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

# Sekhar Chandra Ray

# **Department of Physics University of South Africa**

### Define tomorrow.



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#### MATEDIAL

## **STONE AGE** $\Rightarrow$ **BRONZE AGE** $\Rightarrow$ **IRON AGE**

### ISTONE AGE

The Stone Age lasted for a very long period of time! It stretches from the very beginnings of humanity three million years ago, to the farmers that lived a few thousand years ago. The reason it's called the Stone Age is because during this time. the people used tools made out of stone!

Neolithic (New Stone Age) Begins

#### 500.000 BC

Palaeolithic (Old Stone Age) Begins



• 500,000 BC Early humans migrate into Britain from Europe. They walk over the land, as at this time Britain was connected to European land





During this period, people in Britain used simple tools made out of stone, such as the 'hand axe' This tool would have been used to cut meat, for digging and chopping wood.

130.000 BC



@130.000 BC

This early species of human was known as the Neanderthal Neanderthals looked very similar to today's humans, but they did have different shaped head



25.000 BC

Britain and Northern Europe are plunged into a long Ice Age. The temperature was constantly freezing. Glaciers, snow and ice formed across much of the land, making it a difficult place to survive!



After the Ice Age ends, the temperature on earth begins to

increase. Large amounts of ice started to melt making the sea levels rise.

Because of this, Britain becomes disconnected from mainland Europe.

Lush green forests grow as a result of

Mesolithic (Middle Stone Age) Begins

10.000 BC

10,000 BC

a warmer climate.



8 000 BC Over time, tools and homes became more advanced. People chose flint stone to make their tools because it was very strong, sharp

ided more warmth and better shelte

8.000 BC

Before this place to p plants Ov introduced planting cr and easy to hold. The huts that people made

Neolithic

5.00

4.500 BC





4,500 BC - 3,500 BC

Before this period, people would move from place to place hunting and gathering wild plants. Over time, a new way of life was introduced from Europe. People started planting crops and farming animals such as sheep, cows and pigs.



that were used for tasks such as carrying water, cooking and farming.

nottery and tools Now that stone age people were farming, they started to settle down in communities with other families. Because there were more people, the houses were built using stone and thatched roofs that housed more people, and were a lot warmer! Men and women started crafting pottery items and more complex tools



In a time when people were constantly moving around in search of food and shelter, walking around on foot was slow and painful. Horses were used as faster transport a way to carry people and belongings



ge is built The prehistoric monument Stonehenge is erected

a huge monument that consisted of giant stones arranged into circles. It is believed that the stones were transported from 250 miles away. It is still not known what stonehenge was used for

#### **BRONZE AGEI** 2,500 BC

The Bronze Age was a period of time between the Stone Age and the Iron Age. when bronze was used widely to make tools, weapons and other implements. Bronze is made when copper is heated and mixed with tin, creating a stronger metal than copper.



A group of people migrated from Europe to Britain called the Beaker People, named after their distinctive pottery bell-shaped drinking tools. When they arrived they brought with them the knowledge of making bronze.



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e flint stone to make

as very strong, sharp

uts that people made

nd better shelter

use of bronze tools was a key elopment in human history. Bronze is de by heating copper and tin until it is ten (liquid). The molten can then be poured moulds, which allowed people to make a ne of different shaned tools many more was possible when using just flint and



The house of choice in the Bronze Age was the Roundhouse. This was a large round structure that housed many people. A large fire would have been lit in the centre inside the building that would have been used for cooking and for warmth. The smoke from the pickaxe's to collect rocks containing copper (copper ore). fire would escape through small gaps in the thatched



• 1,800 BC People start mining for copper on a large industrial scale, digging deep beneath the earth's surface. They would use strong bronzi

### 1,000 BC IRON AGE

The Iron Age was the period of time after the Bronze Age. It is the third and last stage of the three-age system. It's named the Iron Age because people started using iron to make tools and weapons: this was a much stronger and reliable metal. We call the people that lived in Iron Age Britain 'Celts'.



800 BC

The Celts wore brightly coloured clothing, made using dyes made from berries and plants. Celts were very clean people, apparently they invented soap! Some people still speak languages that the Celts spoke - Welsh and Gaelic



A hill fort was a type of settlement that was built

on a hill, high up from the rest of the ground. The Celts would construct high walls and dig deep

ditches around the hill to stop nasty people from

hill forts in search of rare, precious metals such

invading their settlements! People would invade



700 BC

Celts made tools and weapons out of a metal called iron. Unlike bronze which is poured, iron is worked into a shape by repeatedly heating and hammering against an anvil (a hard piece of stone). This process is called smithing. Iron is much harder than bronze and keeps a cutting edge for longer, which is great for swords



#### 700 BC

800 BC

as bronze, iron and gold.



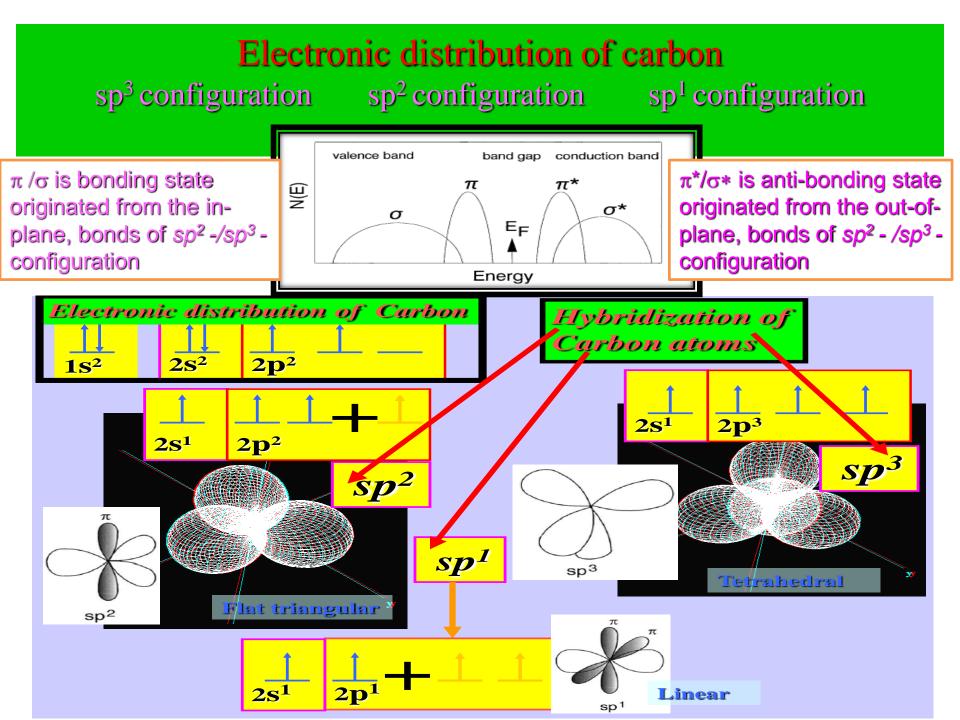


⇒ Each age is levelled by the Material
⇒ that bearing the new technology
⇒ that makes the new society

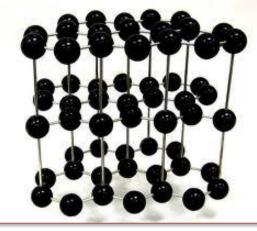
What will be the next age?? What will be next material??

# CARBON AGE or GRAPHENE AGE !!





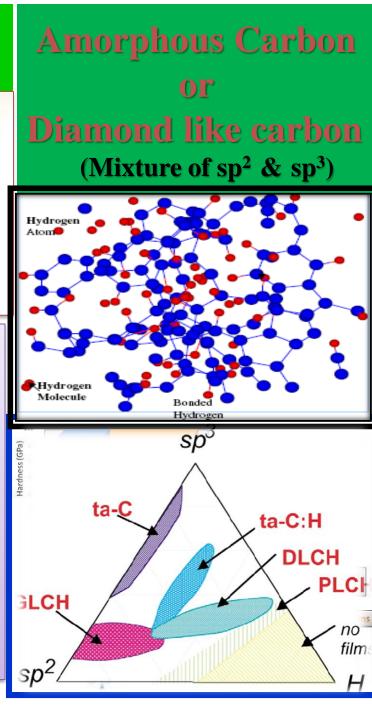
## Graphite (100%sp<sup>2</sup>



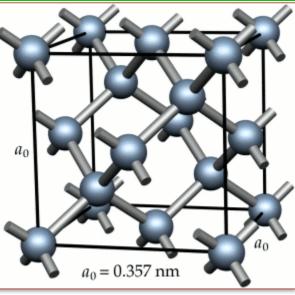
Properties of graphite:
1. Graphite is a soft, slippery, grayish-black substance. It is metallic luster and is opaque
2. Specific gravity is 2.3.
3. Graphite is a good conductor of heat and electricity.
4. Although graphite is a very

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.



# Diamond (100%sp<sup>3</sup>)



### **Properties of diamond:**

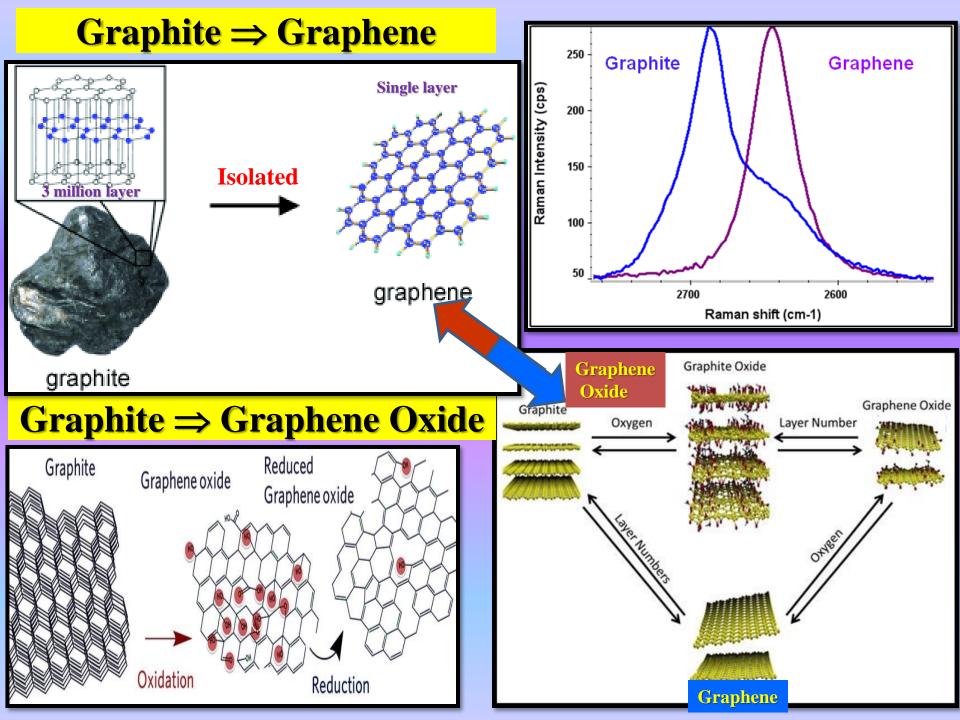
1. It is the hardest substance known.

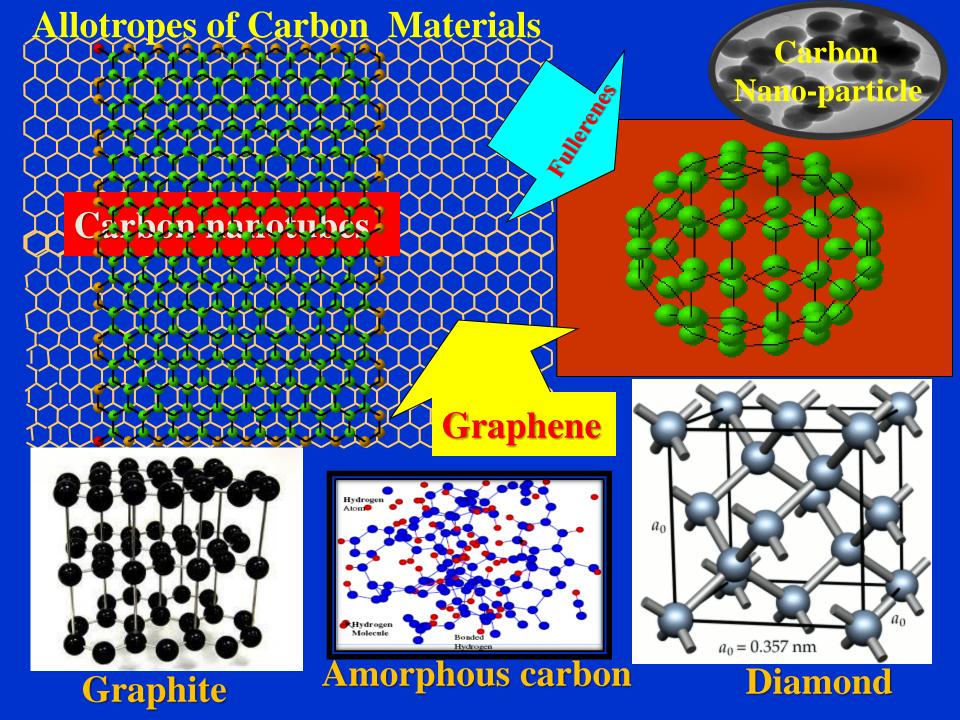
2. It has a high refractive index and gives an extraordinary brilliance.

3. The specific gravity of diamond is 3.52.

4. Diamond is a bad conductor of heat and electricity because it lacks free electrons.

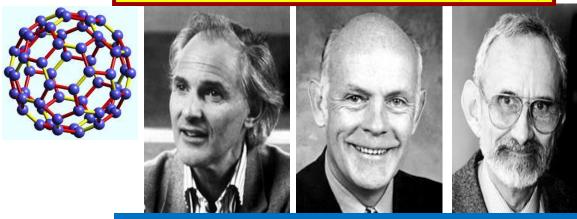
5. Chemically, diamonds are unreactive under ordinary conditions.





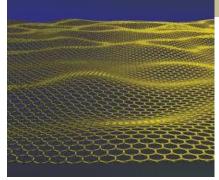
# **Six Giants of carbon materials**

### 1985 – Fullerene (1996)



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

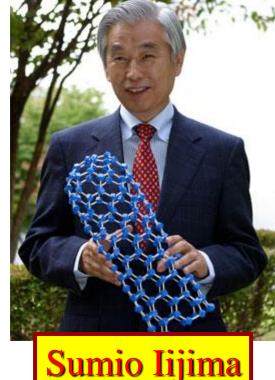
# 2004 – Graphene (2010)











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

- $(0.34 \text{ nm} \cong \text{One million times thinner than a human hair})$
- → Smallest molecule
- →High surface area of ~2500m<sup>2</sup>/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

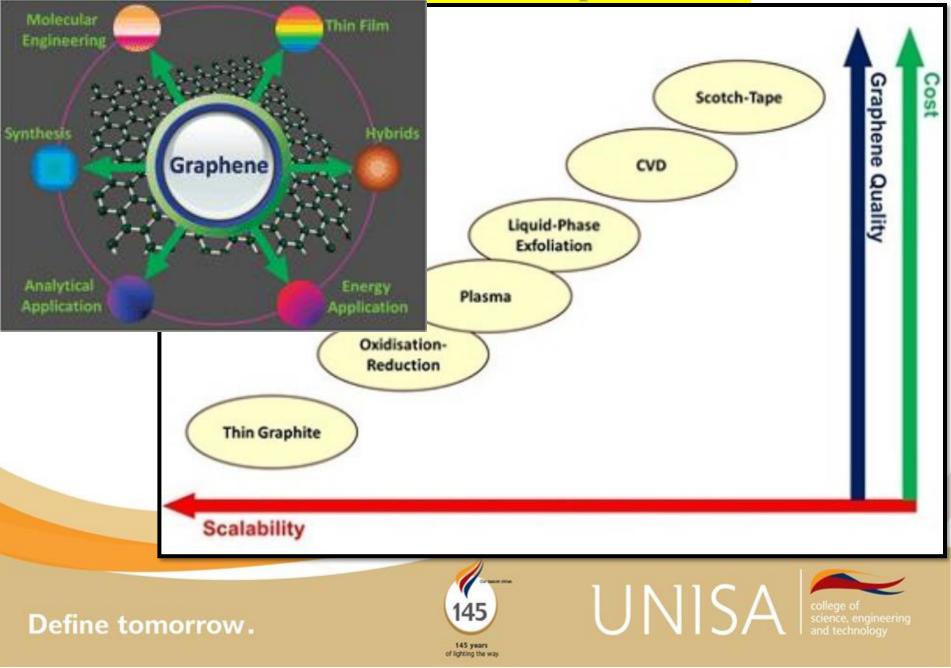


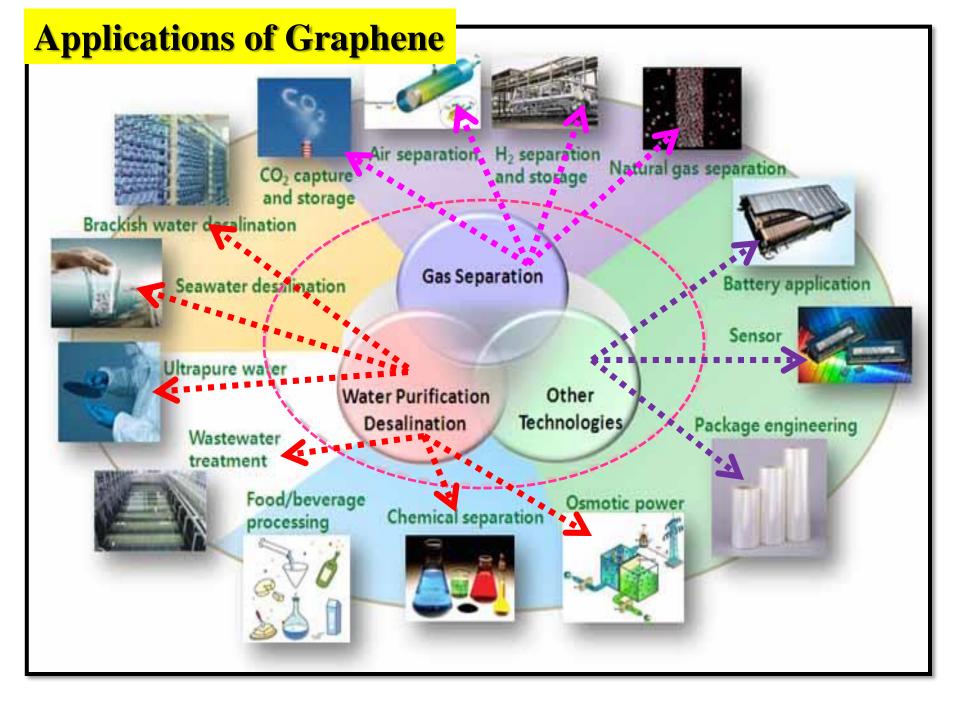
UNISA College of science, e and technological

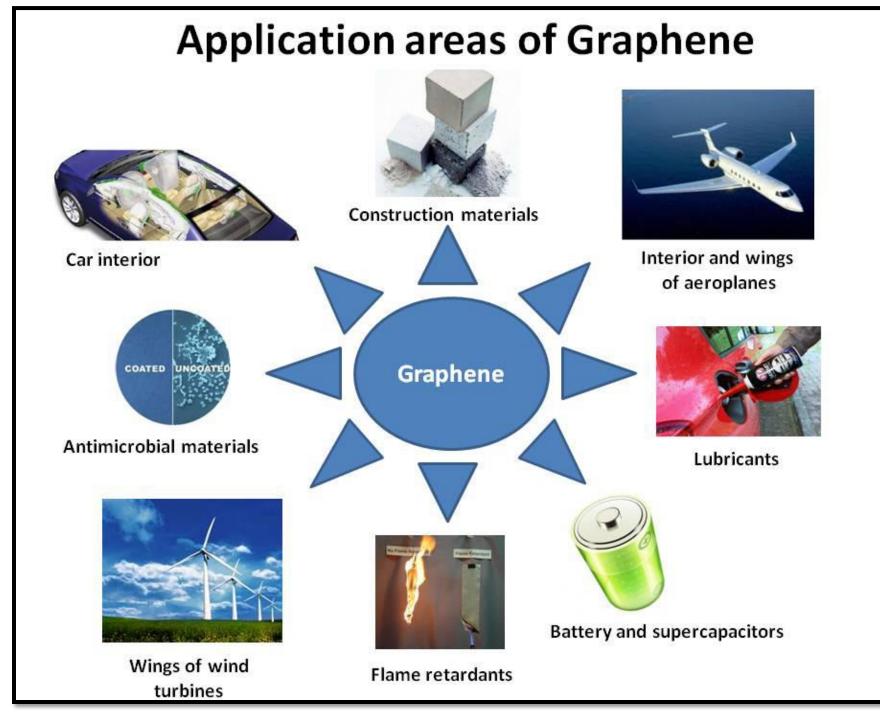


Define tomorrow.

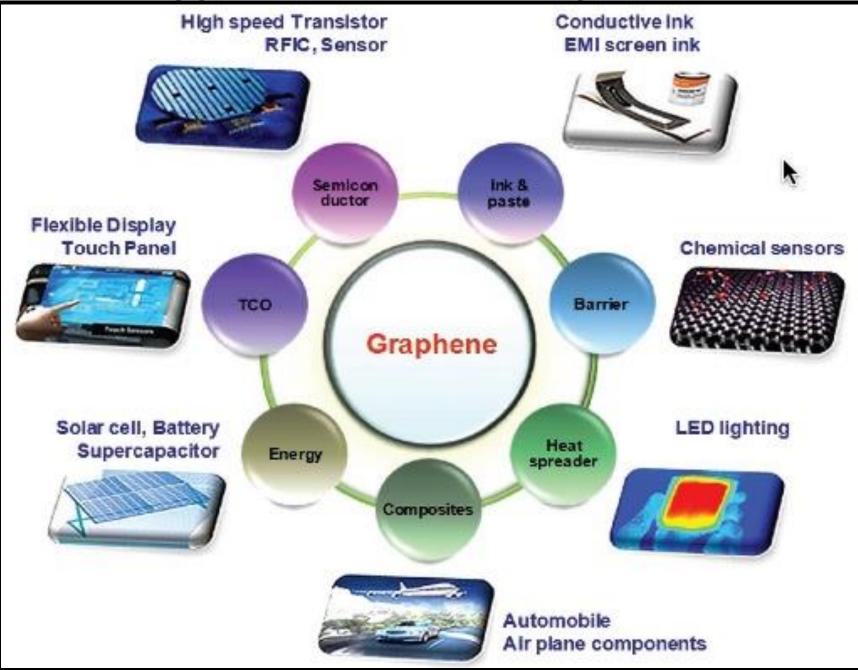
### **Synthesis Process of Graphene**

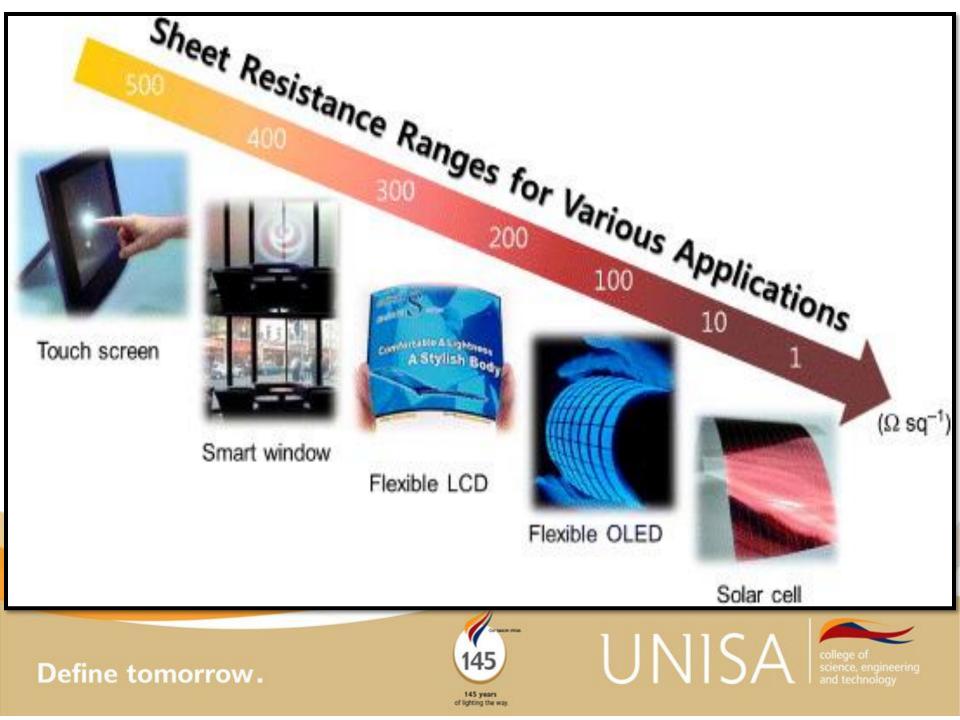




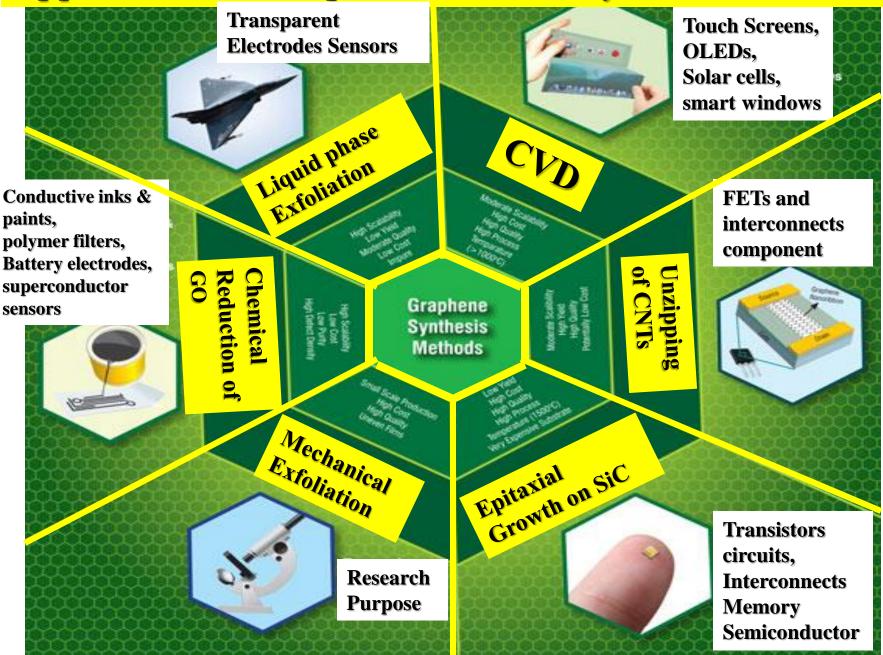


### **Application areas of Graphene**

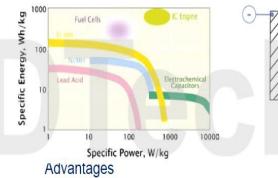




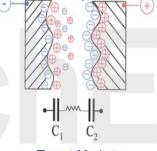
## **Applications of Graphene based on Synthesis Process**



# **Supercapacitors**



- ✓ Fast power delivery but less energy density
- ✓ Wide temperature compliance range
- ✓ Longer lifetime than Li-ion batteries
- ✓ Simplicity



electrolyte

#### Target Markets

- ✓ Mobile phones
- ✓ Camera
- ✓ Vehicles (bus, lifters, cars, trucks)
- ✓ Back-up system
- ✓ Renewable energy

### **ULTRA/SUPER CAPACITORS**

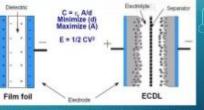
100 years old technology enhanced by modern materials based on polarization electrolytes, high surface area electrodes and extremely small charge seperation

#### Graphene Advantages

- \* High surface area to weight ratio (2600 m<sup>2</sup> /g)
- \* High conductivity
- \* Measured specific capacitance 135 F/g

#### Uses

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

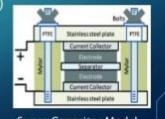


Laser

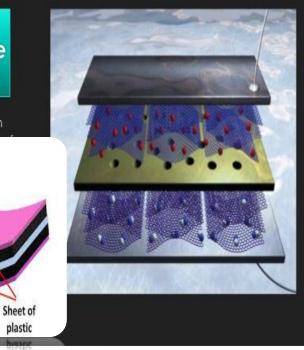
Scribed

Graphene

ECDL (Electro Chemical Double Layer) Capa



Super Capacitor Model



### **Supercapacitor Markets**

plastic

Energy Storage

Due to the extremely high

Separator &

Electrolyte

T-compliance

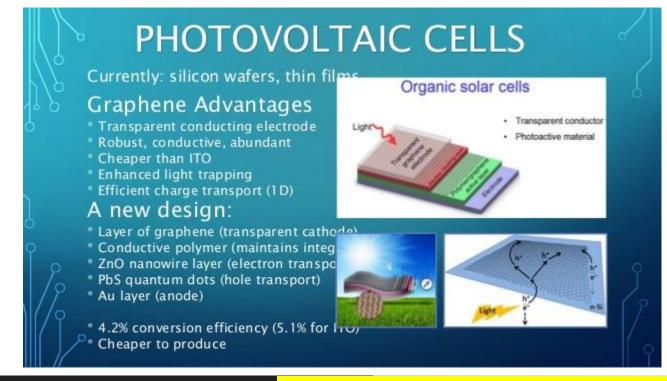
**Devices** 



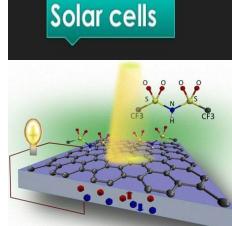


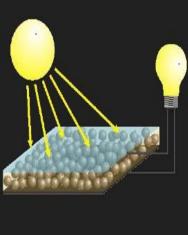






#### Solar cell / Flexible solar cell / Solar panel







### MAJESTIC FUTURE

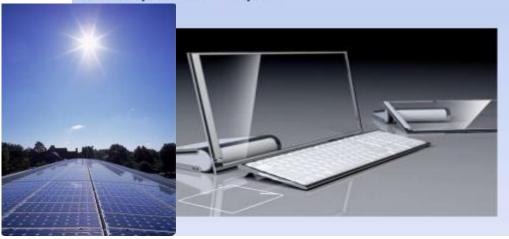
#### Advancements in touch screens

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.



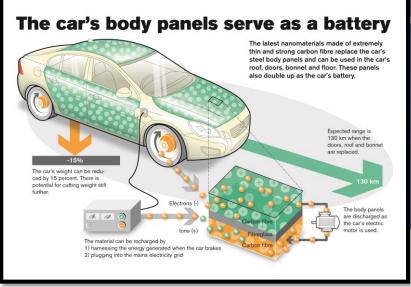




### Mechanical engineering

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

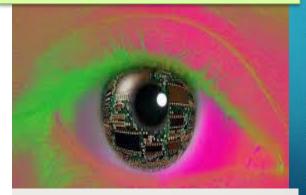








### Superhero Vision Coming in Graphene Contact Lenses





# New sensor could make night vision

# **BIOLOGICAL ENGINEERING**

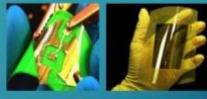
#### Graphene Advantages

\* Large Surface Area \* High Electrical Conductivity

\* Thinness and Strength

#### Uses

- \* Efficient Bioelectric Sensory Devices
- \* Able to monitor Glucose level, chole
- DNA sequencing, Haemoglobin level
- \* Toxic Graphene as anti-cancer treat
- \* Process of Tissue Regenration



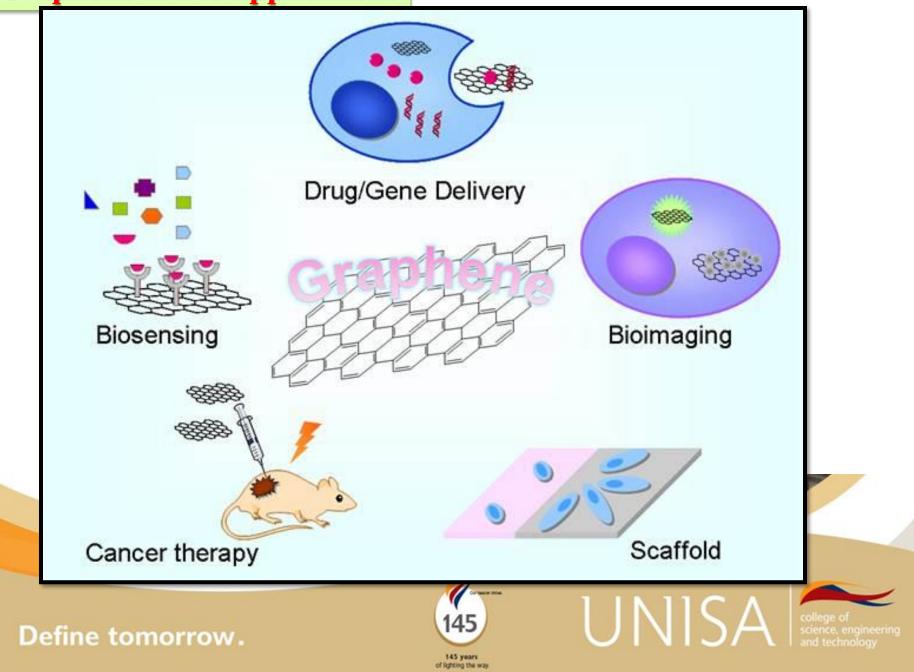




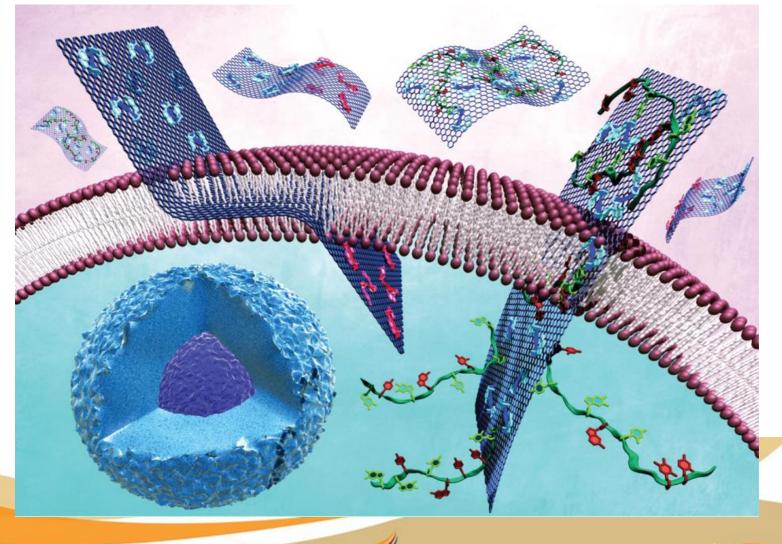
 In 2010, the Chinese Academy of Sciences has found that sheets of graphene oxide are highly effective at killing bacteria such



### **Graphene in Bio-applications**



### Graphene in drug delivery into the interior of a cell



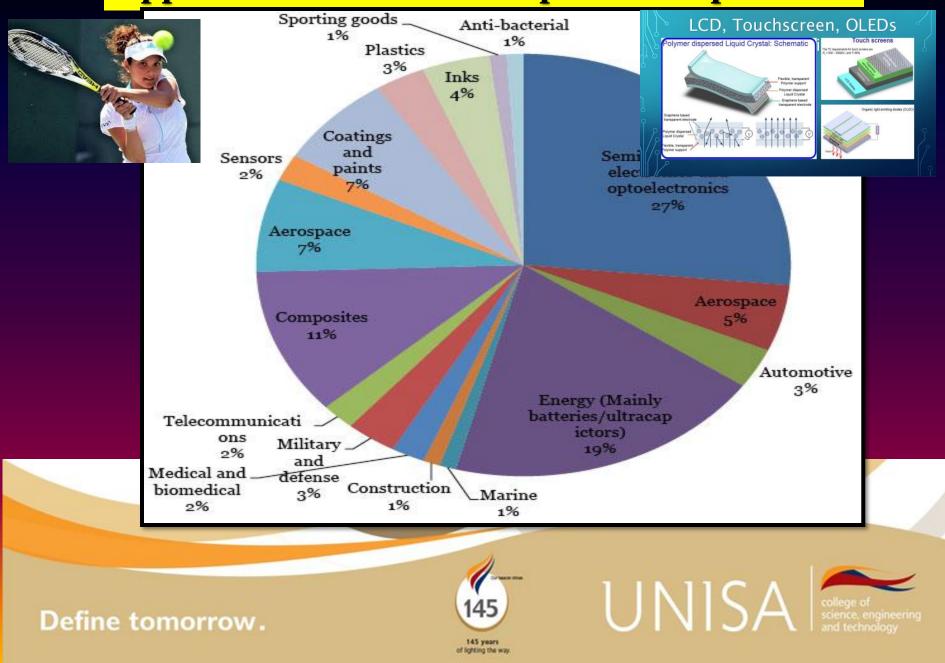
Define tomorrow.



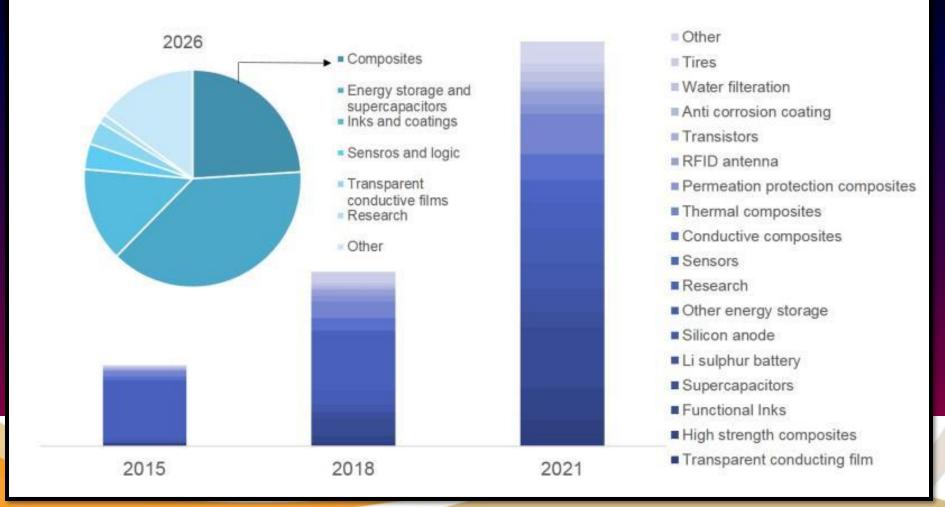




## **Applications chart for Graphene companies**



# A roadmap for graphene

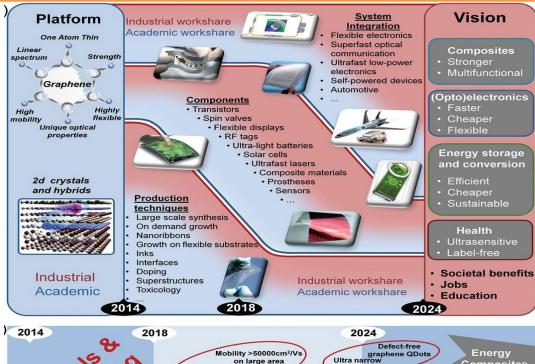


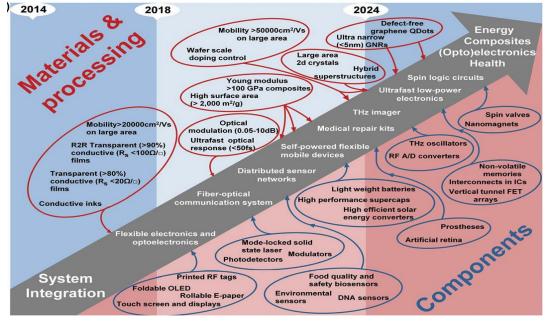
**Define tomorrow.** 



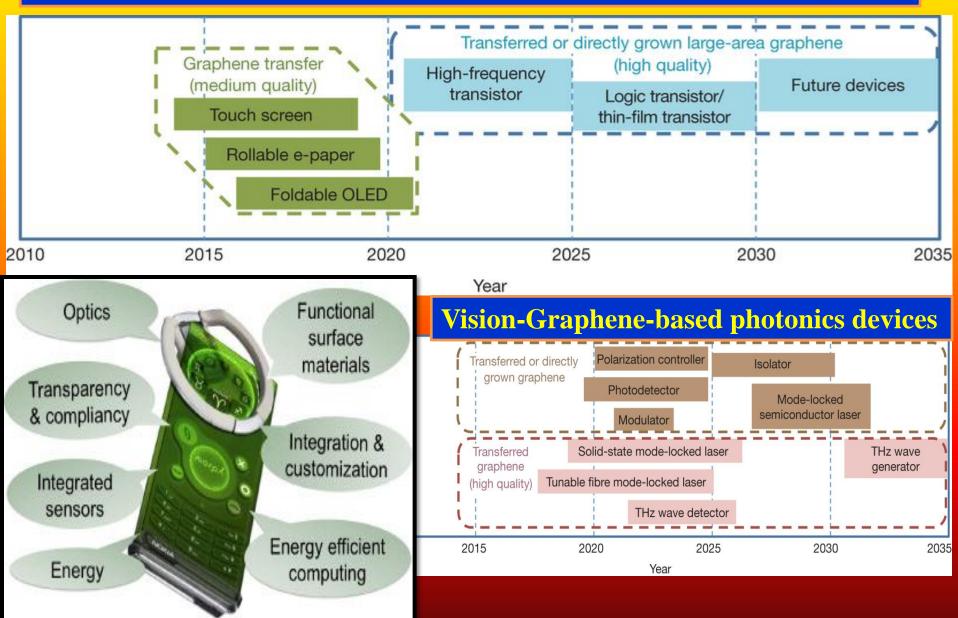
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# **Vision – Future Applications of Graphene**



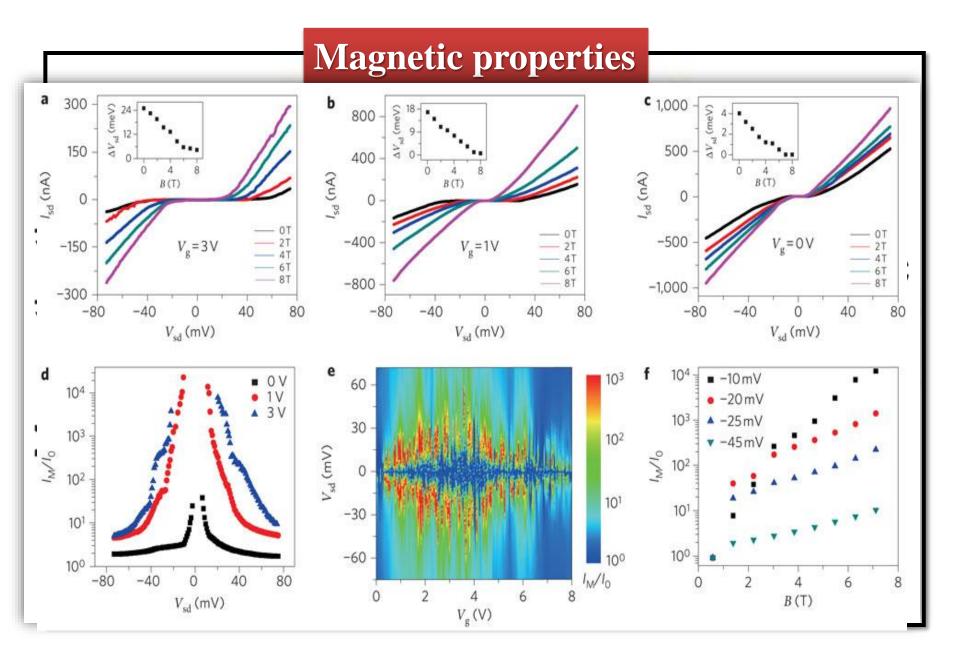


## Vision-Graphene-based display and electronic devices



# (**Prototype Graphene Phone:**within 3 years)

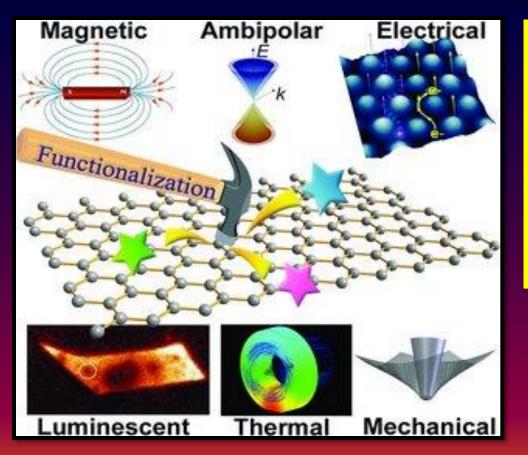




# **Magnetic devices using Graphene**

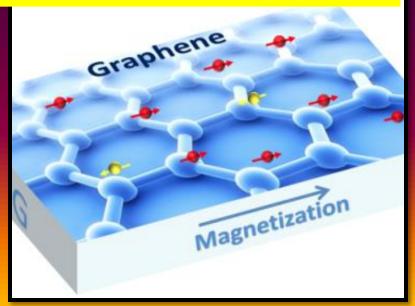


# **Functionalization of Graphene by Hydrogen, Silicon and Nitrogen, Iron, Gold, Cobalt-----**



### Why Carbon / Graphene??

Carbon-based materials are very<br/>promising for spintronic<br/>applications due to their weak<br/>spin-orbit coupling and<br/>potentially providing a long spin<br/>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

(Insulator)

Graphane

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

GraphU

(semiconductor)

Conversion  $sp^2 \rightarrow sp^3$ 

(conductor)

Graph<sup>e</sup>ne

Nr.Hydr

NM

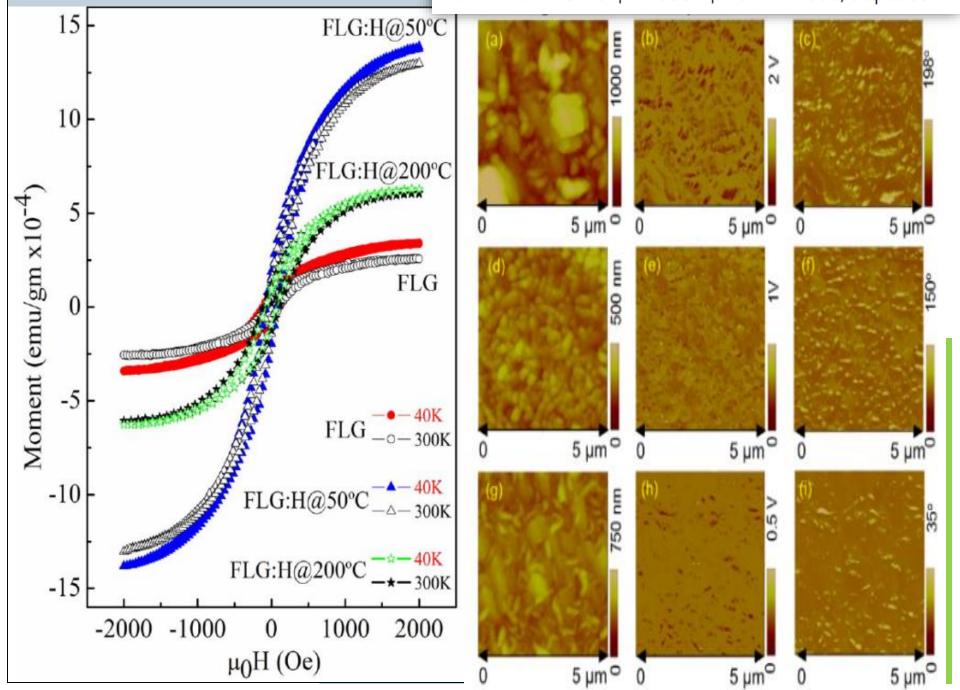
 $m=0\mu_{R}, E=0.49$ 

 $m=0\mu_{R}, E=0.15;$ 

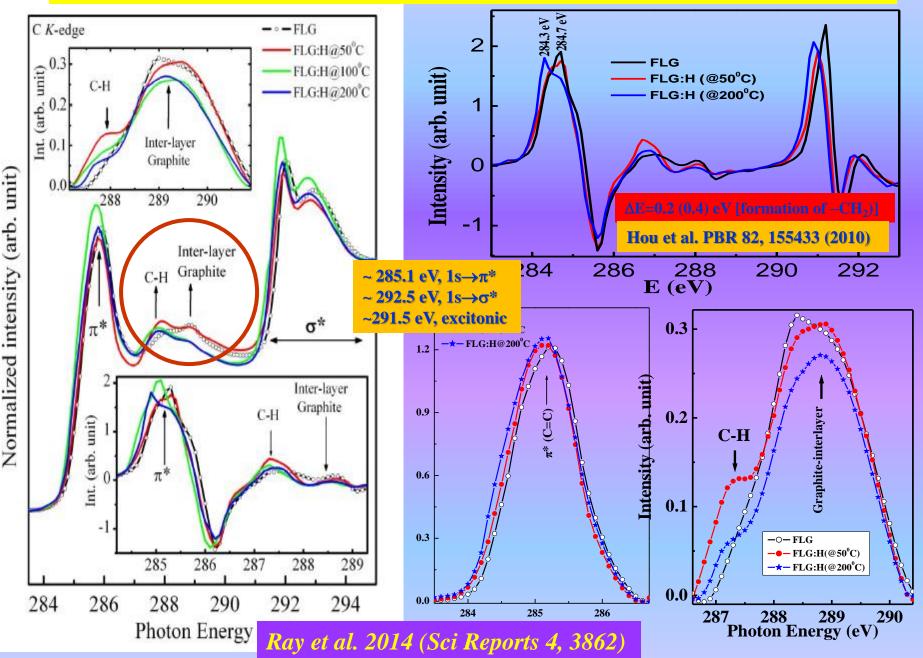
by removing conduction  $\pi$ -bands and opening band gaps

 $=4\mu_{\rm B}, E=0;$ 

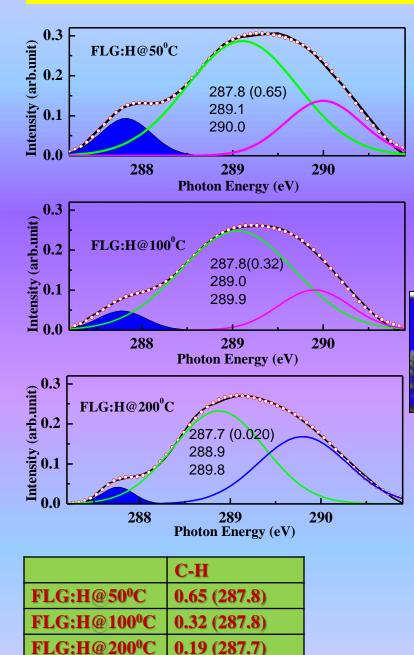
www.nature.com/scientificreports SCIENTIFIC REPORTS | 4:3862 | DOI: 10.1038/srep03862



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

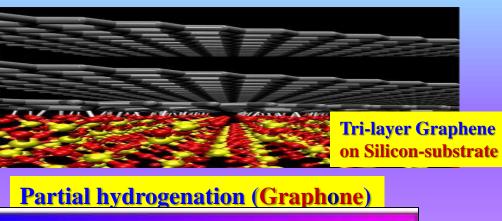


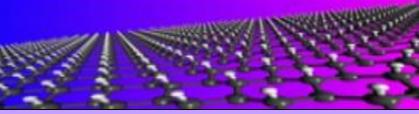
### **Determination of C-H content from C K-edge XANES spectra**



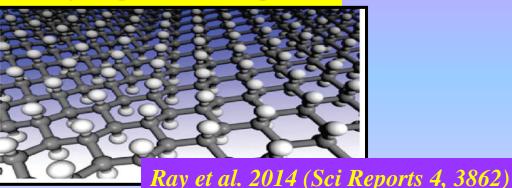
0.19 (287.7)

**CH** ratio  $0.65: 0.32: 0.19 \approx 6: 3: 2$ 

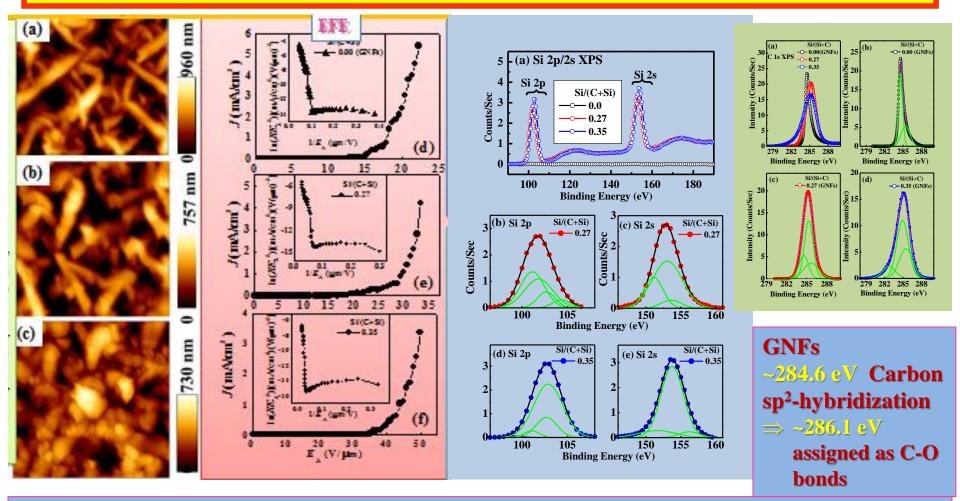




### **Full hydrogenation (Graphane)**



#### **Silicon-Functionalized Graphene Nanoflakes: Electronic Structure**



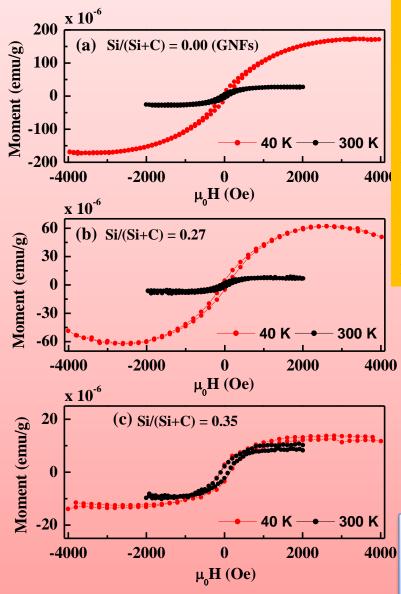
#### **GNFs:Si**

 $\Rightarrow \sim 285.4 \text{ eV}$  carbon sp<sup>2</sup>-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<sup>3</sup>-hybridization

- $\Rightarrow$  ~ 285.0 eV is "defect peaks"
- $\Rightarrow$  ~285.6 eV defined as Si-C-O bonding peak
- $\Rightarrow$  ~286.8 eV is the C-O bonds

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

#### Silicon-Functionalized Graphene: Ferro-Magnetic Behaviour



 $\Rightarrow$  M<sub>S</sub> values are reduced with increasing coercivity (H<sub>c</sub>) as the Si-content is increased, implying the loss of magnetization with silicon content.

 $\Rightarrow$ With increase of Si-content, non-defect Si-C tetrahedral bonding along with SiO are formed that make sp<sup>3</sup>-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

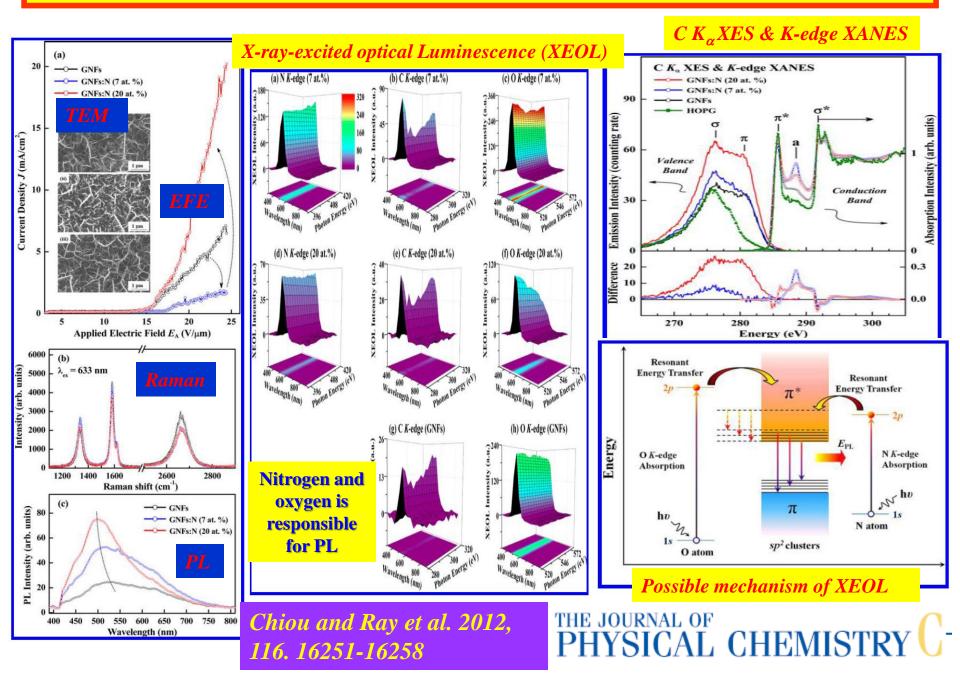
Saturation magnetization  $(M_S)$ , Coercivity  $(H_C)$  and Remanence  $(M_R)$  of GNFs and GNFs:Si.

Sample	$\frac{Si}{(Si+C)}$	M <sub>s</sub> (x10 <sup>-6</sup> emu/g)		H <sub>c</sub> (Oe)		M <sub>R</sub> (x10 <sup>-6</sup> emu/g)	
	Ratio	<b>40K</b>	<b>300K</b>	40K	300K	<b>40K</b>	<b>300K</b>
GNFs	0.00	172.53	27.19	66.00	81.27	9.38	5.83
<b>GNFs:Si</b>	0.27	62.05	6.92	90.00	108.00	4.62	2.25
<b>GNFs:Si</b>	0.35	13.00	12.00	149.00	101.00	2.85	2.20

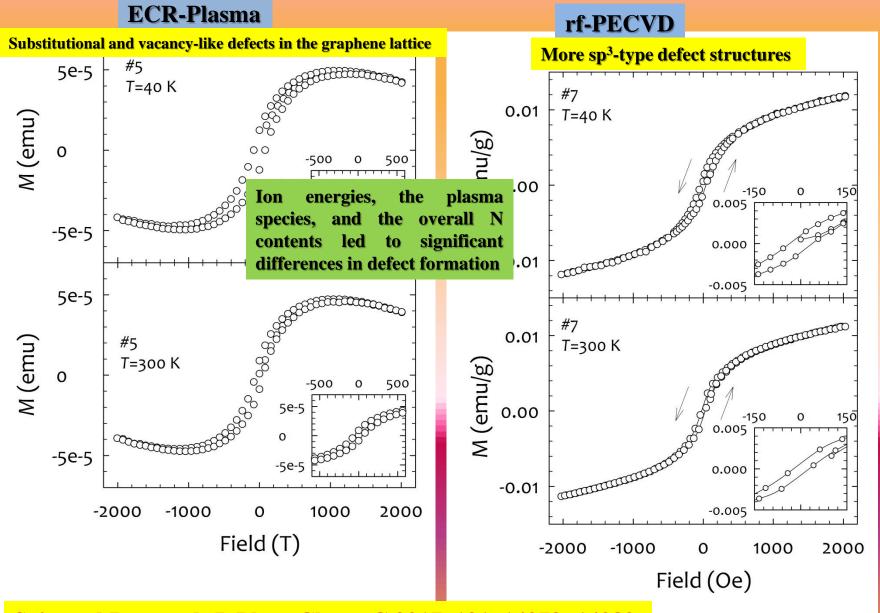
Ferromagnetic materials with high coercivity are called magnetically hard materials, and are used to make permanent magnets. Materials with low coercivity are said to be magnetically soft and are are used in transformer and inductor cores, ling heads, microwave devices, and magnetic shielding.

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

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

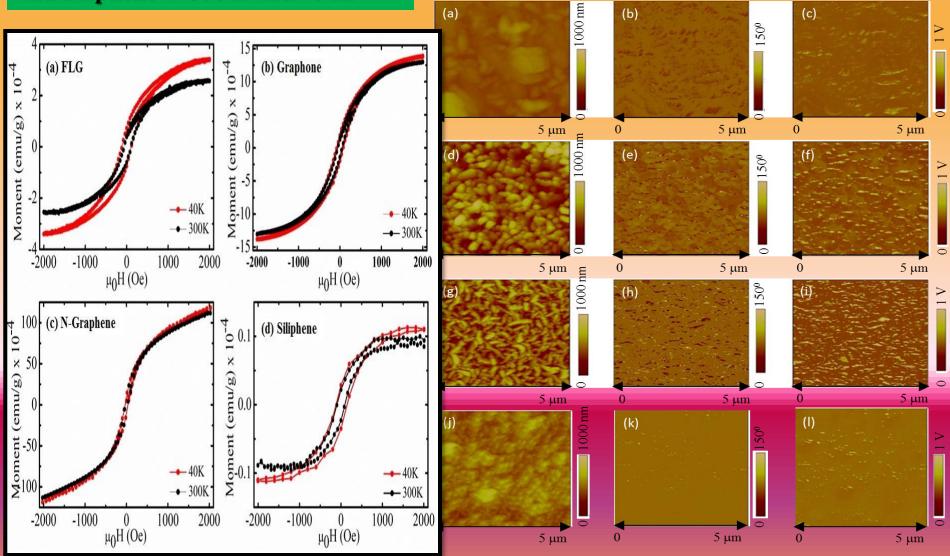


### **Nitrogen Functionalized Graphene: Ferro-Magnetic Behaviour**



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

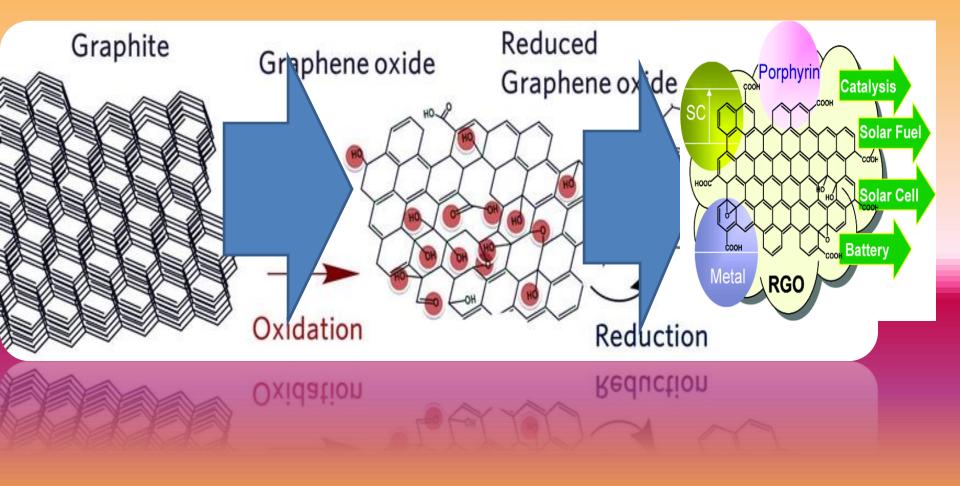


Ray et al. 2016, RSC Adv., 2016, 6, 70913-70924

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

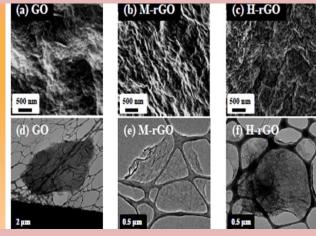
Sample/	H <sub>c</sub> (Coercivity)	M <sub>s</sub> (Saturation	M <sub>r</sub> (Remnant	
Temperature	(Oe)	magnetisation)	magnetisation)	
		(emu/gm)	(emu/gm)	
FLG				
40K	112.37	3.47 x 10 <sup>-4</sup>	0.52 x 10 <sup>-4</sup>	
300K	62.98	2.60 x 10 <sup>-4</sup>	<b>0.42</b> x 10 <sup>-4</sup>	
Graphone				
40K	76.19	13.94 x 10 <sup>-4</sup>	1.91 x 10 <sup>-4</sup>	
300K	52.88	12.91 x 10 <sup>-4</sup>	<b>1.28 x 10</b> -4	
N-Graphene				
40K	40.00	118.62 x 10 <sup>-4</sup>	9.74 x 10 <sup>-4</sup>	
300K	25.42	111.91 x 10 <sup>-4</sup>	6.04 x 10 <sup>-4</sup>	
Siliphene				
40K	120.03	0.11 x 10 <sup>-4</sup>	0.03 x 10 <sup>-4</sup>	
300K	94.75	0.09 x 10 <sup>-4</sup>	0.02 x 10 <sup>-4</sup>	
	Ray et al. 2016, RSC Adv., 2016, 6, 70913-			

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

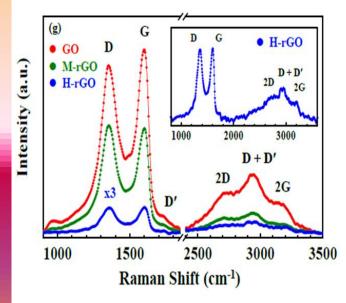


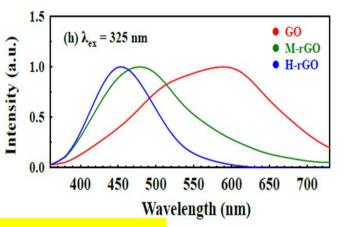
### **SEM, TEM, Raman and PL of Graphene Oxides**

FE-SEM images: Change of surface morphology



**TEM images: Change of surface morphology** 





**GO:** A significant number of disorder-induced defect states within the  $\pi$ - $\pi$ \* gap and exhibits a predominant broad **PL spectrum** centered at longer wavelengths.

**rGO:** The number of disorder-induced states within the  $\pi$ - $\pi$ \* gap decreases, and an increased number of small sp<sup>2</sup> clusters in the rGO result in blue luminescence.

#### **Photoluminescence:**

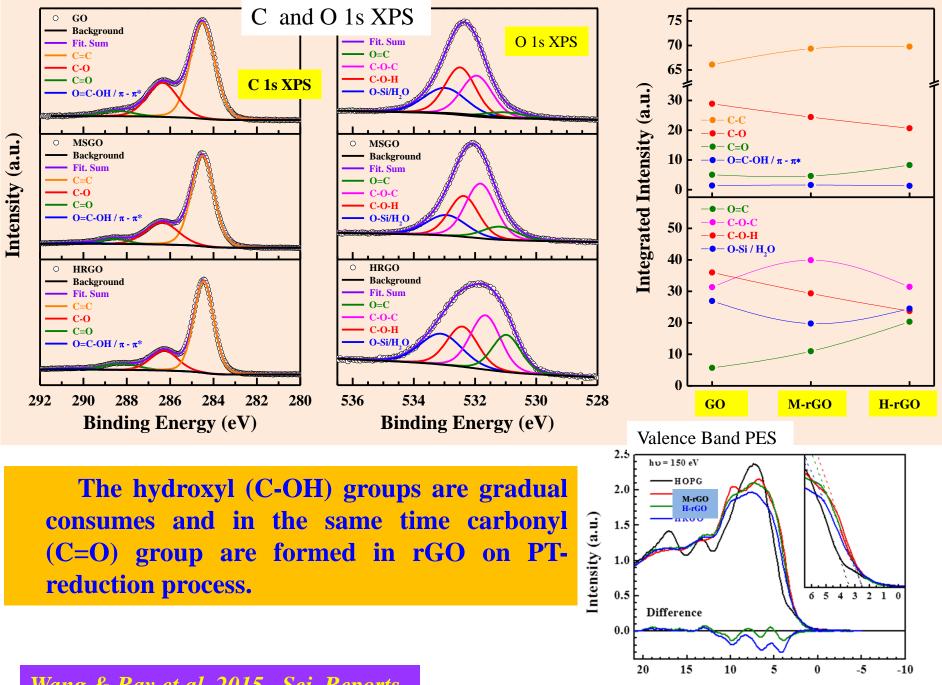
P-T reduction process does not always remove all of the oxygen and oxygen containing functional groups from the GO but that the process can increase the number of  $\pi^*(C-OH)$  and  $\pi^*(C-O-C)$  bonds upon the rearrangement of oxygen and oxygen-containing functional groups with carbon; this consequence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

<b>B-Band: 1587 cm<sup>-1</sup> is</b> ttributed to the E <sub>2g</sub> honon of sp <sup>2</sup> states	D-band: 1327 cm <sup>-1</sup> is A <sub>1g</sub> symmetry disorder - defects/ vacancies in grain boundaries	
	U	

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

#### Chuang and Ray et al. 2014, Sci. Reports

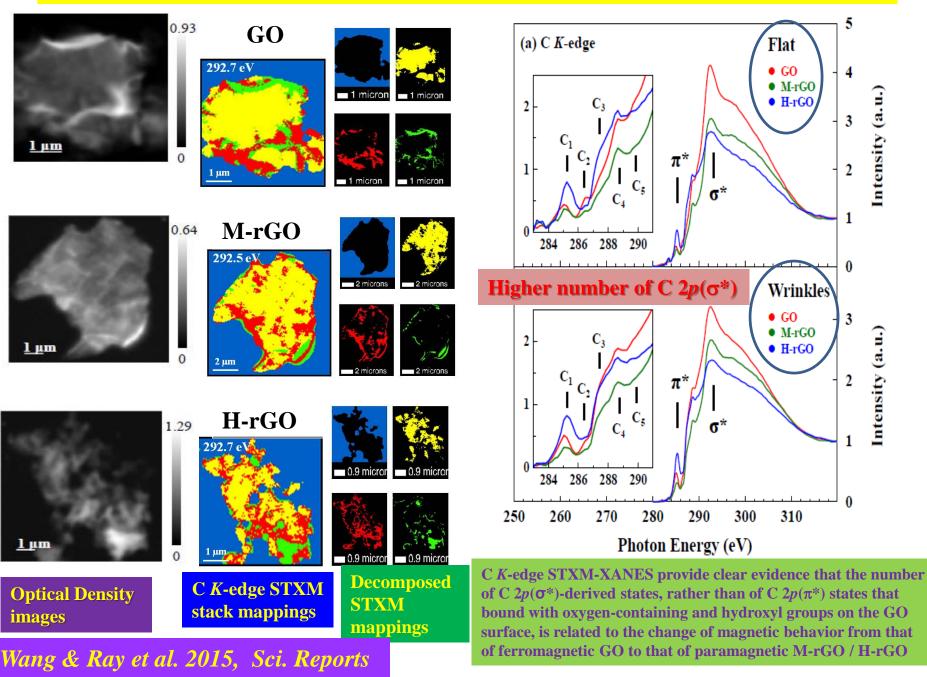
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Wang & Ray et al. 2015, Sci. Reports

Binding Energy (eV)

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



### **Magnetic behavior of Graphene Oxides**

Origin of magnetic behavior in Graphene Oxides !!

### In general,

- ⇒Symmetry breaking at the edges
- $\Rightarrow$  Vacancy
- $\Rightarrow$  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  $\mu_B$  and 0.56  $\mu_B$  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

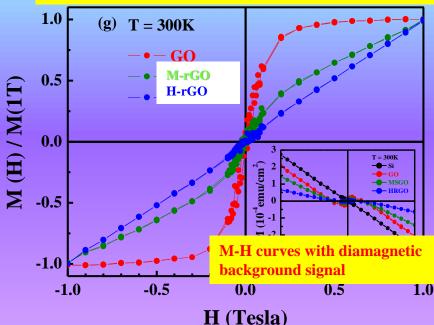
**Ref:** (i) Santos, E. J. G. eta l. *New J. Phys.* 2012, *14*, 043022. (ii) Wang, M. et at. *Nanotechnology* 2011, *22*, 105702. (iii) Boukhvalov, D. W. et al. *ACS Nano* 2011, *5*, 2440

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



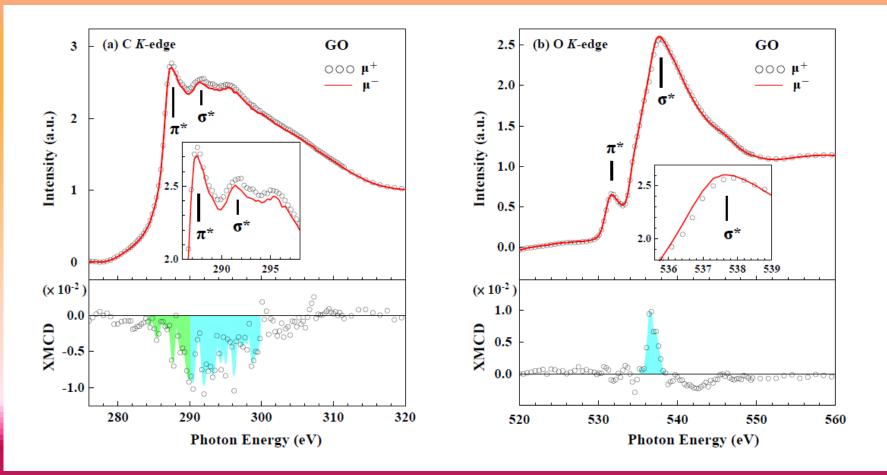
Absence of d and f electrons but strongly supports the intrinsic  $d^0$  magnetism of GO

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.

### GO is usually considered as an diamagnetic insulator / semiconductor material

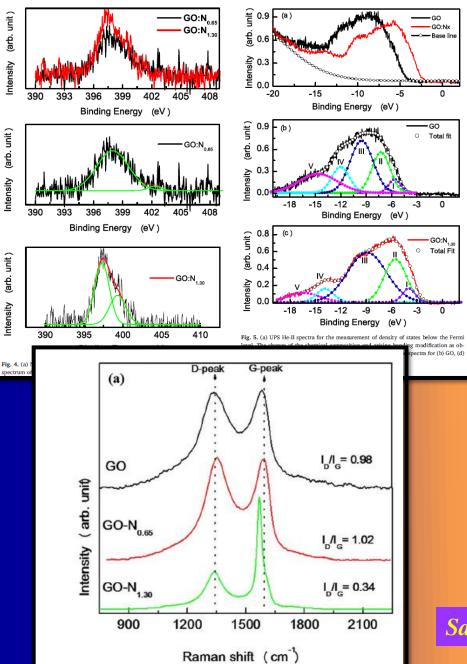
### **X-ray Magnetic Circular Dichroism (XMCD) of Graphene Oxides**

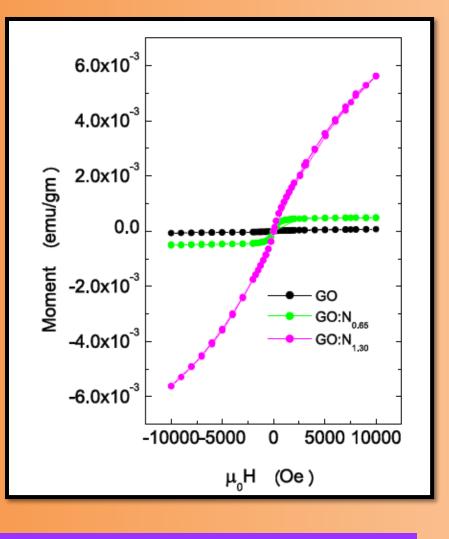


**C and O K-edge:** X-ray magnetic circular dichroism (XMCD) spectra with the photo-helicity of incident x-rays parallel ( $\mu^+$ ) and anti-parallel ( $\mu^-$ ) to the direction of magnetization of GO

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Wang & Ray et al. 2015, Sci. Reports
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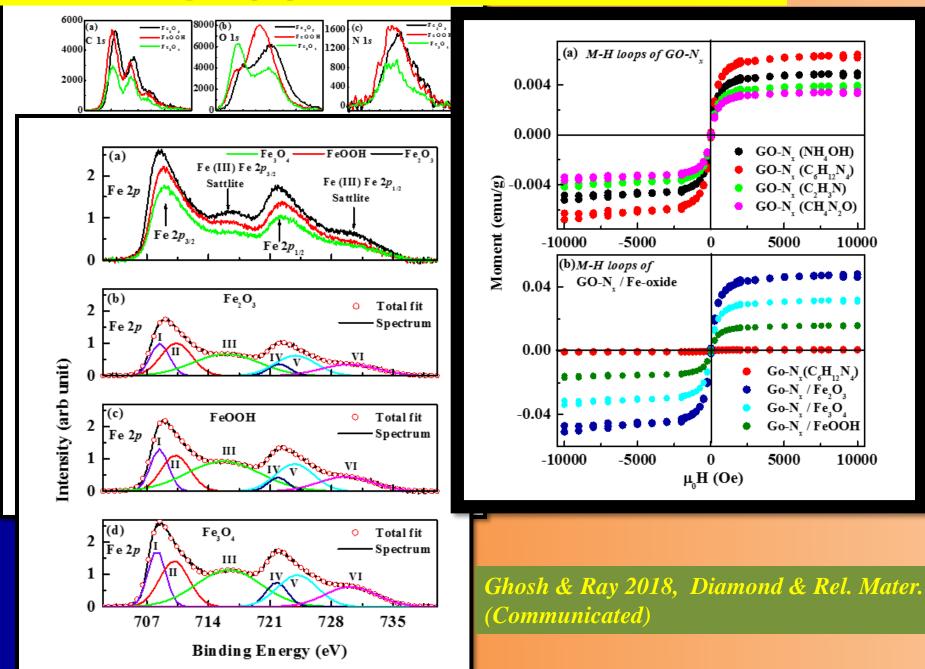
#### **Electronic and magnetic properties of nitrogen functionalized graphene-oxide**





Sarma & Ray 2017, Diamond & Rel. Mater.

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



### Origin of magnetic properties in carbon implanted ZnO nanowires

C K-edge

(x10<sup>3</sup>)

280

(IV)

Thin

Thin

550

290

300

Photon Energy (eV)

**(V)** 

Bulk

Bulk

2.2

2.0

1.8

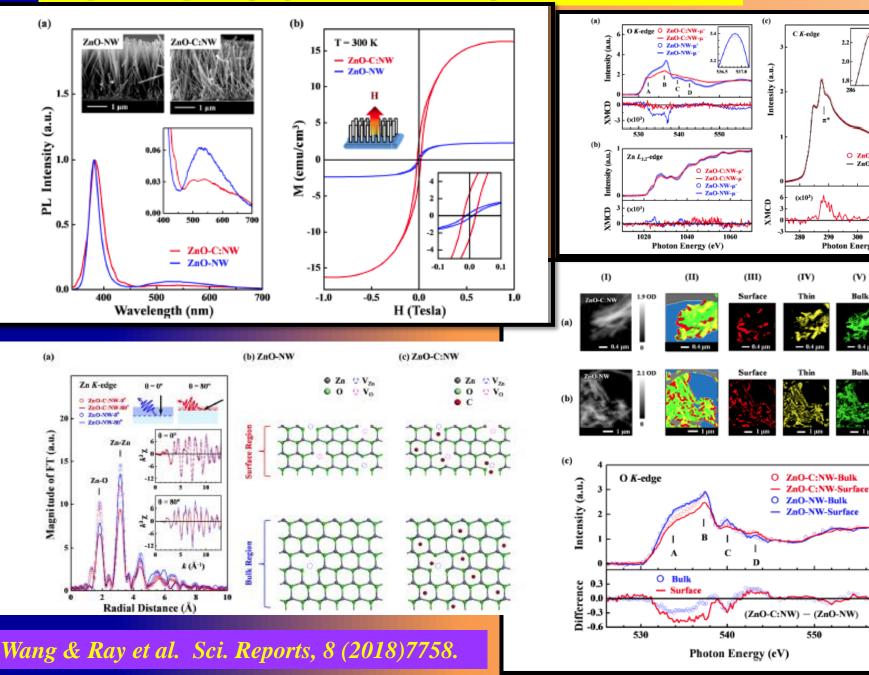
286 288 290

O ZnO-C:NW-µ\*

- ZnO-C:NW-µ

310

320

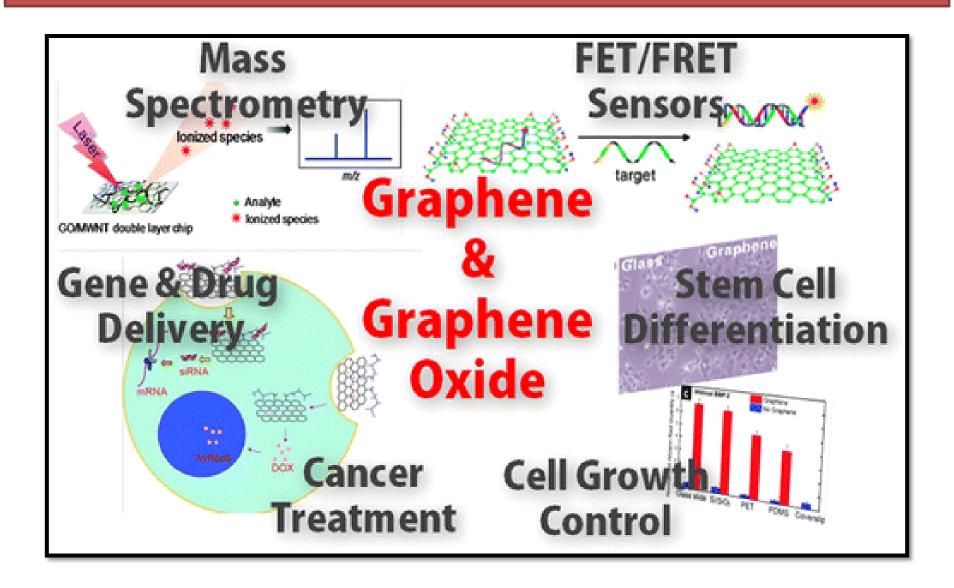


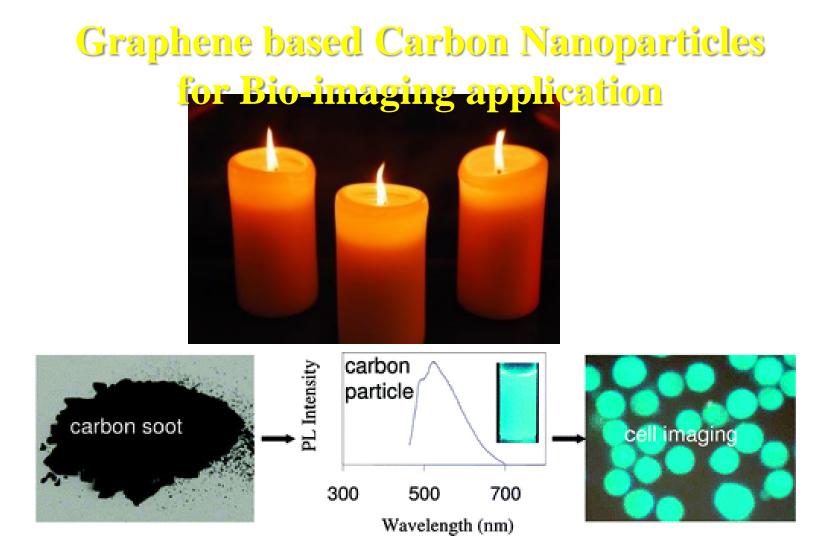
# CONCLUSION

- 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**

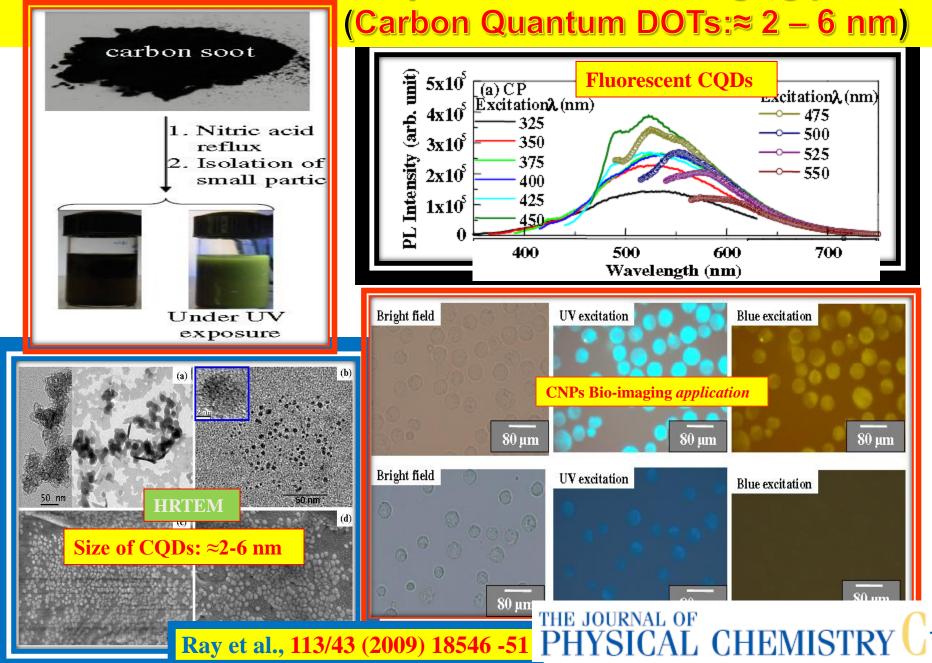


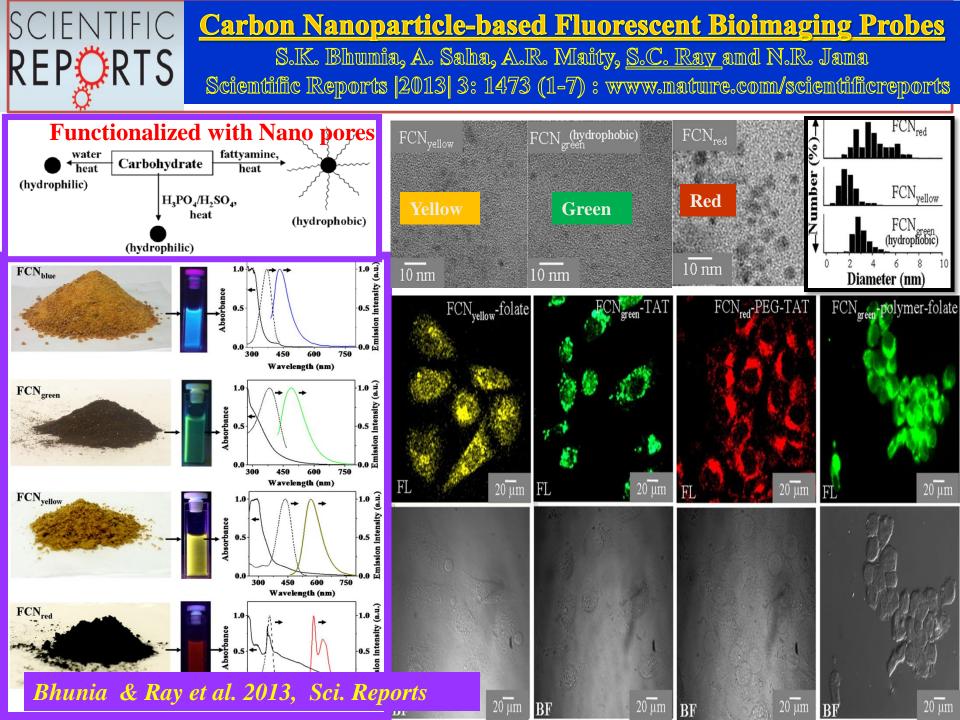


Ray et al.

J. Phys. Chem. C 2009, 113, 18546-18551

**Fluorescent Carbon Nanoparticles for Bio-imaging probes** 





# Vision – Applications of Graphene (within 50 years)



# Vision – Applications of Graphene (within 50 years)!

## THANK YOU FOR YOUR ATTENTION



**GRAPHENE** The 'miracle material' that could revolutionize our world

is it? Is aver of carbon arranged in a honeycomb lattice. When millions of these are stacked one on top of another they form graphite - a mineral consisting of carbon which is found in pencils.

Graphene is a one-atom thick

Graphene was discovered in 2004 at the UK's University of Manchester by physicists Andre Geim and Konstantin Novoselov when they isolated a single-layer of graphene using Scotch Tape before going on to demonstrate its remarkable conductive and resilient properties.

What

Geim and Novoselov's work earned them the Nobel Prize in physics in 2010 and today researchers are in a race to realize its technical and commercial capabilities.







college of science, engineering and technology