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

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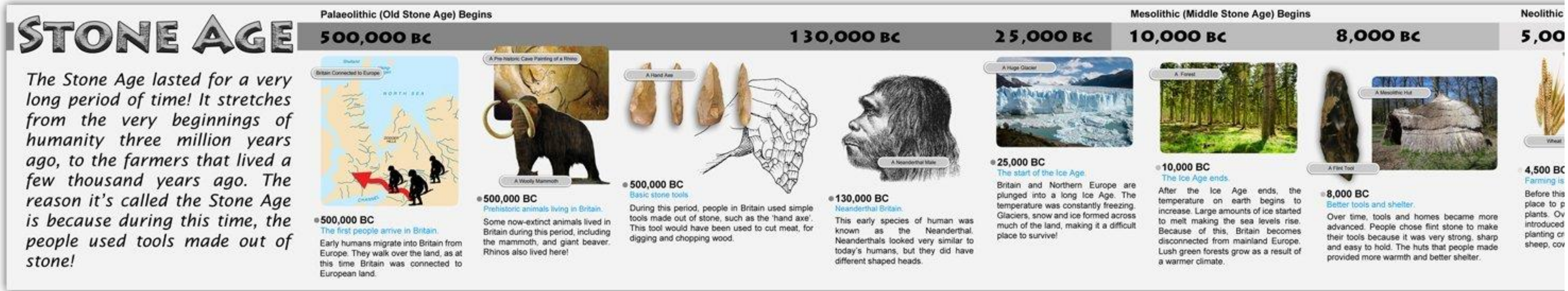
Define tomorrow.

145 years of lighting the way.

UNISA college of science, engineering and technology

STONE AGE ⇒ BRONZE AGE ⇒ IRON AGE



⇒ **Each age is levelled by the Material**
⇒ **that bearing the new technology**
⇒ **that makes the new society**

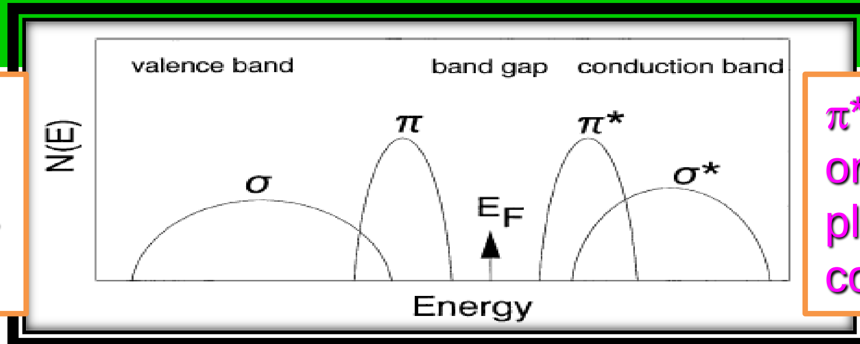
What will be the next age??
What will be next material??

CARBON AGE
or
GRAPHENE AGE !!

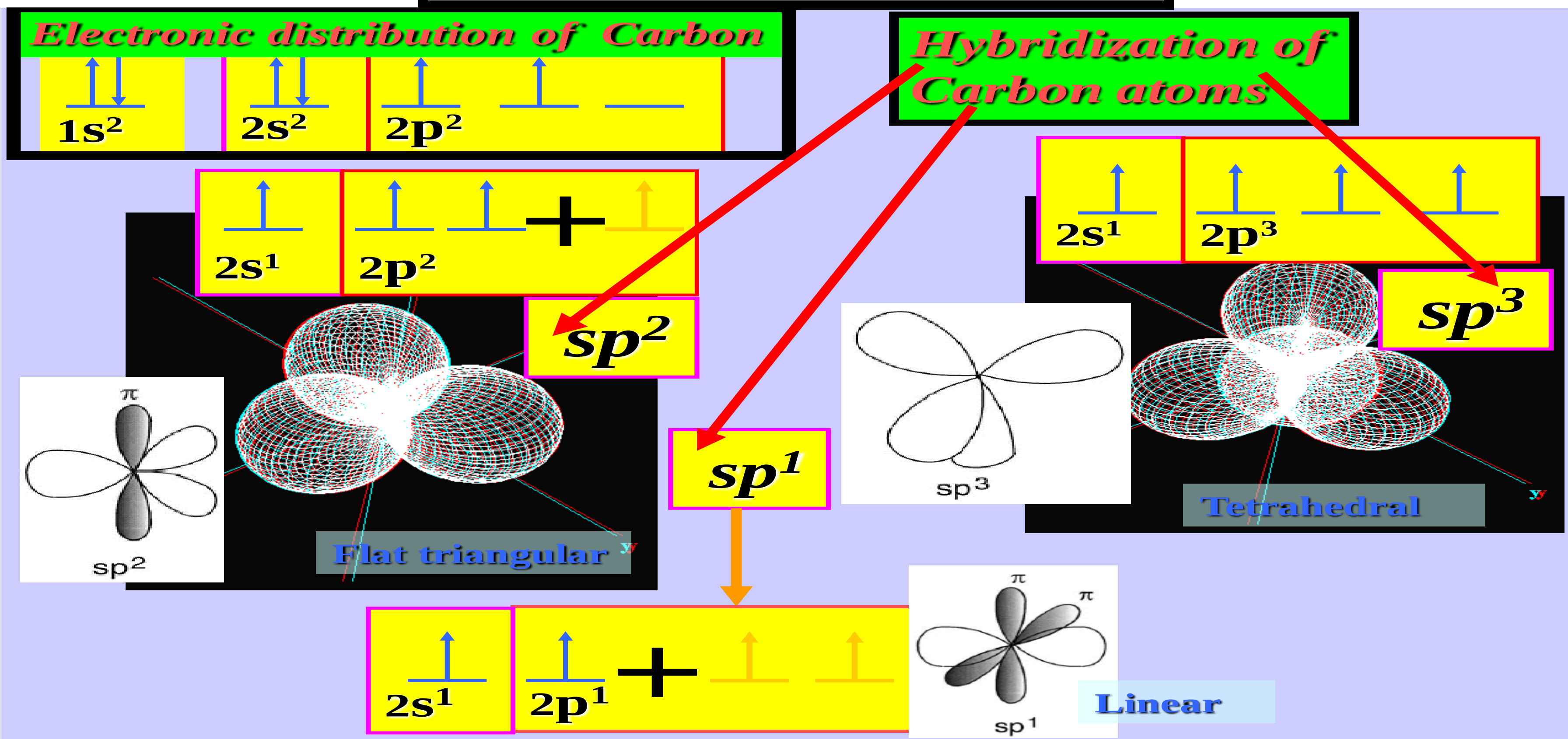
Electronic distribution of carbon

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



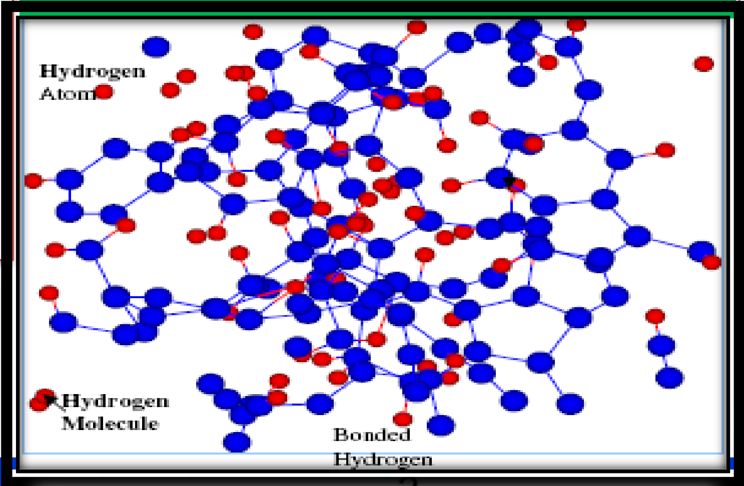
Graphite (100%sp²

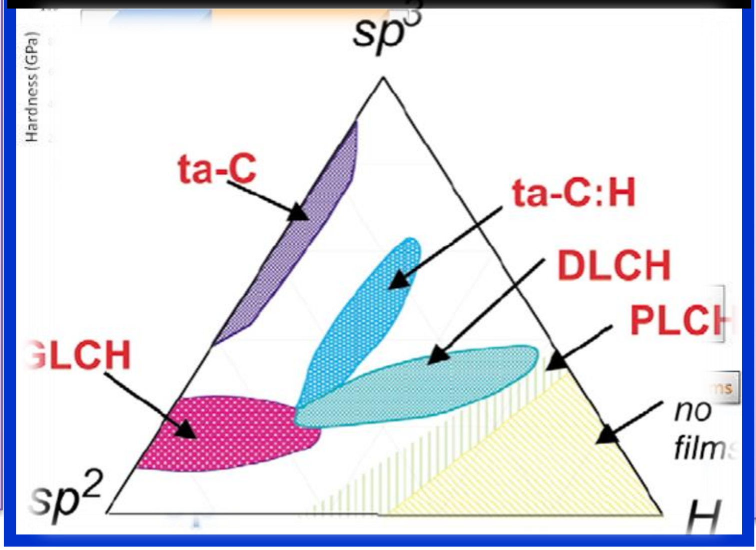
Properties of graphite:

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.

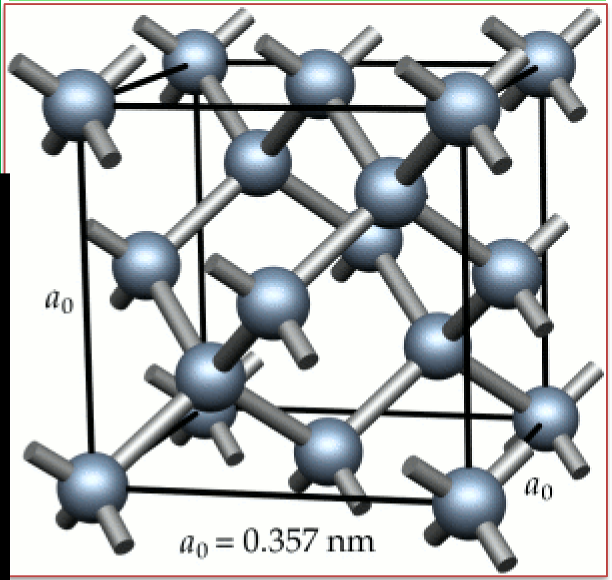
Amorphous Carbon or Diamond like carbon

(Mixture of sp^2 & sp^3)





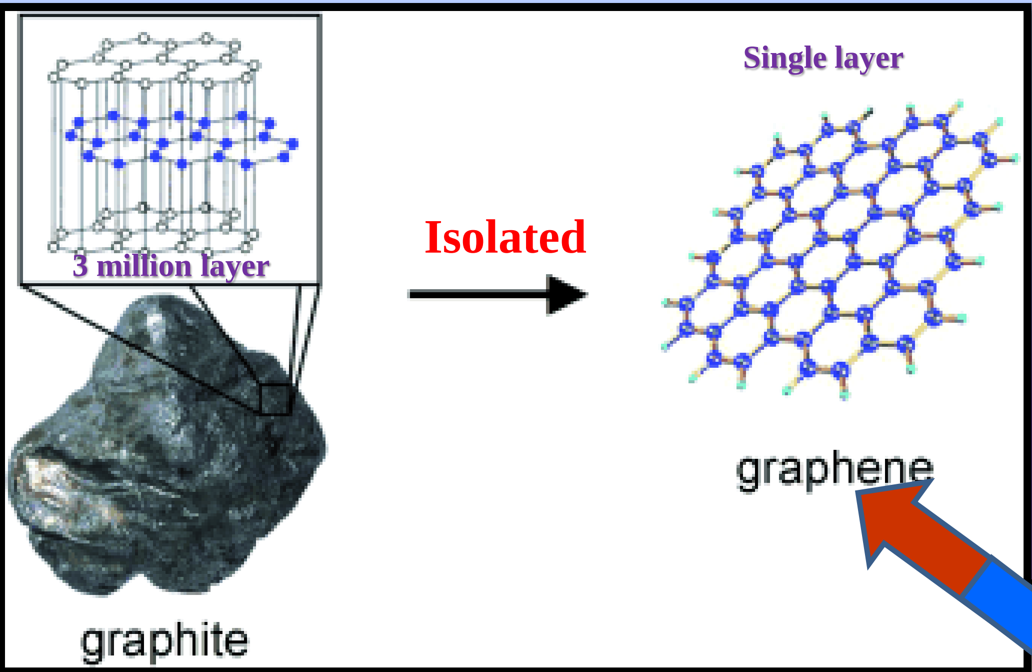
Diamond (100%sp³)

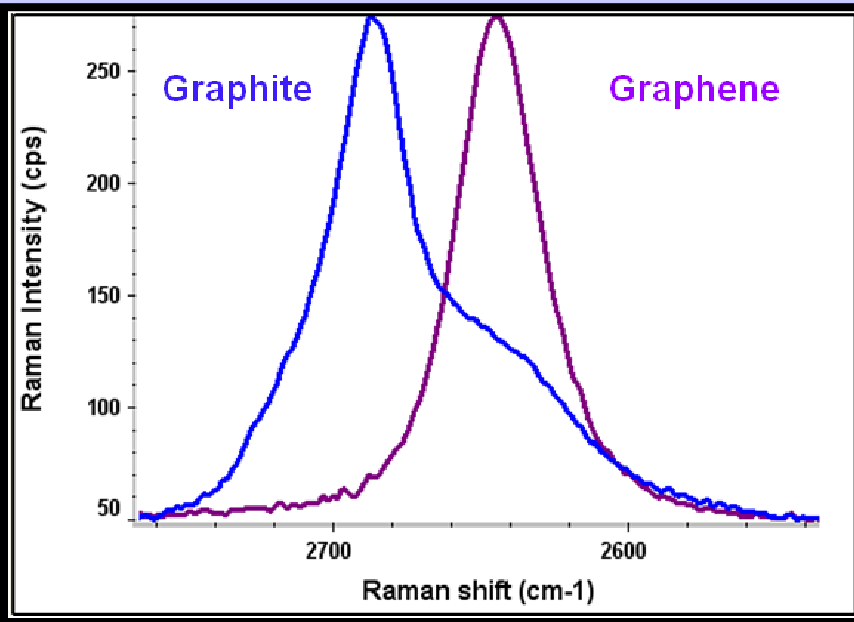


Properties of diamond:

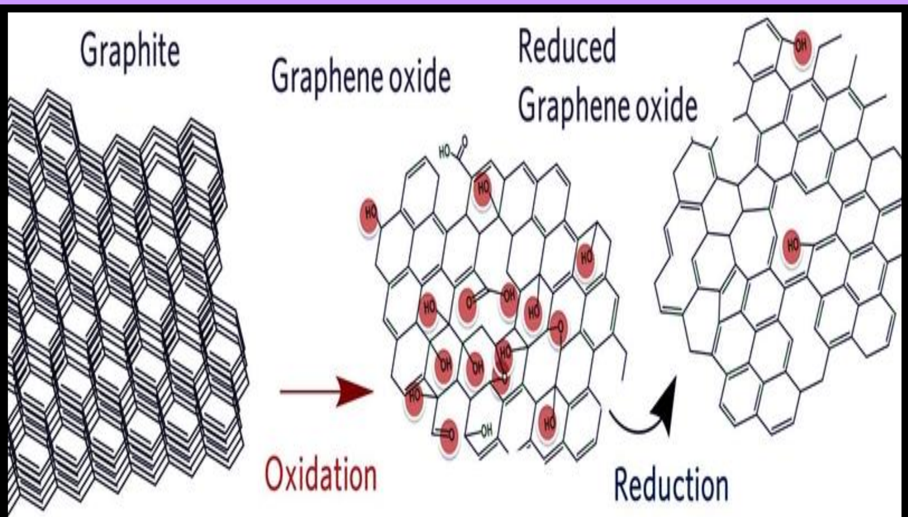
1. It is the hardest substance known.
2. It has a high refractive index and gives an extraordinary brilliance.
3. The specific gravity of diamond is 3.52.
4. Diamond is a bad conductor of heat and electricity because it lacks free electrons.
5. Chemically, diamonds are un-reactive under ordinary conditions.

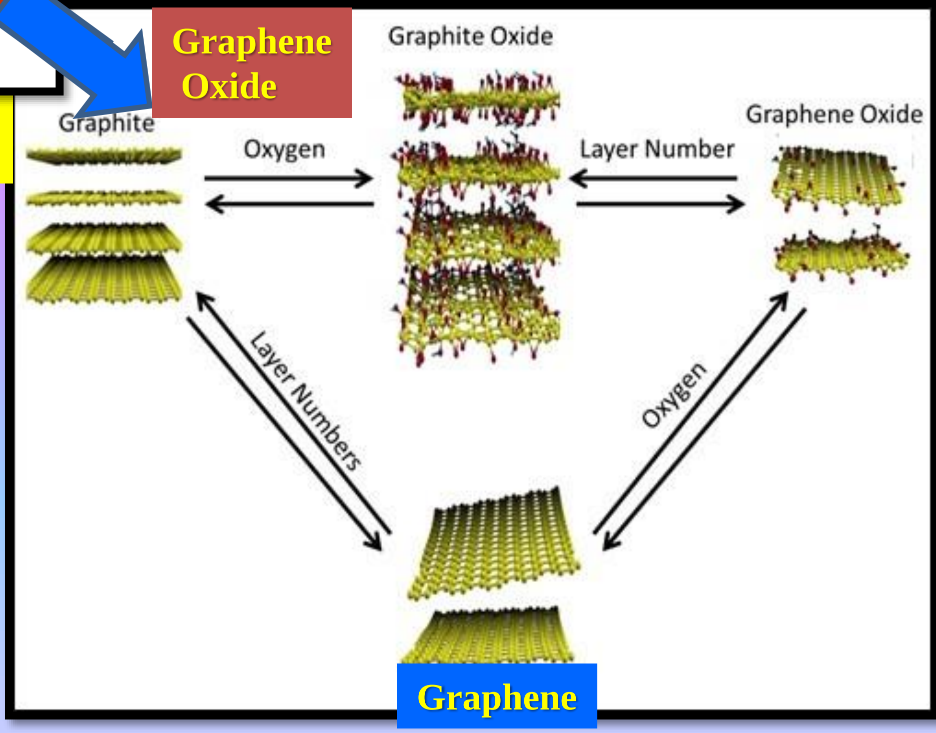
Graphite ⇒ Graphene

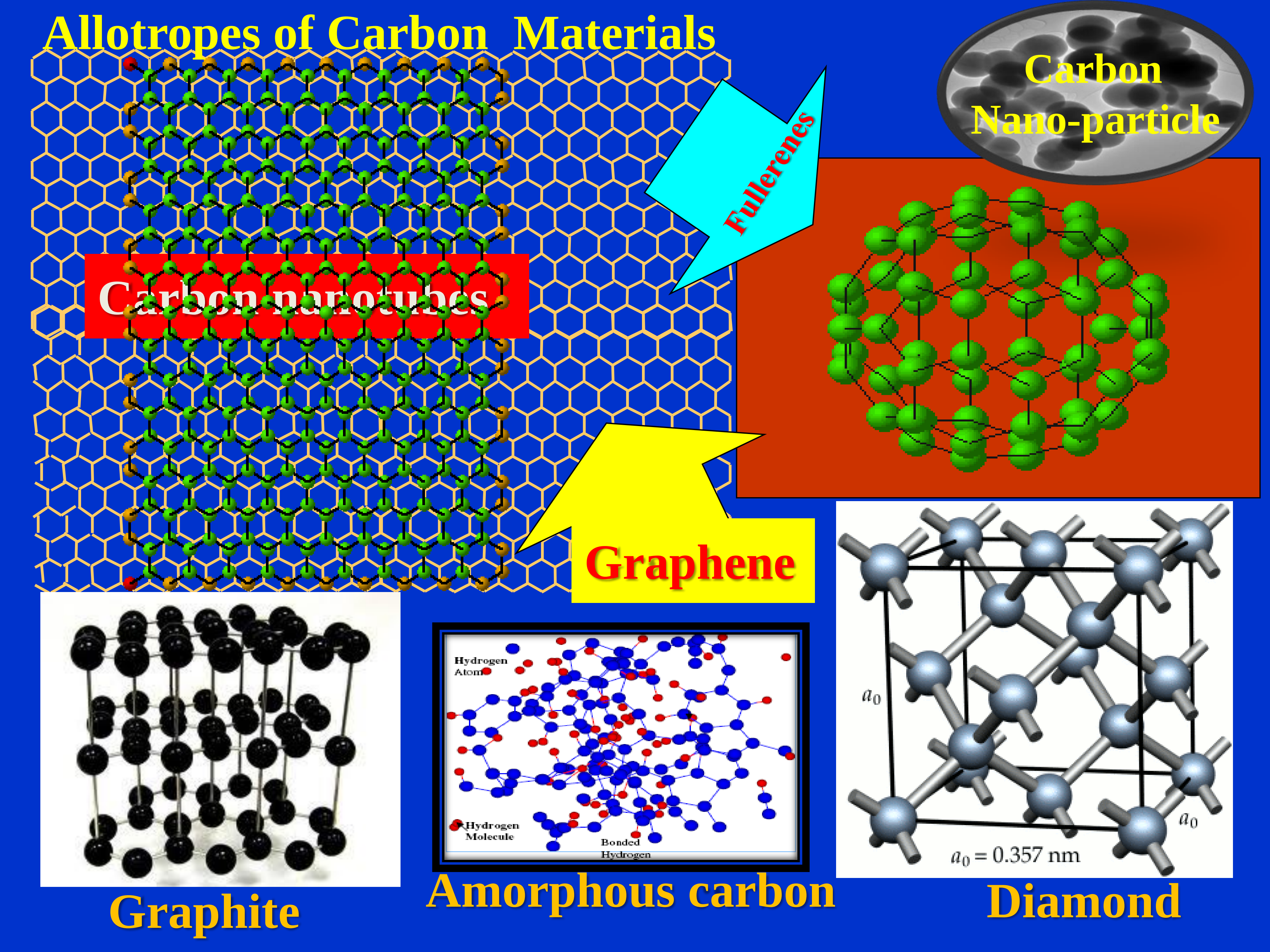




Graphite ⇒ Graphene Oxide

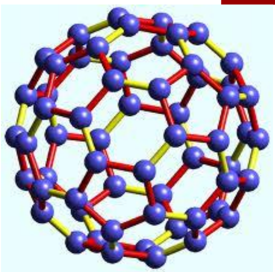


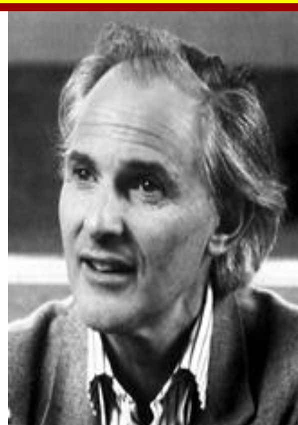


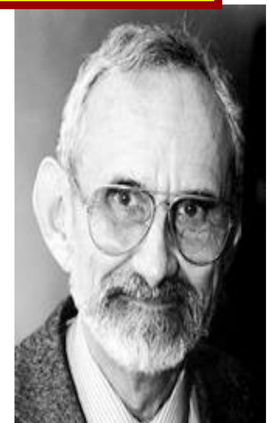

Allotropes of Carbon Materials
Carbon Nano-particle
Fullerenes
Carbon nanotubes
Graphene
Hydrogen Atom
Hydrogen Molecule
Bonded Hydrogen
a_0
a_0
$a_0 = 0.357$ nm
Graphite
Amorphous carbon
Diamond

Six Giants of carbon materials

1985 – Fullerene (1996)

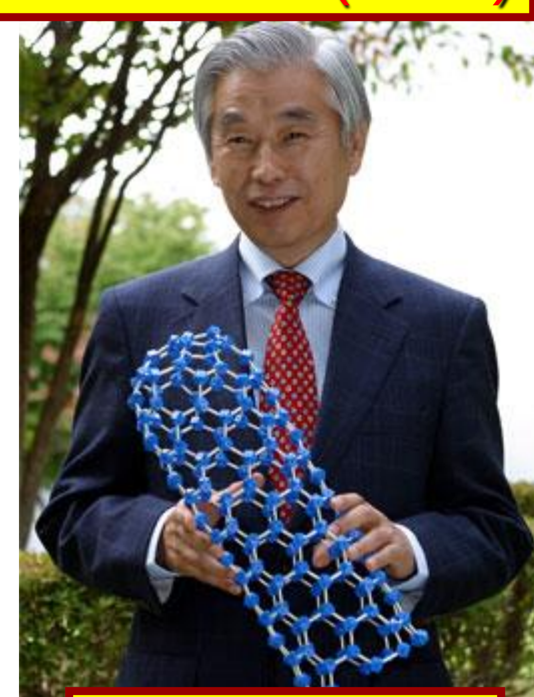






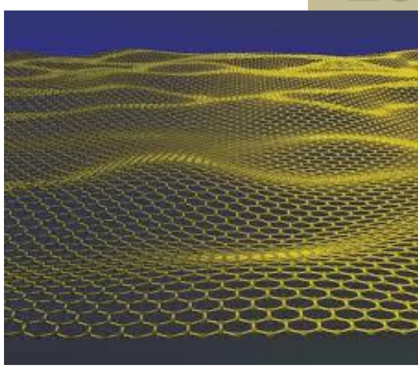
H. W. Kroto, R. E. Smalley and R. F. Curl

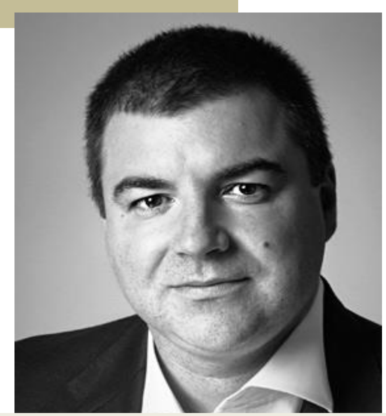
1990 – CNTs (1991)



Sumio Iijima

isolated
2004 – Graphene (2010)





Andre Geim Konstantin Novoselov

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

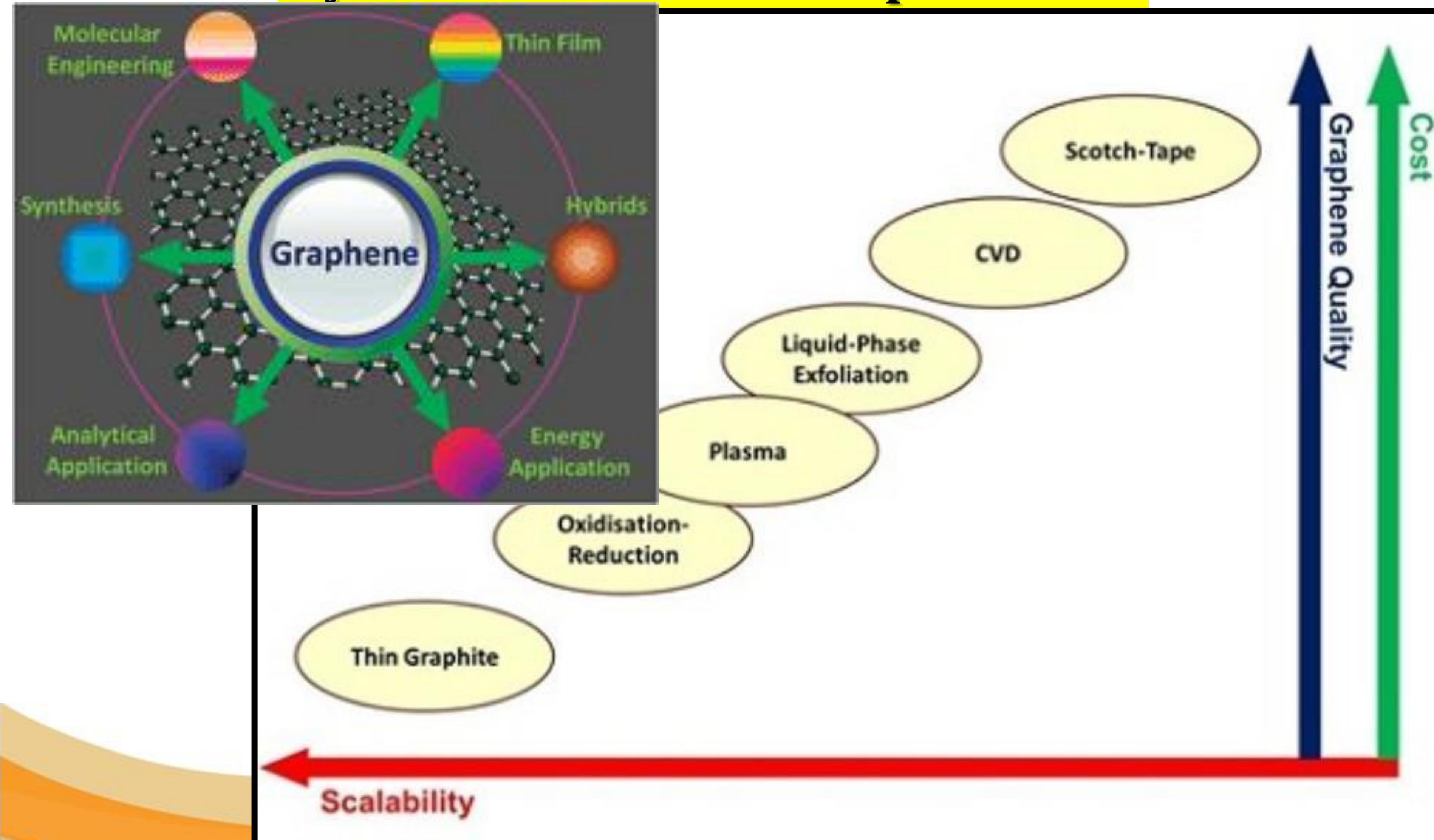
(highly stretchable, transparent and impermeable)

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

→Able to filter harmful organic materials

→ Superconductor

Synthesis Process of Graphene



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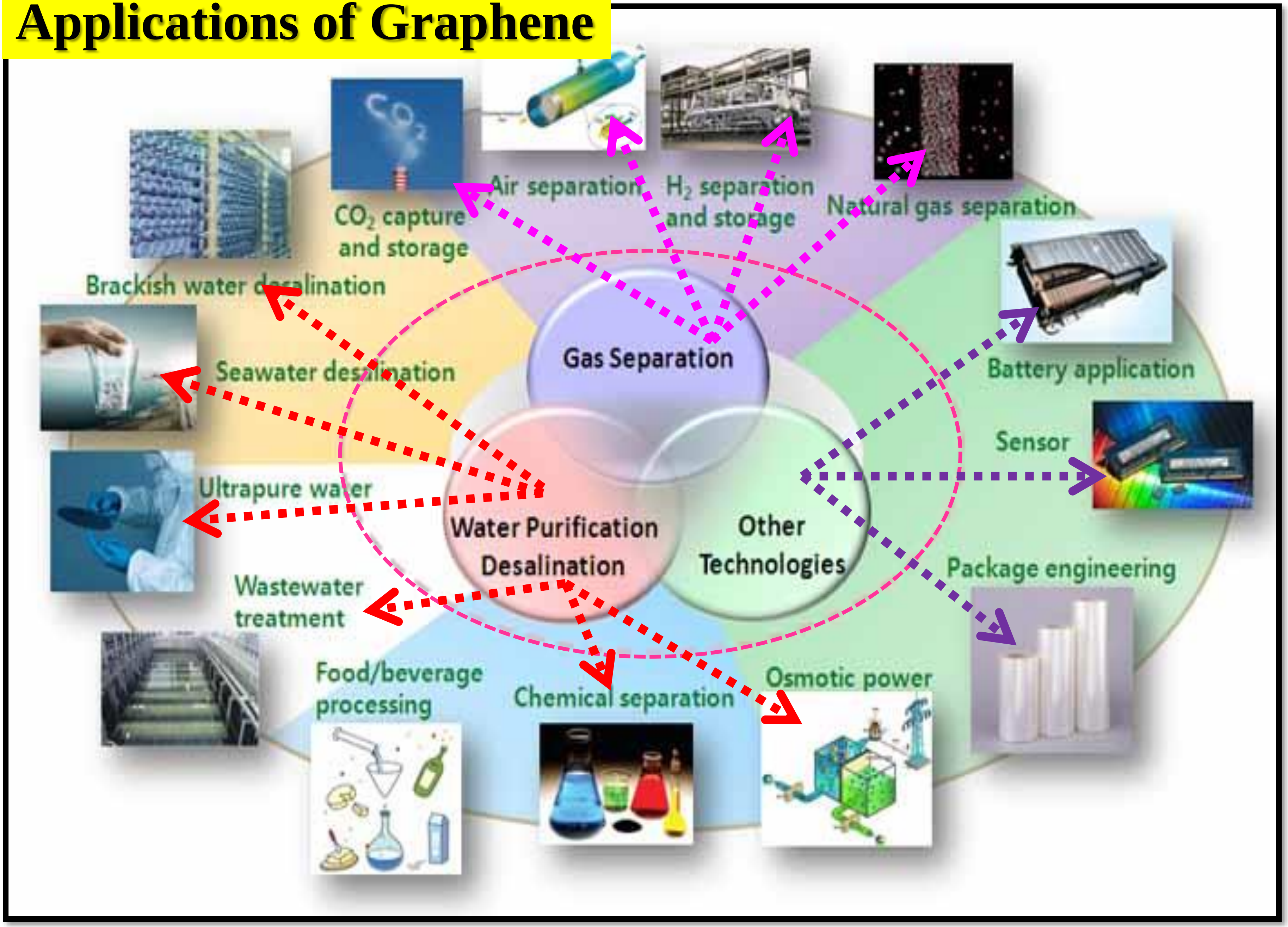
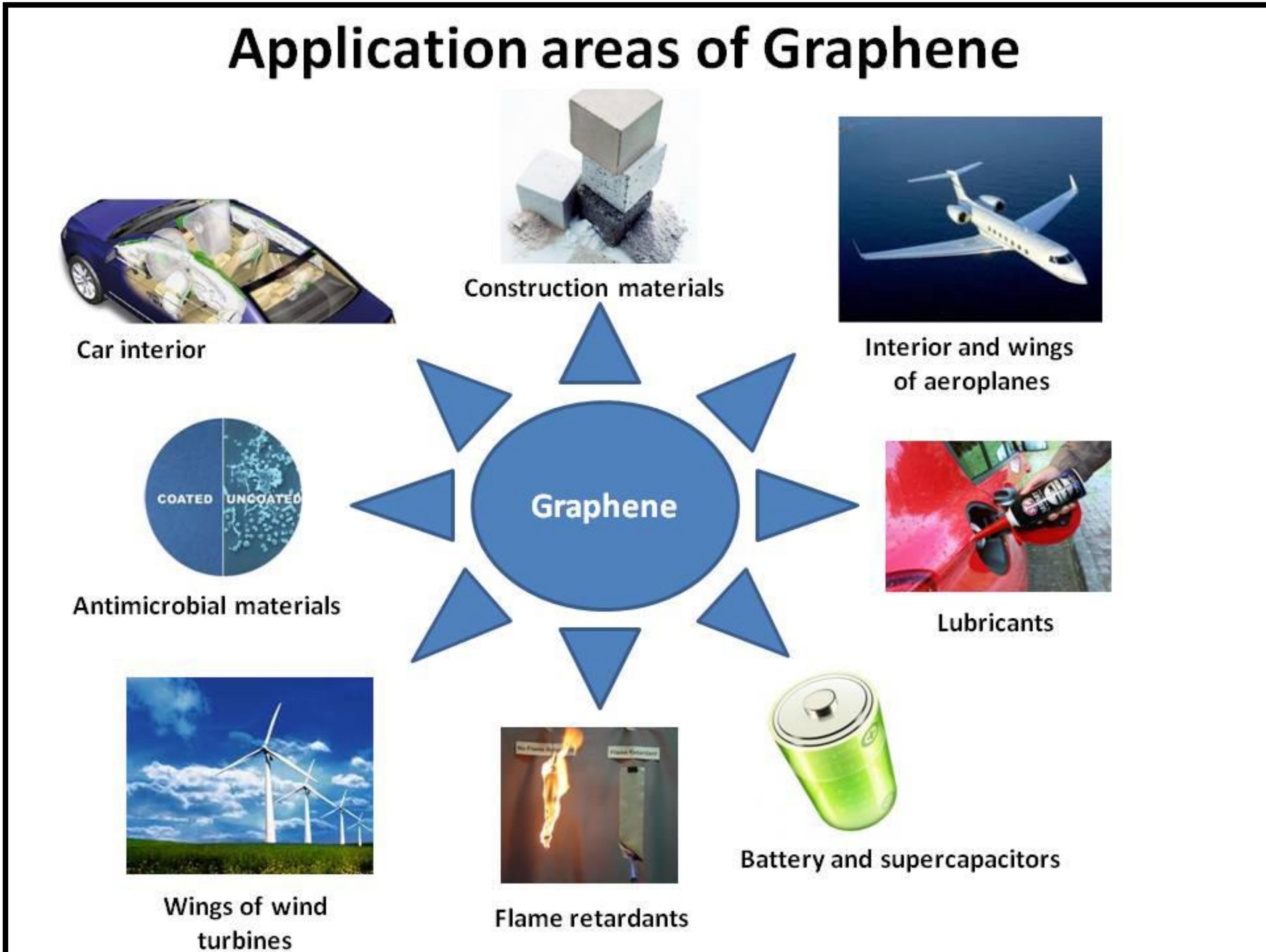
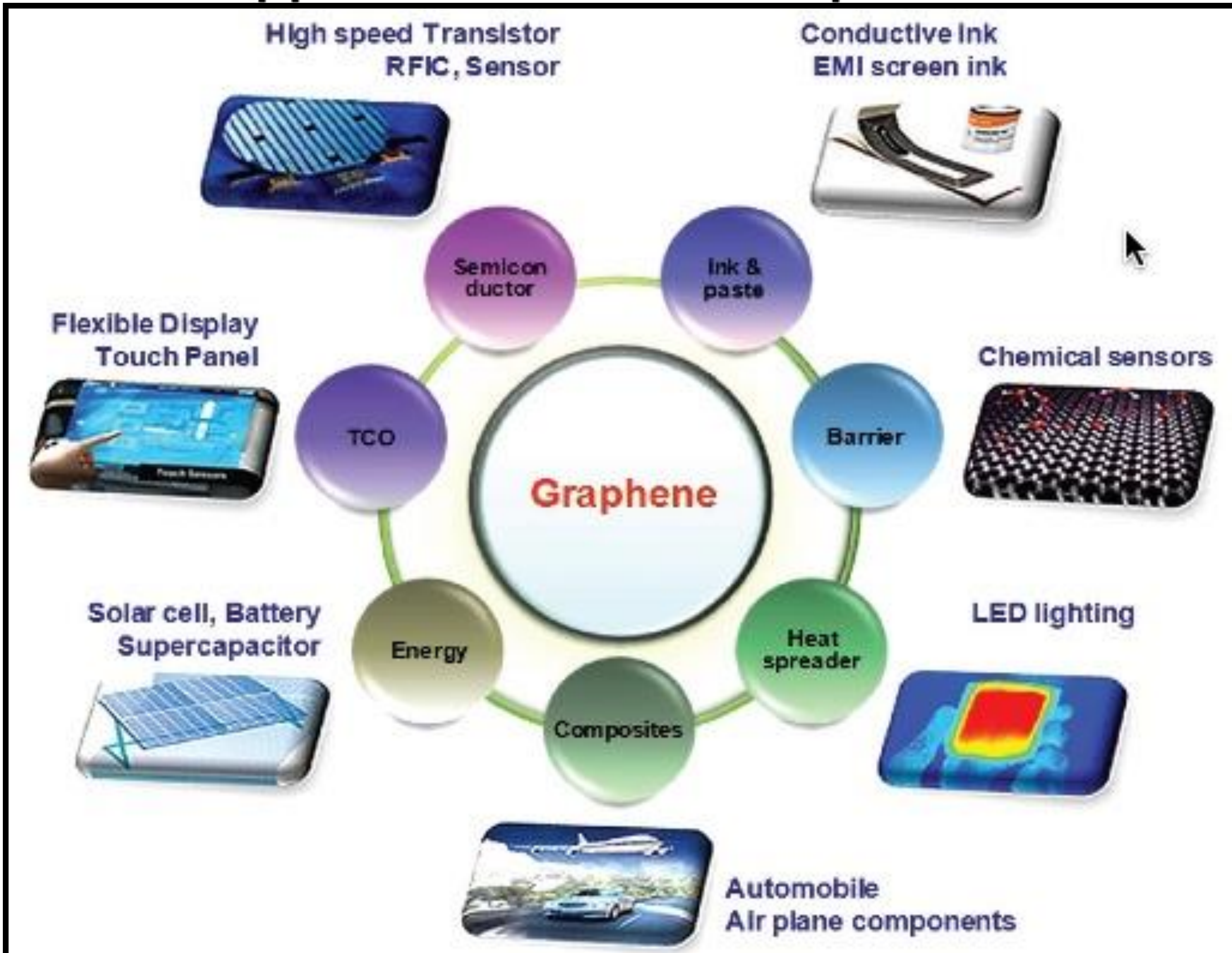
Applications of Graphene

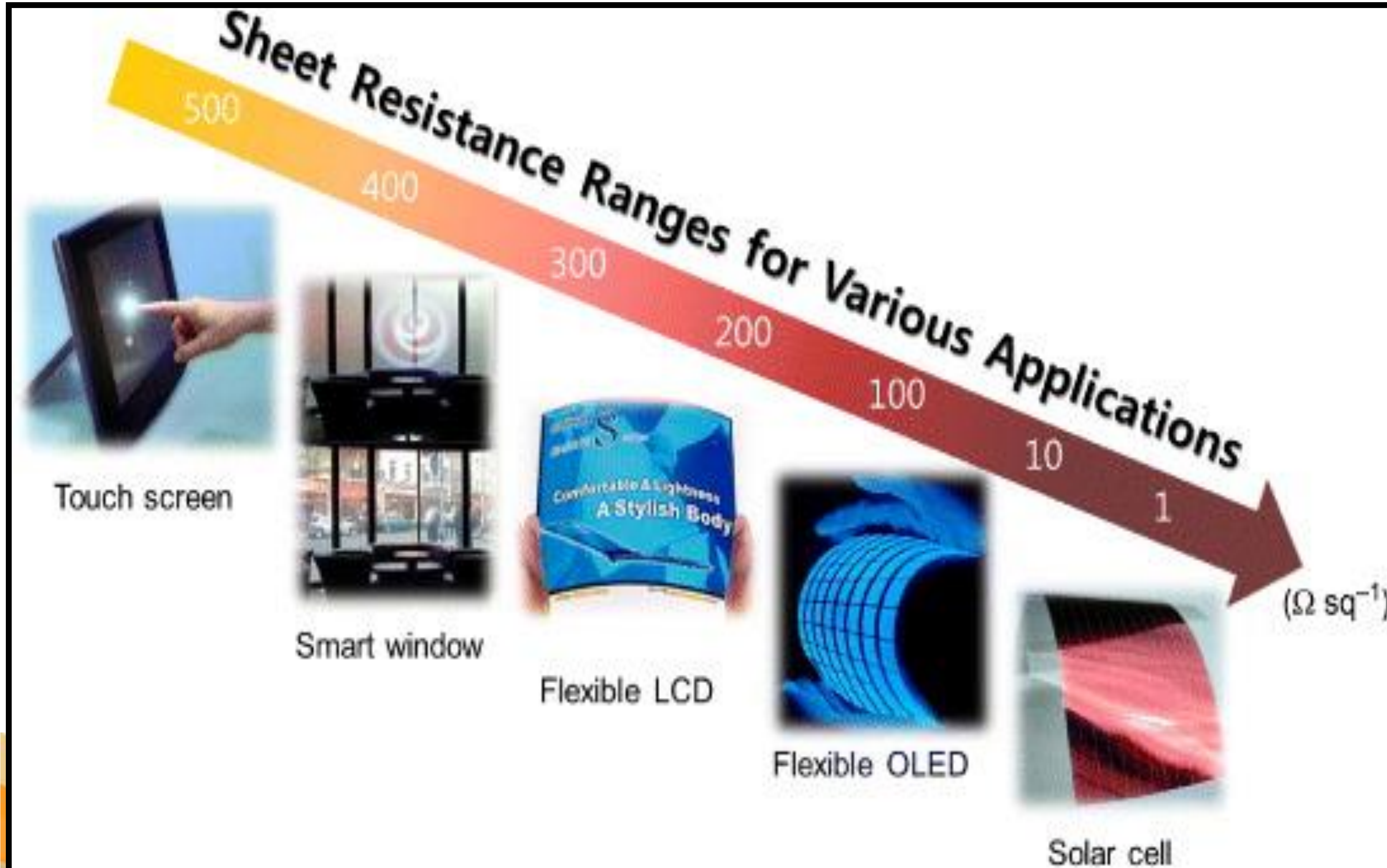




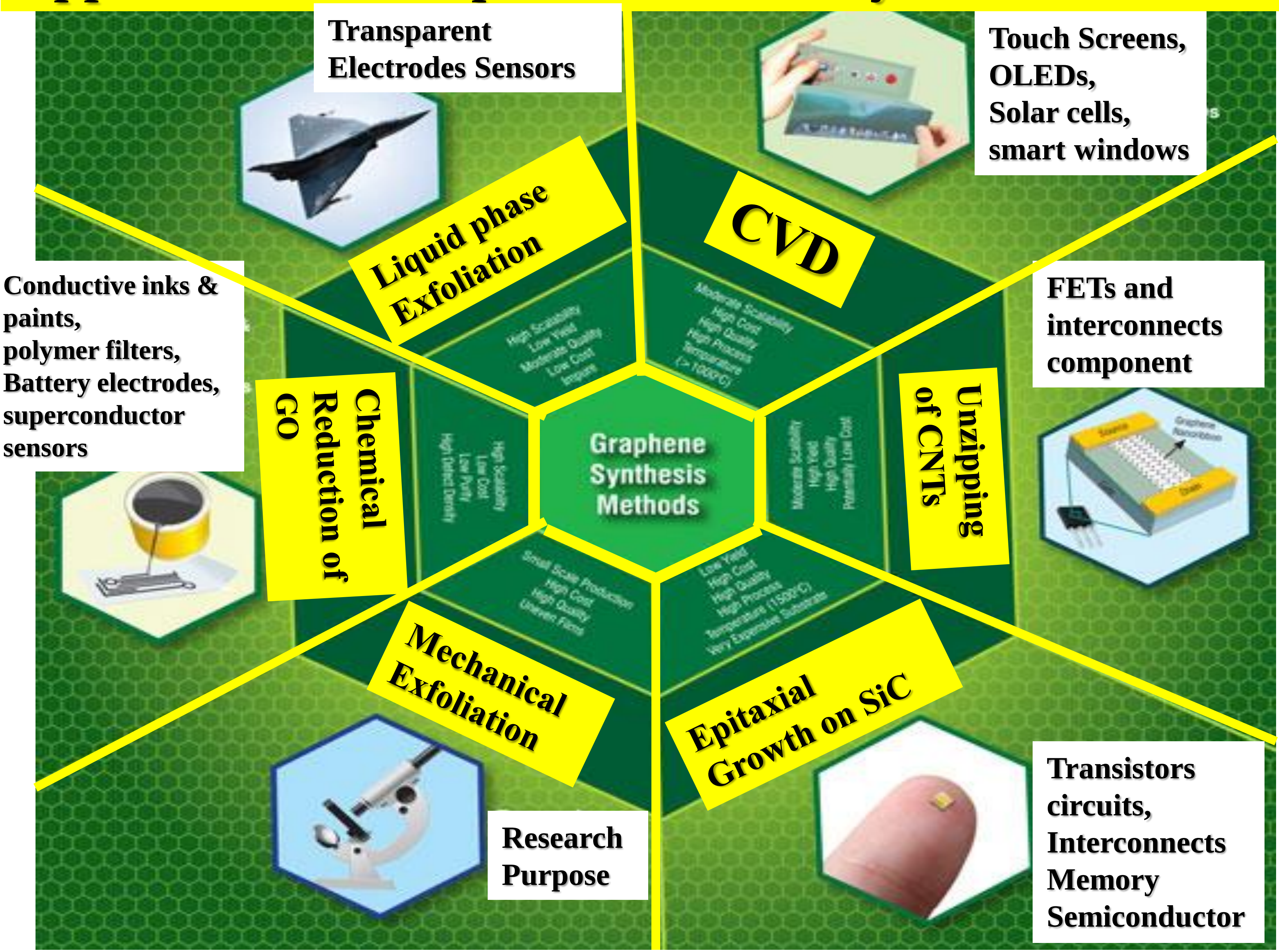
Application areas of Graphene
Construction materials
Car interior
Interior and wings of aeroplanes
Graphene
COATED
UNCOATED
Antimicrobial materials
Lubricants
Battery and supercapacitors
Wings of wind turbines
Flame retardants

Application areas of Graphene

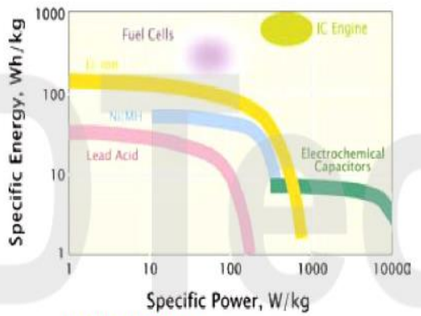


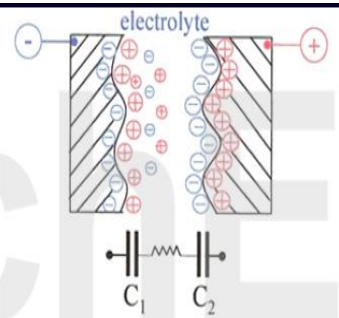

Sheet Resistance Ranges for Various Applications
500
400
300
200
100
10
1
(Ω sq⁻¹)
Touch screen
Smart window
Flexible LCD
A Stylish Body
Flexible OLED
Solar cell

Applications of Graphene based on Synthesis Process



Supercapacitors

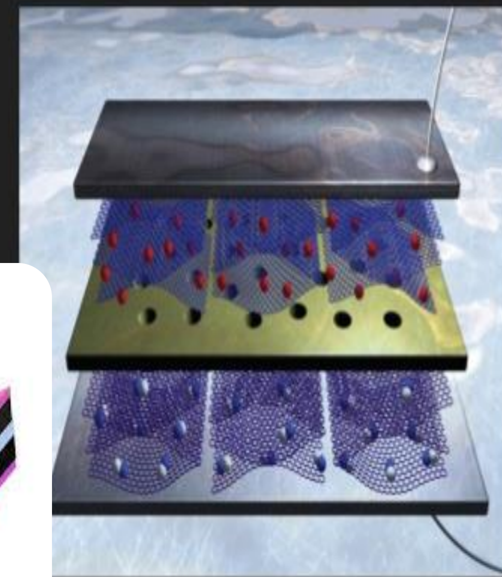


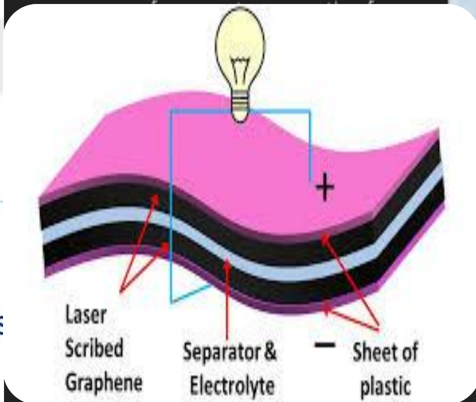


Advantages	Target Markets
✓ Fast power delivery but less energy density	✓ Mobile phones
✓ Wide temperature compliance range	✓ Camera
✓ Longer lifetime than Li-ion batteries	✓ Vehicles (bus, lifters, cars, trucks
✓ Simplicity	✓ Back-up system
	✓ Renewable energy

Energy Storage Devices

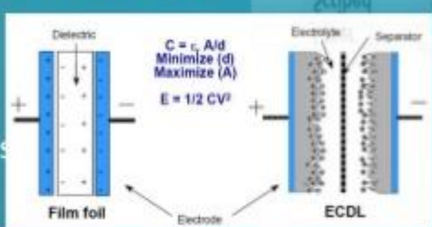
✓ Due to the extremely high





ULTRA/SUPER CAPACITORS

100 years old technology enhanced by modern materials based on polarization electrolytes, high surface area electrodes and extremely small charge seperation



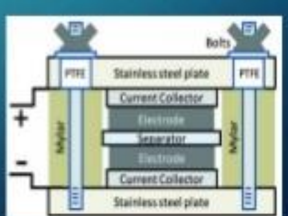
ECDL (Electro Chemical Double Layer) Capa

Graphene Advantages

* High surface area to weight ratio (2600 m^2 /g)
* High conductivity
* Measured specific capacitance 135 F/g

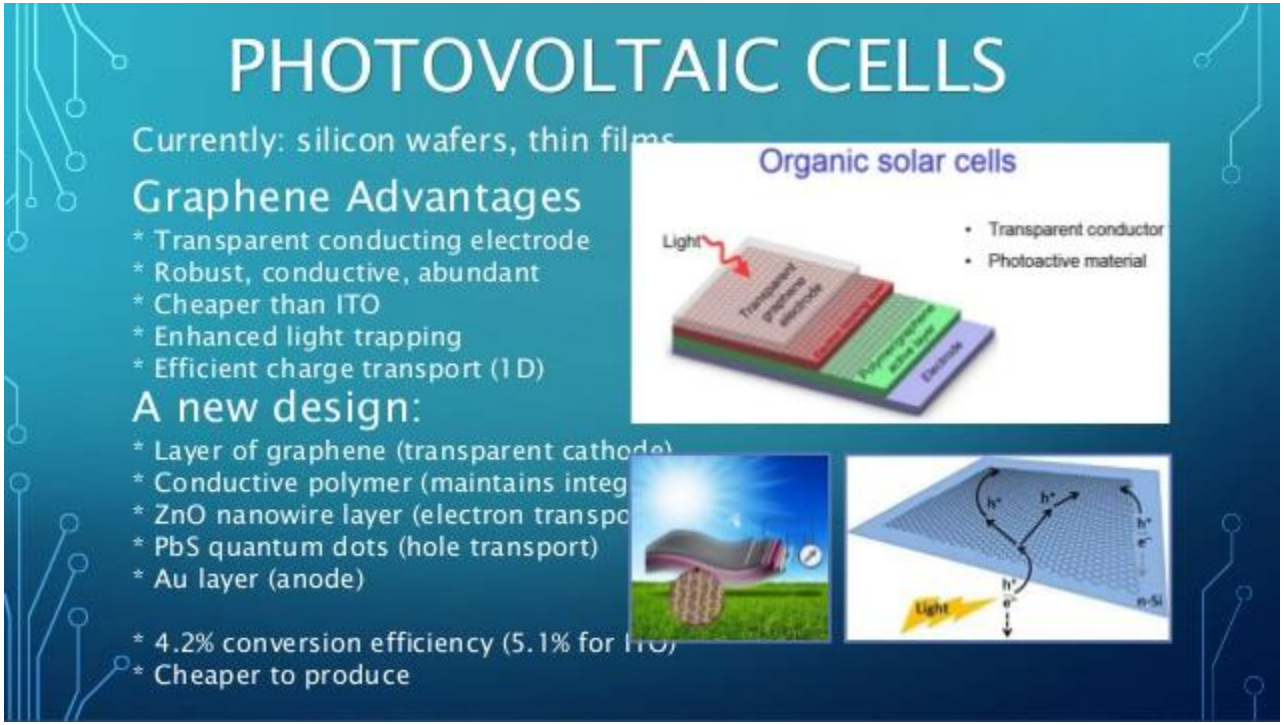
Uses

* Electric vehicles
* Backup powering
* High power capability
* Cell phones

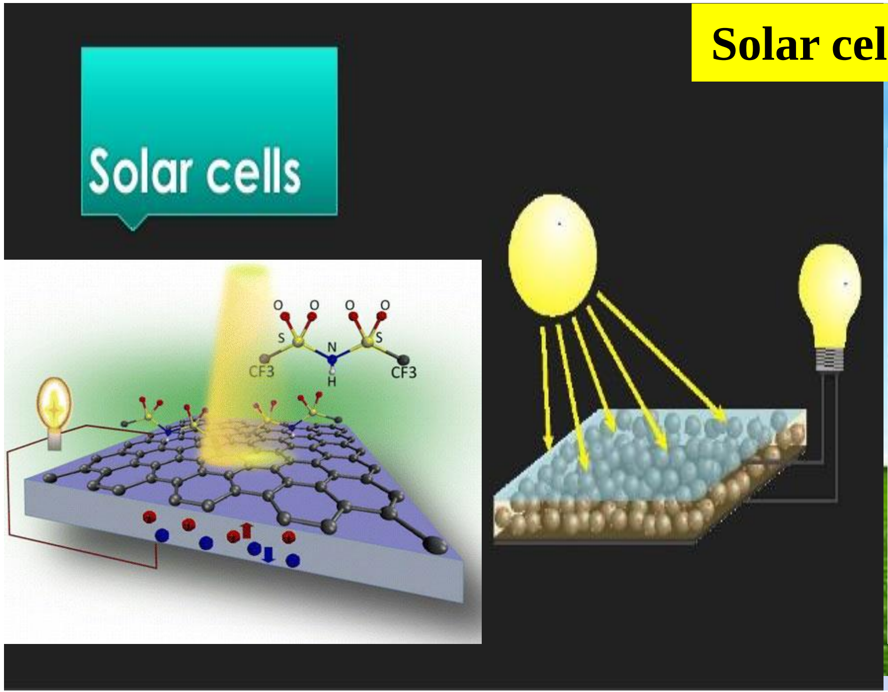


Super Capacitor Model

Supercapacitor Markets



Solar cell / Flexible solar cell / Solar panel



MAJESTIC FUTURE

- Advancements in touch screens

It is practically transparent and a good conductor

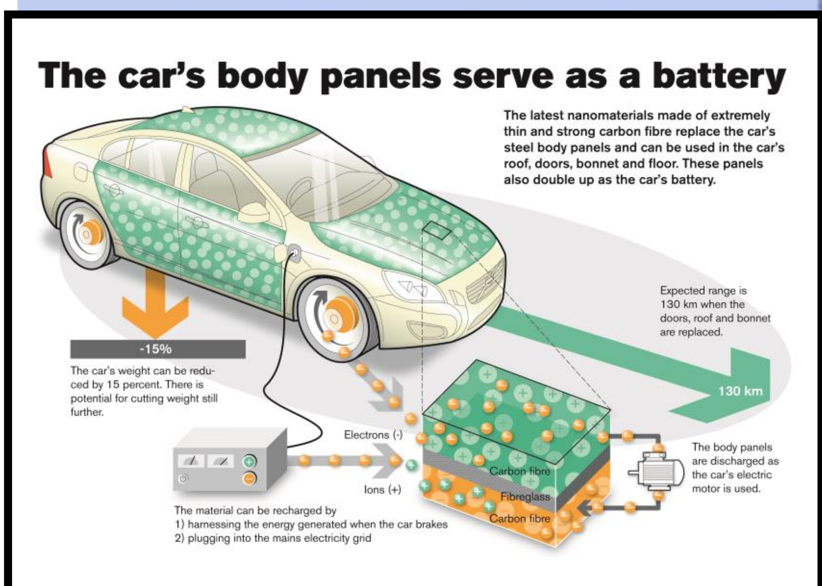
Transparent-Flexible Touch Screen

Electronics Engineering

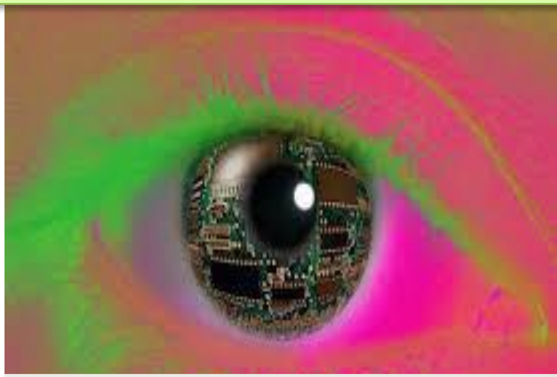
- Will definitely replace silicon and germanium as device material.
- Conducting material on PCBs.
- Single molecule sensors
- Touchscreens
- Graphene transistor.
- Graphene integrated circuits.
- Graphene chips.

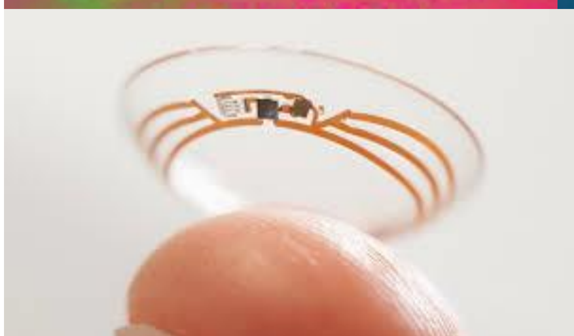
Mechanical engineering

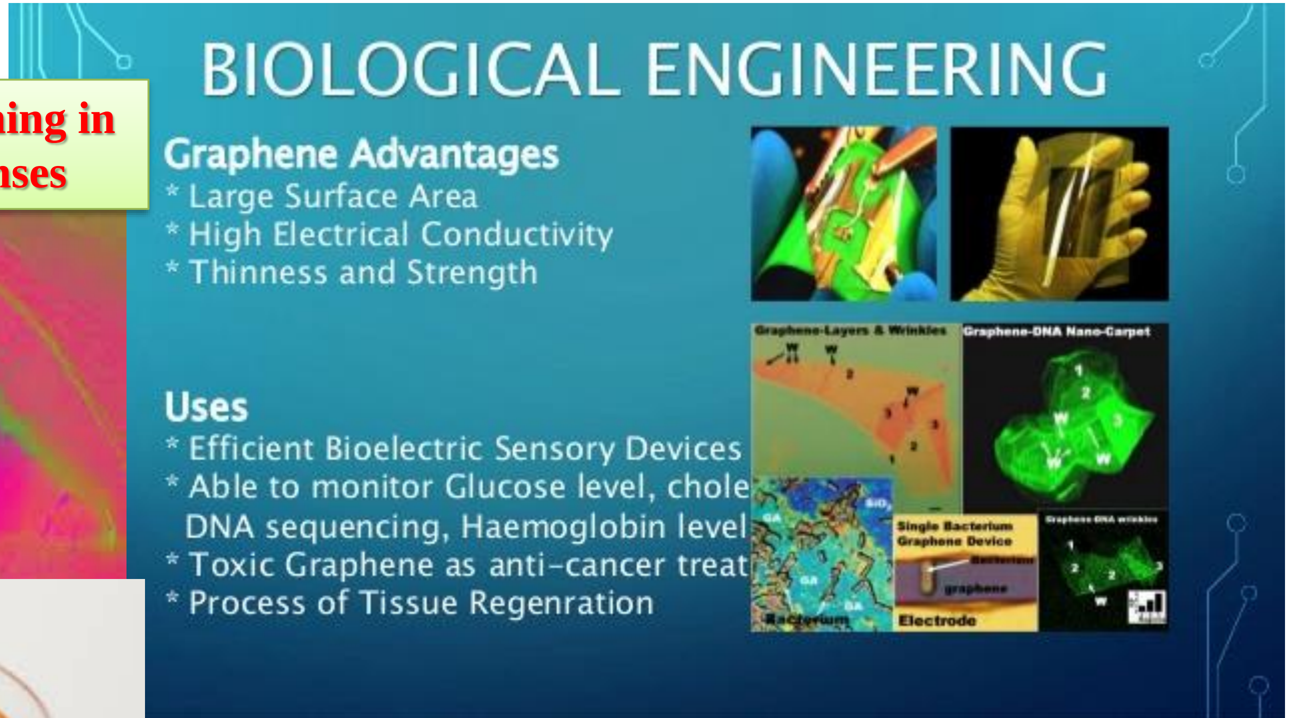
- In Manufacturing process as Manufacturing material.
- As a composite material for machines ,cars.
- Defense.
- Airplanes, space shuttles , satellite.

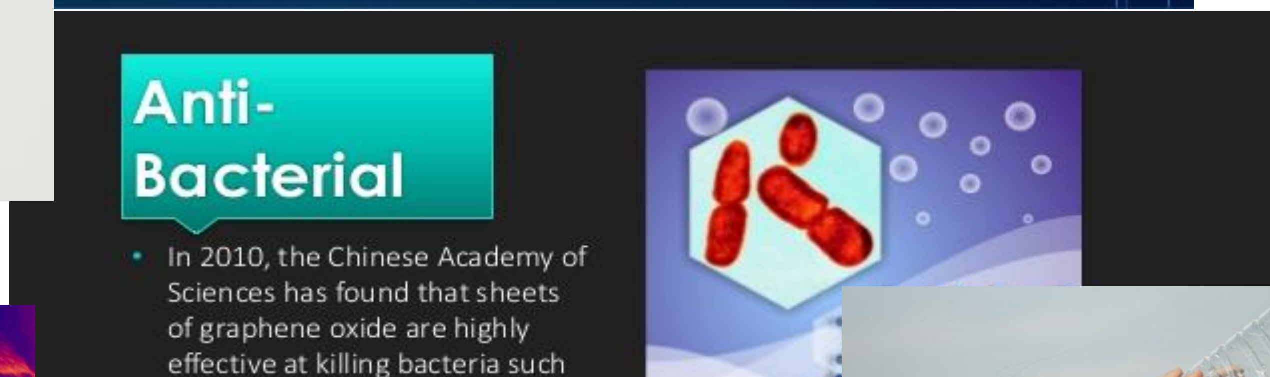


Superhero Vision Coming in Graphene Contact Lenses

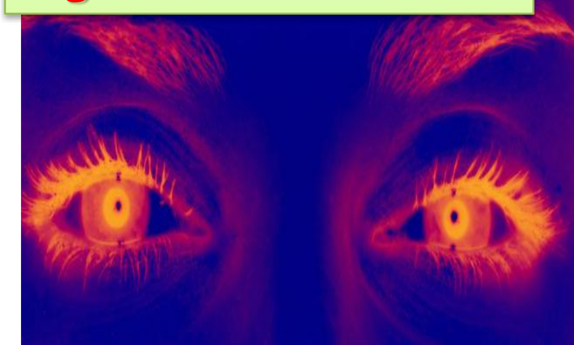




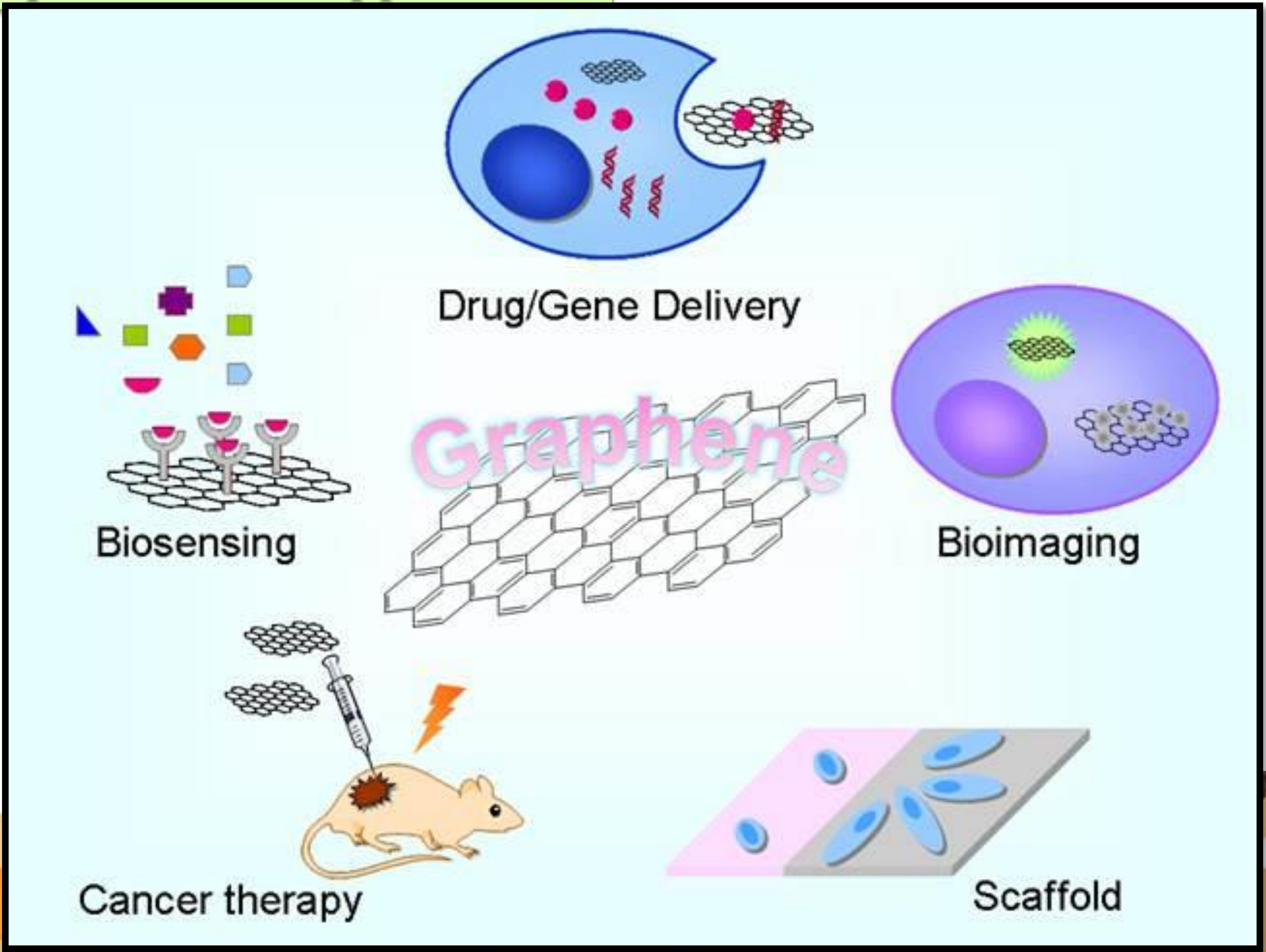




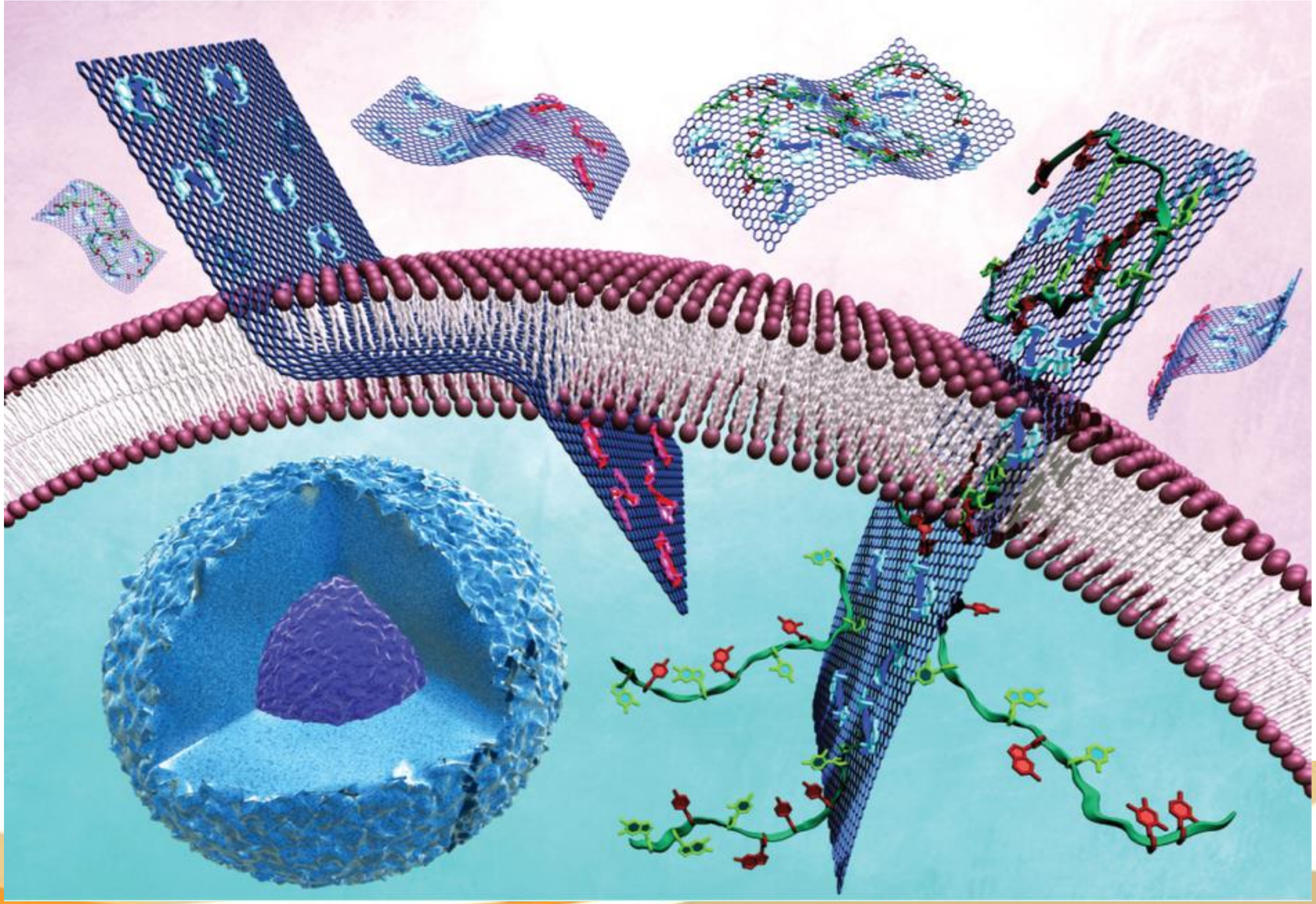
New sensor could make night vision



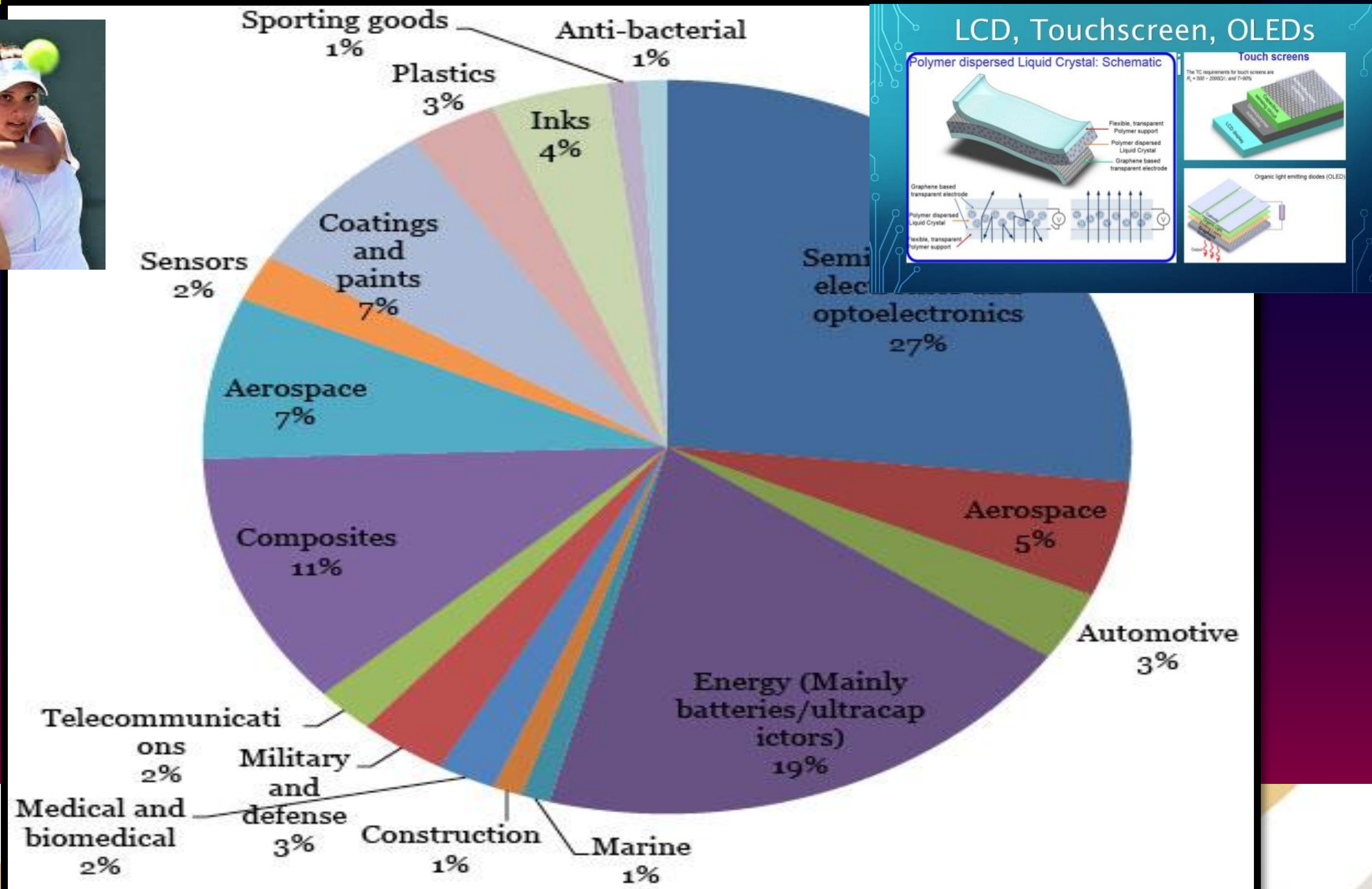
Graphene in Bio-applications



Graphene in drug delivery into the interior of a cell



Applications chart for Graphene companies



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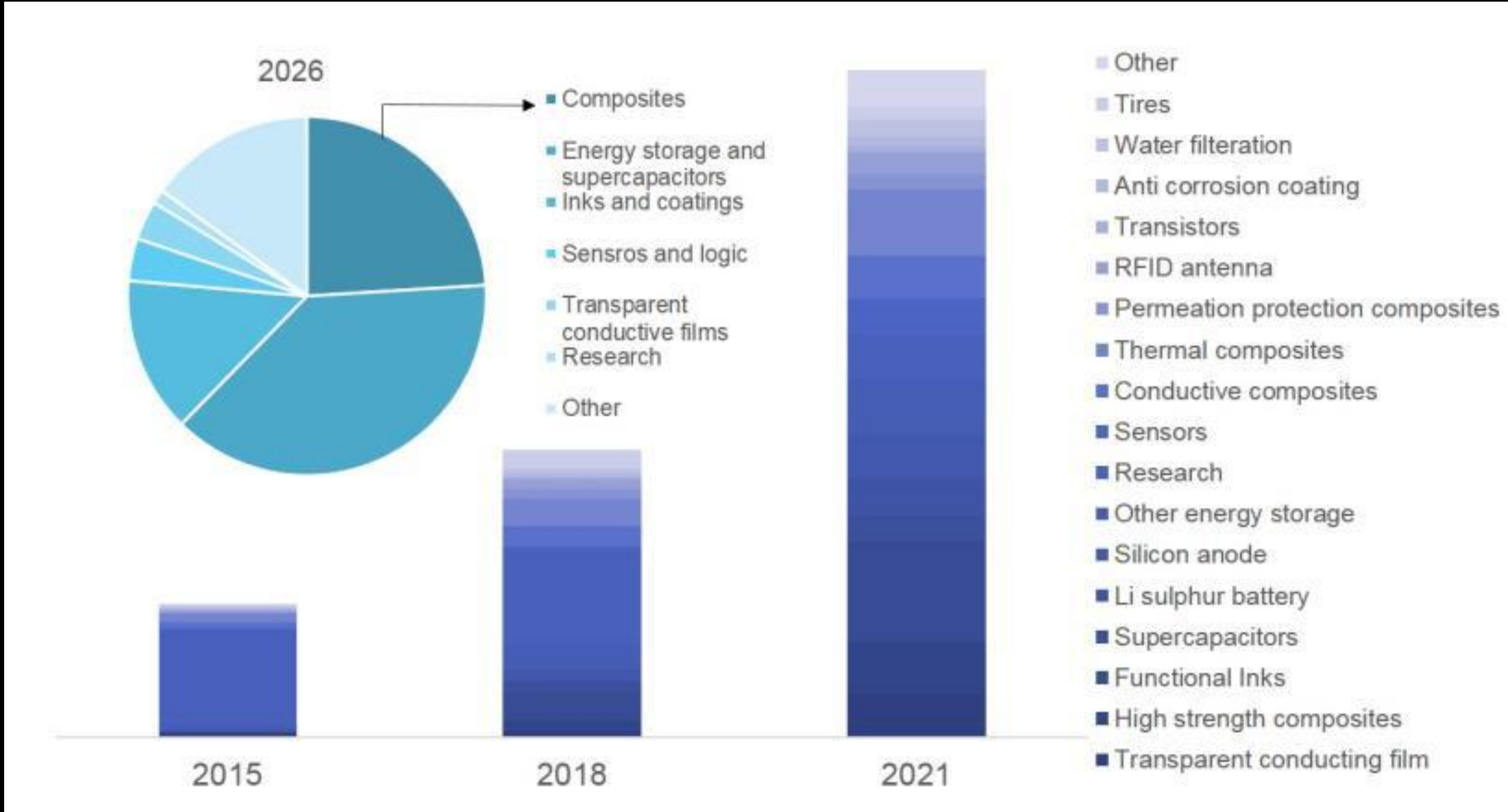
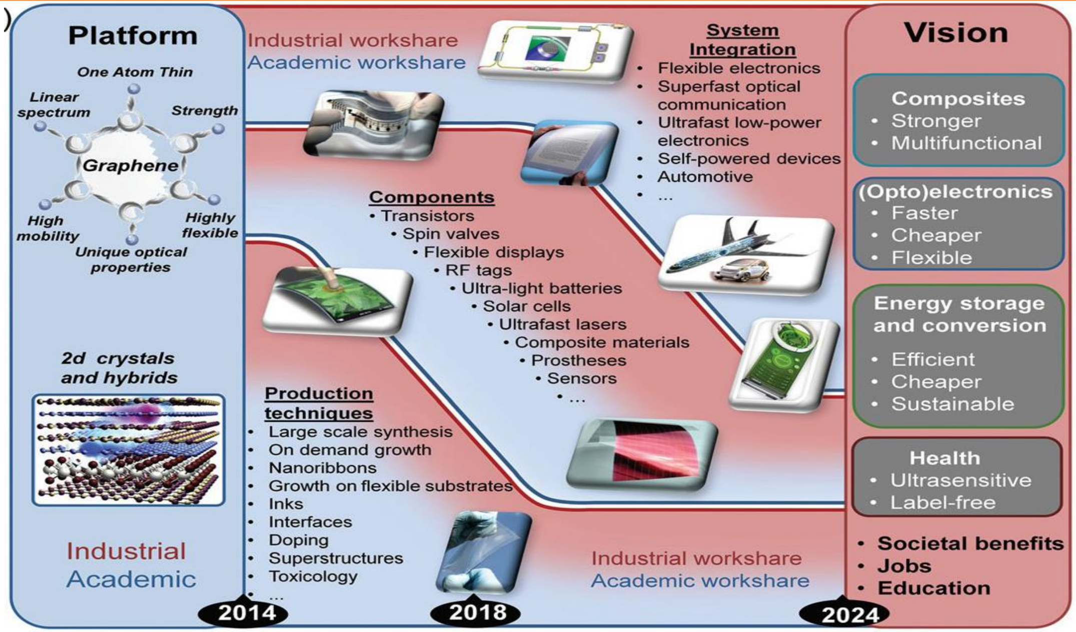
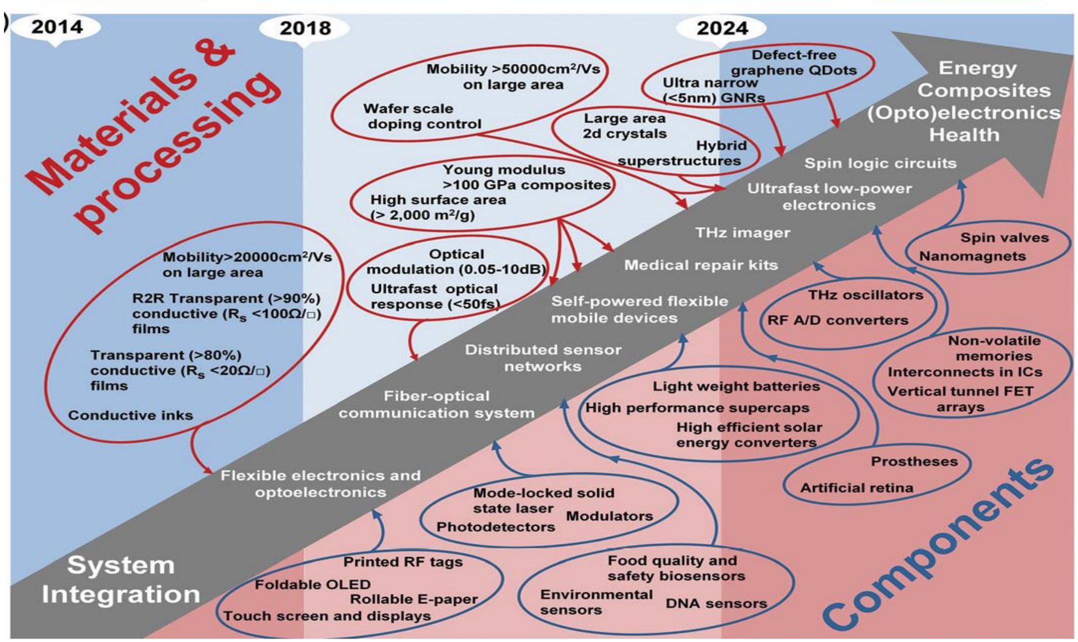
A roadmap for graphene

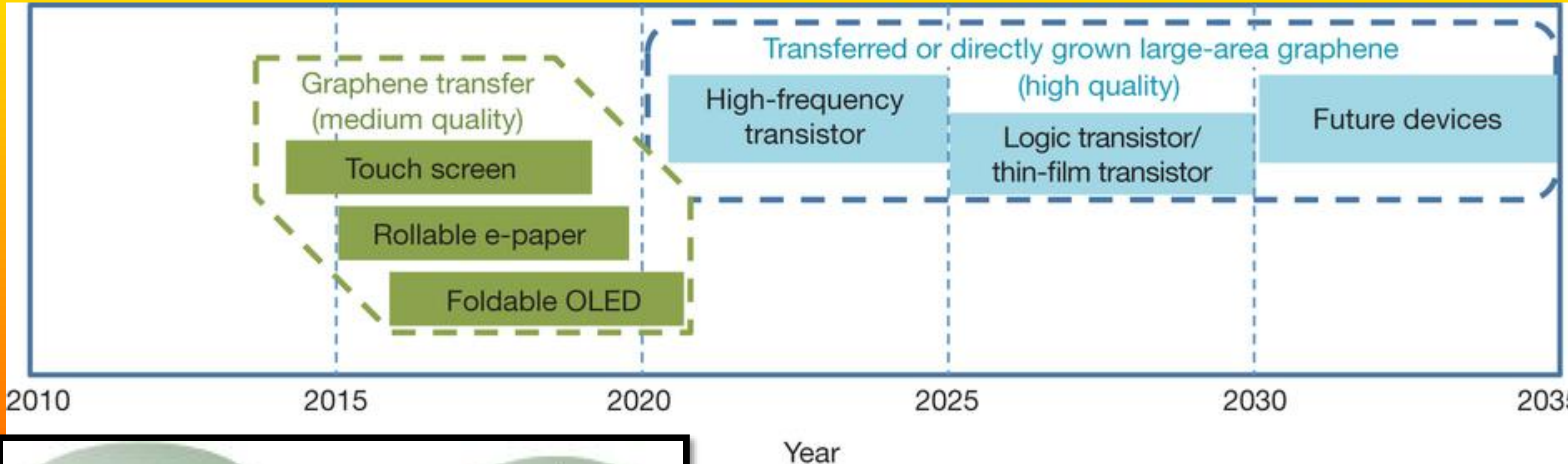


Vision – Future Applications of Graphene

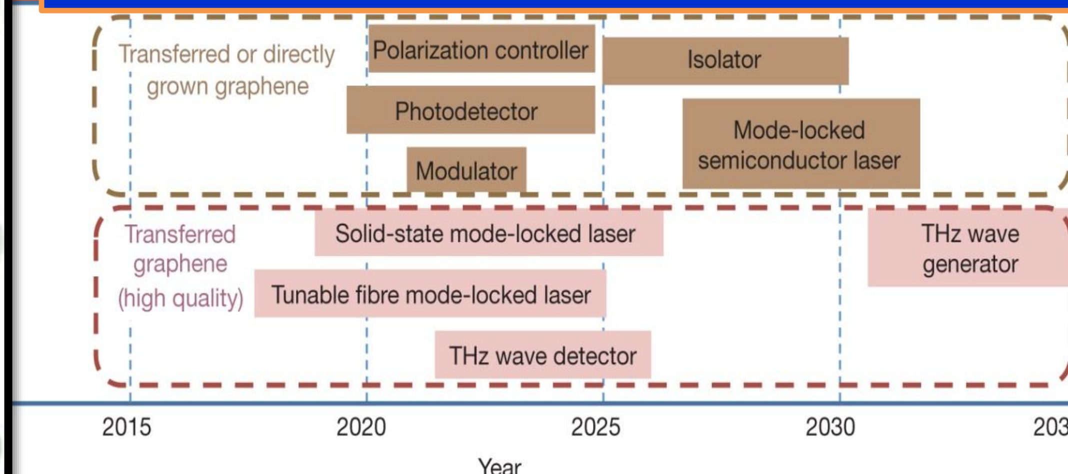




Vision-Graphene-based display and electronic devices



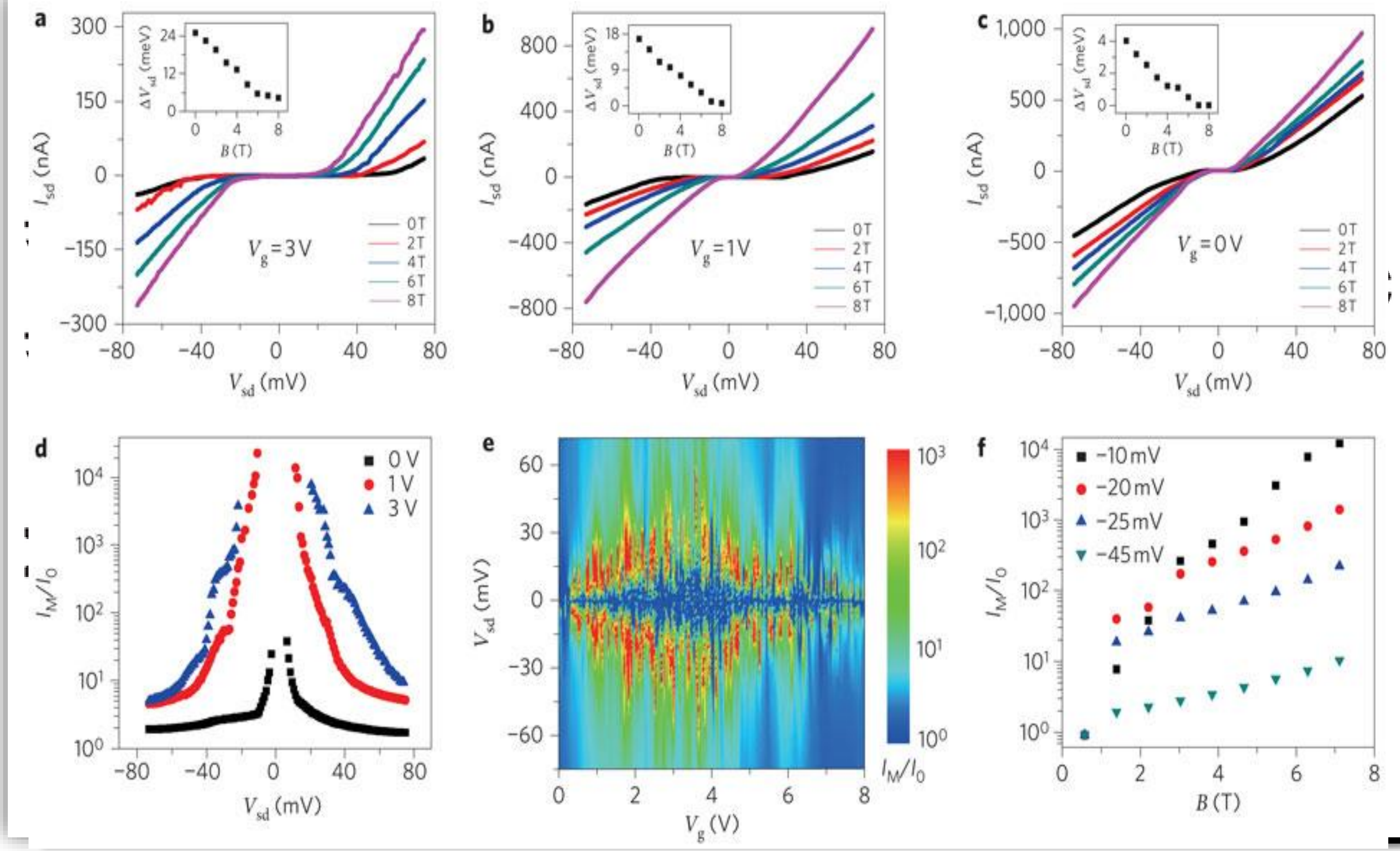
Vision-Graphene-based photonics devices



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

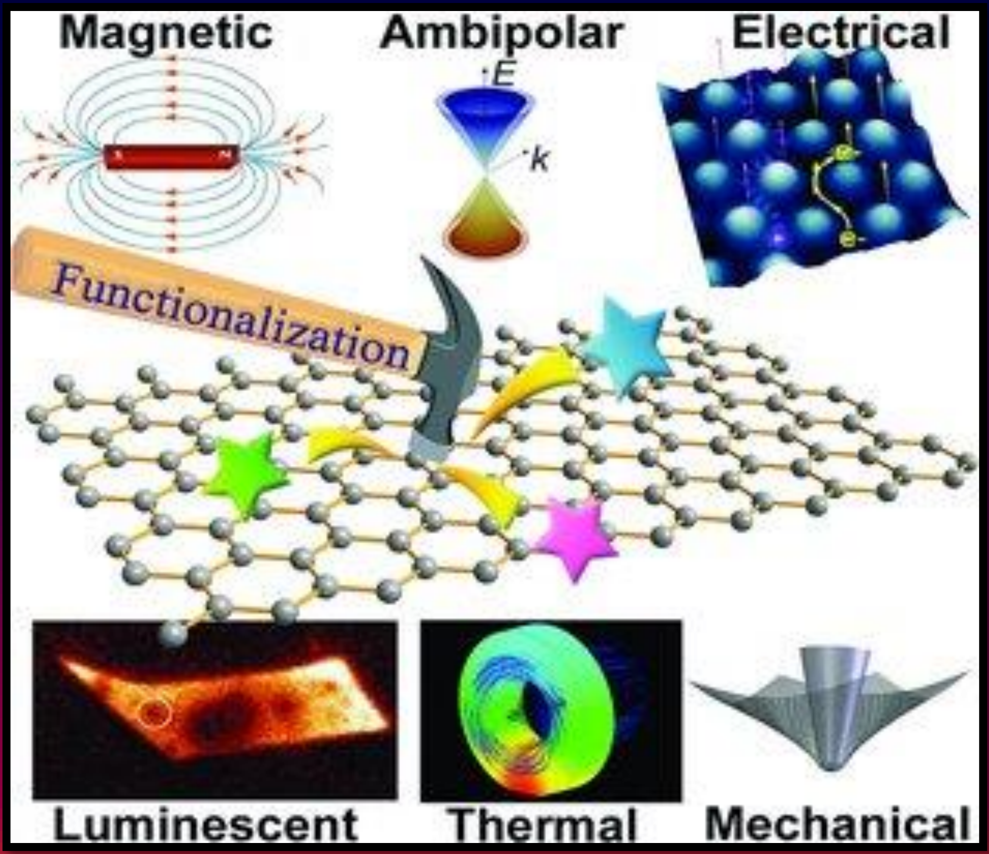
(Prototype Graphene Phone:within 3 years)

Magnetic properties



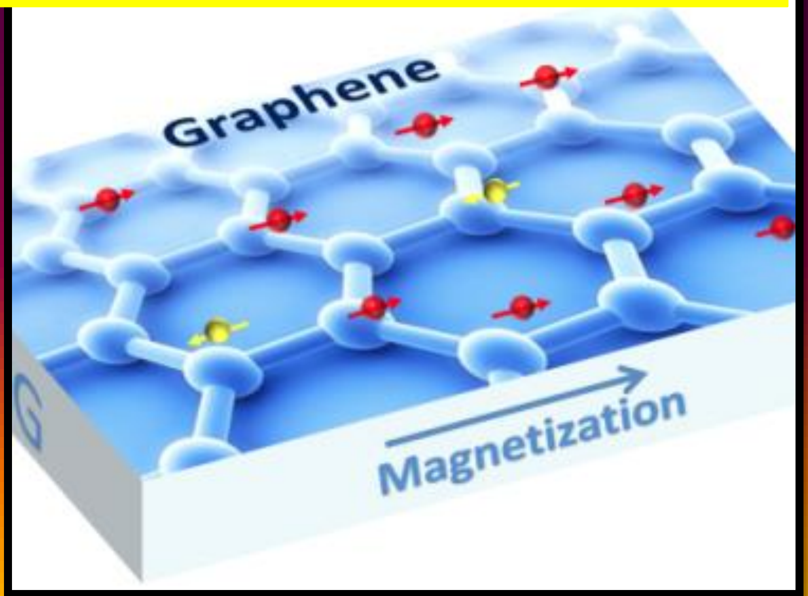
Magnetic devices using Graphene

Functionalization of Graphene by Hydrogen, Silicon and Nitrogen, Iron, Gold, Cobalt-----



Why Carbon / Graphene??

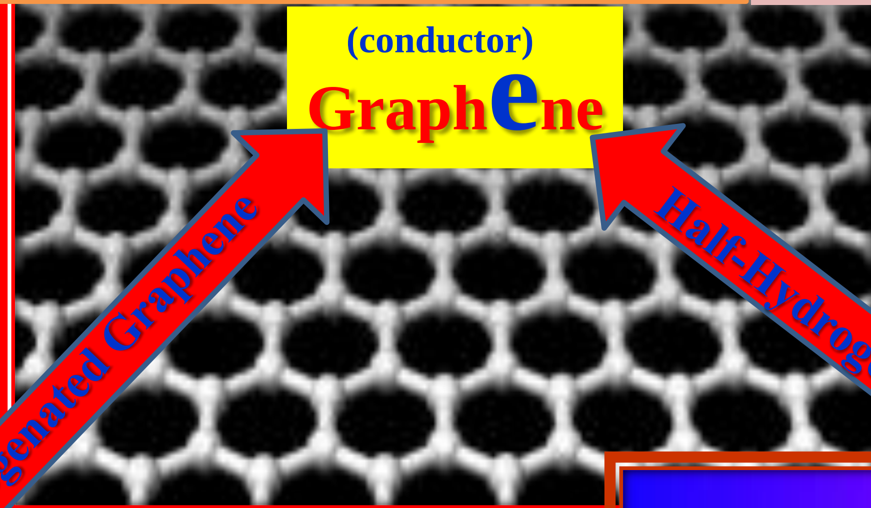
Carbon-based materials are very promising for spintronic applications due to their weak spin-orbit coupling and potentially providing a long spin life time



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

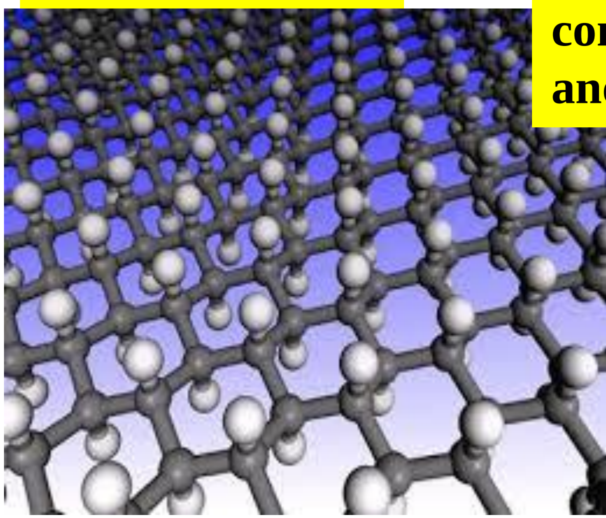
Fully Hydrogenated Graphene

Half-Hydrogenated Graphene

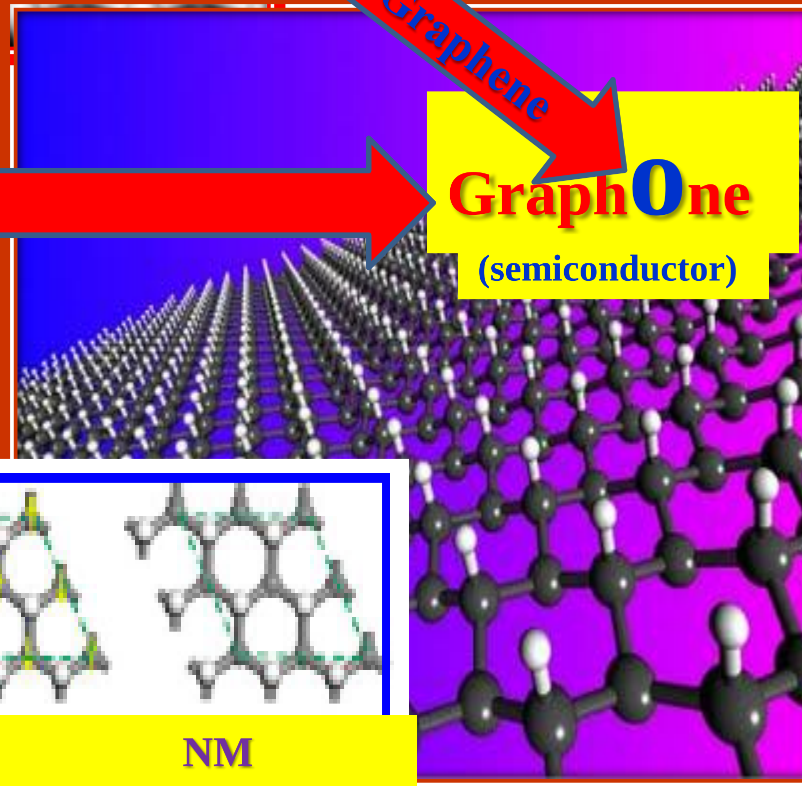
Conversion $sp^2 \rightarrow sp^3$

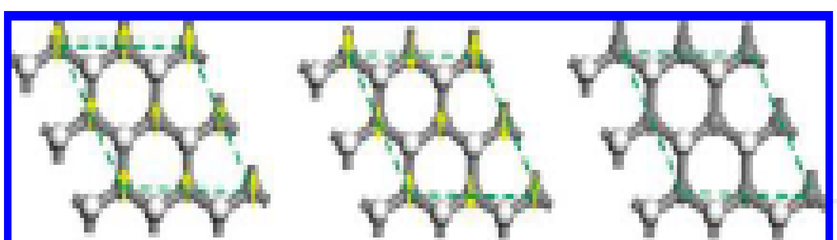
by removing conduction π-bands and opening band gaps

(Insulator)
GraphAne



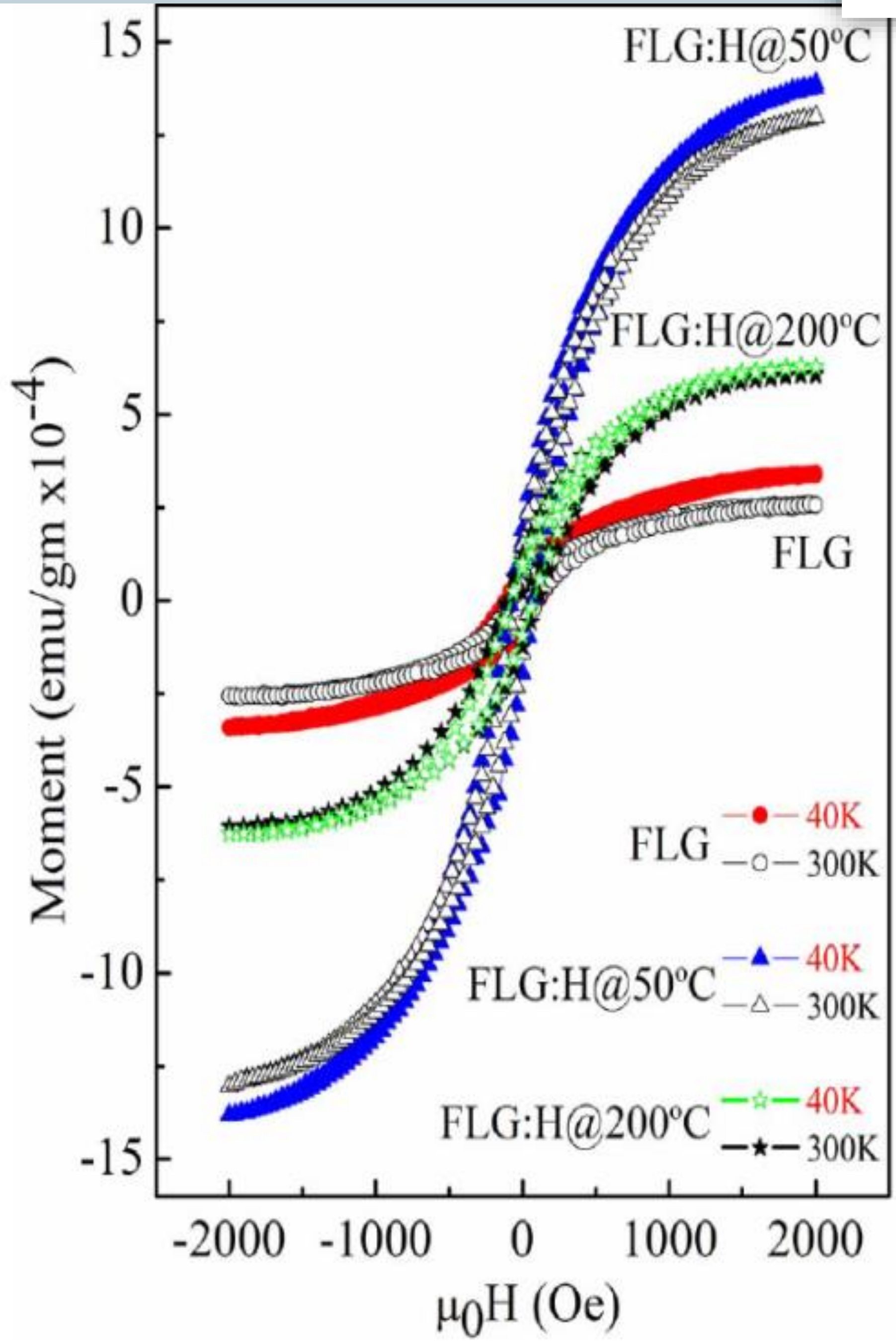
GraphOne
(semiconductor)

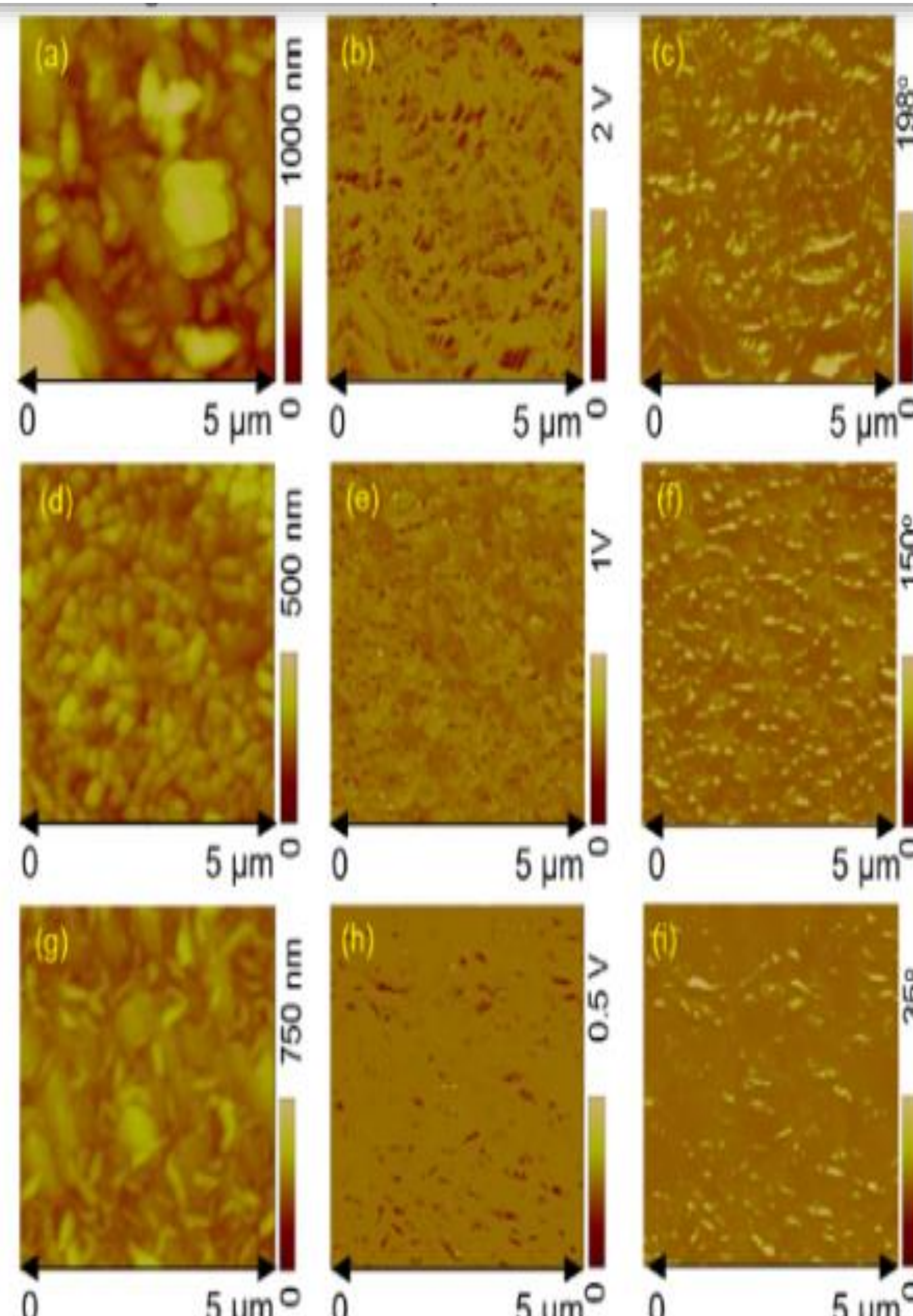




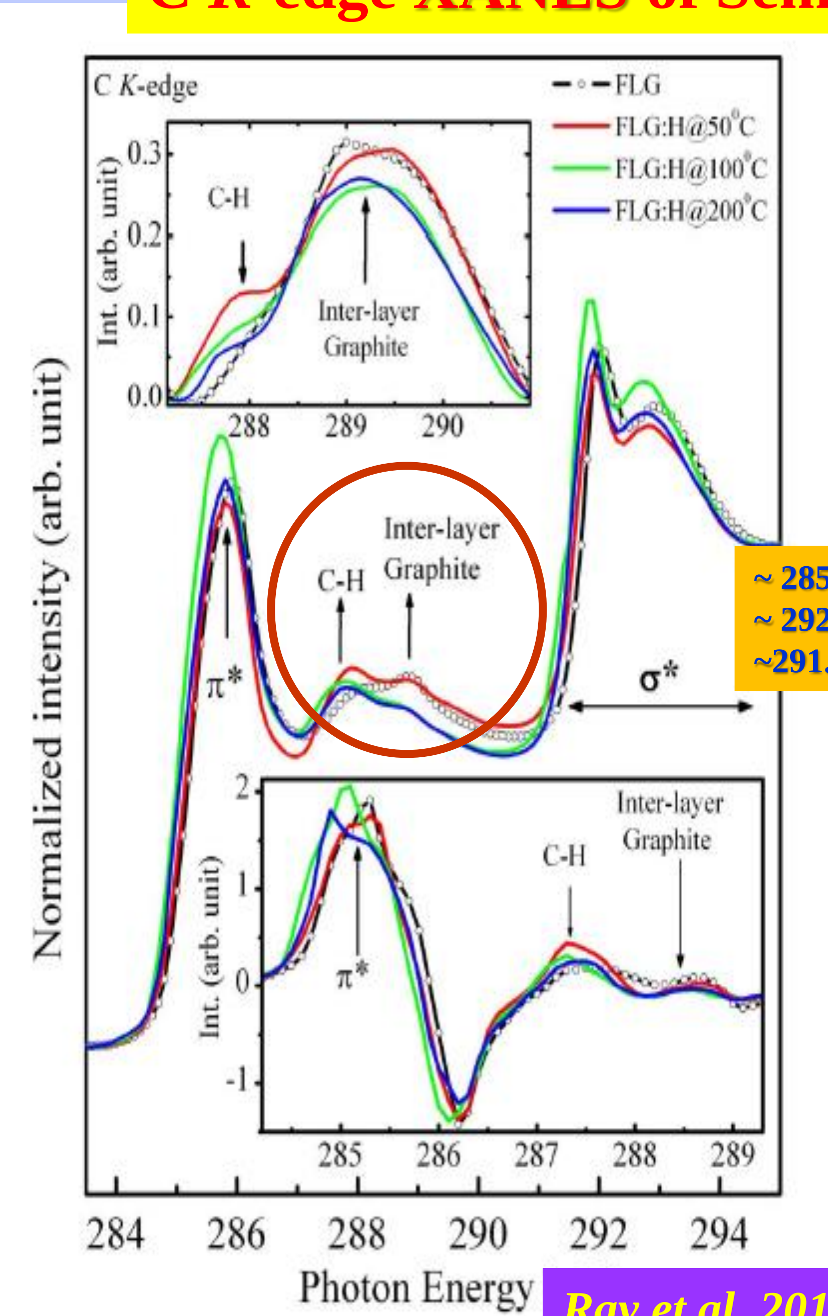
FM	AF	NM
$m=4\mu_B, E=0$;	$m=0\mu_B$, $E=0.15$;	$m=0\mu_B$, $E=0.49$

SCIENTIFIC REPORTS | 4 : 3862 | DOI: 10.1038/srep03862

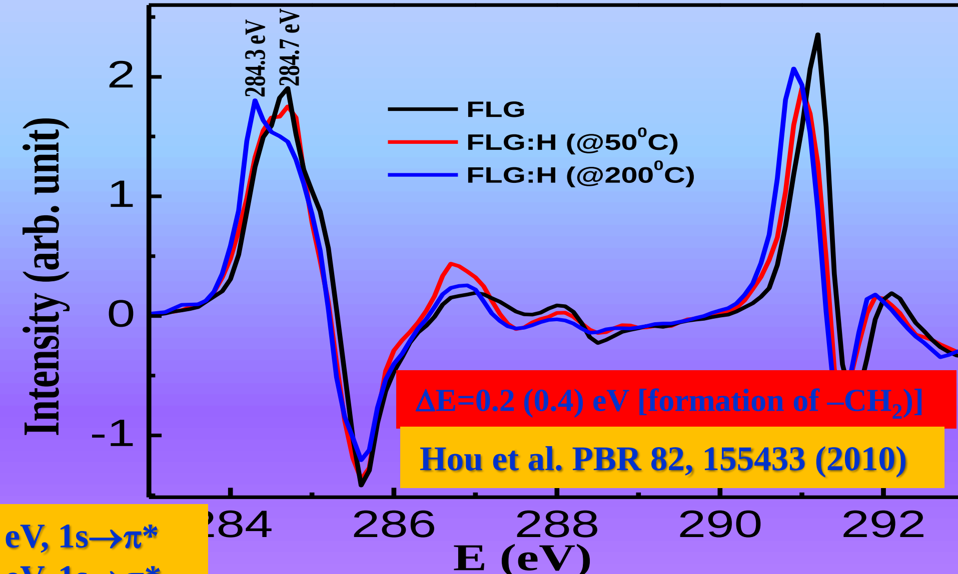




C *K*-edge XANES of Semi-hydrogenated Graphene Sheet



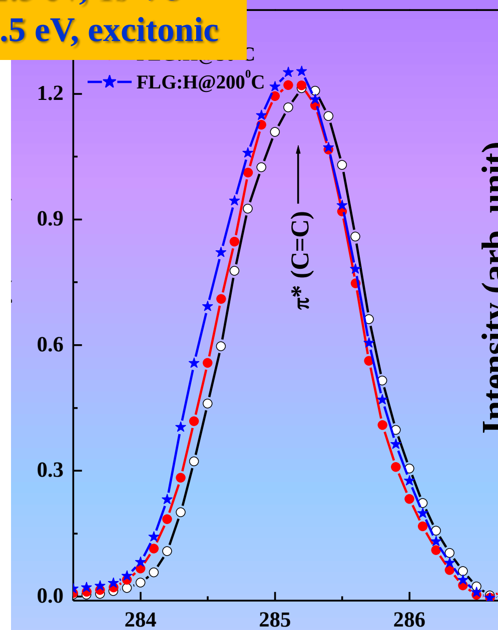
Ray et al. 2014 (Sci Reports 4, 3862)

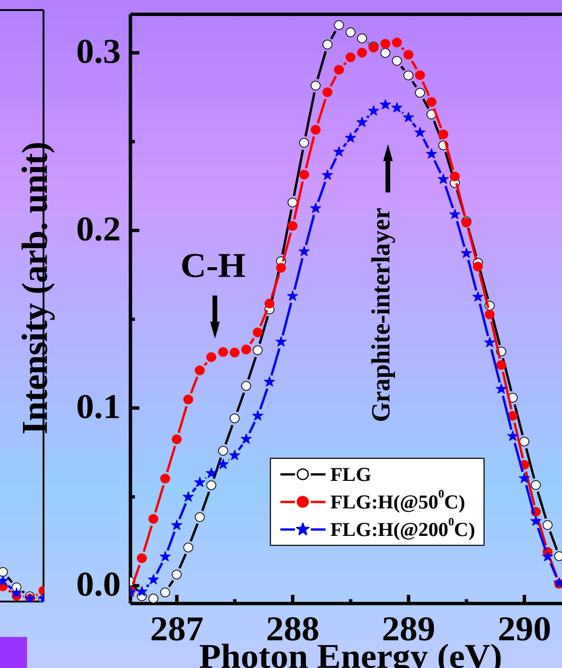


ΔE=0.2 (0.4) eV [formation of $-CH_2$)]

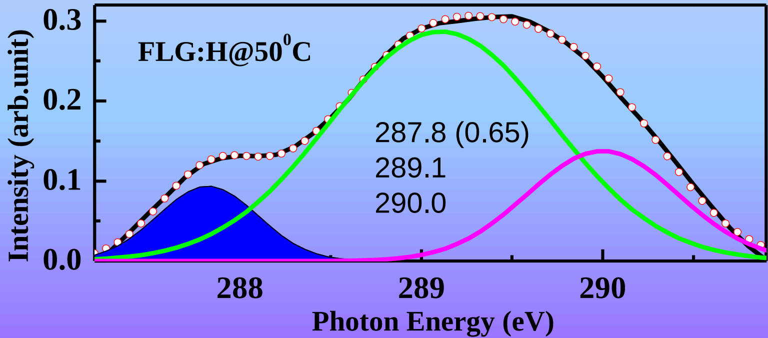
Hou et al. PBR 82, 155433 (2010)

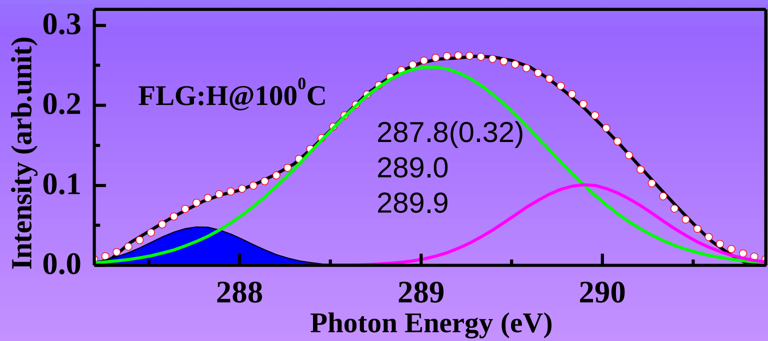
~ 285.1 eV, 1s→π*
~ 292.5 eV, 1s→σ*
~291.5 eV, excitonic

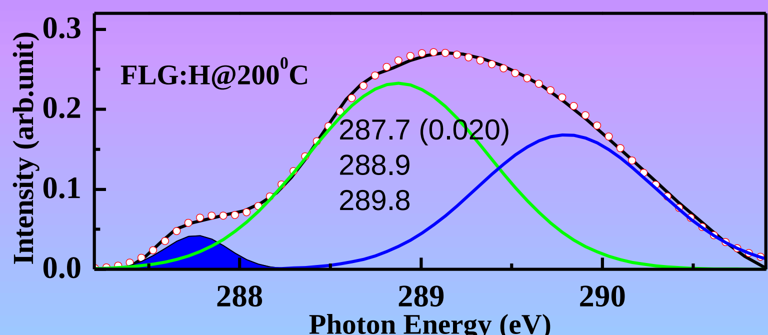




Determination of C-H content from C *K*-edge XANES spectra



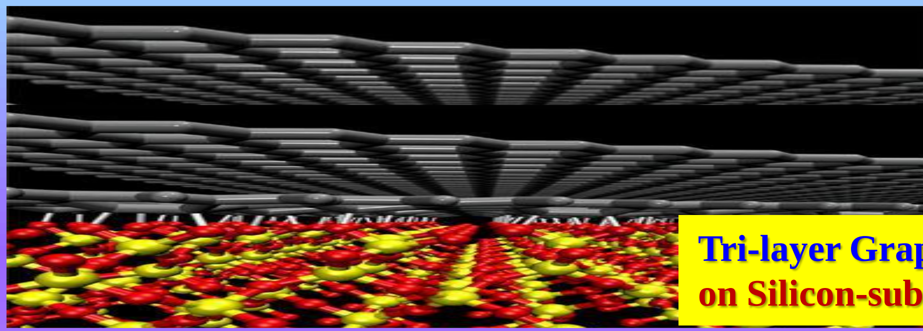




	C-H
FLG:H@50^{0}C	0.65 (287.8)
FLG:H@100^{0}C	0.32 (287.8)
FLG:H@200^{0}C	0.19 (287.7)

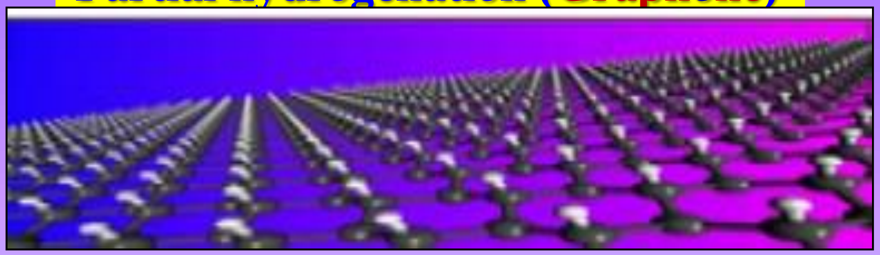
CH ratio

0.65 : 0.32 : 0.19 ≈ 6 : 3 : 2

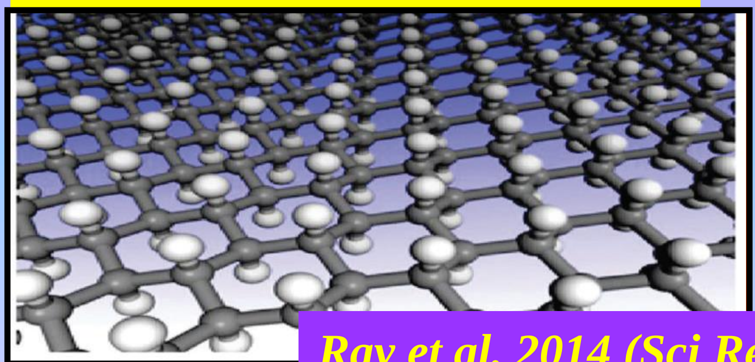


Tri-layer Graphene on Silicon-substrate

Partial hydrogenation (Graphone)

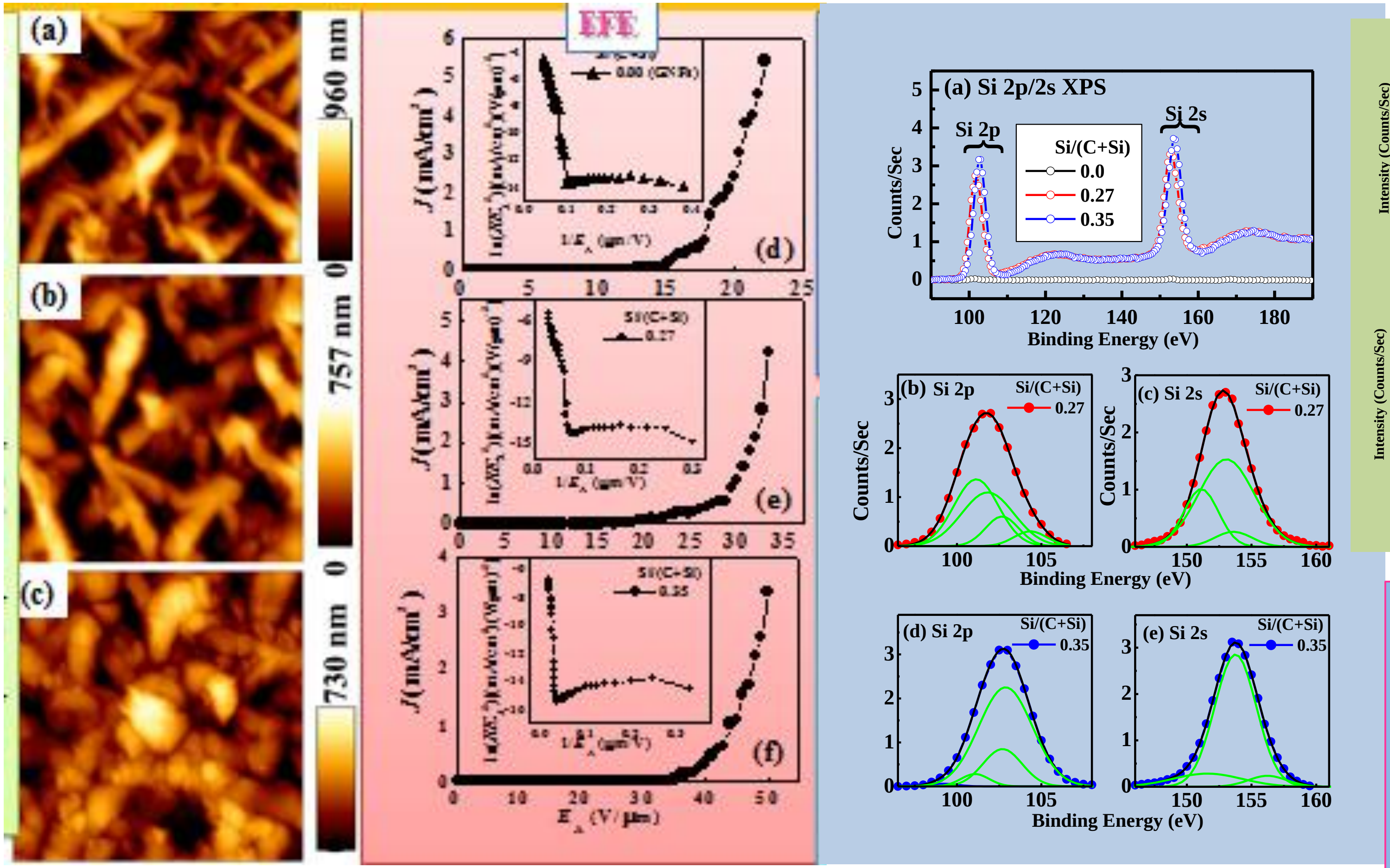


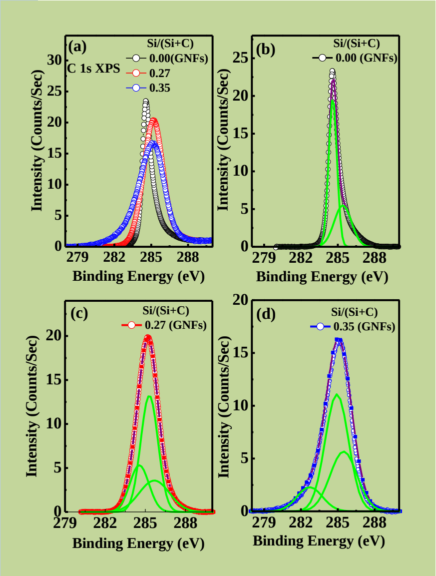
Full hydrogenation (Graphane)



Ray et al. 2014 (Sci Reports 4, 3862)

Silicon-Functionalized Graphene Nanoflakes: Electronic Structure





GNFs

~284.6 eV Carbon sp^2-hybridization

⇒ ~286.1 eV assigned as C-O bonds

GNFs:Si

⇒ ~285.4 eV carbon sp^2-hybridization is shifted to the higher energy and became broader for GNFs:Si having Si/(Si+C) is 0.35 indicating the formation of Carbon sp^3-hybridization

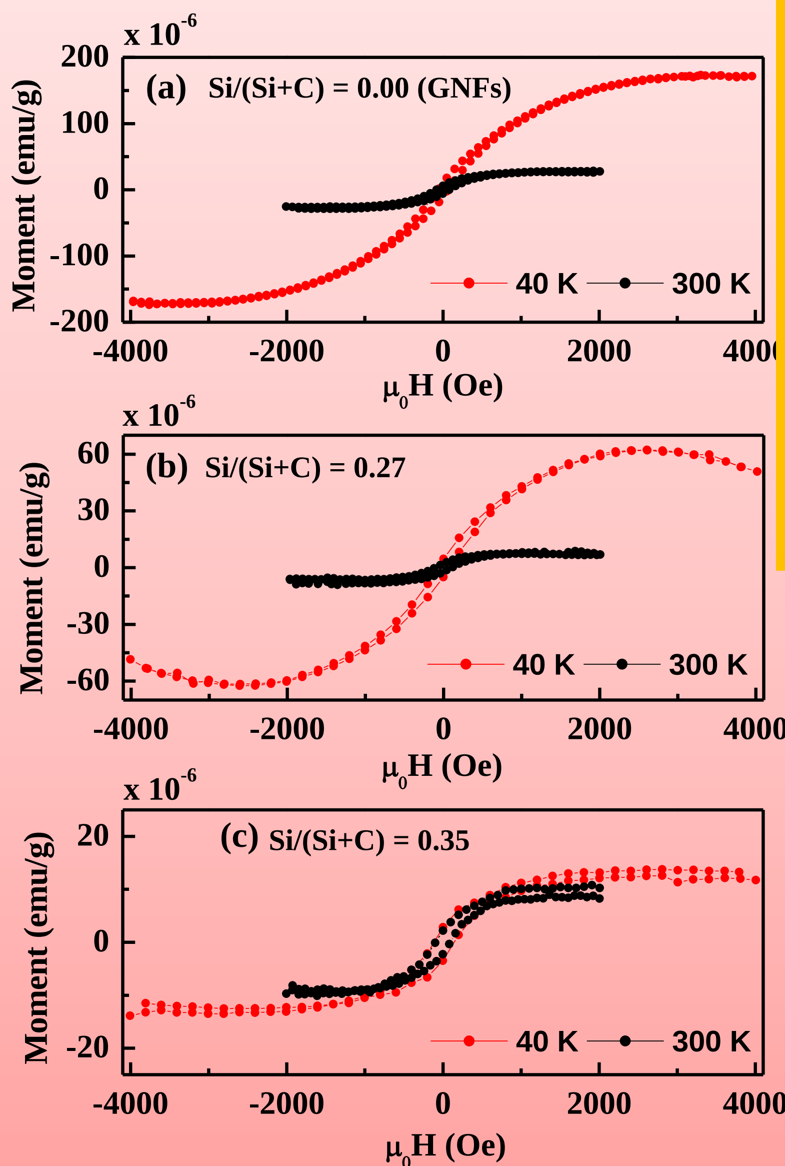
⇒ ~ 285.0 eV is "defect peaks"

⇒ ~285.6 eV defined as Si-C-O bonding peak

⇒ ~286.8 eV is the C-O bonds

***Ray et al.* J App. Phys. 118, 115302 (2015)**

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**

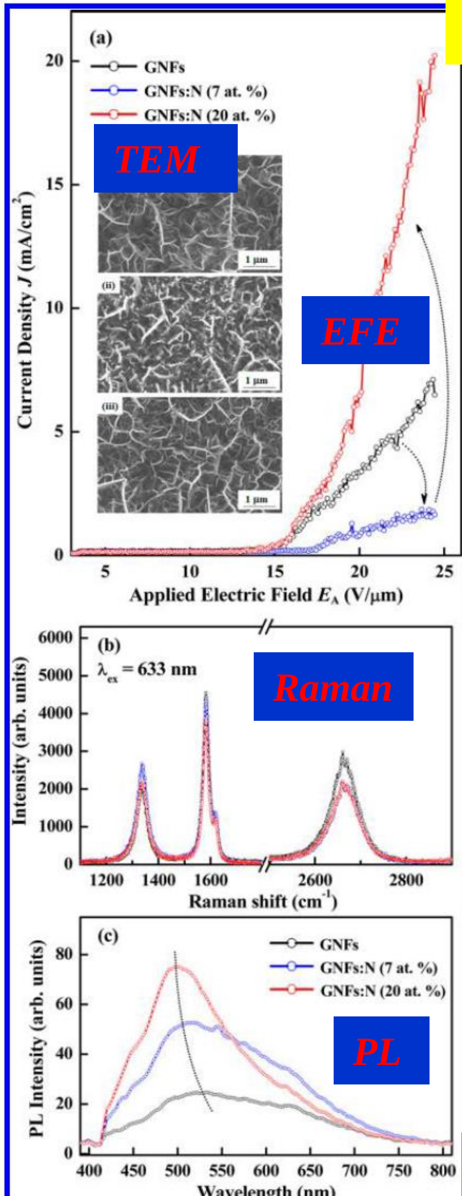
Saturation magnetization (M_S), Coercivity (H_C) and Remanence (M_R) of GNFs and GNFs:Si.

Sample	$\frac{Si}{(Si+C)}$ Ratio	M_s($x10^{-6}$ emu/g)		H_c (Oe)		M_R($x10^{-6}$ 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

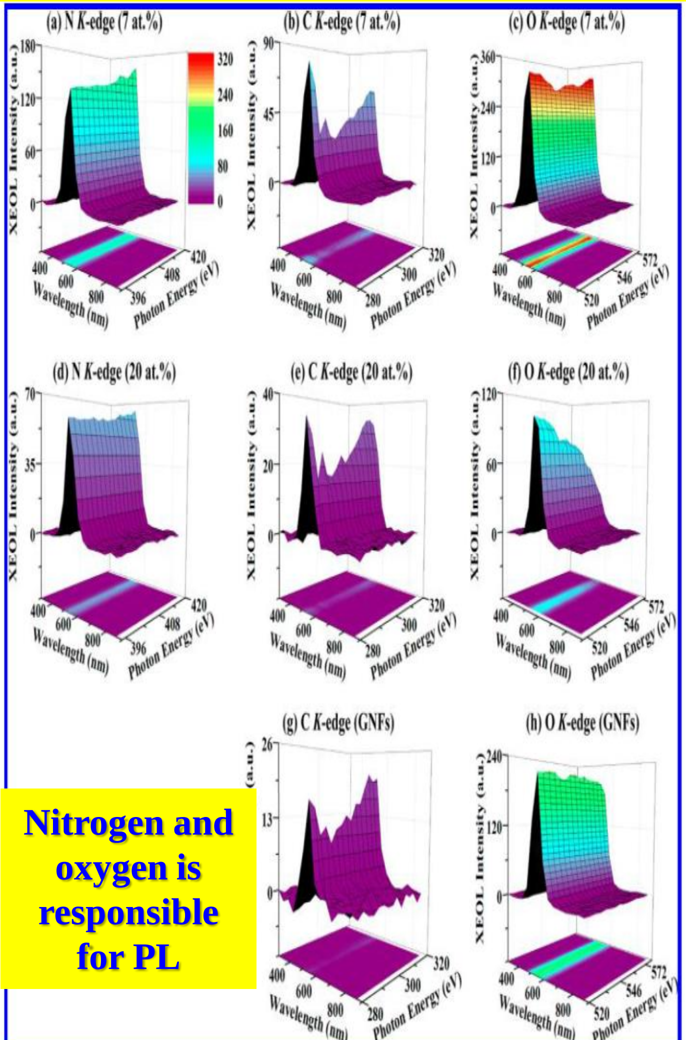
Ferromagnetic materials with high coercivity are called magnetically hard materials, and are used to make permanent magnets. Materials with low coercivity are said to be magnetically soft and are are used in transformer and inductor cores, ... ling heads, microwave devices, and magnetic shielding.

Ray et al. 2015 (J App. Phys. 118, 115302 (2015))

Nitrogen-Functionalized Graphene : Tunable PL and Electronic Structure, Magnetic Behaviors

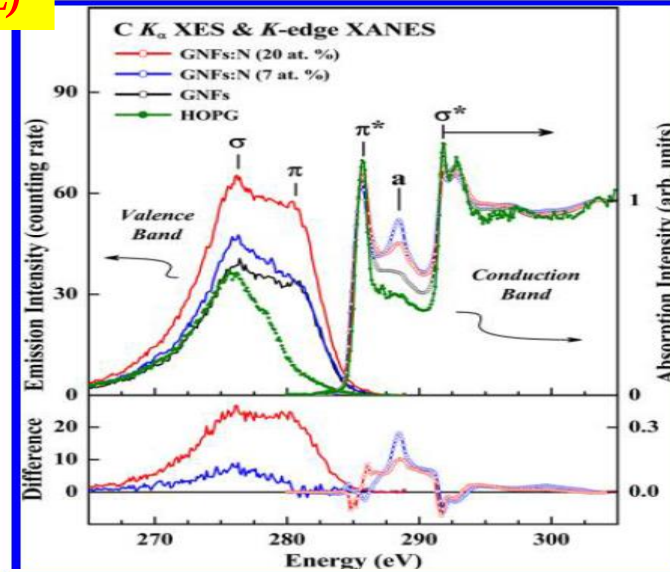


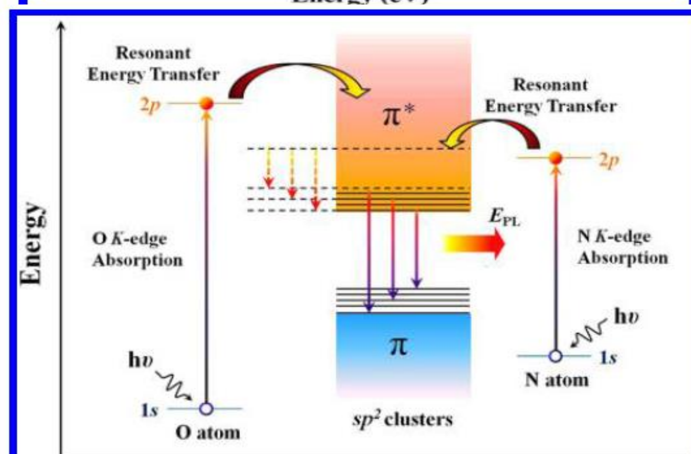
X-ray-excited optical Luminescence (XEOL)



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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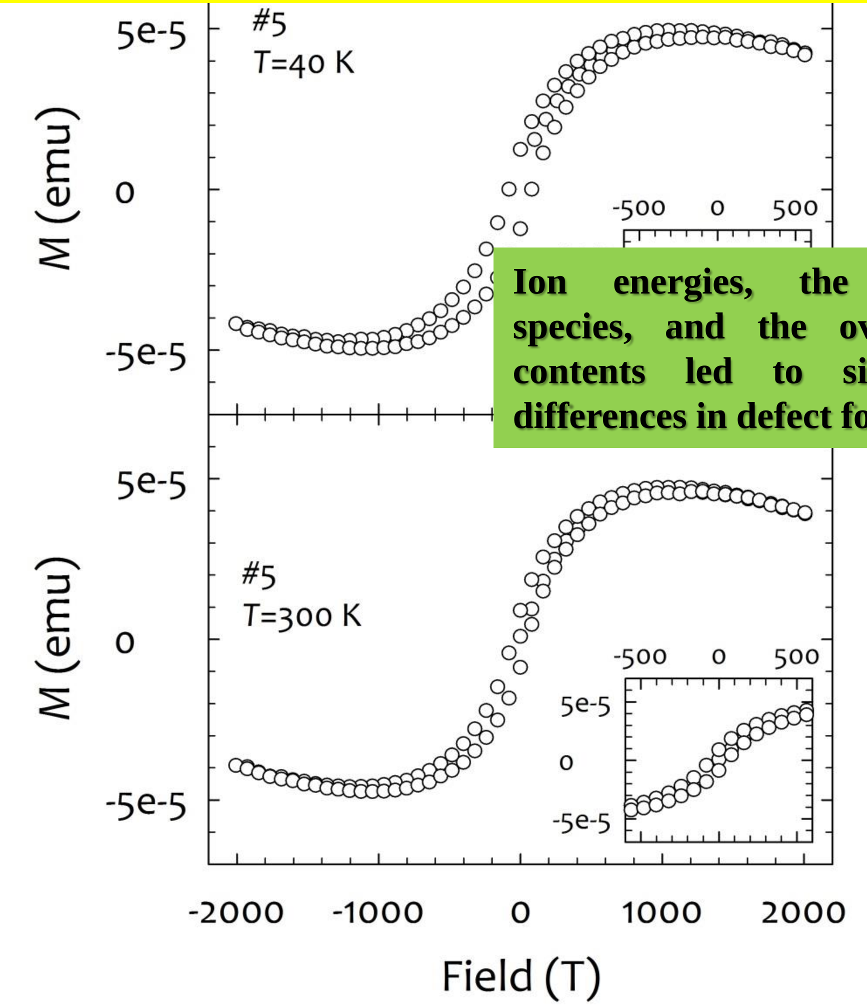
Nitrogen Functionalized Graphene: Ferro-Magnetic Behaviour

ECR-Plasma

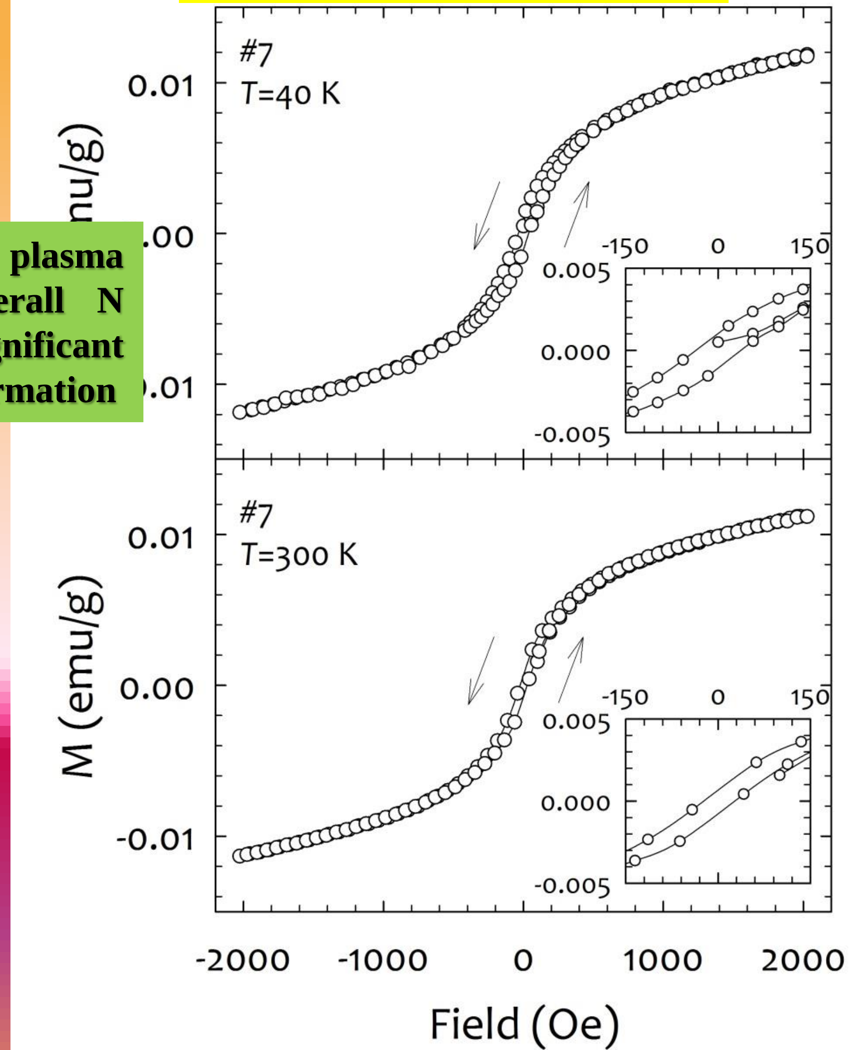
Substitutional and vacancy-like defects in the graphene lattice



Ion energies, the plasma species, and the overall N contents led to significant differences in defect formation

rf-PECVD

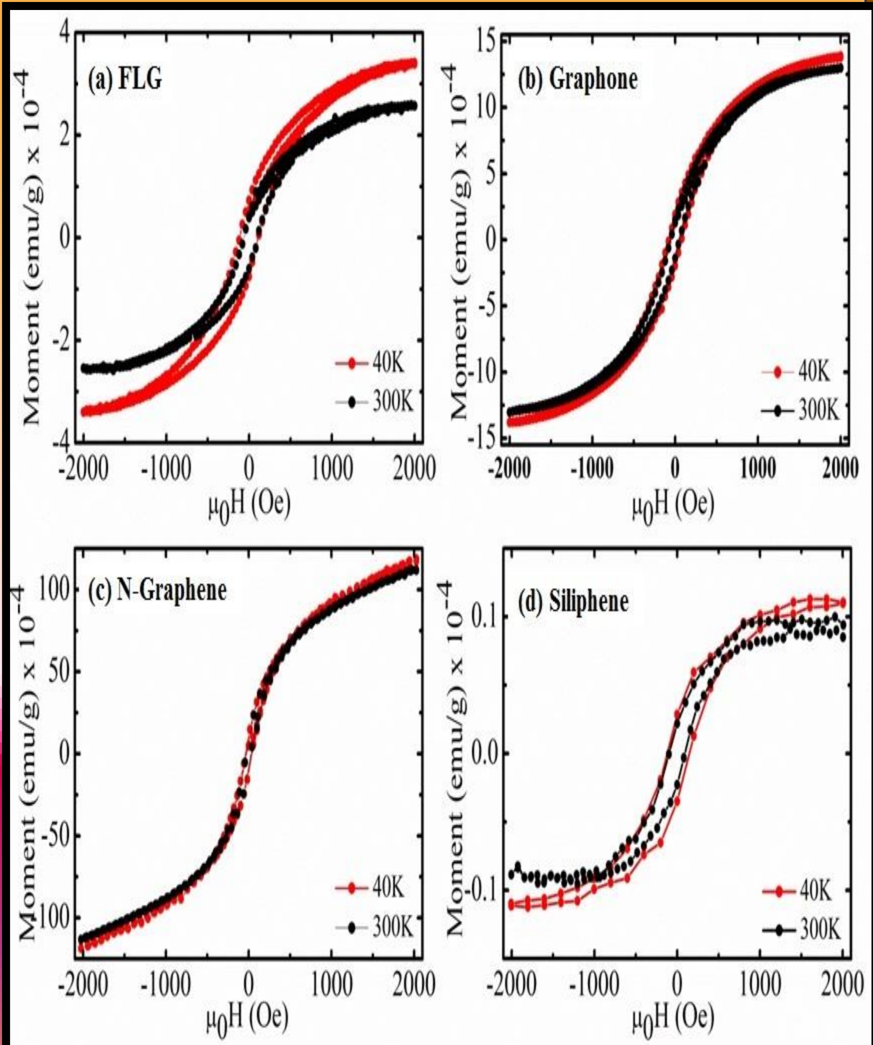
More sp^3-type defect structures

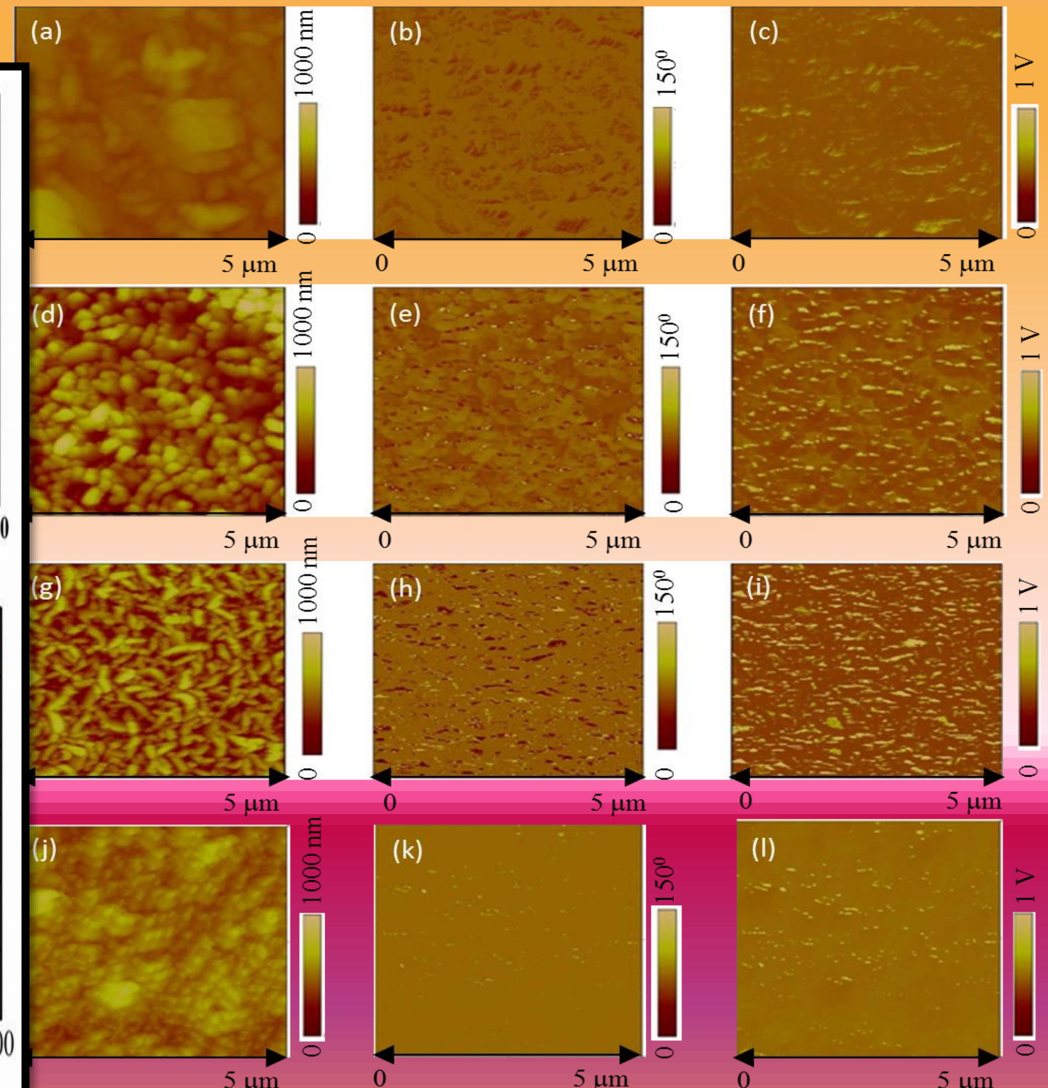


Soin and Ray et al. J. Phys. Chem. C 2017, 121, 14073−14082

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





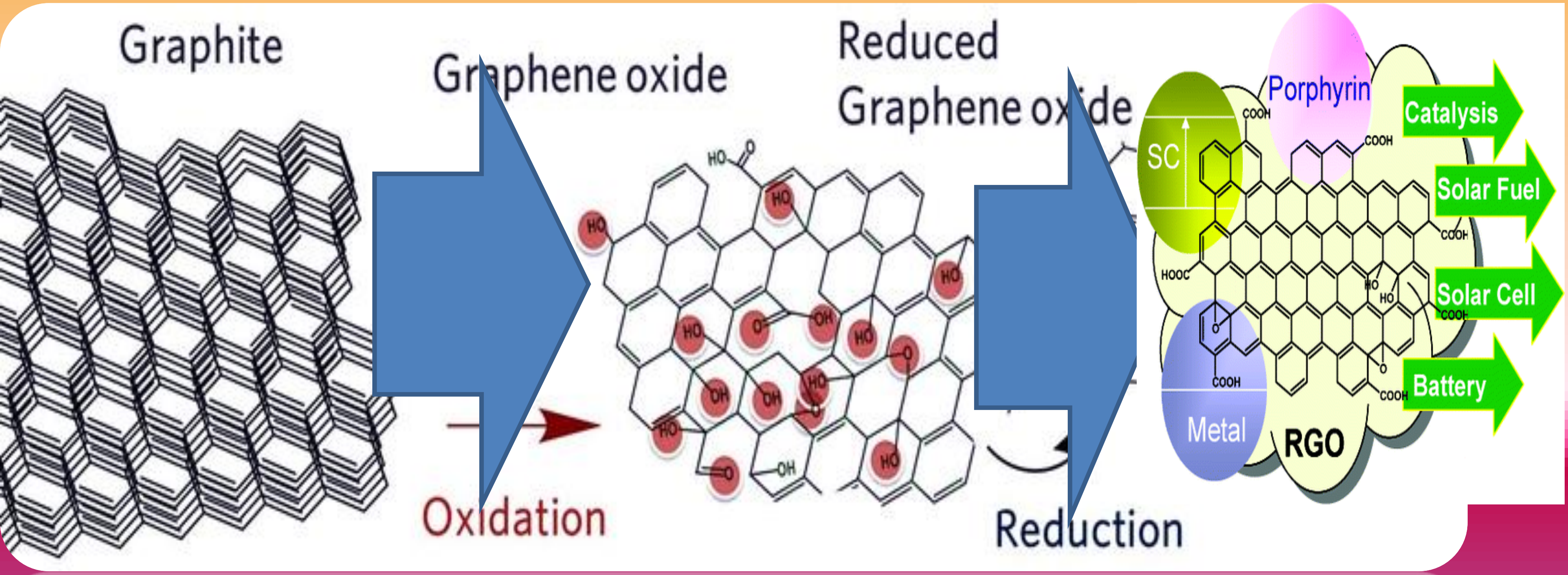
Ray et al. 2016, **RSC Adv., 2016, 6, 70913–70924**

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}

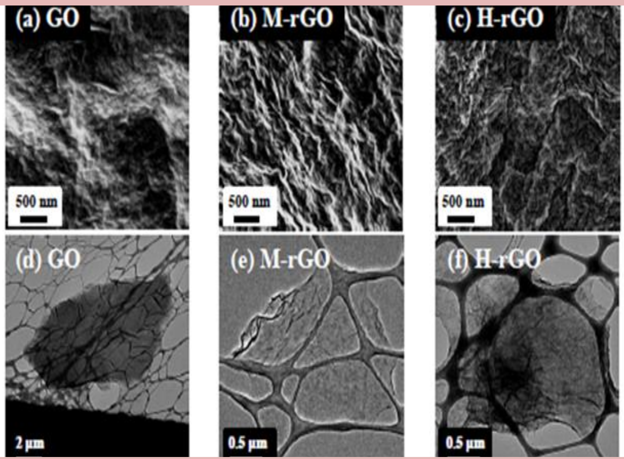
Ray et al. 2016, **RSC Adv., 2016, 6, 70913–70924**

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

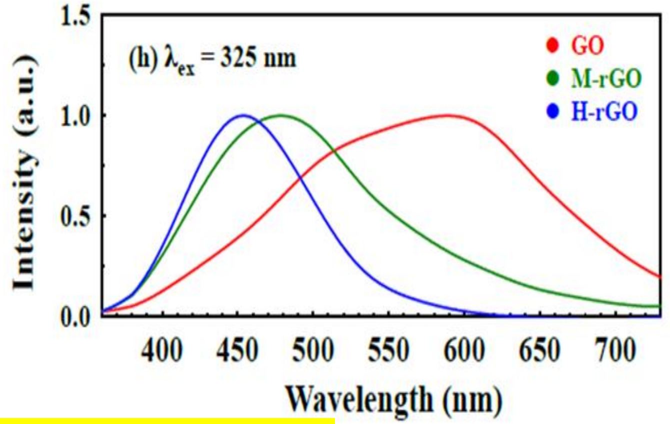


SEM, TEM, Raman and PL of Graphene Oxides

FE-SEM images: Change of surface morphology



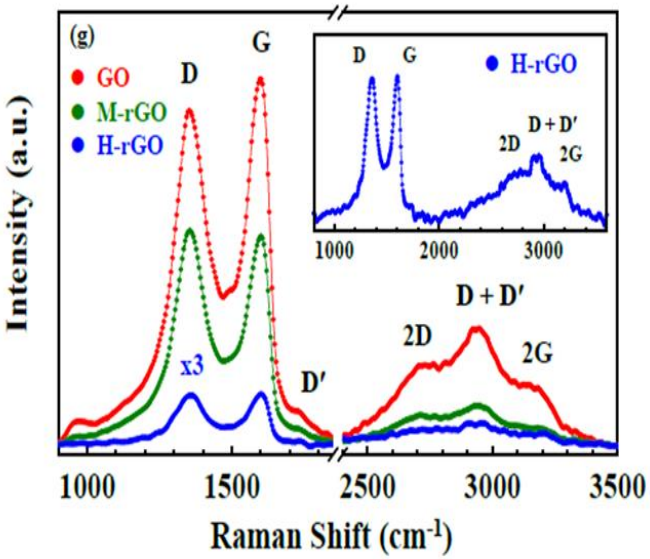
TEM images: Change of surface morphology



GO: A significant number of disorder-induced defect states within the π–π* gap and exhibits a predominant broad PL spectrum centered at longer wavelengths.
rGO: The number of disorder-induced states within the π–π* gap decreases, and an increased number of small sp^2 clusters in the rGO result in blue luminescence.

Photoluminescence:

P-T reduction process does not always remove all of the oxygen and oxygen containing functional groups from the GO but that the process can increase the number of π*(C-OH) and π*(C-O-C) bonds upon the rearrangement of oxygen and oxygen-containing functional groups with carbon; this consequence may also play a role in enhancing the transfer of resonance energy from O sites to the sp^2 clusters in the graphene lattice, which results in broad PL emission.

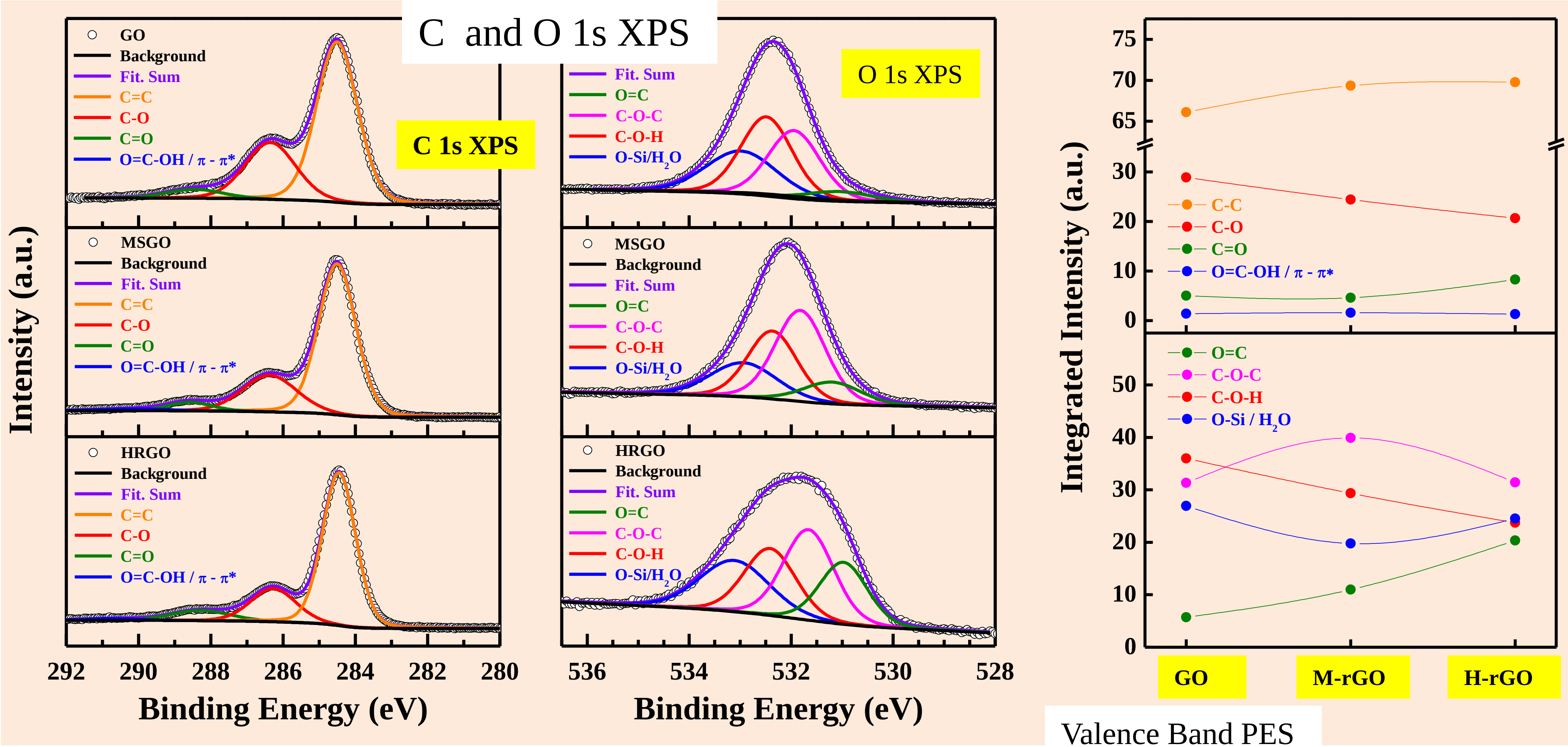


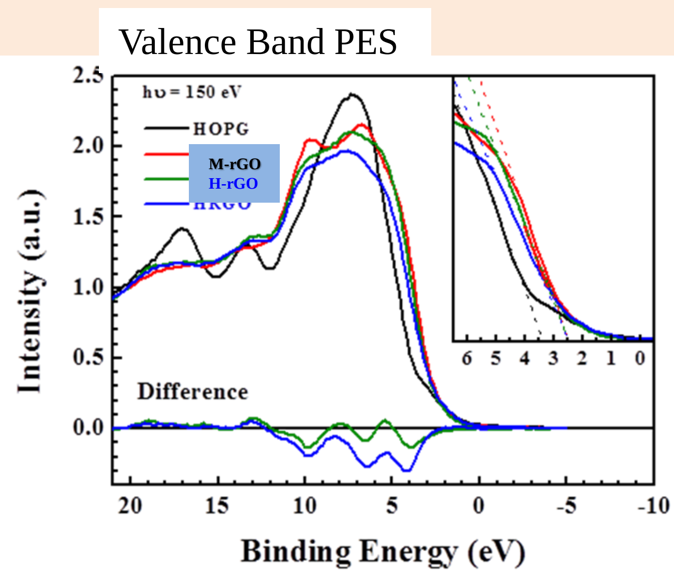
G-Band: 1587 cm^{-1} is attributed to the E_{2g} phonon of sp^2 states

D-band: 1327 cm^{-1} is A_{1g} symmetry disorder - defects/ vacancies in grain boundaries

Removal of oxygen and/or oxygen-containing functional groups and is based on the restoration of the C=C sp^2 bonds in the Graphene hexagonal lattice

Chuang and Ray et al. 2014, Sci. Reports

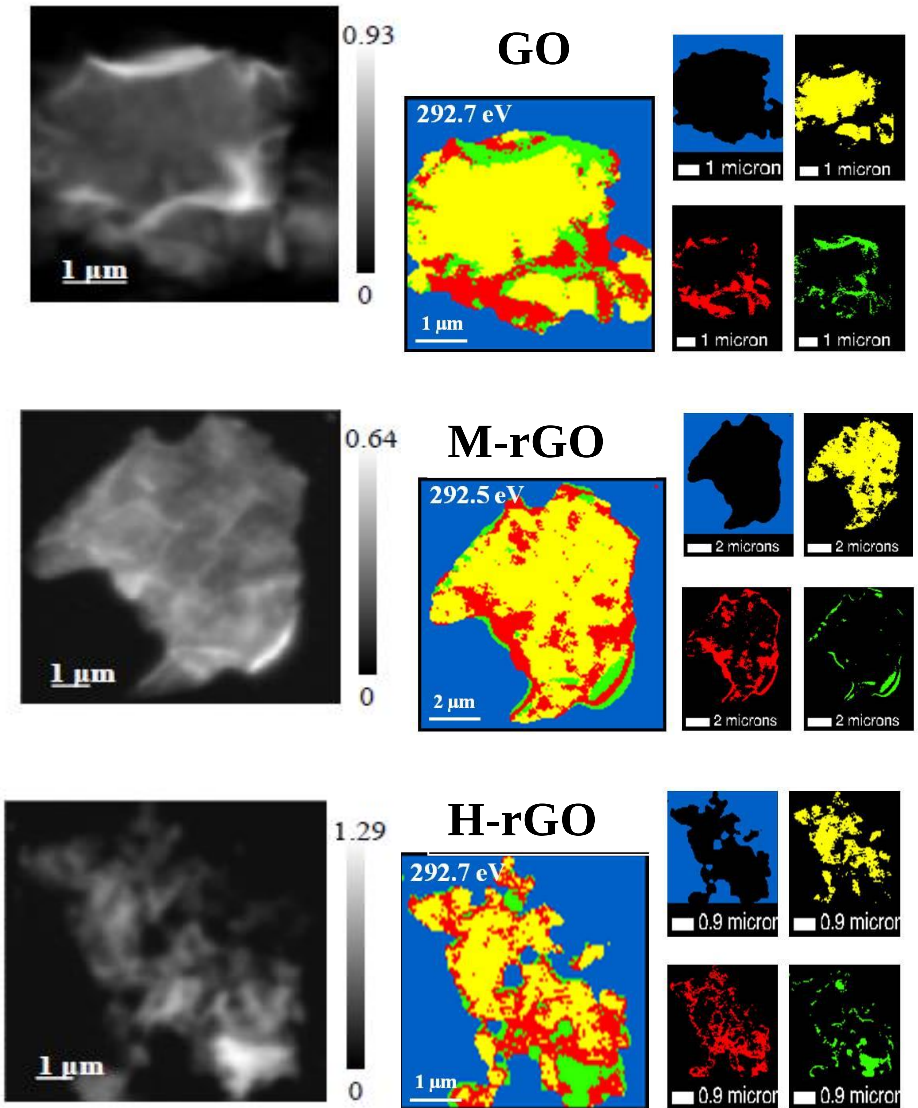




The hydroxyl (C-OH) groups are gradual consumes and in the same time carbonyl (C=O) group are formed in rGO on PT-reduction process.

Wang & Ray et al. 2015, Sci. Reports

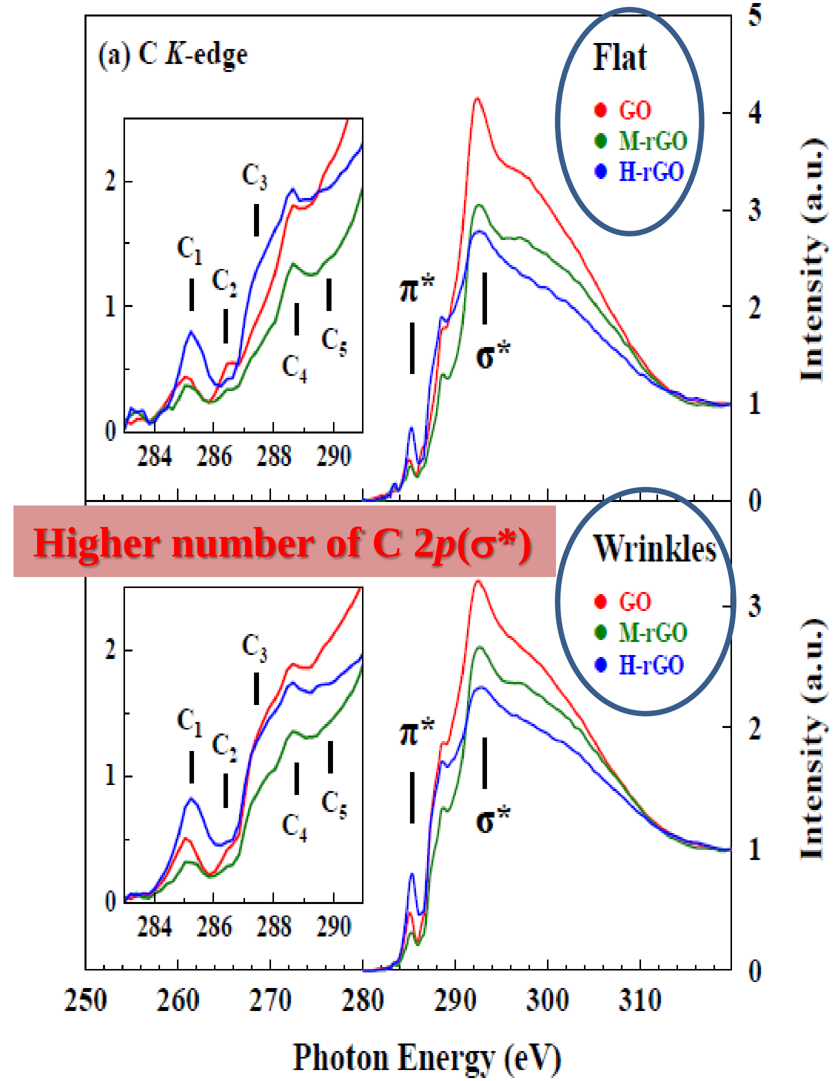
C and O *K*-edge Scanning Tunneling X-ray microscopy (STXM) -XANES spectra



Optical Density images

C *K*-edge STXM stack mappings

Decomposed STXM mappings



C *K*-edge STXM-XANES provide clear evidence that the number of C 2*p*(σ*)-derived states, rather than of C 2*p*(π*) states that bound with oxygen-containing and hydroxyl groups on the GO surface, is related to the change of magnetic behavior from that of ferromagnetic GO to that of paramagnetic M-rGO / H-rGO

Wang & Ray et al. 2015, Sci. Reports

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 !!

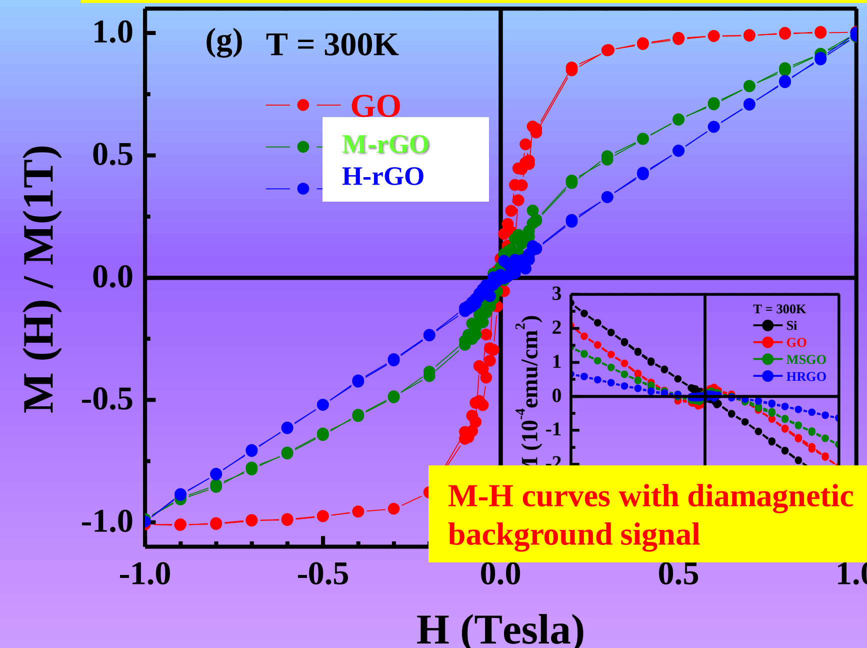
(iv) The most stable magnetic configuration corresponds to seven OH-groups

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

Wang & Ray et al. 2015, Sci. Reports

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



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

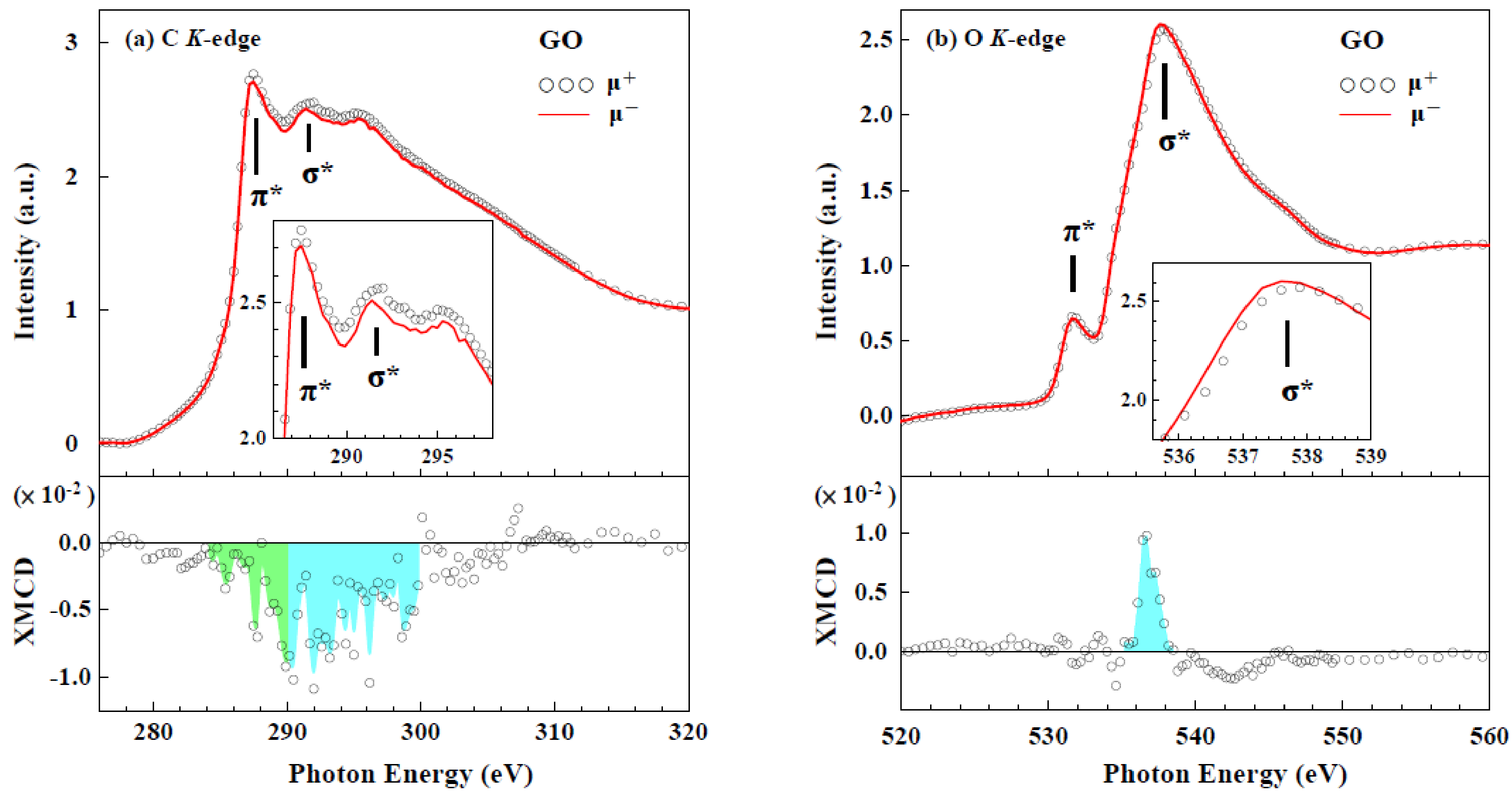
Room temperature FM in GO

Coercivity ~150 Oe

Saturated Magnetic field about ~3000 Oe

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

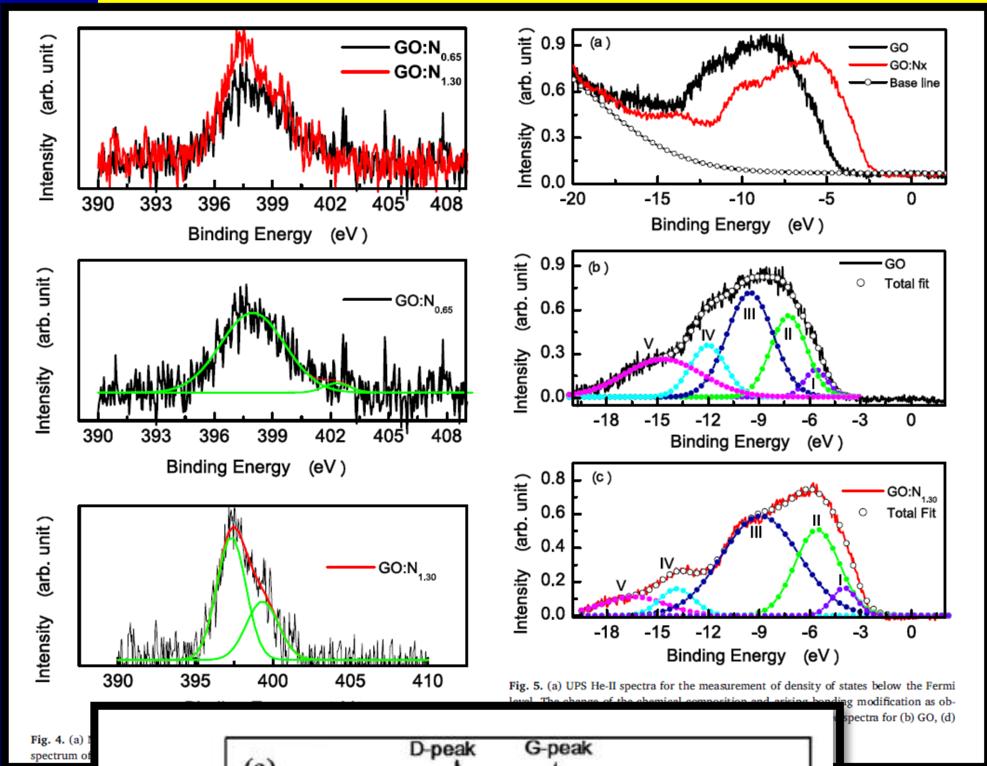
X-ray Magnetic Circular Dichroism (XMCD) of Graphene Oxides

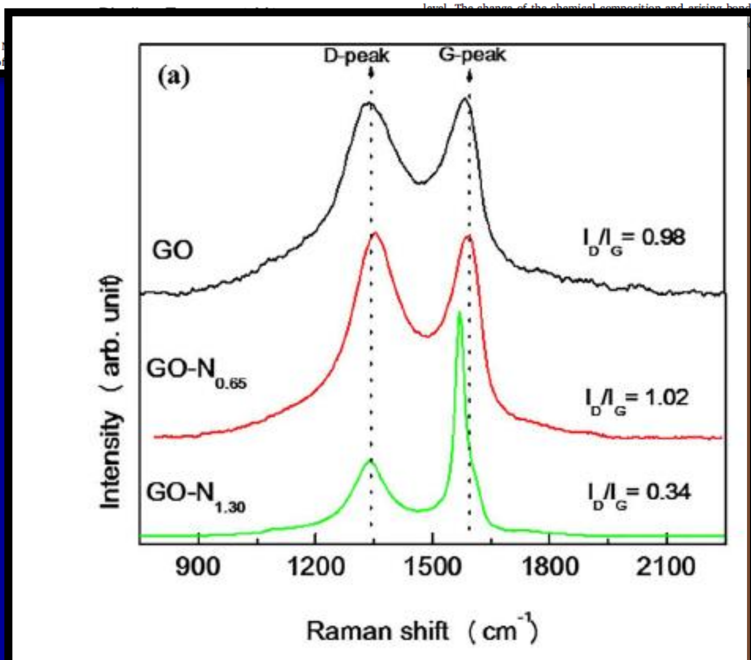


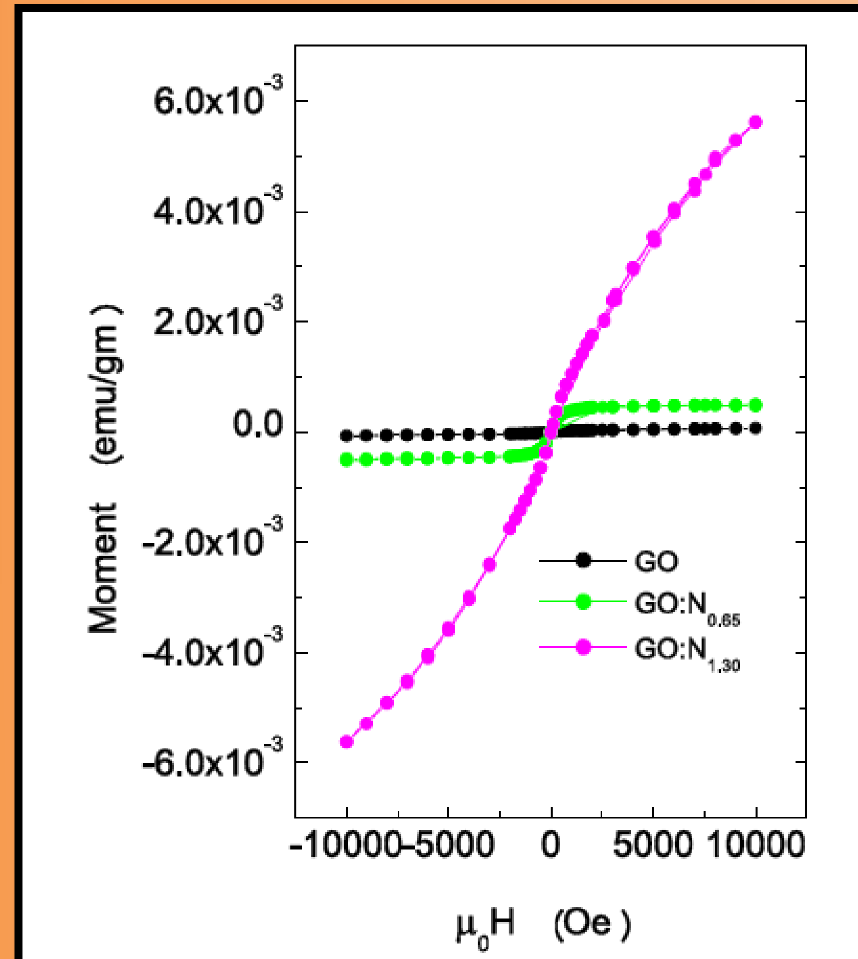
C and O *K*-edge: X-ray magnetic circular dichroism (XMCD) spectra with the photo-helicity of incident x-rays parallel (μ^+) and anti-parallel (μ^-) to the direction of magnetization of GO

Wang & Ray et al. 2015, Sci. Reports

Electronic and magnetic properties of nitrogen functionalized graphene-oxide

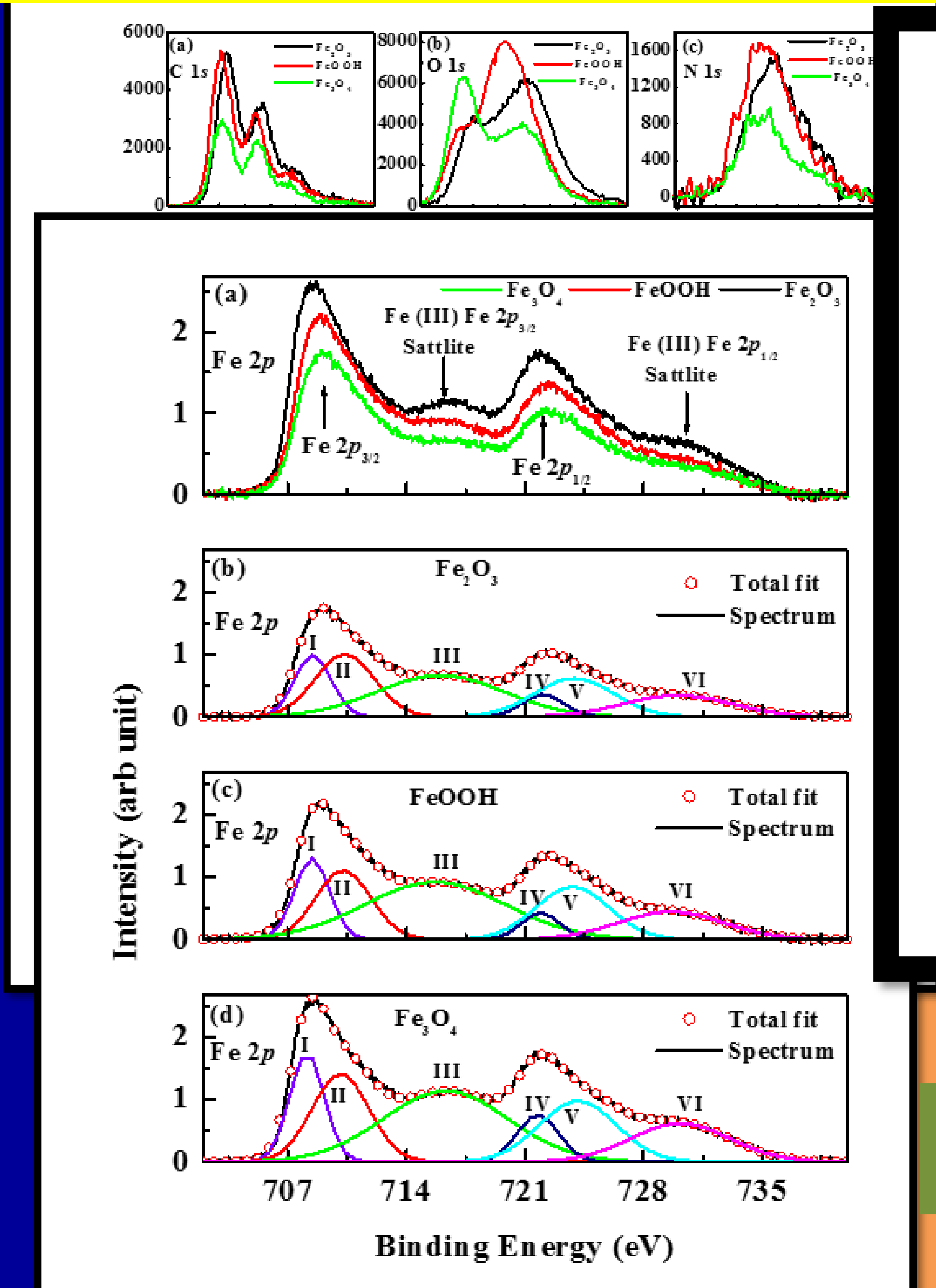


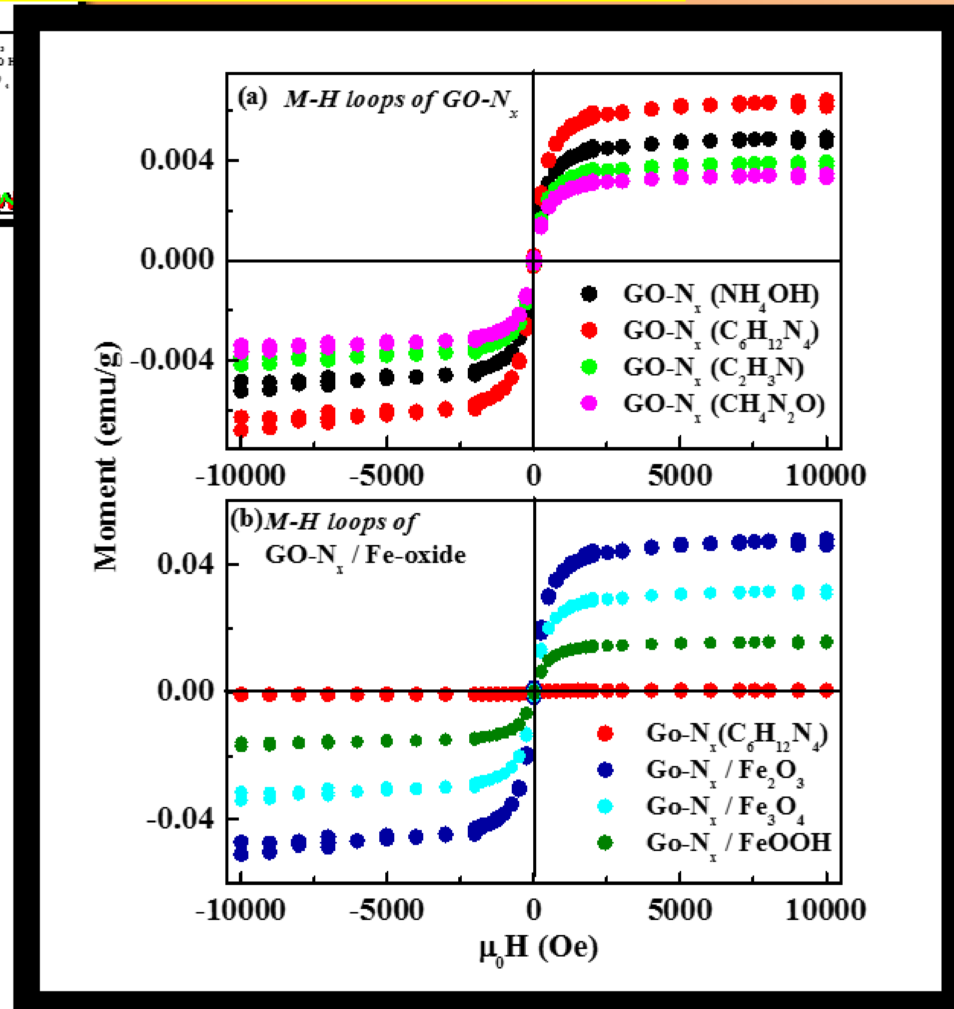




Sarma & Ray 2017, Diamond & Rel. Mater.

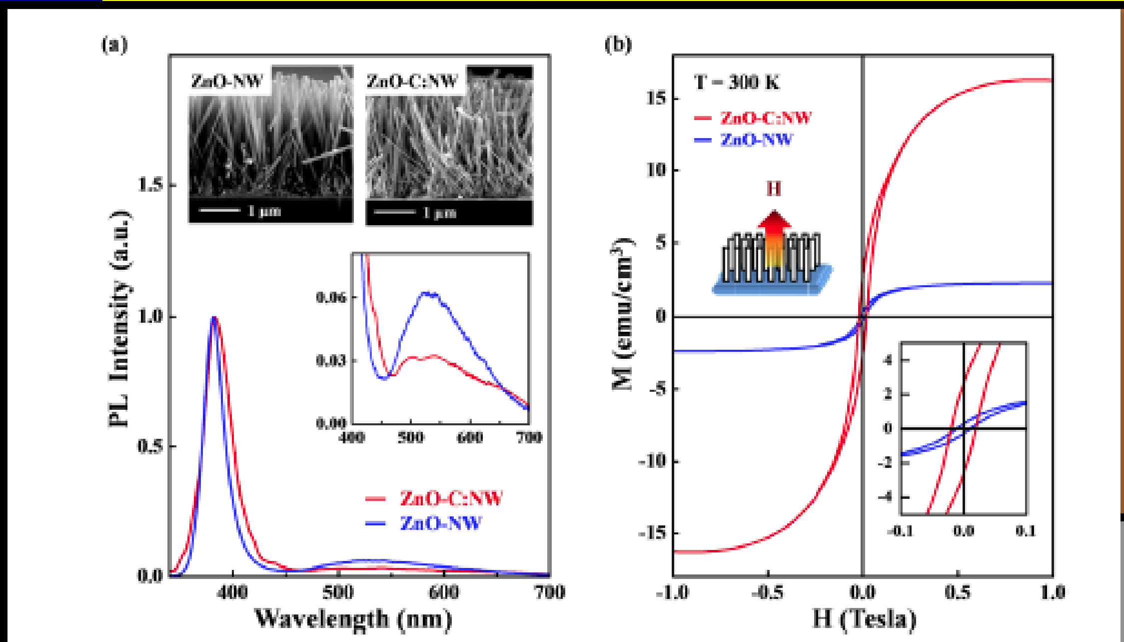
Electronic and magnetic properties of GO:Nx functionalized with Iron oxide

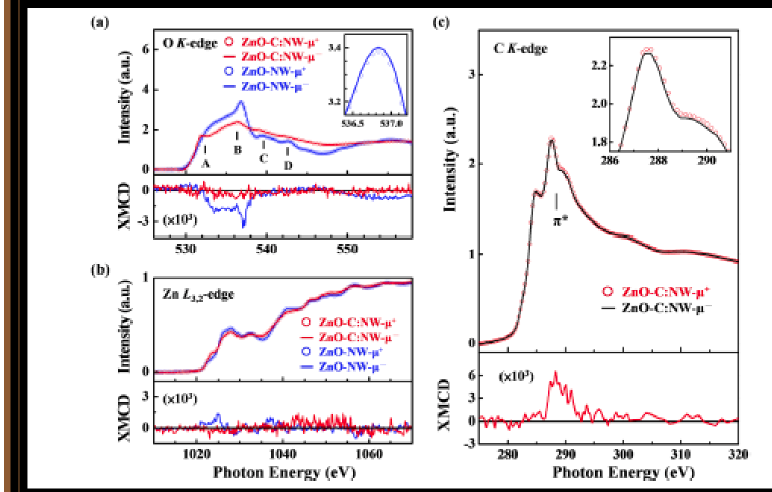


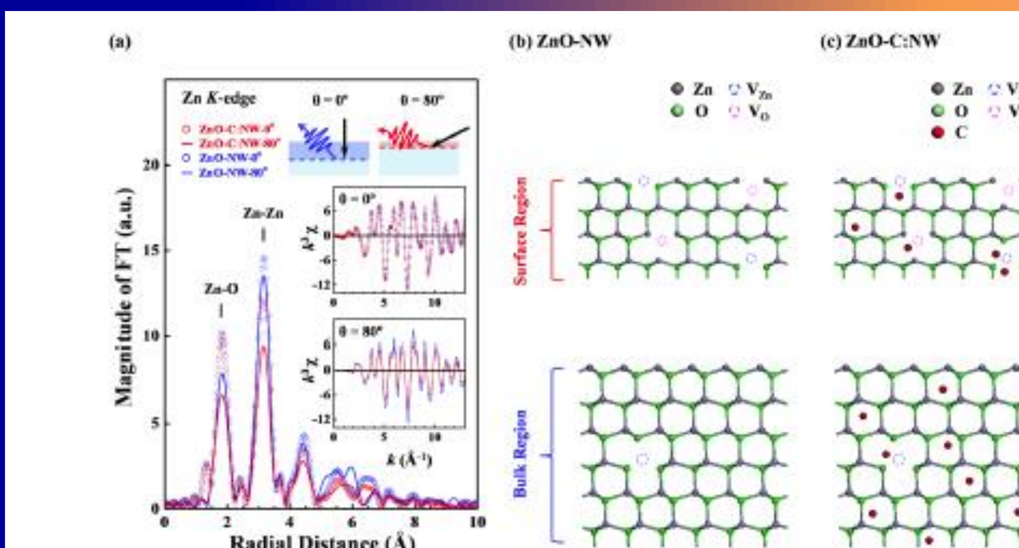


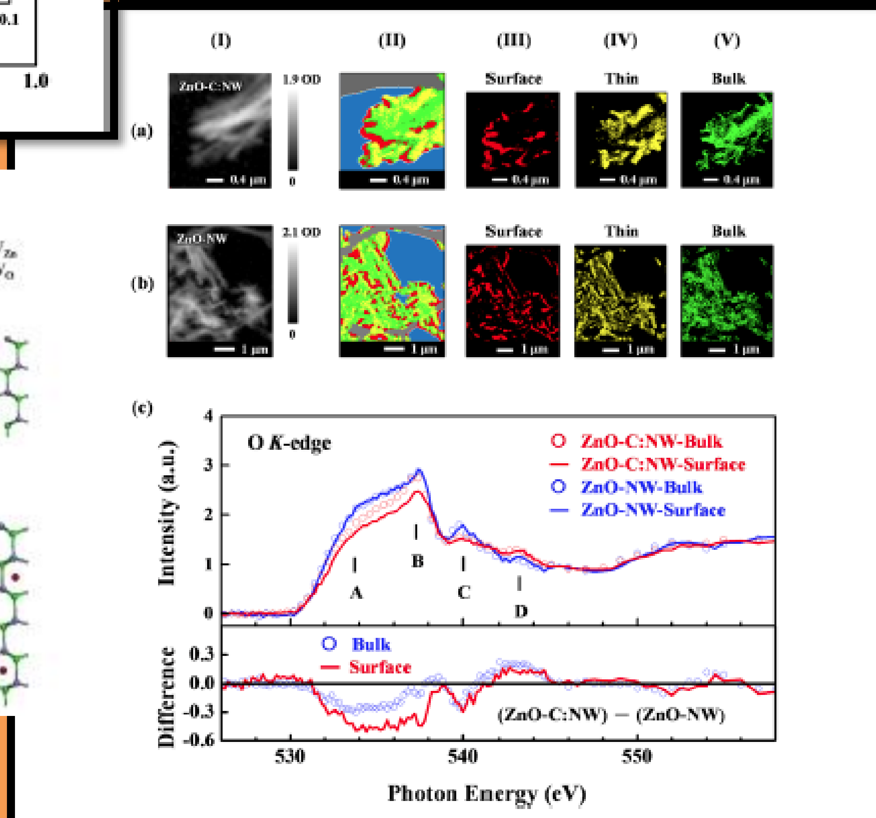
Ghosh & Ray 2018, Diamond & Rel. Mater. (Communicated)

Origin of magnetic properties in carbon implanted ZnO nanowires









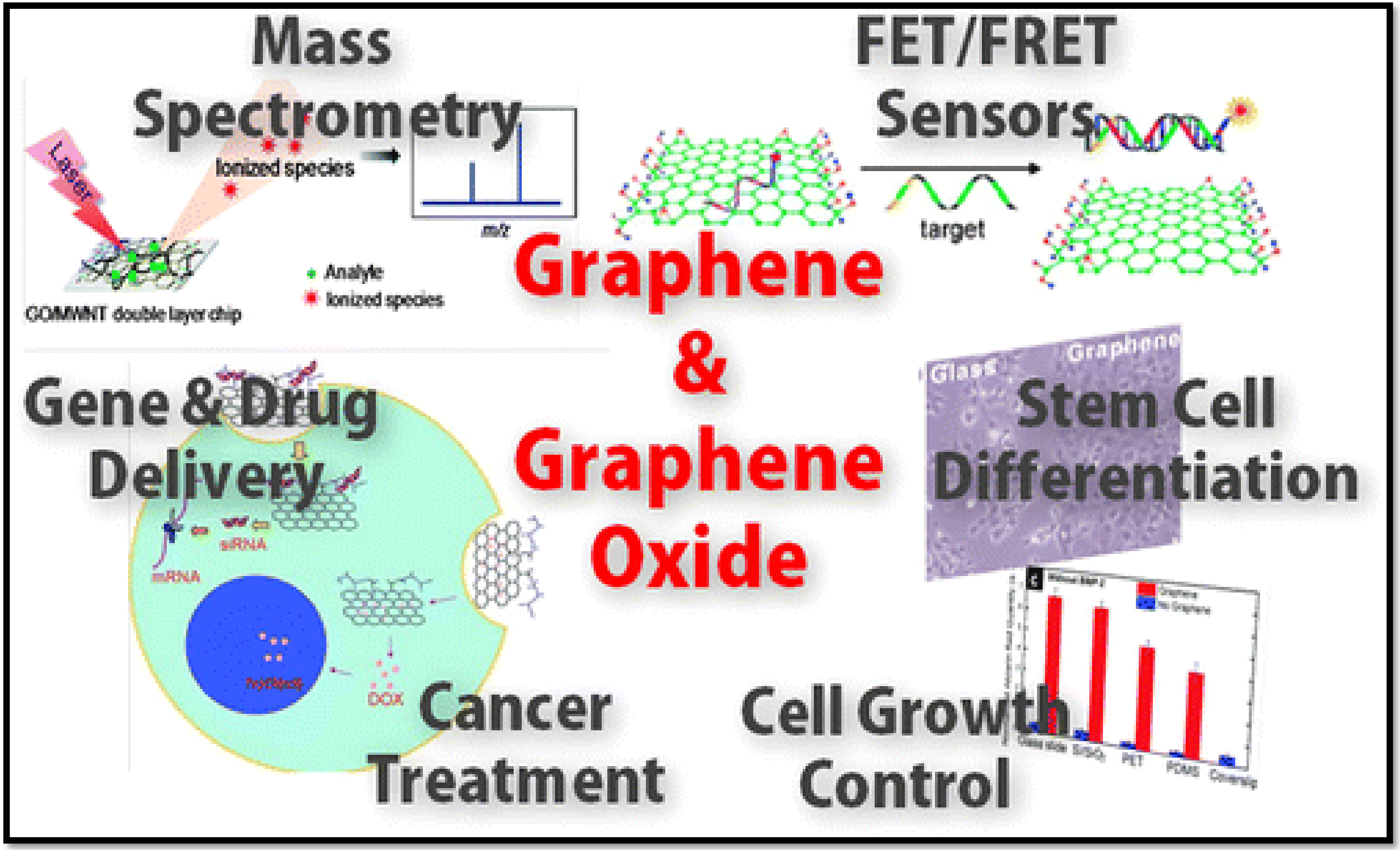
Wang & Ray et al. Sci. Reports, 8 (2018)7758.

CONCLUSION

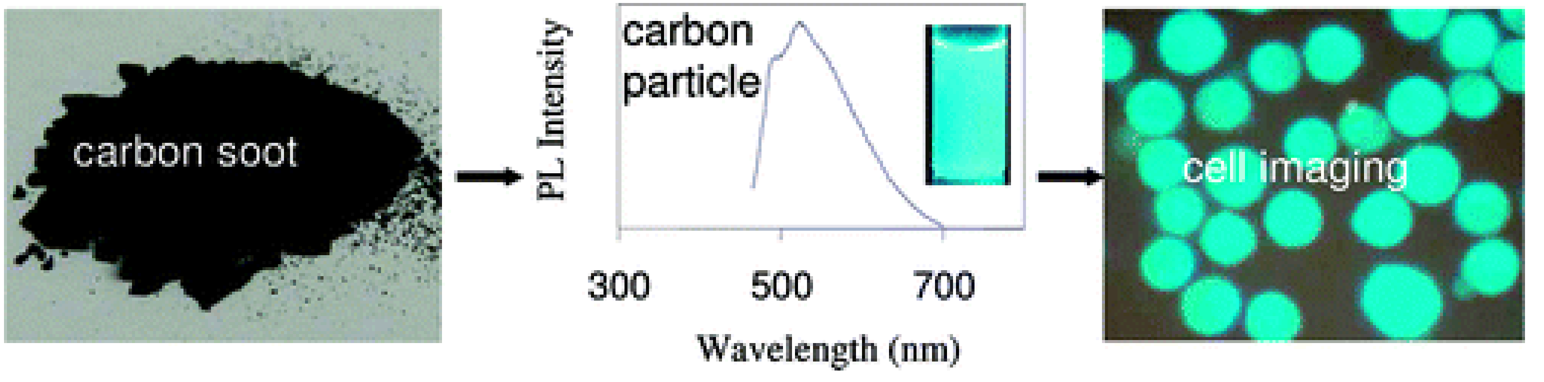
- Graphene is a new hope for electronic devices and could possibly replace or rejuvenate Silicon based devices. It seems to be a better material than Silicon and CNT.
- Lack of Natural Band Gap prevents Graphene to replace Silicon based devices very now.
- Successful prototypes include Superconductor, 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.

Graphene is a promising and useful material for new types of systems, circuits and devices where several functionalities can be combined into a single materials

Graphene/Graphene based Carbon for Bio-imaging application



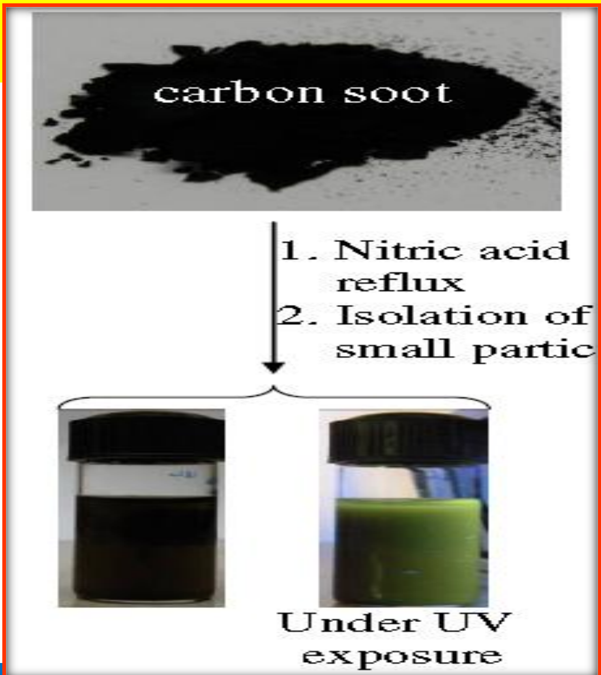
Graphene based Carbon Nanoparticles for Bio-imaging application

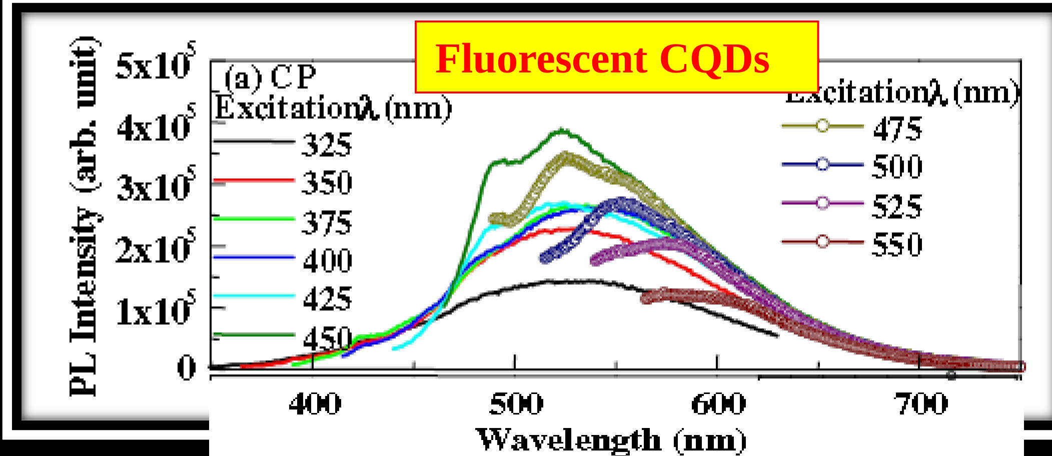


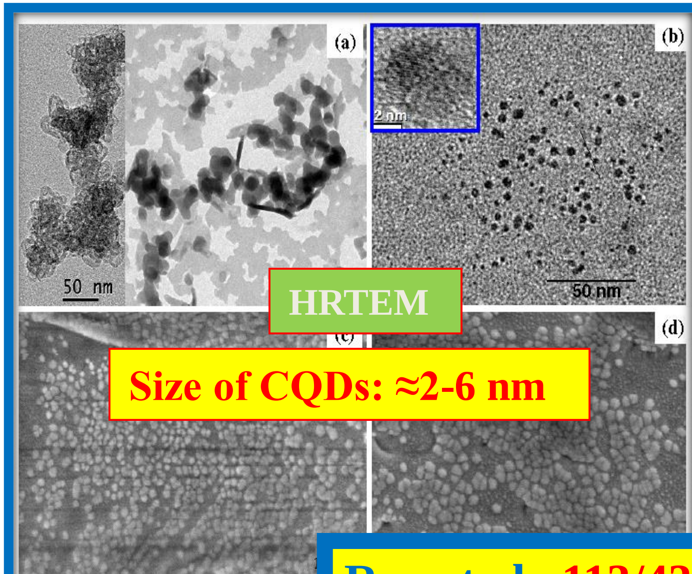
Ray et al. *J. Phys. Chem. C* **2009**, *113*, 18546–18551

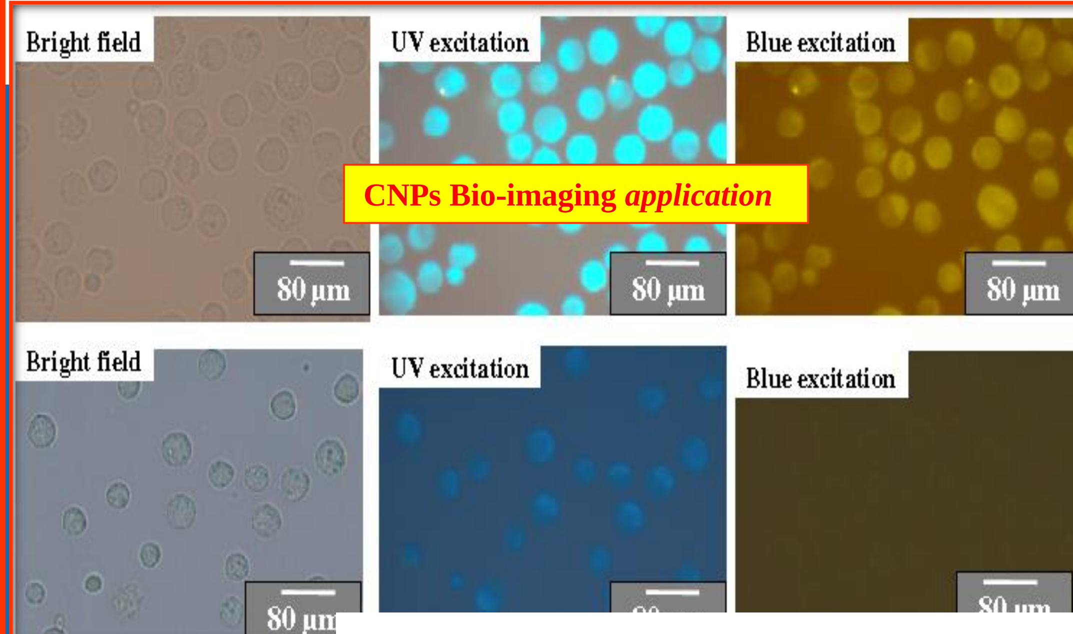
Fluorescent Carbon Nanoparticles for Bio-imaging probes

(Carbon Quantum DOTs:≈ 2 – 6 nm)









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

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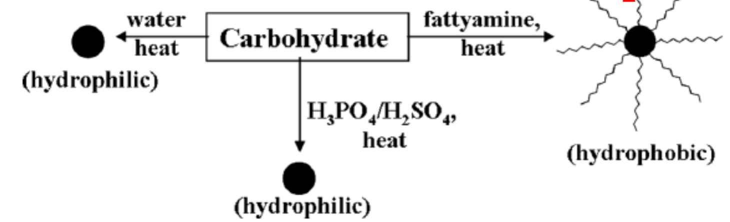
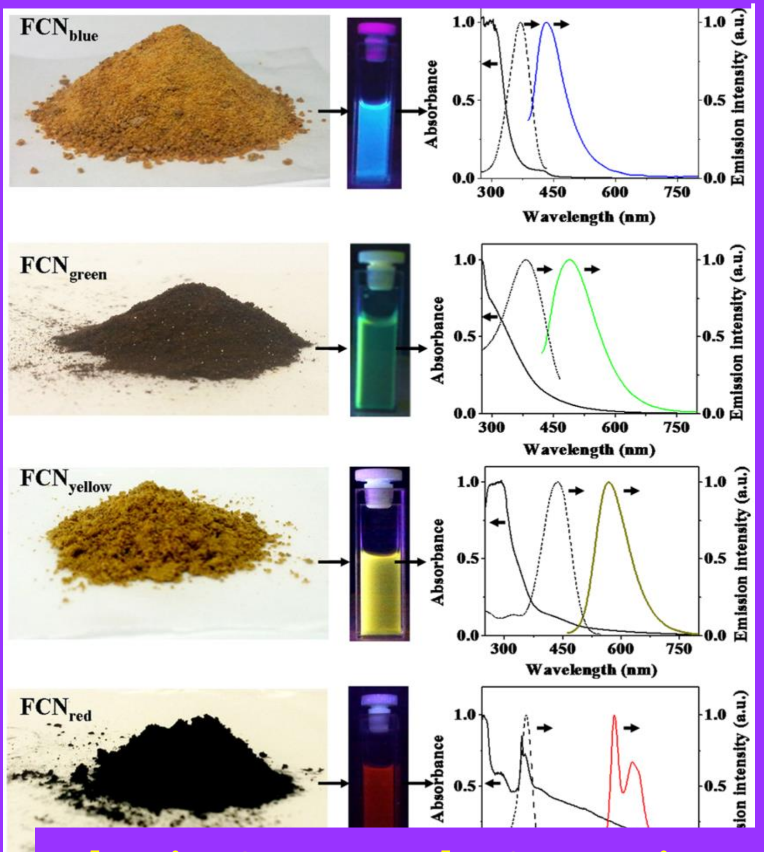
Carbon Nanoparticle-based Fluorescent Bioimaging Probes

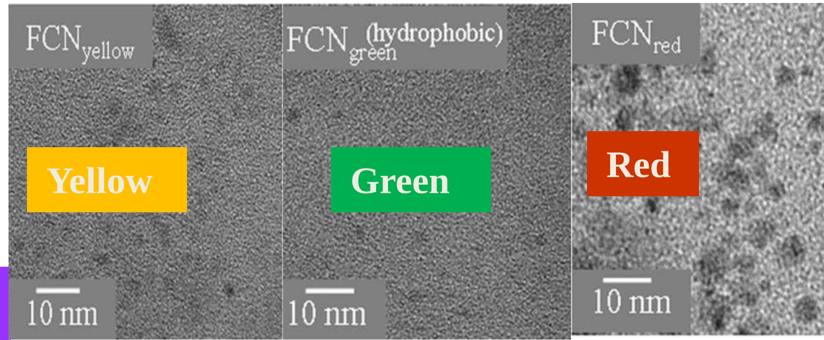
S.K. Bhunia, A. Saha, A.R. Maity, S.C. Ray and N.R. Jana

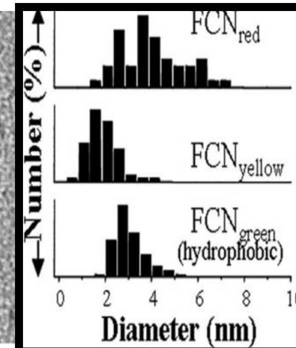
Scientific Reports |2013| 3: 1473 (1-7) : www.nature.com/scientificreports

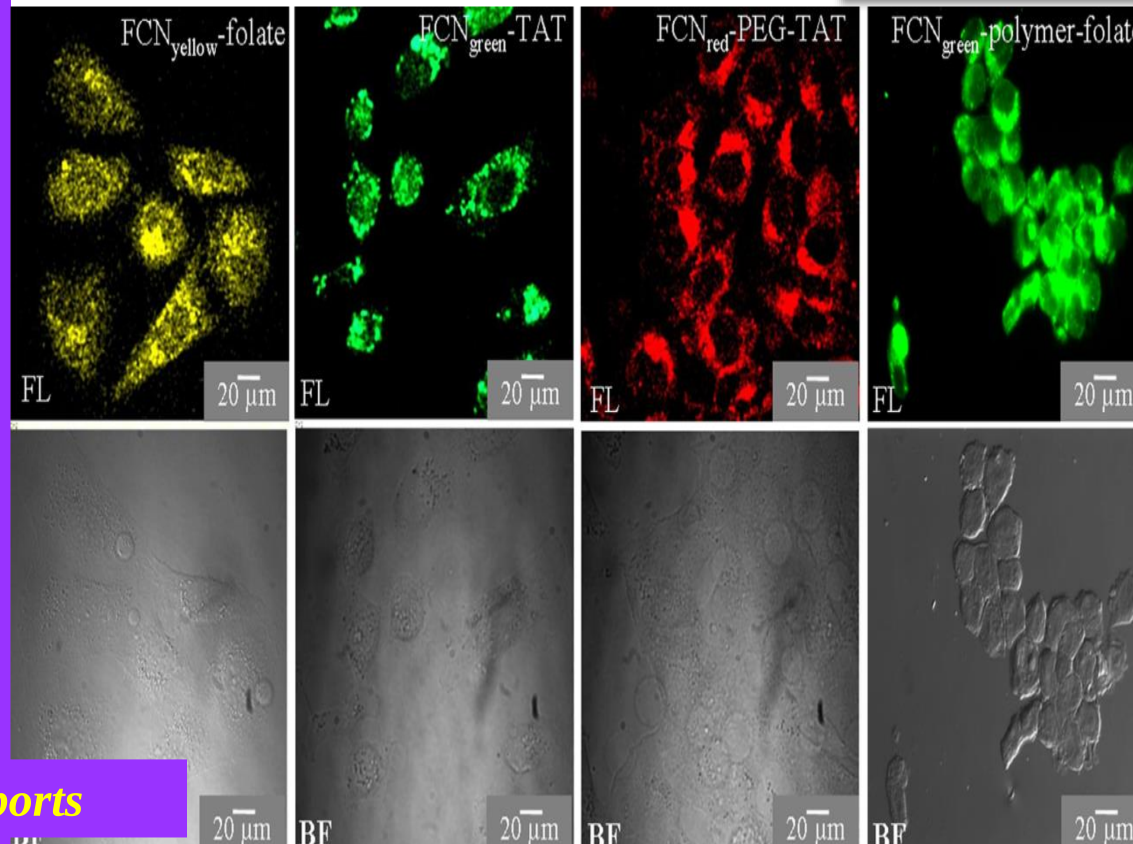
Functionalized with Nano pores





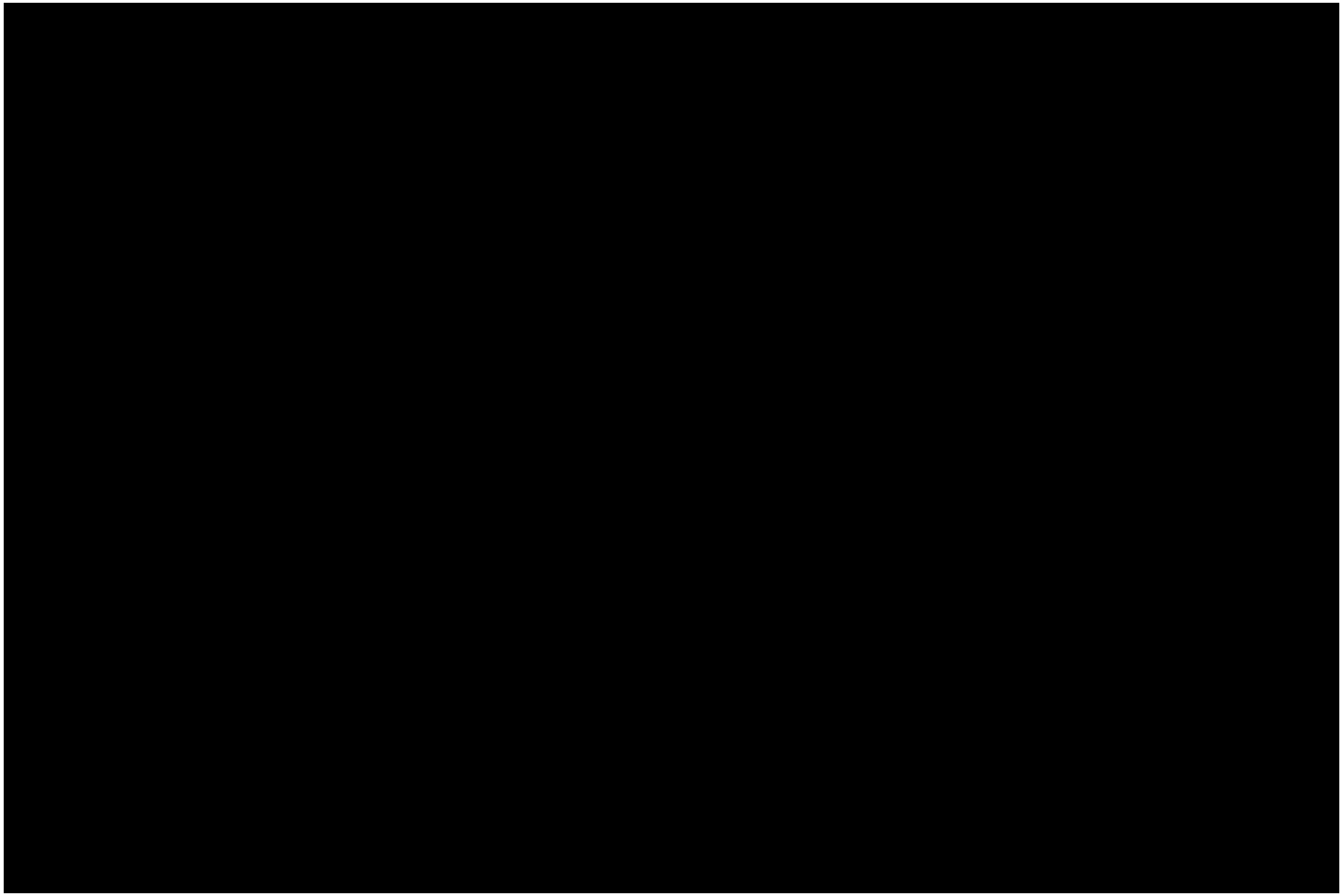






Bhunia & Ray et al. 2013, Sci. Reports

Vision – Applications of Graphene (within 50 years)



Vision – Applications of Graphene (within 50 years)!

THANK YOU FOR YOUR ATTENTION