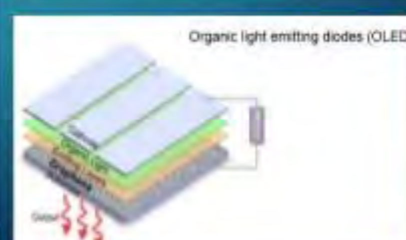
Uses

* Touchscreens
* Liquid Crystal Display (LCD)
* Organic Light Emitting Diodes (OLEDs)

LCD, Touchscreen, OLEDs







Smart Packaging

- Fragmented markets with many different requirements, therefore needs for different products


× Products need to be conceived, developed and manufactures---very few companies are moving up the value chain
× Amount of ink per item is very small
× Graphene occupies an awkward market position, lying between low cost carbon paste and high-conductivity

PHOTOVOLTAIC CELLS

Currently: silicon wafers, thin fil

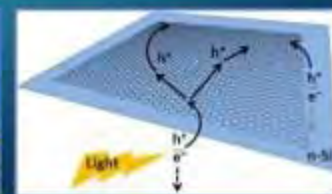
Graphene Advantages

* Transparent conducting electrode
* Robust, conductive, abundant
* Cheaper than ITO
* Enhanced light trapping
* Efficient charge transport (1D)

A new design:

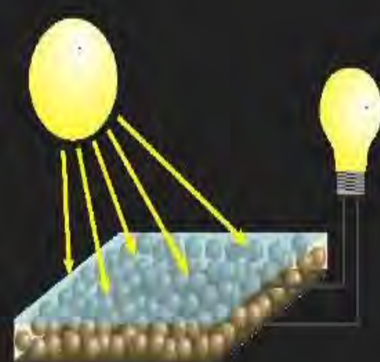
* Layer of graphene (transparent catho
* Conductive polymer (maintains integ
* ZnO nanowire layer (electron transpo
* PbS quantum dots (hole transport)
* Au layer (anode)

* 4.2% conversion efficiency (5.1% for
* Cheaper to produce



Solar cells

- Graphene turned to be a promising material for photoelectrochemical energy conversion in dye sensitized solar cells.
- The transparent, conductive, and ultrathin graphene films are fabricated from exfoliated graphite oxide, followed by thermal reduction.
- The obtained films exhibit a high conductivity of 550 S/cm and a transparency of more than 70% over 1000-3000 nm.



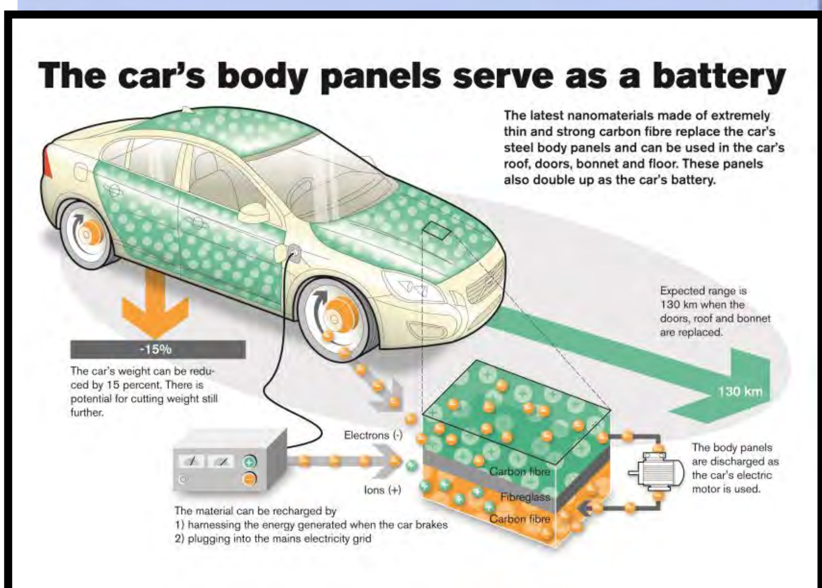
Solar cells

➢ The large scale production of highly transparent graphene films by chemical vapour deposition three years ago. In this process, researchers create ultra-thin graphene sheets by first depositing carbon atoms in the form of graphene films on a nickel plate from methane gas. Then they lay down a protective layer of thermo plastic over the graphene layer and dissolve the nickel underneath in an acid bath. In the final step they attach the plastic-protected graphene to a very flexible polymer sheet, which can then be incorporated into a OPV cell (graphene photovoltaics).

➢ High transperancy will increase efficiency of solar cells

Mechanical engineering

- In Manufacturing process as Manufacturing material.
- As a composite material for machines ,cars.
- Defense.
- Airplanes, space shuttles , satellite.



MAJESTIC FUTURE

- Advancements in touch screens

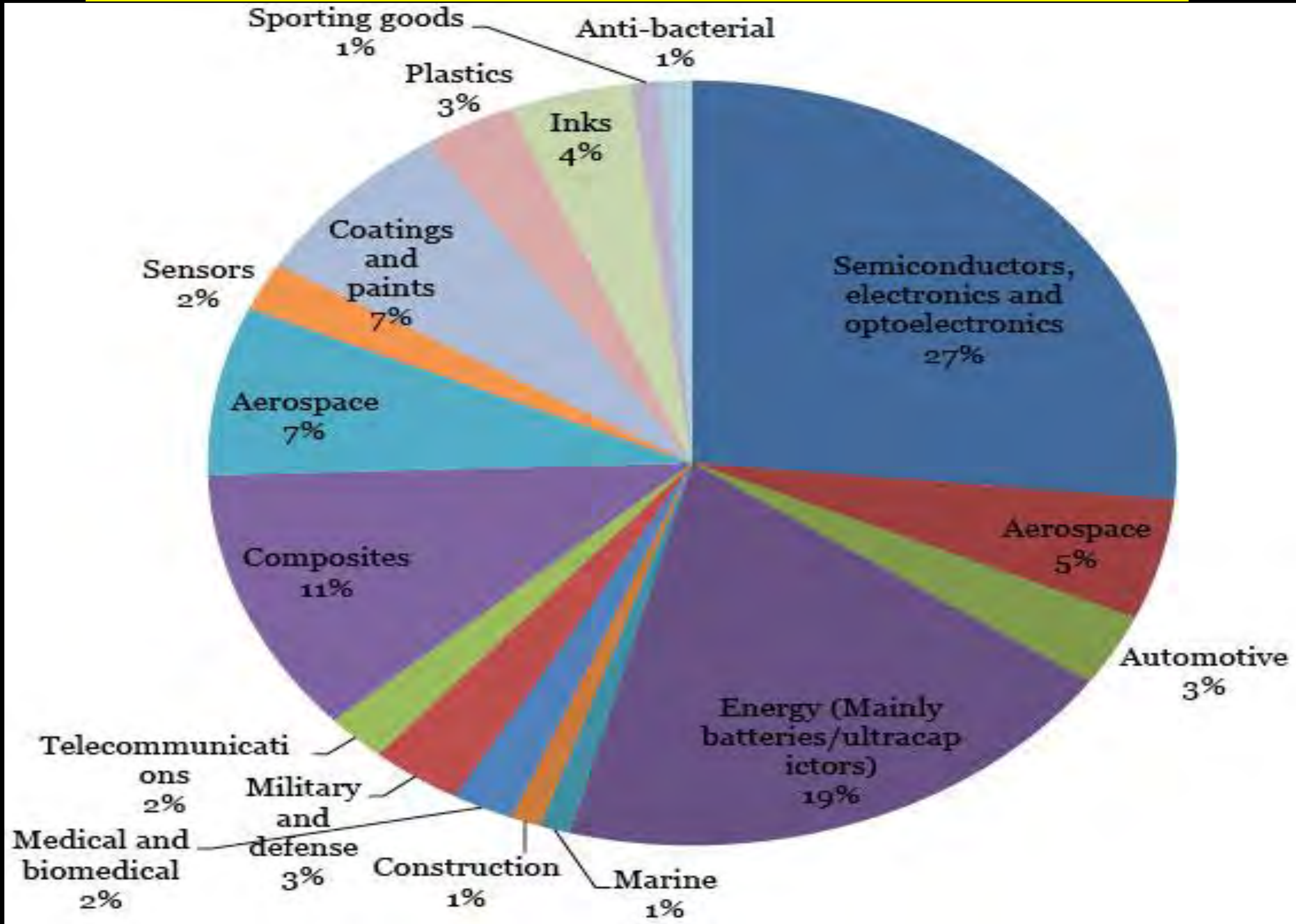
It is practically transparent and a good conductor

Transparent-Fexiable Touch Screen

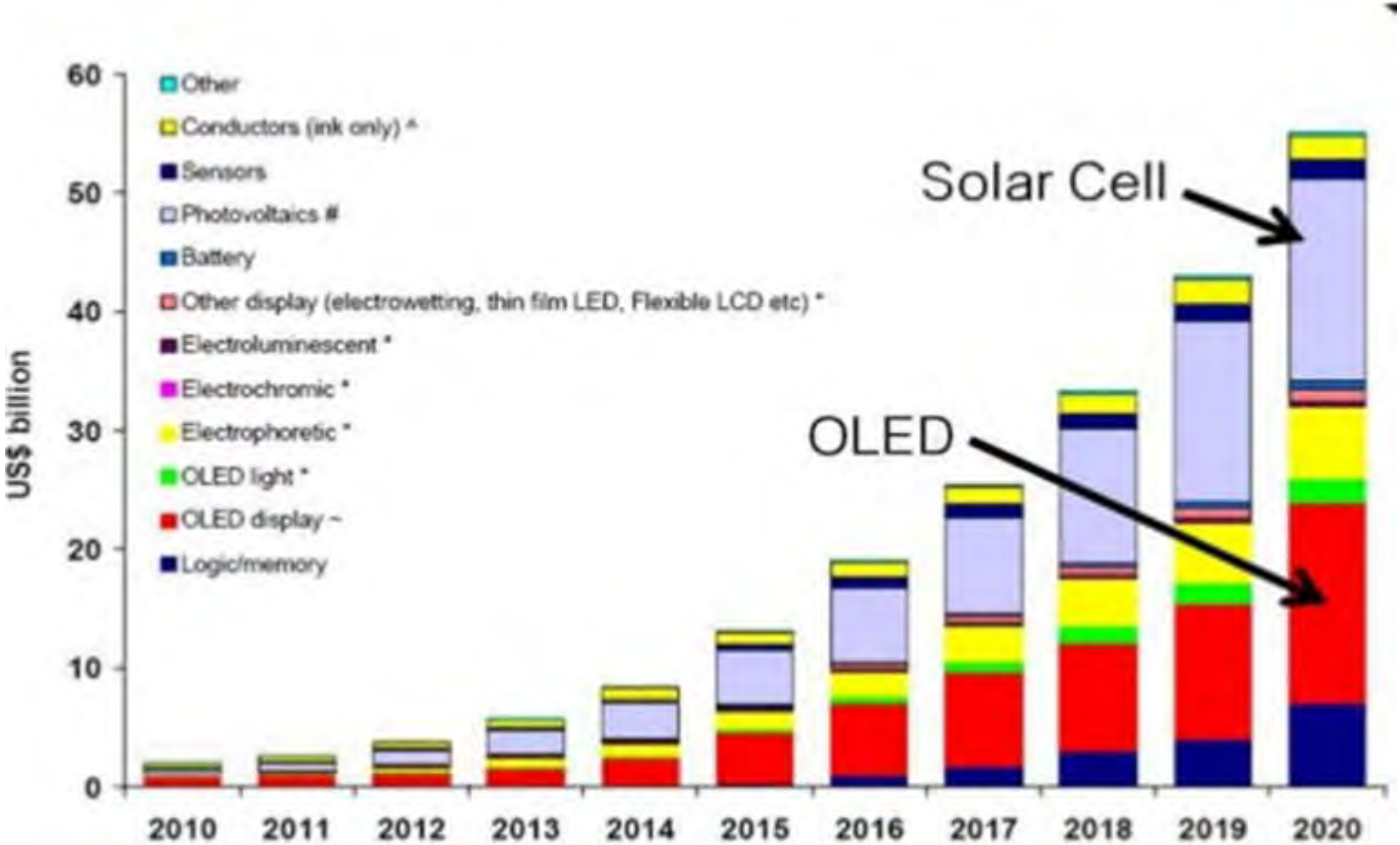
Electronics Engineering

- Will definitely replace silicon and germanium as device material.
- Conducting material on PCBs.
- Single molecule sensors
- Touchscreens
- Graphene transistor.
- Graphene integrated circuits.
- Graphene chips.

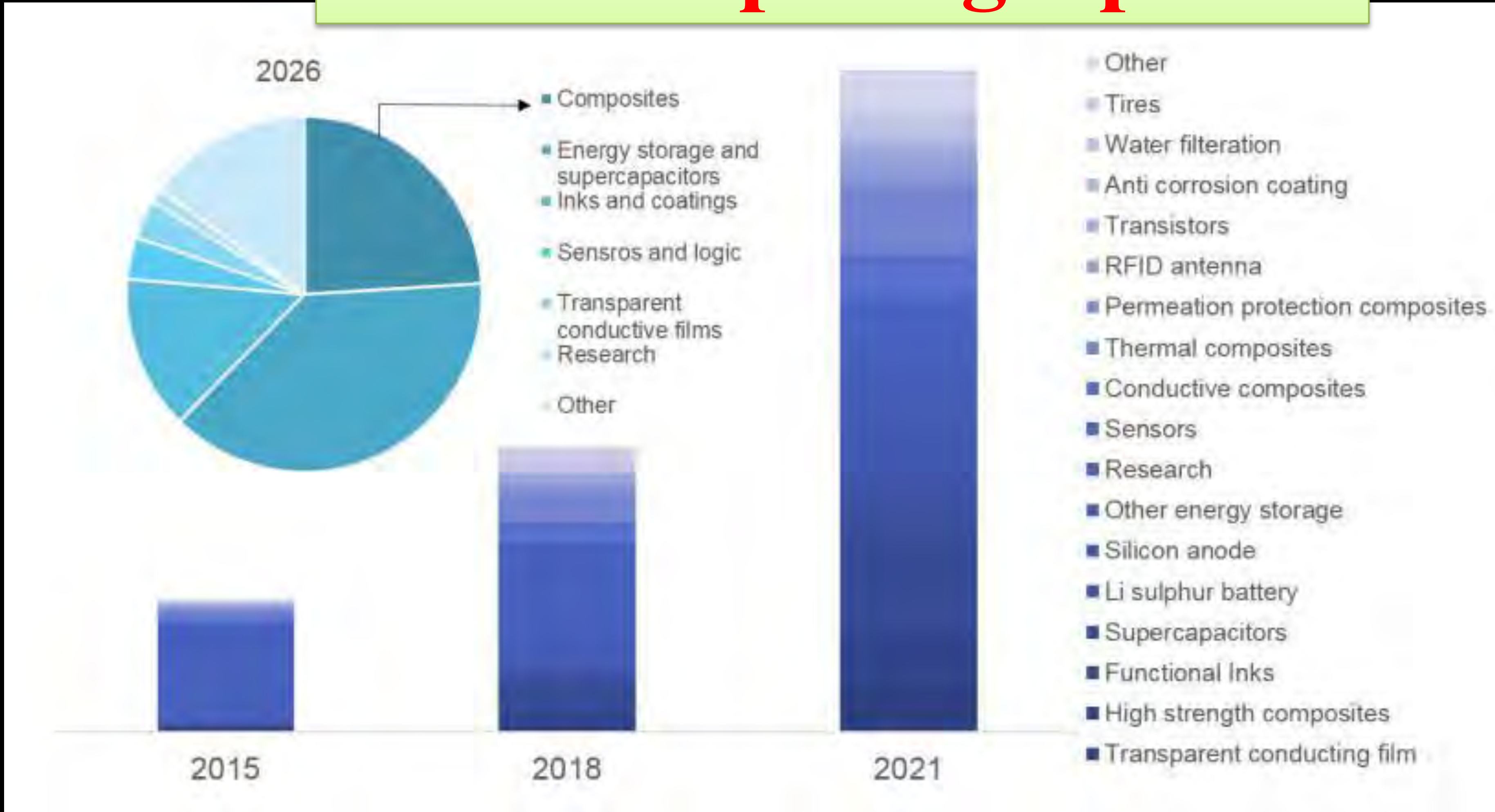
Applications chart for Graphene companies



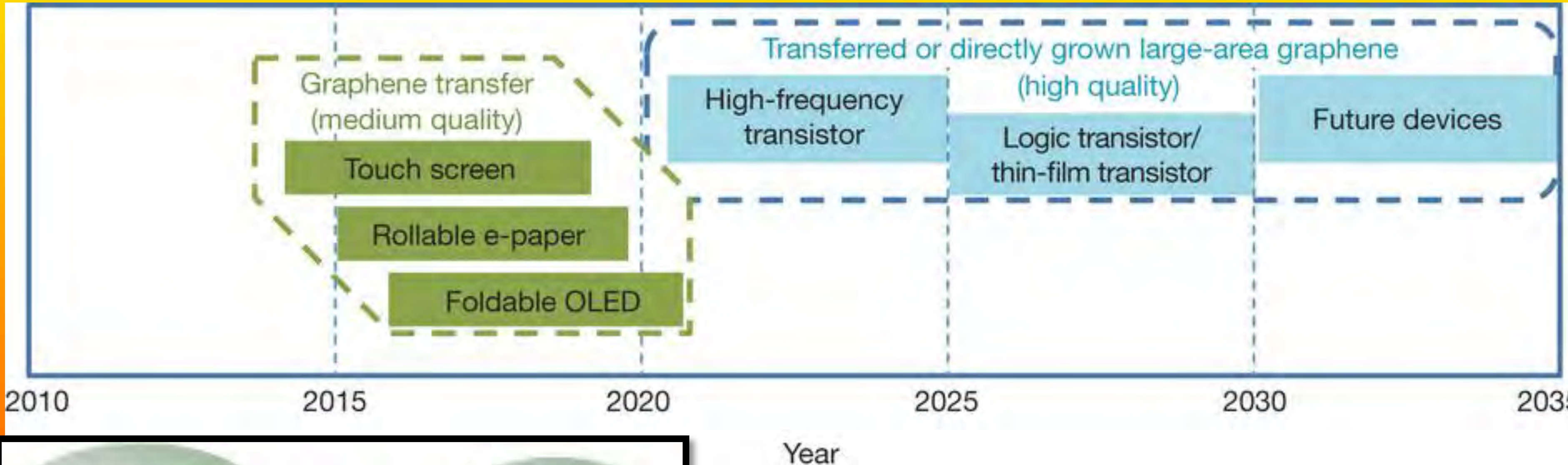
What to expect from Graphene --Major Applications



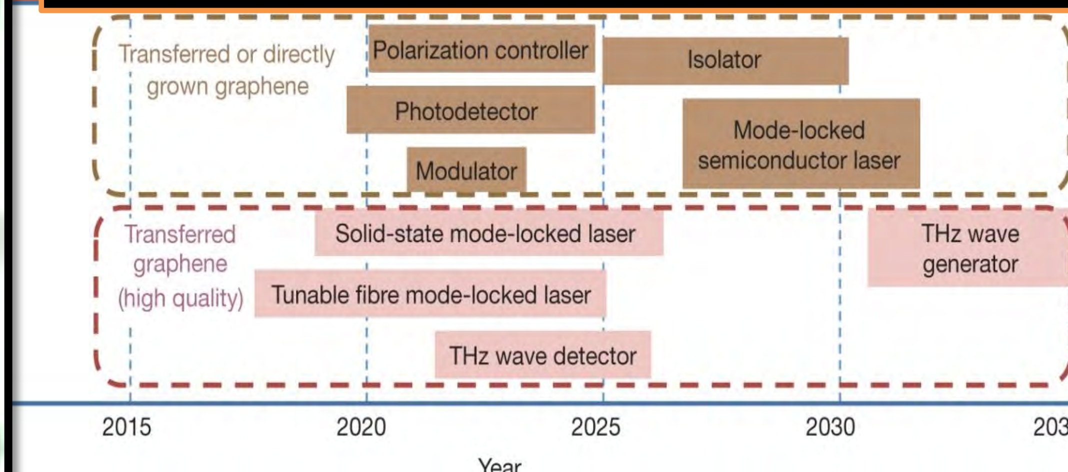
A roadmap for graphene



Vision-Graphene-based display and electronic devices



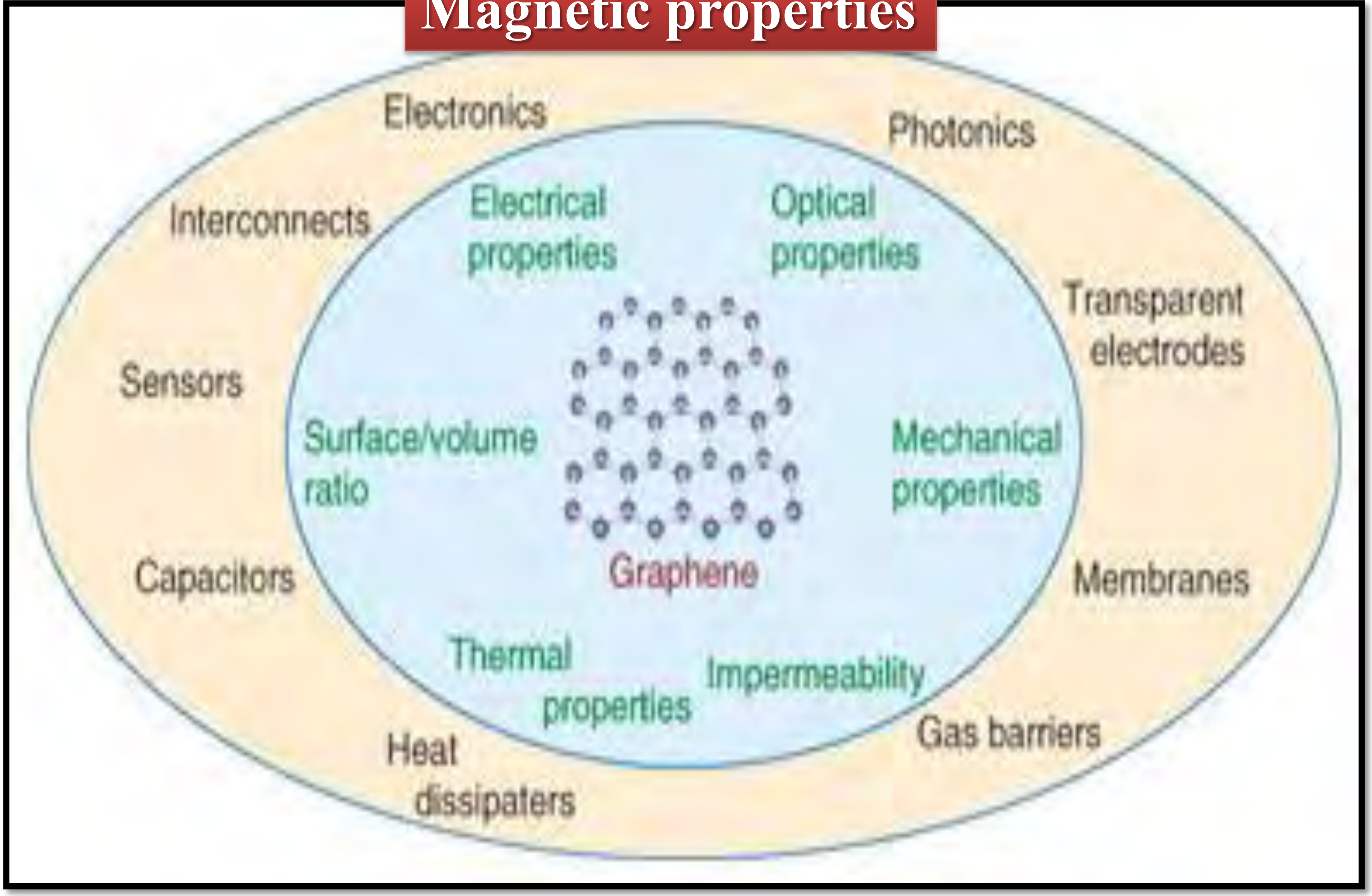
Vision-Graphene-based photonics devices



K S Novoselov *et al. Nature* **490**, 192-200 (2012)

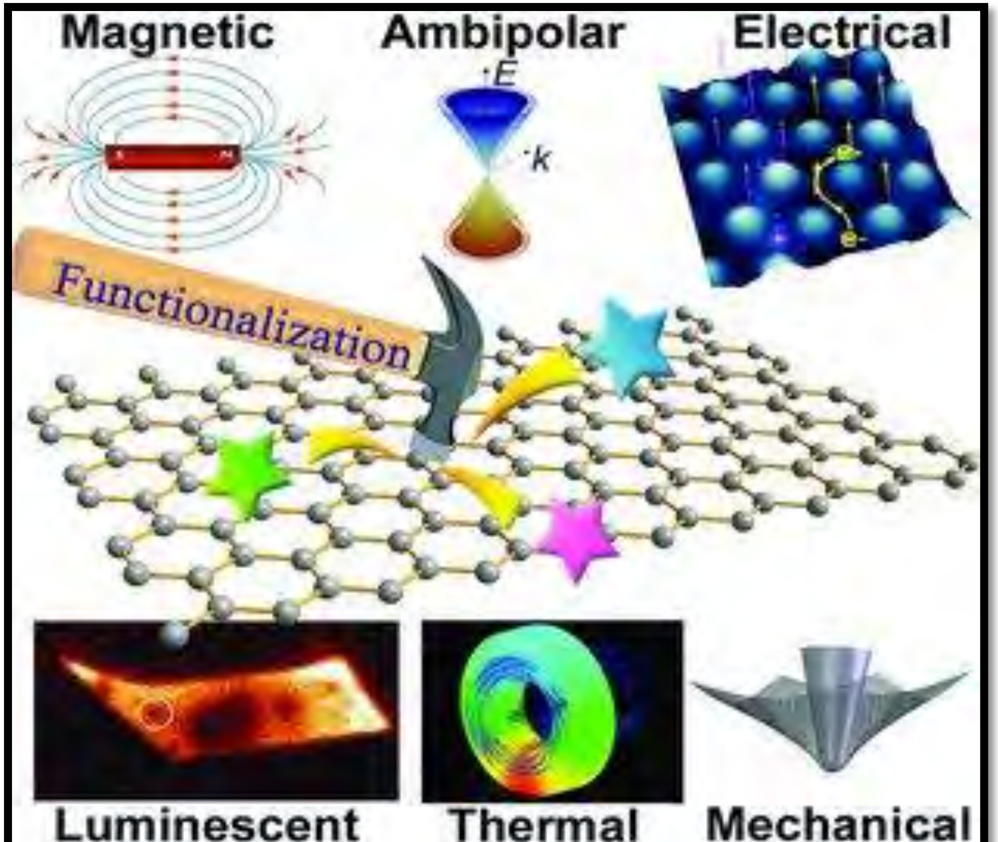
My Contribution on Graphene Research

Magnetic properties



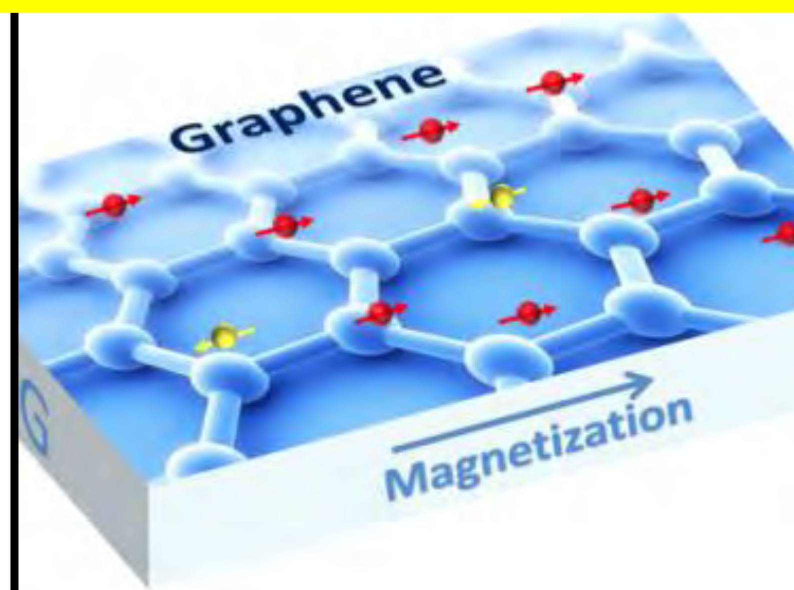
Magnetic Storage device applications using Graphene

Functionalization of Graphene by Hydrogen, Silicon and Nitrogen ------



Why Carbon / Graphene??

Carbon-based materials are very promising for spintronic applications due to their weak spin-orbit coupling and potentially providing a long spin life time

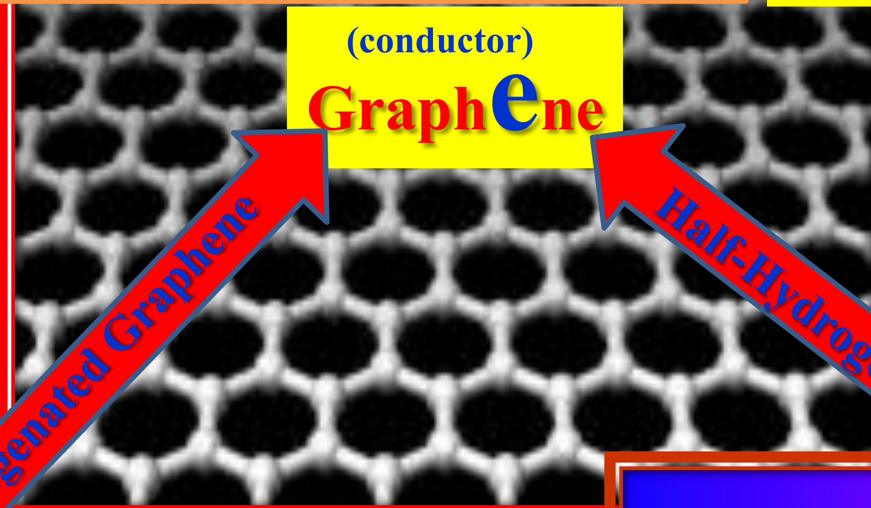


Graphene-Graphone-Graphane

Ferromagnetism of Graphone by Zhou et al. Nano Letters 2009, 9/11, 3867

Graphene: 2D crystal made of carbon atoms arranged in a honeycomb lattice

(conductor)
Graphene



Graphone: The semi-hydrogenation of graphene (hydrogen atoms are the white dots) makes the material ferromagnetic

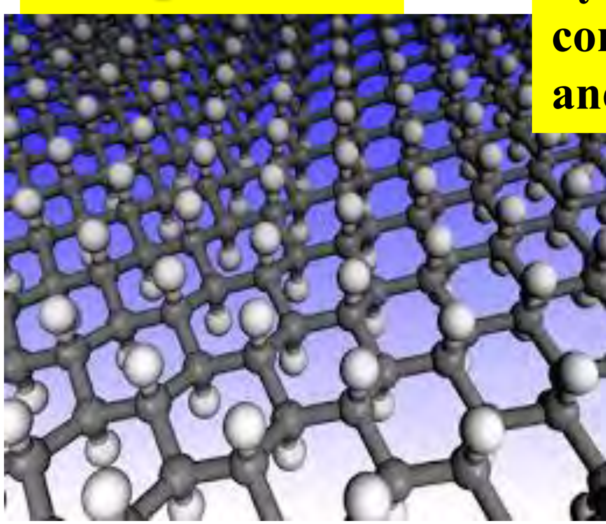
Fully Hydrogenated Graphene

Half-Hydrogenated Graphene

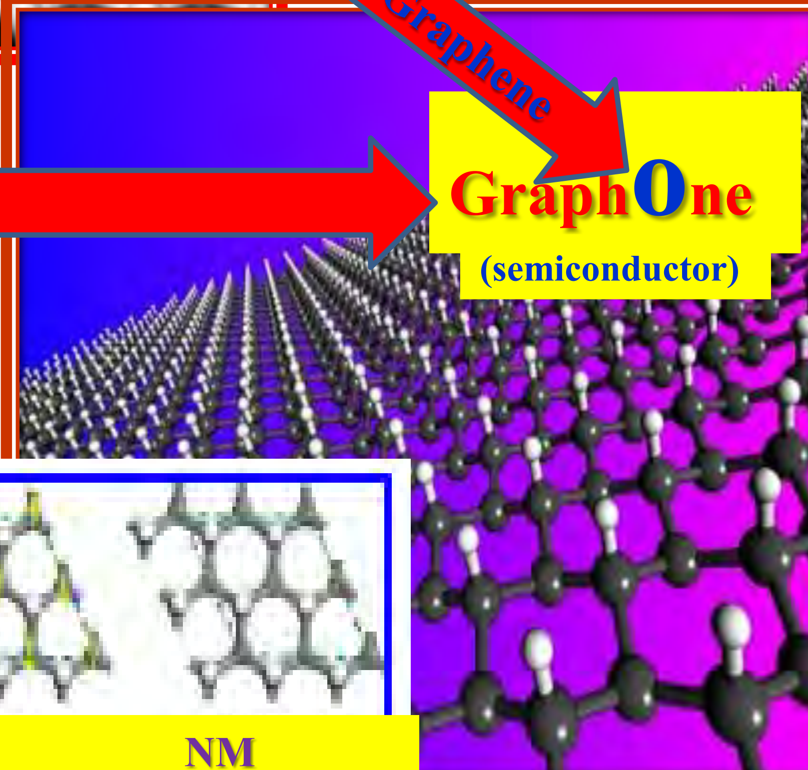
Conversion $sp^2 \rightarrow sp^3$

by removing conduction π-bands and opening band gaps

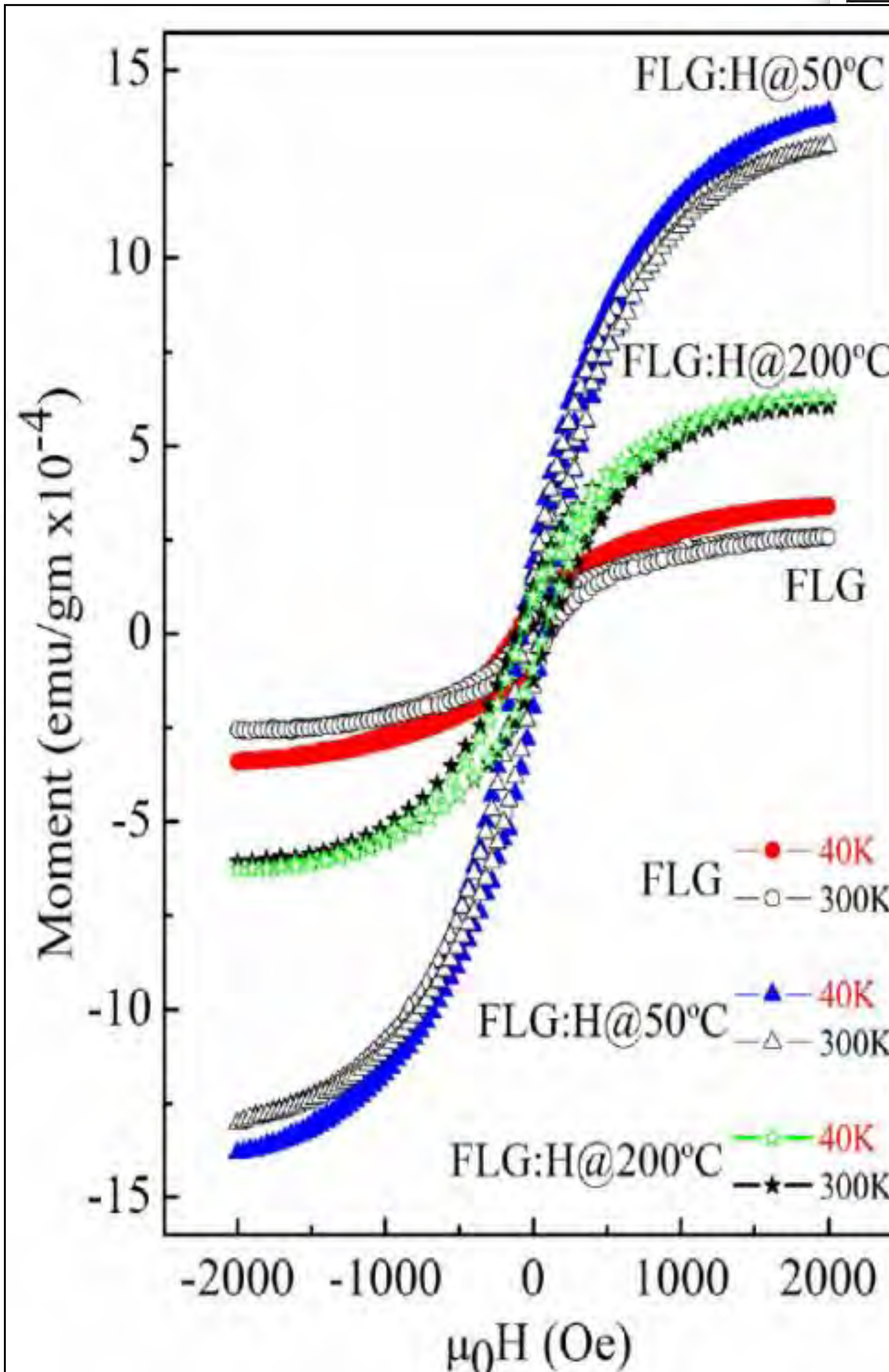
(Insulator)
Graphane



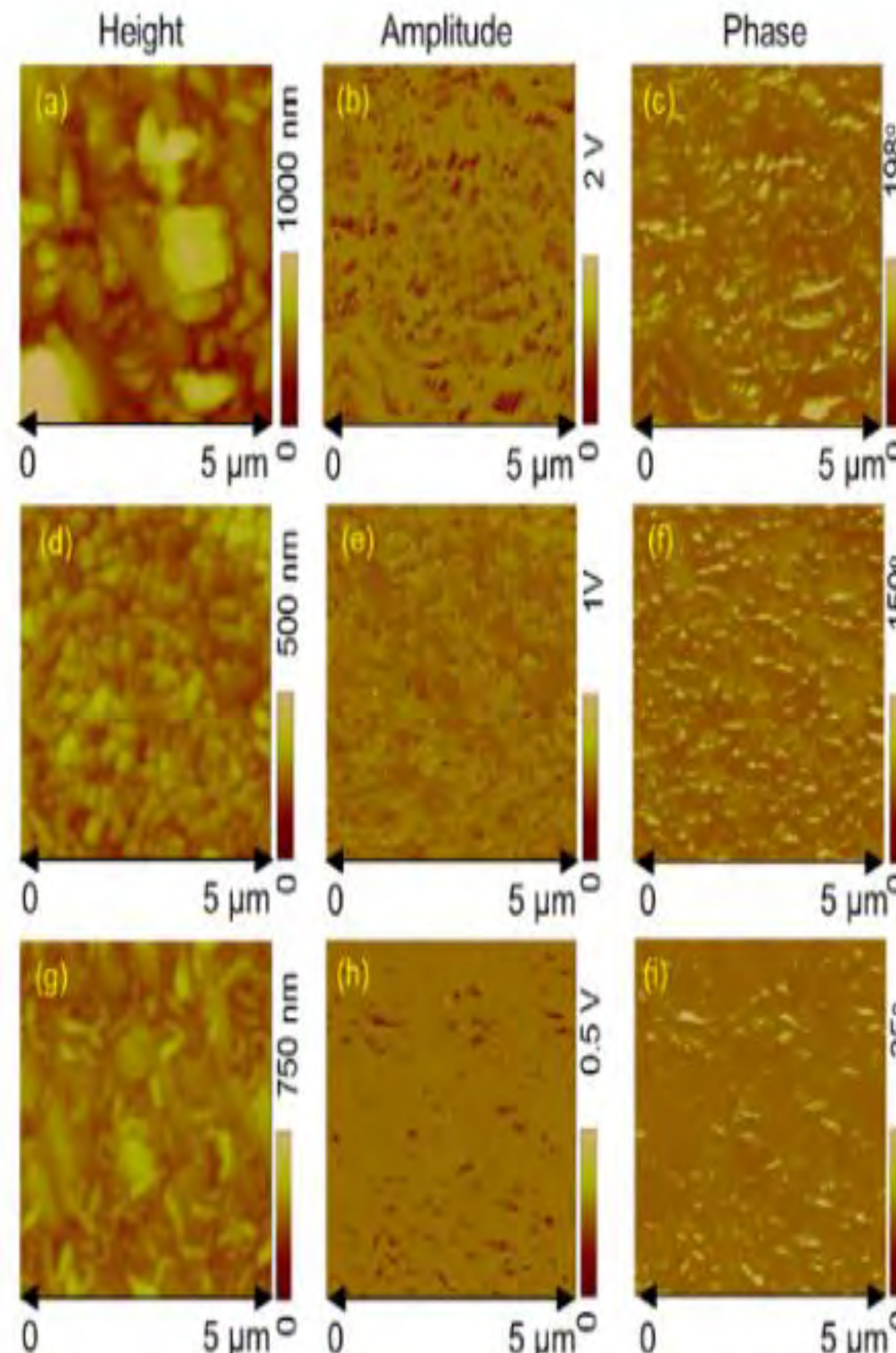
Graphone
(semiconductor)



FM	AF	NM
$m=4\mu_B, E=0;$	$m=0\mu_B, E=0.15;$	$m=0\mu_B, E=0.49$

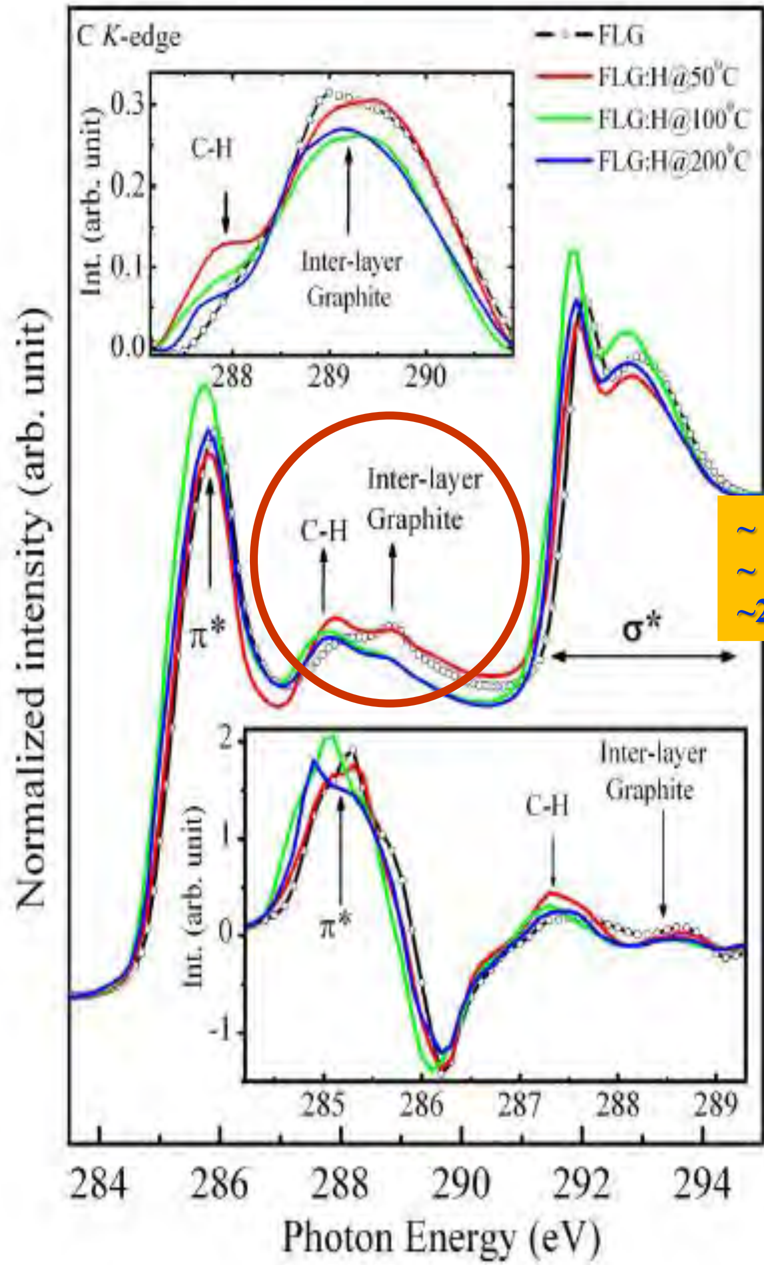


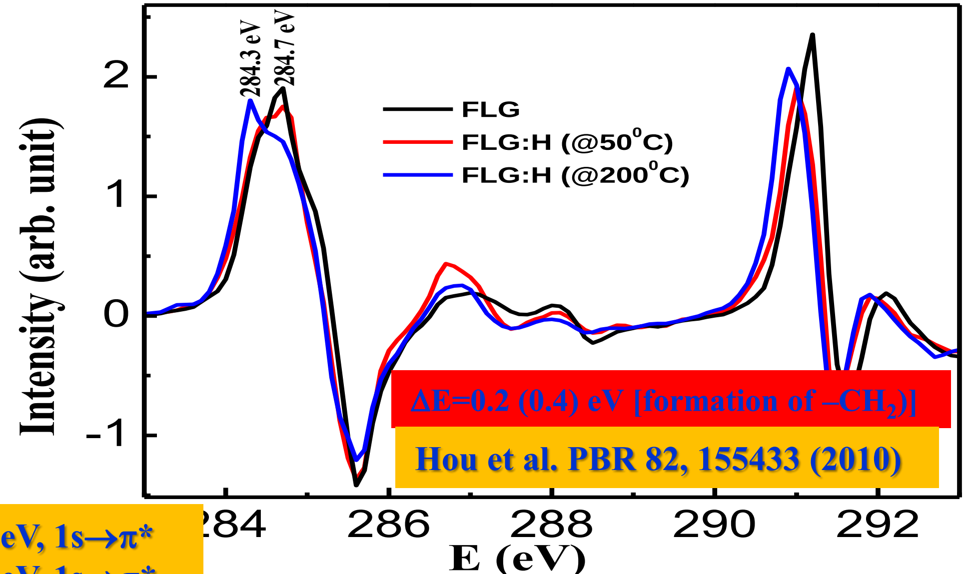
FLG:H@50ºC
FLG:H@200ºC
FLG
Moment (emu/gm x10^{-4})
μ_0H (Oe)
FLG —●— 40K
—○— 300K
FLG:H@50ºC —▲— 40K
—△— 300K
FLG:H@200ºC —☆— 40K
—★— 300K



Height
Amplitude
Phase
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
1000 nm
2 V
198º
500 nm
1V
150º
750 nm
0.5 V
35º
0
5 μm

C *K*-edge XANES of Semi-hydrogenated Graphene Sheet

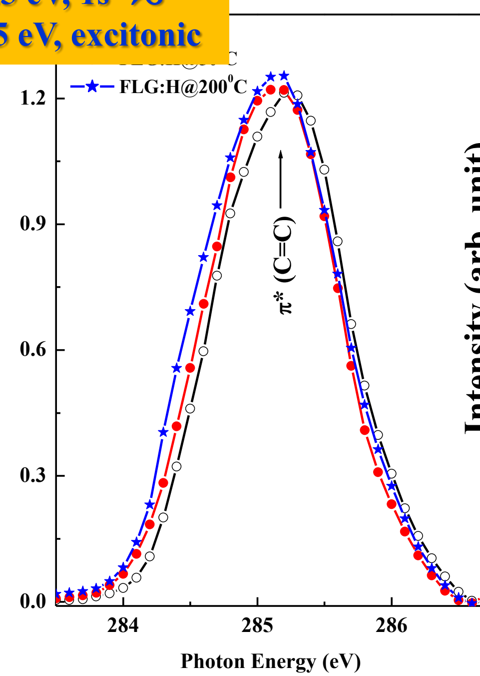


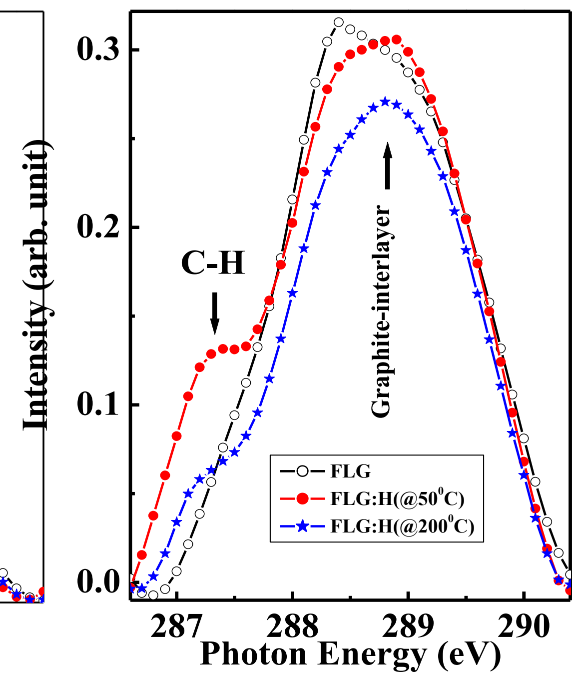


ΔE=0.2 (0.4) eV [formation of $-CH_2$)]

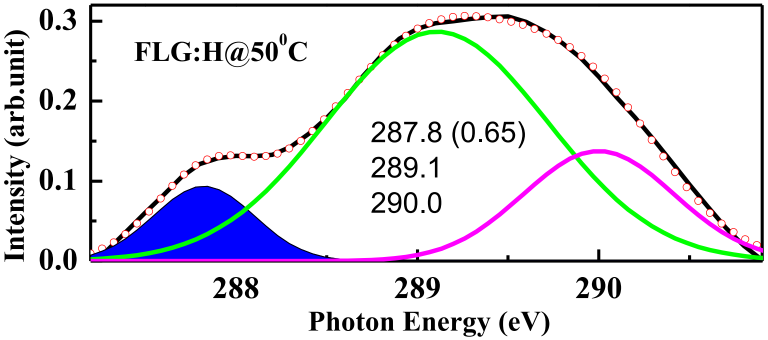
Hou et al. PBR 82, 155433 (2010)

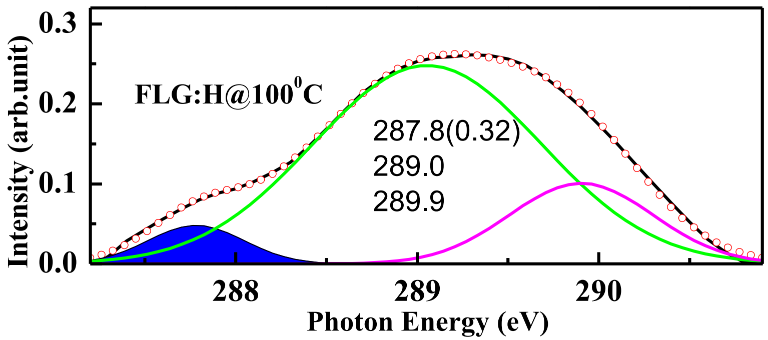
~ 285.1 eV, 1s→π*
~ 292.5 eV, 1s→σ*
~291.5 eV, excitonic

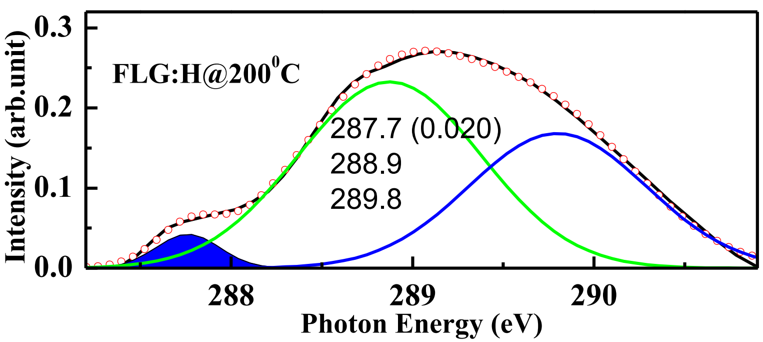




Determination of C-H content from C *K*-edge XANES spectra

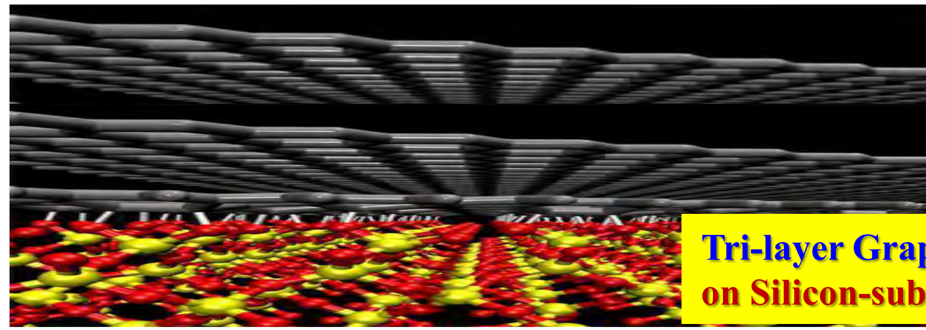






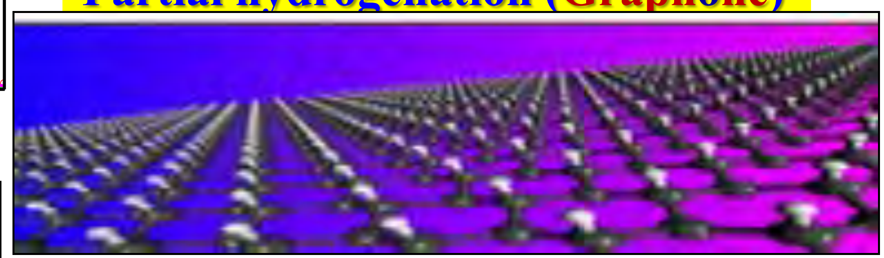
	C-H
FLG:H@50⁰C	0.65 (287.8)
FLG:H@100⁰C	0.32 (287.8)
FLG:H@200⁰C	0.19 (287.7)

CH ratio
0.65 : 0.32 : 0.19 ≈ 6 : 3 : 2

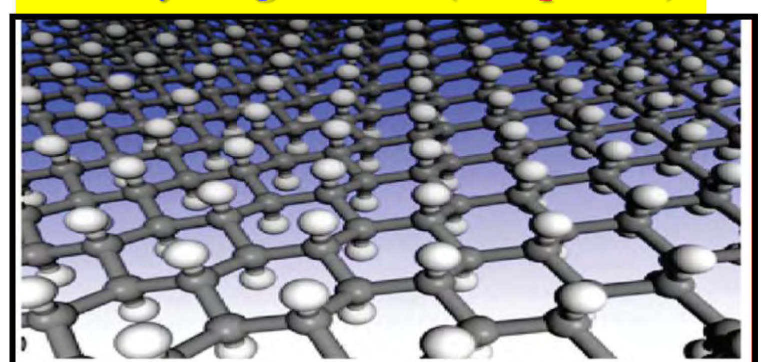


Tri-layer Graphene on Silicon-substrate

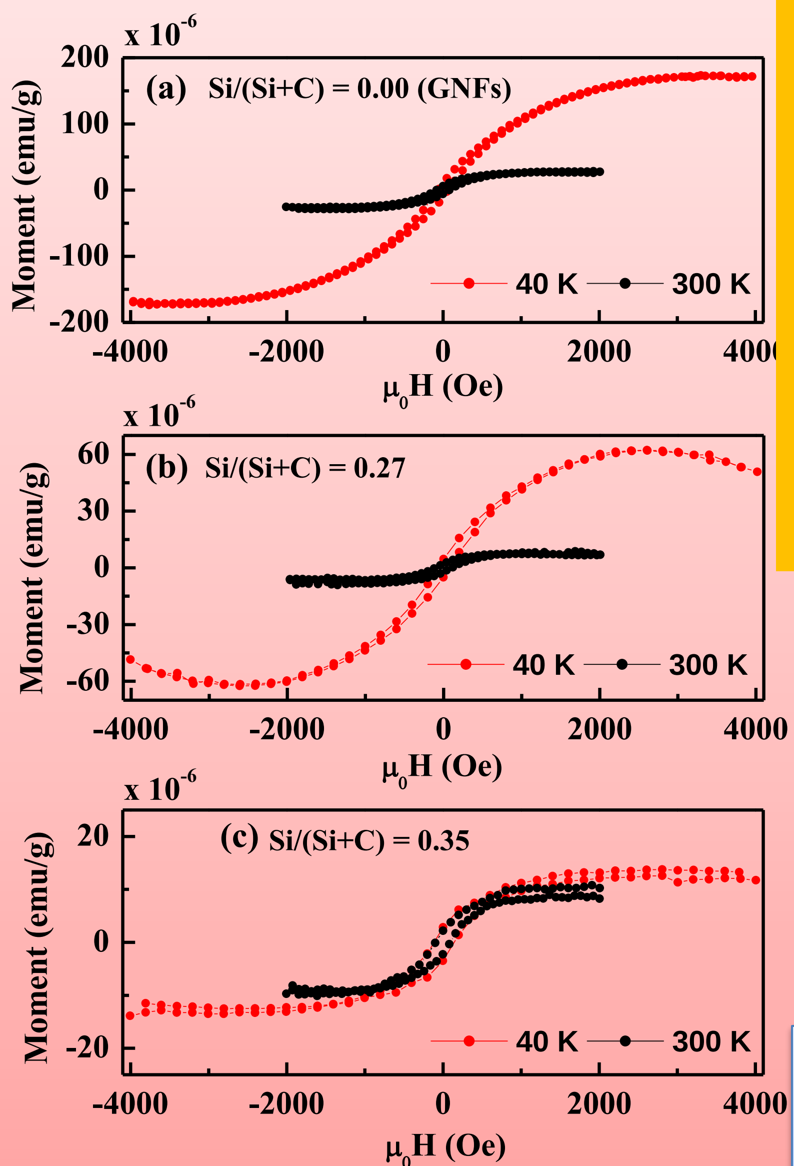
Partial hydrogenation (Graphone)



Full hydrogenation (Graphane)



Silicon-Functionalized Graphene: Ferro-Magnetic Behaviour



⇒M_S values are reduced with increasing coercivity (H_c) as the Si-content is increased, implying the loss of magnetization with silicon content.

⇒With increase of Si-content, non-defect Si-C tetrahedral bonding along with SiO are formed that make sp^3-rich structured GNFs materials that are responsible for reducing the magnetisation of GNFs.

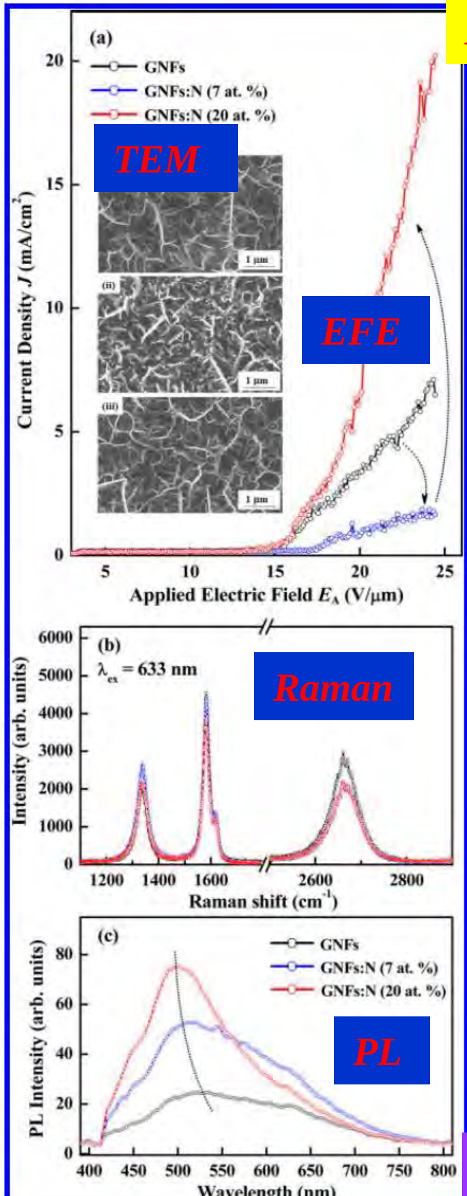
⇒Formation of Si-O-C due to air exposure known as a defect structure that is responsible for the reducing of ferromagnetic behaviours

Saturation magnetization (M_S), Coercivity (H_C) and Remanence (M_R) of GNFs and GNFs:Si.

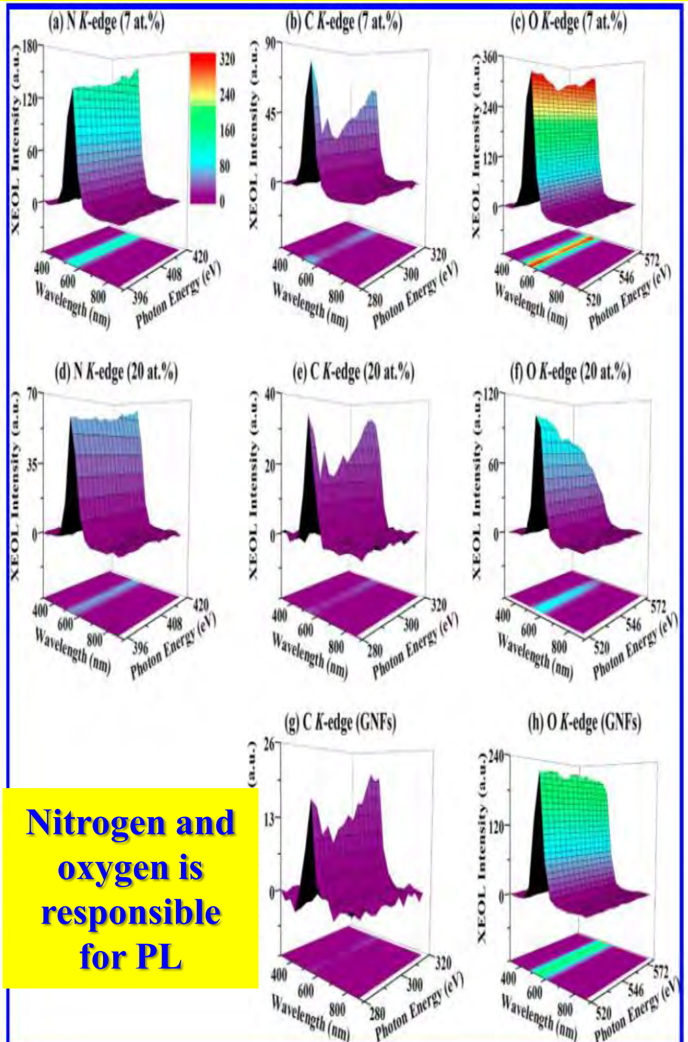
Sample	$\frac{Si}{(Si+C)}$ Ratio	M_s ($\times 10^{-6}$ emu/g)		H_c (Oe)		M_R ($\times 10^{-6}$ emu/g)	
		40K	300K	40K	300K	40K	300K
GNFs	0.00	172.53	27.19	66.00	81.27	9.38	5.83
GNFs:Si	0.27	62.05	6.92	90.00	108.00	4.62	2.25
GNFs:Si	0.35	13.00	12.00	149.00	101.00	2.85	2.20

Ferromagnetic materials with high coercivity are called magnetically hard materials, and are used to make permanent magnets. Materials with low coercivity are said to be magnetically soft and are are used in transformer and inductor cores, recording heads, microwave devices, and magnetic shielding.

Nitrogen-Functionalized Graphene : Tunable PL and Electronic Structure

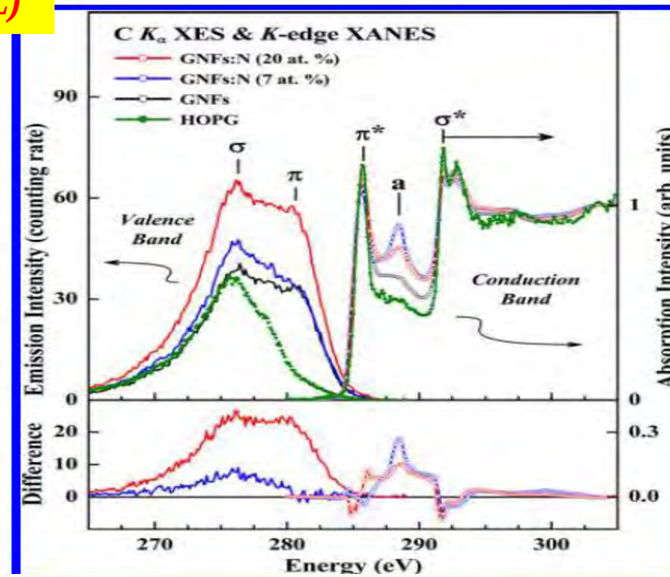


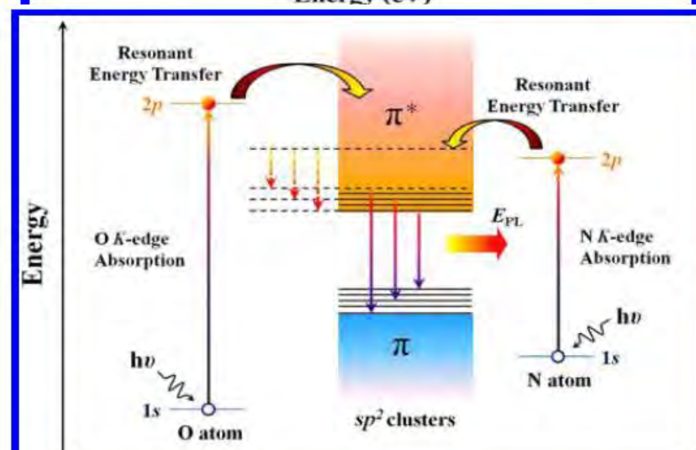
X-ray-excited optical Luminescence (XEOL)



Nitrogen and oxygen is responsible for PL

C K_α XES & K-edge XANES





Possible mechanism of XEOL

Chiou and Ray et al. 2012, 116. 16251-16258

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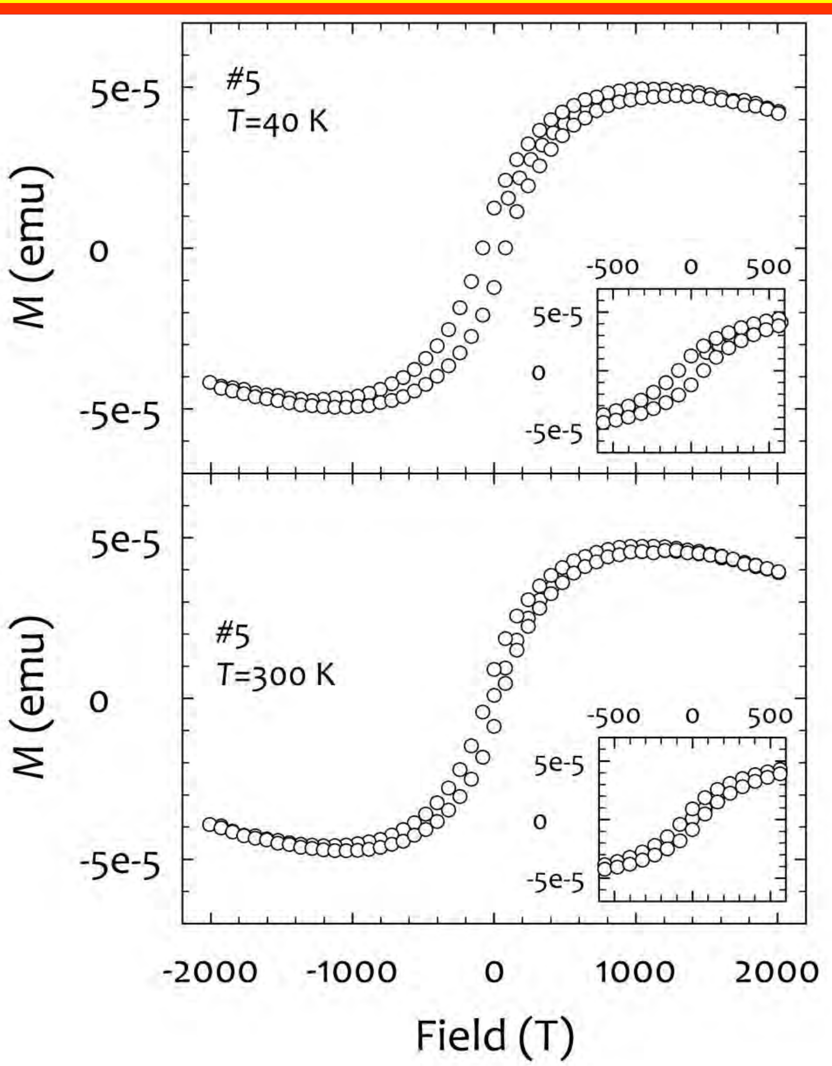
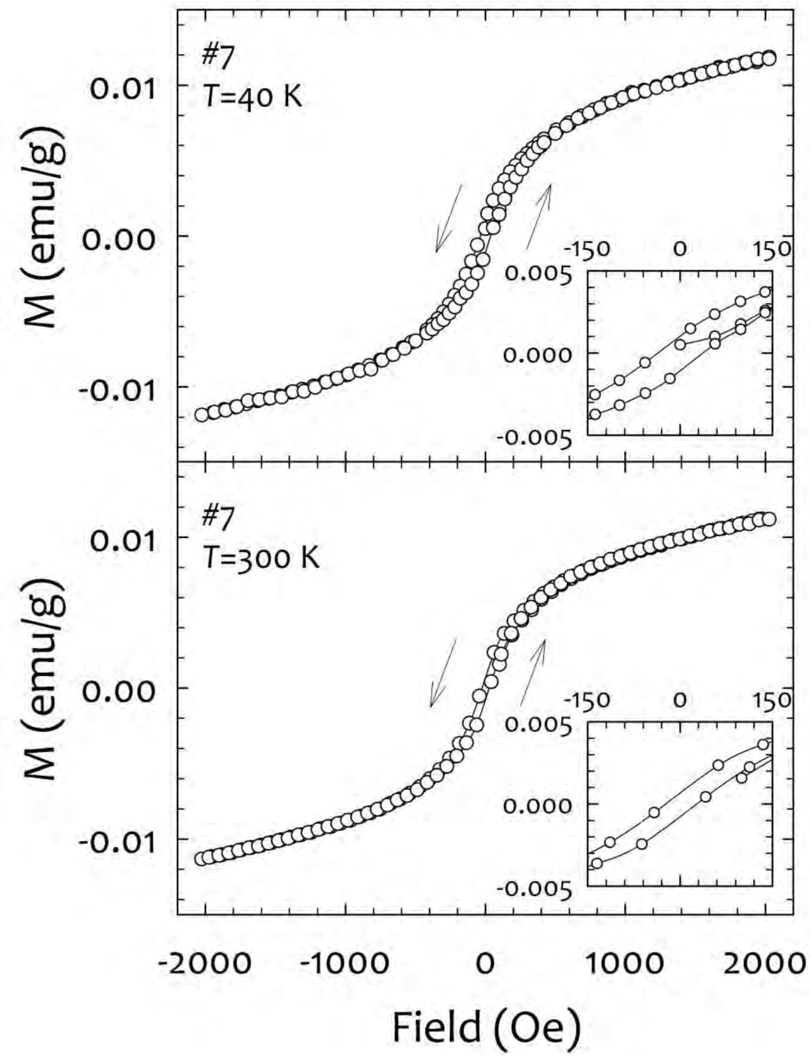
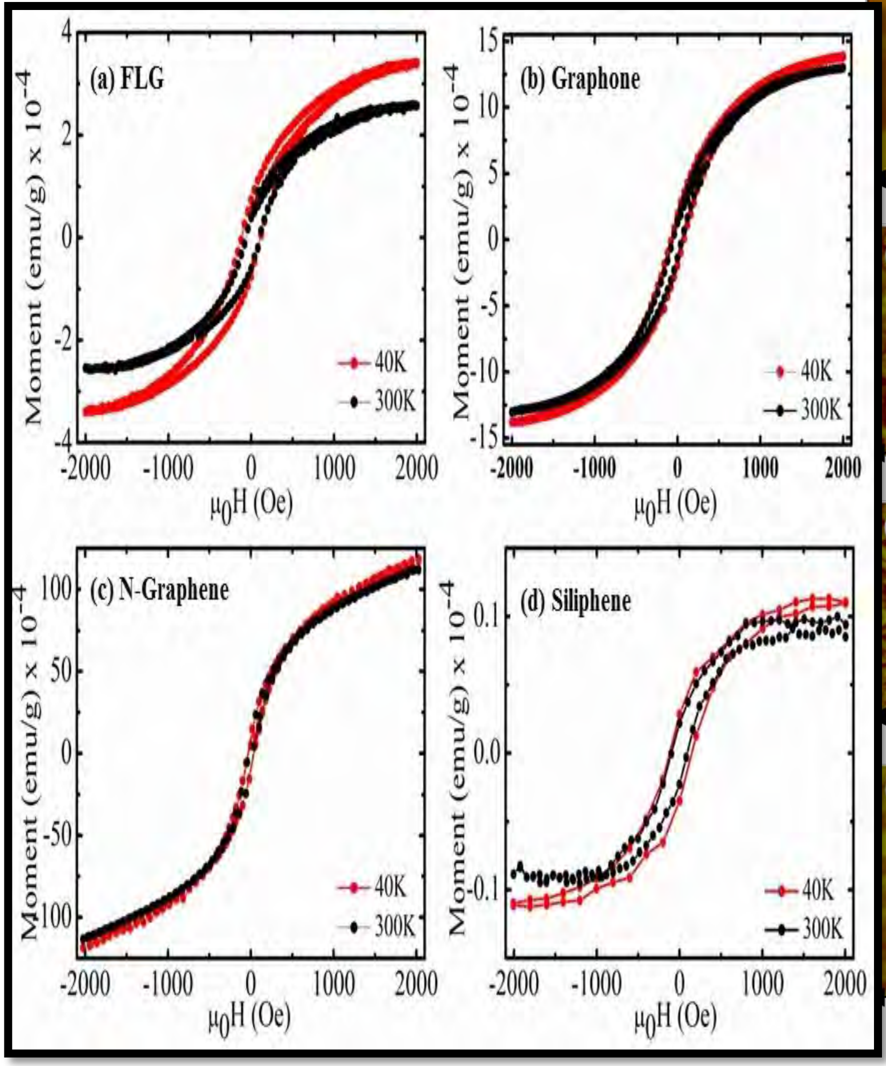
Nitrogen Functionalized Graphene: Ferro-Magnetic Behaviour

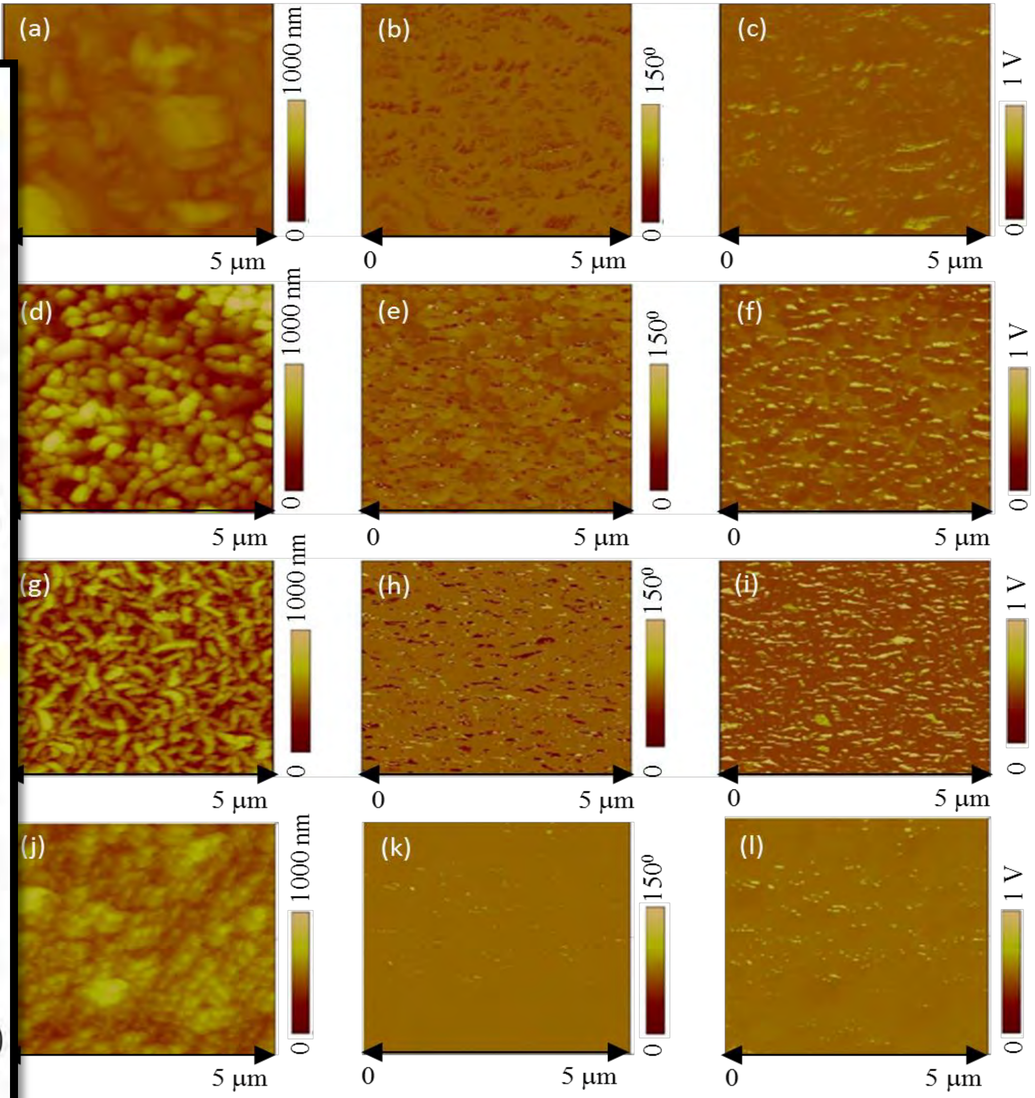




Magnetic hysteresis loops of pristine Graphene, Graphone, N-graphene and Siliphene at 300 K and 40 K.

Magnetic Force Microscopy images of pristine Graphene, Graphone, N-graphene and Siliphene



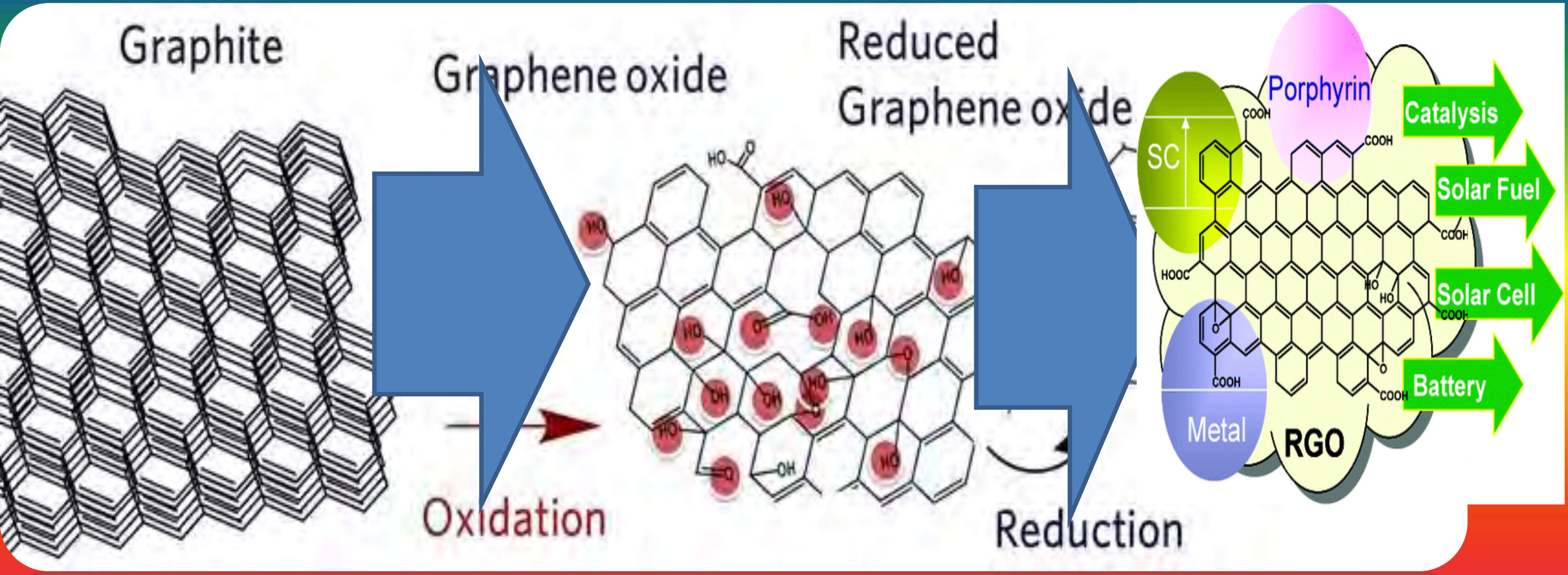


Ray et al. NPG Asia Materials (Under consideration)

Magnetic properties of the pristine and plasma treated graphenes at 40 K and 300 K

Sample/ Temperature	H_c (Coercivity) (Oe)	M_s (Saturation magnetisation) (emu/gm)	M_r (Remnant magnetisation) (emu/gm)
FLG			
40K	112.37	3.47×10^{-4}	0.52×10^{-4}
300K	62.98	2.60×10^{-4}	0.42×10^{-4}
Graphone			
40K	76.19	13.94×10^{-4}	1.91×10^{-4}
300K	52.88	12.91×10^{-4}	1.28×10^{-4}
N-Graphene			
40K	40.00	118.62×10^{-4}	9.74×10^{-4}
300K	25.42	111.91×10^{-4}	6.04×10^{-4}
Siliphene			
40K	120.03	0.11×10^{-4}	0.03×10^{-4}
300K	94.75	0.09×10^{-4}	0.02×10^{-4}

Role of Oxygen Functional groups (C-O, O-C-OH, C-OH) of Graphene / Graphene Oxides: Magnetic behavior



Magnetic behavior of Graphene Oxides

GO is usually considered as an diamagnetic insulator / semiconductor material

Origin of magnetic behavior in Graphene Oxides !!

In general,

⇒ **Symmetry breaking at the edges**

⇒ **Vacancy**

⇒ **Substitution and absorption of atoms**

⇒ Origin of magnetism due to presence of Oxygen functional groups

DFT calculations:

(i) The local spin moment of the carboxyl (COOH) and hydroxyl (OH) functional groups adsorbed on the GRAPHENE are 1.00 μ_B and 0.56 μ_B respectively.

(ii) Two hydroxyl groups at non neighboring carbon atoms (having one carbon in between) favors the magnetism in GO

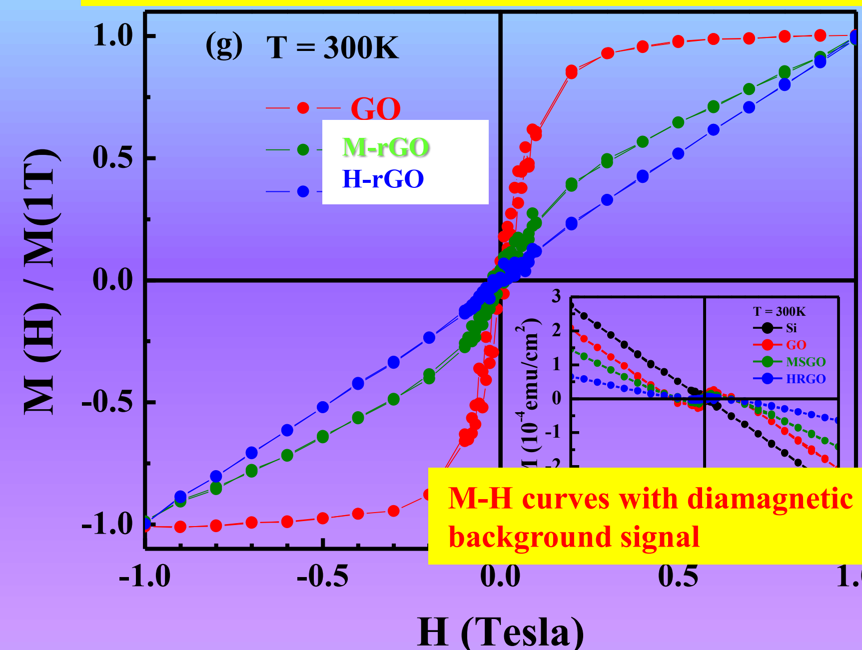
(iii) Hydroxyl groups present at neighboring carbon atoms shows no magnetism !!

(iv) The most stable magnetic configuration corresponds to seven OH-groups

Ref: (i) Santos, E. J. G. eta l. *New J. Phys.* 2012, *14*, 043022.
(ii) Wang, M. et at. *Nanotechnology* 2011, *22*, 105702.
(iii) Boukhvalov,D. W. et al. *ACS Nano* 2011, *5*, 2440

Carbon-based materials are very promising for spintronic applications due to their weak spin-orbit coupling and potentially providing a long spin life time

After subtracting the diamagnetic (Si-substrate) contribution



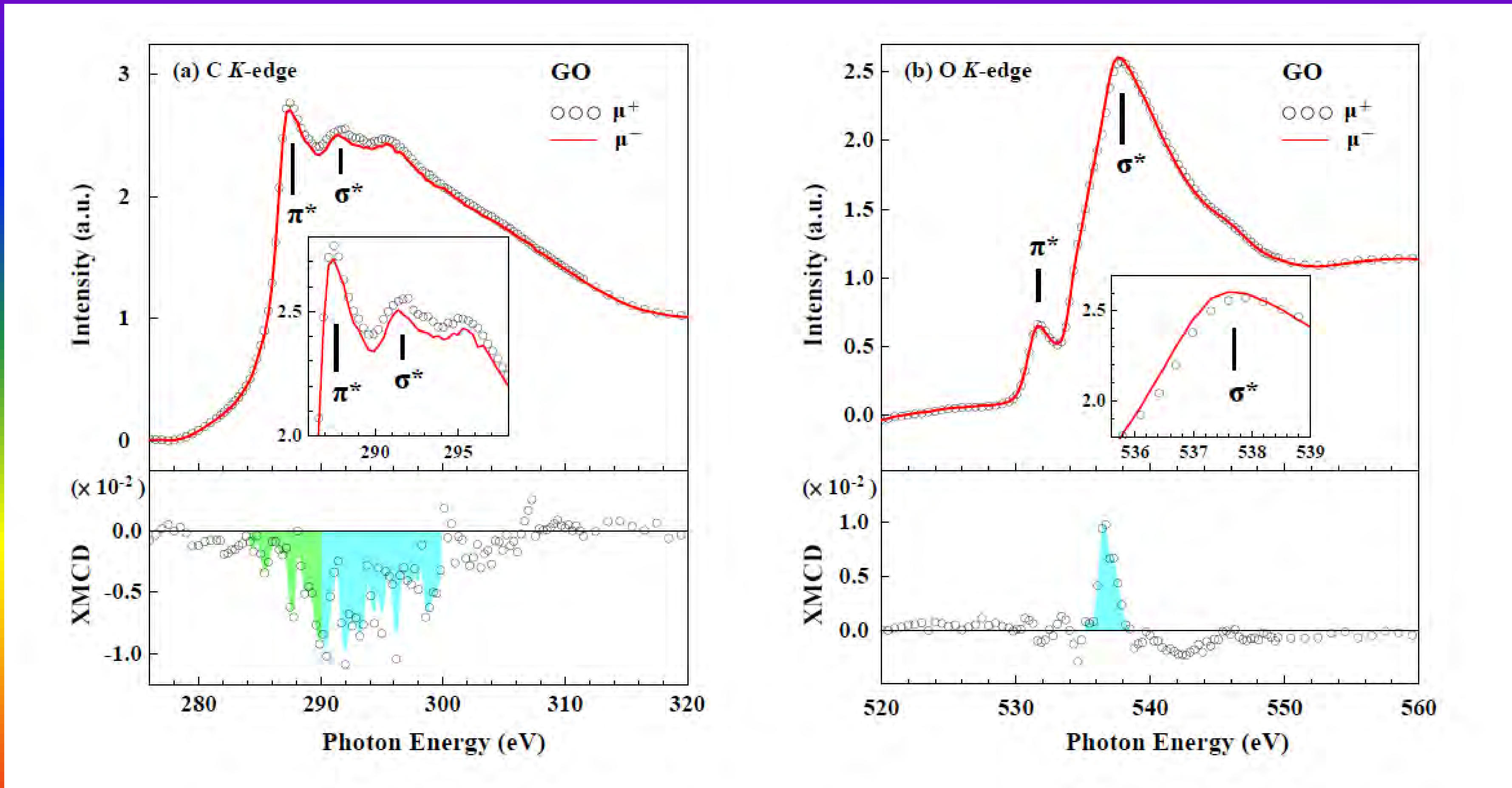
M-H curves with diamagnetic background signal

Absence of ***d*** and ***f*** electrons but strongly supports the intrinsic d^0 magnetism of GO

Room temperature FM in GO
Coercivity ~150 Oe
Saturated field about 3000 Oe

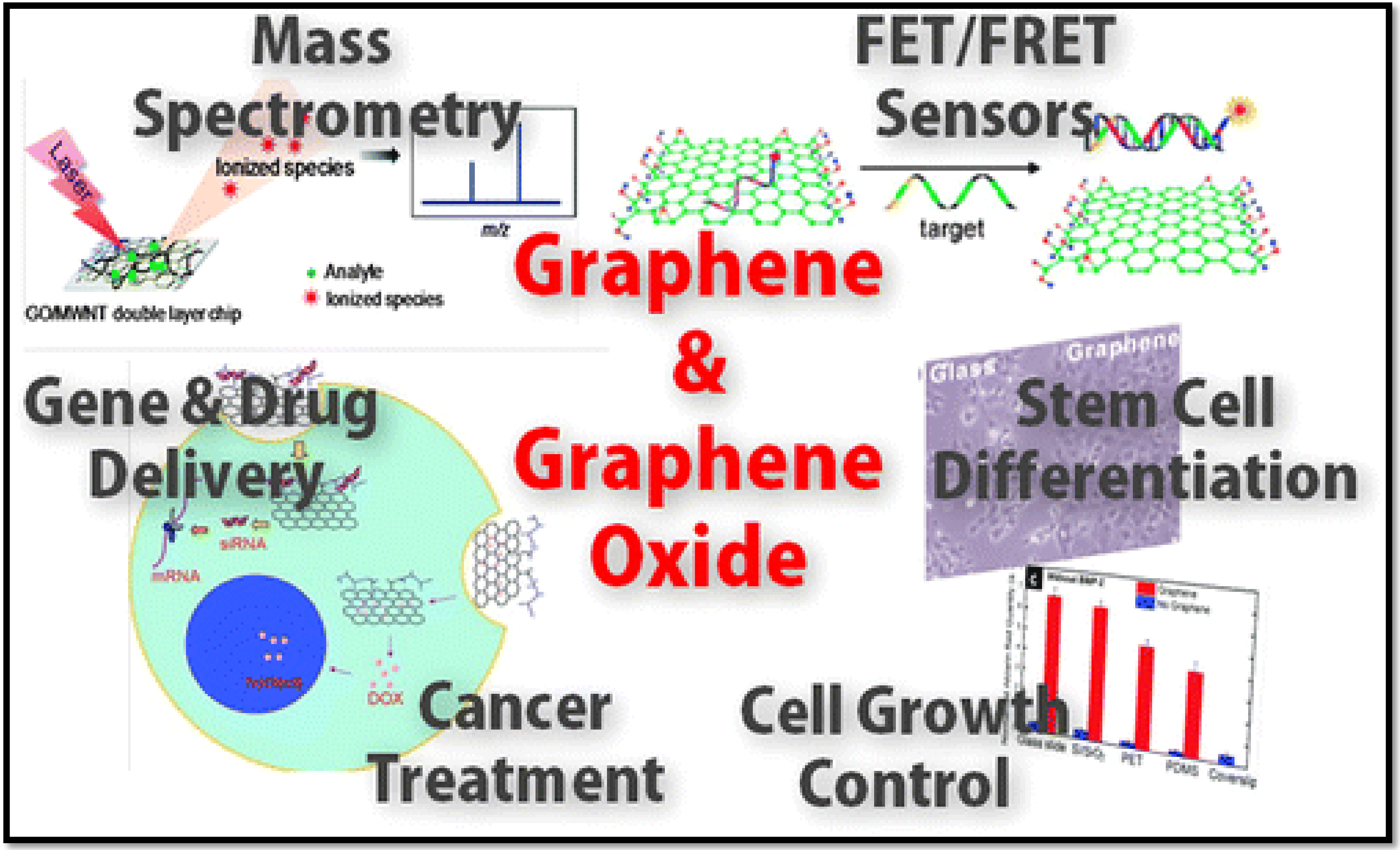
Ferromagnetic behavior gradually decreases (paramagnetic behavior) for MrGO / HrGO on PT-reduction process.

X-ray Magnetic Circular Dichroism (XMCD) of Graphene Oxides

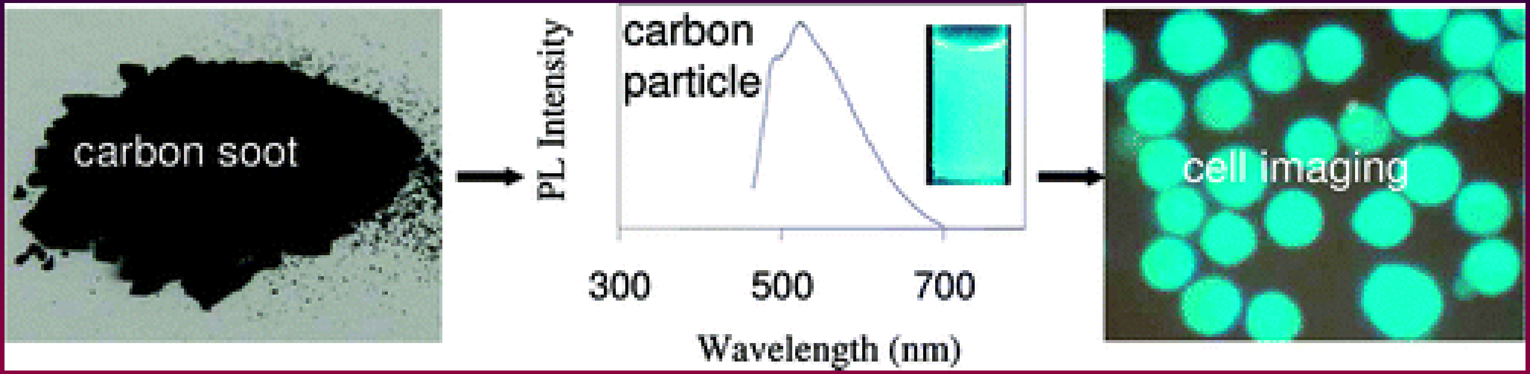


C and O *K*-edge: X-ray magnetic circular dichroism (XMCD) spectra with the photo-helicity of incident x-rays parallel (μ^+) and anti-parallel (μ^-) to the direction of magnetization of GO

Graphene/Graphene based Carbon for Bio-imaging application



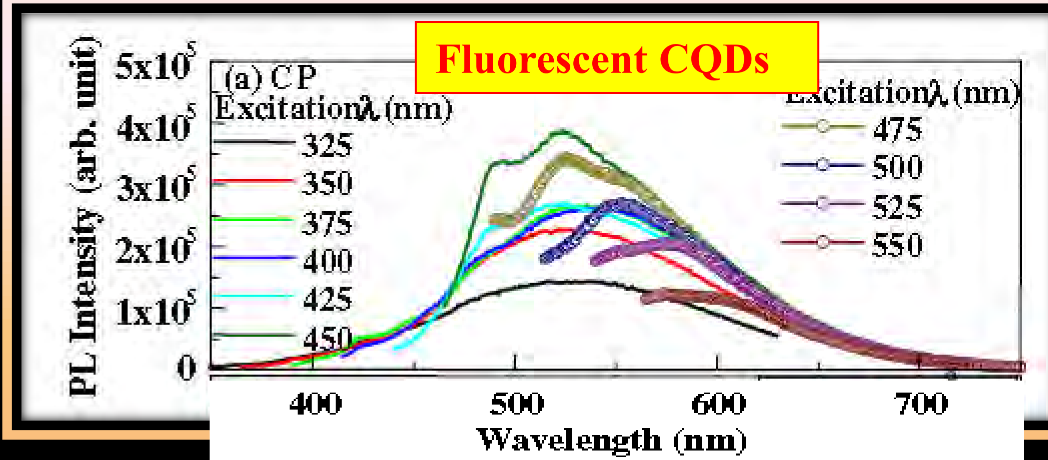
Graphene based Carbon Nanoparticles for Bio-imaging application

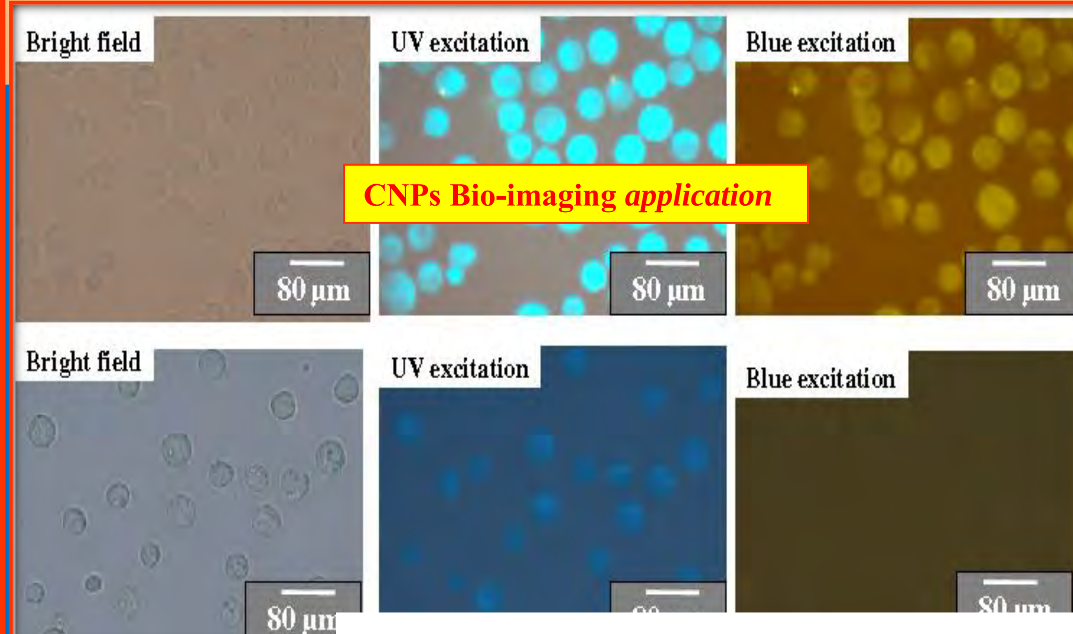


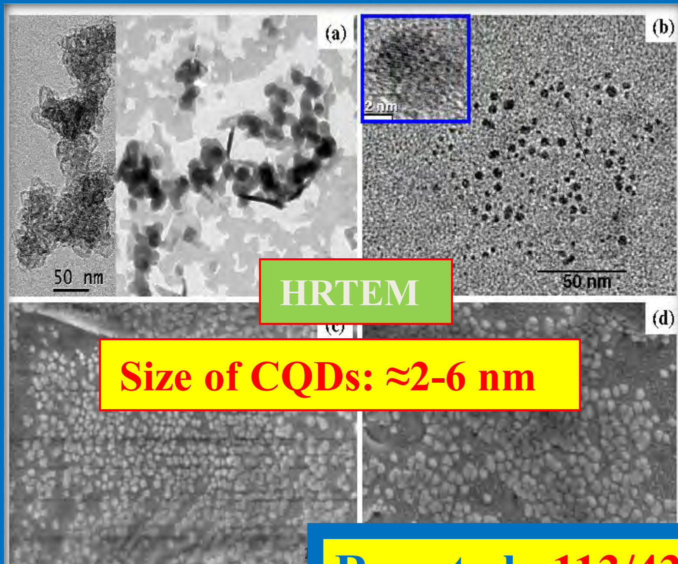
Ray et al. *J. Phys. Chem. C* 2009, *113*, 18546–18551

Fluorescent Carbon Nanoparticles for Bio-imaging probes

(Carbon Quantum DOTs:≈ 2 – 6 nm)







Ray et al., 113/43 (2009) 18546 -51

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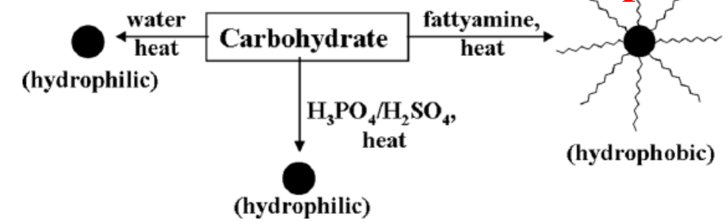
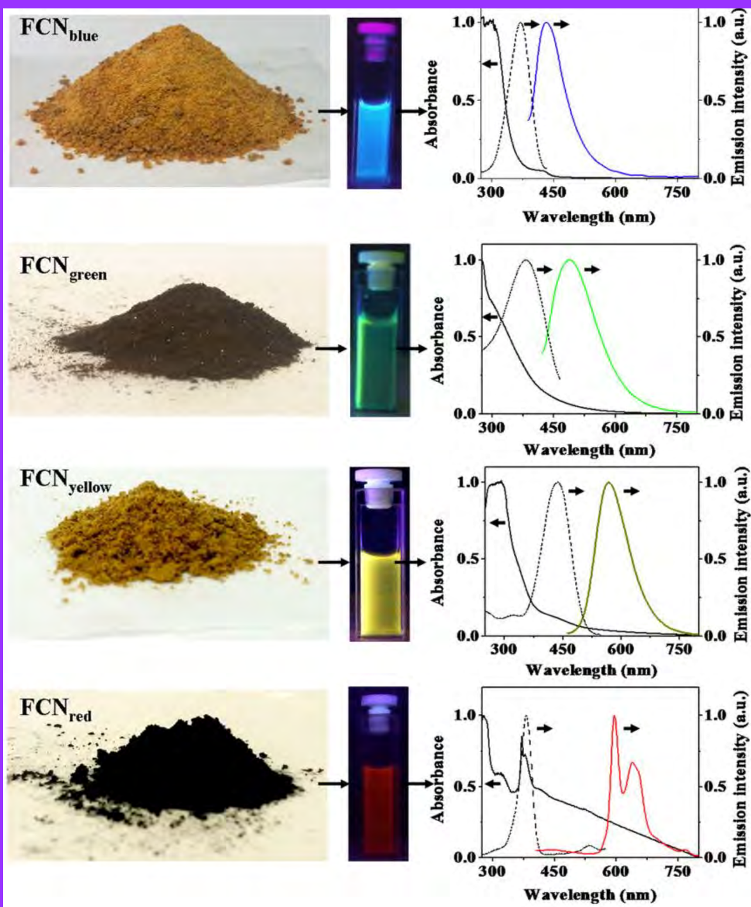
Carbon Nanoparticle-based Fluorescent Bioimaging Probes

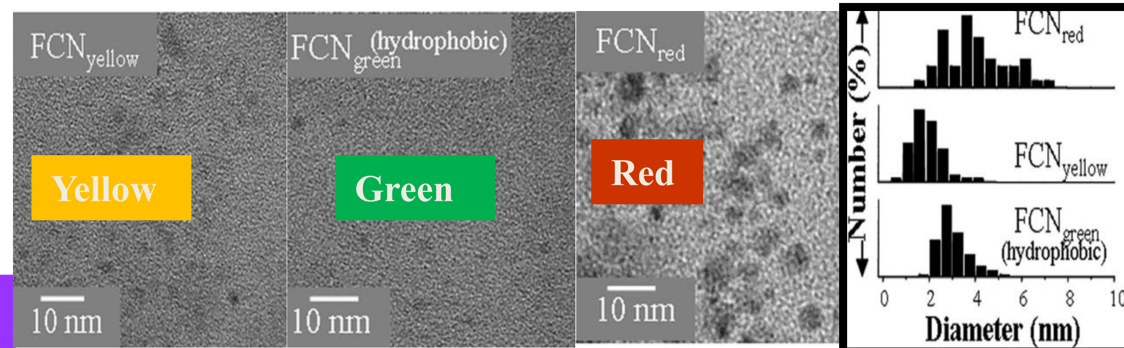
S.K. Bhunia, A. Saha, A.R. Maity, S.C. Ray and N.R. Jana

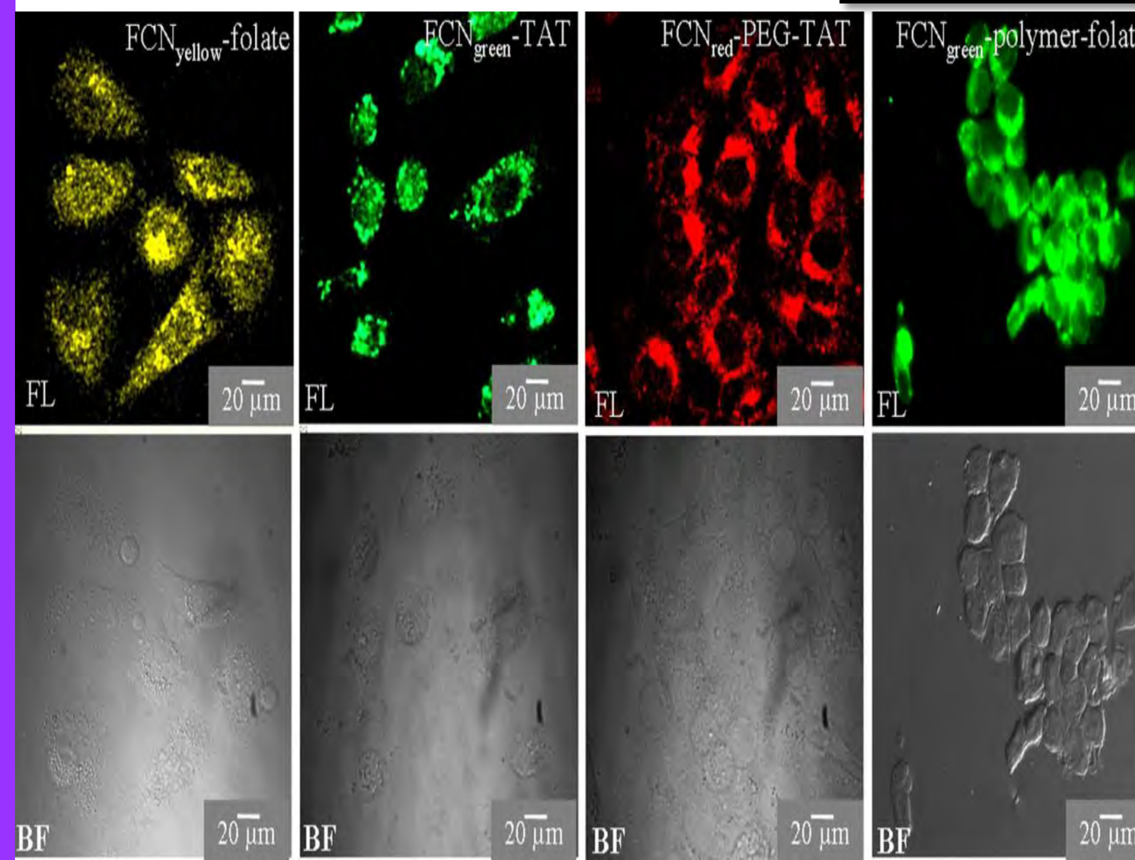
Scientific Reports |2013| 3: 1473 (1-7) : www.nature.com/scientificreports

Functionalized with Nano pores









CONCLUSION

- Graphene is a new hope for electronic devices and could possibly replace or rejuvenate Silicon based devices. It seems to be a better material than Silicon and CNT.
- **Graphene useful in Bio-imaging probe and bio-medicine application**
- Successful prototypes include Superconductor, Flexible Displays and Ultra-Capacitor.
- It shall introduce new era of devices for electronics, space, bio-medical and energy harvesting.
- Graphene devices might surround us very soon.

THANK YOU FOR YOUR ATTENTION