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

Sekhar Chandra Ray

Department of Physics
University of South Africa
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

\( \pi/\sigma \) is bonding state originated from the in-plane, bonds of sp^2 - /sp^3 - configuration

\( \pi^*/\sigma^* \) is anti-bonding state originated from the out-of-plane, bonds of sp^2 - /sp^3 - configuration

Electronic distribution of Carbon

Hybridization of Carbon atoms

\( 1s^2 \)

\( 2s^2 \)

\( 2p^2 \)

\( 2s^1 \)

\( 2p^2 \)

\( sp^2 \)

\( sp^3 \)

\( sp^1 \)

Flat triangular

Tetrahedral

Linear
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 sp² & sp³)

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 unreactive under ordinary conditions.
Graphite $\Rightarrow$ Graphene

Graphite $\Rightarrow$ Graphene Oxide

Graphite

Graphene oxide

Reduced Graphene oxide

Graphite Oxide

Oxygen

Layer Number

Graphene Oxide

Layer Numbers

Oxygen

Graphene

Oxidation

Reduction
Allotropes of Carbon Materials

- Diamond
- Graphite
- Carbon nanotubes
- Amorphous carbon
- Graphene
- Fullerenes
- Carbon Nano-particle
Six Giant on carbon materials

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

- Sumio Iijima
  1990 – CNTs (1991)

- Andre Geim    Konstantin Novoselov

- Graphite - 2010

- Diamond - 2010

- Carbon fiber - 2010

- Carbon black - 2010

- Nanotube - 2010

- Graphene - 2010

- Fullerene - 2010

- Six Giant on carbon materials

- Carbon nanotube
- Graphene
- Fullerene

- Publication year
- Number of publications


- 1000 2000 3000 4000 5000 6000
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 ~2500 m²/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

- Liquid phase Exfoliation
- Chemical Reduction of GO
- Mechanical Exfoliation
- Epitaxial Growth on SiC
- CVD
- Unzipping of CNTs
- Transistors circuits, Interconnects Memory Semiconductor
- GO
- Conductive inks & paints, polymer filters, Battery electrodes, superconductor sensors
- Transparent Electrodes Sensors
- Touch Screens, OLEDs, Solar cells, smart windows
- Research Purpose
Applications of Graphene based on Properties

- Electronics
  - Interconnects
  - Optical properties
  - Transparent electrodes
- Photonics
- Sensors
- Capacitors
- Mechanical properties
- Membranes
- Surface/volume ratio
- Thermal properties
- Impermeability
- Gas barriers
- Heat dissipators
OPTICAL ELECTRONICS

Graphene Advantages
* Optically transmit more than 90% of light
* Conductivity more than $1 \times 10^6 \Omega^{-1} \text{m}^{-1}$
* 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

[Diagram of Polymer dispersed Liquid Crystal: Schematic]

[Diagram of Touch screens]

[Diagram of Organic light emitting diodes (OLED)]
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 films

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 cathode)
* Conductive polymer (maintains integrity)
* ZnO nanowire layer (electron transport)
* PbS quantum dots (hole transport)
* Au layer (anode)

* 4.2% conversion efficiency (5.1% for ITO)
* 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.

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 transparency 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.

The car's body panels serve as a battery

The latest nanomaterials made of extremely thin and strong carbon fibre replace the car's steel body panels and can be used in the car's roof, doors, bonnet and floor. These panels also double up as the car's battery.

- The car's weight can be reduced by 15 percent. There is potential for cutting weight still further.
- The material can be recharged by:
  - harnessing the energy generated when the car brakes
  - plugging into the mains electricity grid
- Expected range is 130 km when the doors, roof and bonnet are replaced
- The body panels can double as the car's electric motor is used
MAJESTIC FUTURE

- Advancements in touch screens

- It is practically transparent and a good conductor

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.

Transparent-Fexiable Touch Screen
Applications chart for Graphene companies

- Semiconductors, electronics and optoelectronics: 27%
- Energy (mainly batteries/ultracapacitors): 19%
- Aerospace: 5%
- Composite: 11%
- Coatings and paints: 7%
- Aerospace: 7%
- Telecommunications: 2%
- Medical and biomedical: 2%
- Marine: 1%
- Construction: 1%
- Military and defense: 3%
- Inks: 4%
- Plastics: 3%
- Anti-bacterial: 1%
- Sporting goods: 1%
What to expect from Graphene -- Major Applications

- Solar Cell
- OLED

Bar chart showing the projected market growth from 2010 to 2020 for various applications of graphene, with emphasis on solar cells and OLEDs.
A roadmap for graphene
My Contribution on Graphene Research

Magnetic properties

- Interconnects
- Sensors
- Capacitors
- Electronics
- Photonics
- Electrical properties
- Optical properties
- Surface/volume ratio
- Mechanical properties
- Transparent electrodes
- Membranes
- Thermal properties
- Impermeability
- Heat dissipaters
- Gas barriers
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: 2D crystal made of carbon atoms arranged in a honeycomb lattice

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

Conversion $sp^2 \rightarrow sp^3$ by removing conduction $\pi$-bands and opening band gaps


Graphene-Graphone-Graphane

FM: $m=4\mu_B, E=0$
AF: $m=0\mu_B, E=0.15$
NM: $m=0\mu_B, E=0.49$
Raman Spectroscopy

Free spins available via the conversion of sp$^2$ to sp$^3$ hybridized structures, and the possibility of unpaired electrons from defects induced upon hydrogenation are thought to be likely mechanisms for the observed ferromagnetic orders.

Ray et al. 2014

Magnetic Force Microscopy
C K-edge XANES of Semi-hydrogenated Graphene Sheet

\[ \Delta E \approx 0.2 \text{ (0.4) eV} \] [formation of –CH$_2$]

Hou et al. PBR 82, 155433 (2010)

\( \approx 285.1 \text{ eV}, \ 1s \rightarrow \pi^* \)

\( \approx 292.5 \text{ eV}, \ 1s \rightarrow \sigma^* \)

\( \approx 291.5 \text{ eV}, \text{ excitonic} \)
Determination of C-H content from C K-edge XANES spectra

<table>
<thead>
<tr>
<th>C-H</th>
<th>FLG:H@50°C</th>
<th>0.65 (287.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FLG:H@100°C</td>
<td>0.32 (287.8)</td>
</tr>
<tr>
<td></td>
<td>FLG:H@200°C</td>
<td>0.19 (287.7)</td>
</tr>
</tbody>
</table>

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

Partial hydrogenation (Graphone)

Full hydrogenation (Graphane)

Tri-layer Graphene on Silicon-substrate
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 sp³-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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/(Si+C) Ratio</th>
<th>M_s (x10^6 emu/g)</th>
<th>H_c (Oe)</th>
<th>M_R (x10^6 emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNFs</td>
<td>0.00</td>
<td>172.53</td>
<td>66.00</td>
<td>9.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.19</td>
<td>81.27</td>
<td>5.83</td>
</tr>
<tr>
<td>GNFs:Si</td>
<td>0.27</td>
<td>62.05</td>
<td>90.00</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.92</td>
<td>108.00</td>
<td>2.25</td>
</tr>
<tr>
<td>GNFs:Si</td>
<td>0.35</td>
<td>13.00</td>
<td>149.00</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.00</td>
<td>101.00</td>
<td>2.20</td>
</tr>
</tbody>
</table>

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

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

X-ray-excited optical Luminescence (XEOL)

Possible mechanism of XEOL

Nitrogen and oxygen is responsible for PL

Nitrogen-Functionalized Graphene: Tunable PL and Electronic Structure

C Kα XES & K-edge XANES

TEM

EFE

Raman

PL

THE JOURNAL OF PHYSICAL CHEMISTRY
Nitrogen Functionalized Graphene: **Ferro-Magnetic Behaviour**
Magnetic hysteresis loops of pristine Graphene, Graphone, N-graphene and Siliphene at 300 K and 40 K. 

Ray et al. NPG Asia Materials (Under consideration)
## Magnetic properties of the pristine and plasma treated graphenes at 40 K and 300 K

<table>
<thead>
<tr>
<th>Sample/ Temperature</th>
<th>$H_c$ (Coercivity) (Oe)</th>
<th>$M_s$ (Saturation magnetisation) (emu/gm)</th>
<th>$M_r$ (Remnant magnetisation) (emu/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40K</td>
<td>112.37</td>
<td>3.47 x 10^{-4}</td>
<td>0.52 x 10^{-4}</td>
</tr>
<tr>
<td>300K</td>
<td>62.98</td>
<td>2.60 x 10^{-4}</td>
<td>0.42 x 10^{-4}</td>
</tr>
<tr>
<td>Graphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40K</td>
<td>76.19</td>
<td>13.94 x 10^{-4}</td>
<td>1.91 x 10^{-4}</td>
</tr>
<tr>
<td>300K</td>
<td>52.88</td>
<td>12.91 x 10^{-4}</td>
<td>1.28 x 10^{-4}</td>
</tr>
<tr>
<td>N-Graphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40K</td>
<td>40.00</td>
<td>118.62 x 10^{-4}</td>
<td>9.74 x 10^{-4}</td>
</tr>
<tr>
<td>300K</td>
<td>25.42</td>
<td>111.91 x 10^{-4}</td>
<td>6.04 x 10^{-4}</td>
</tr>
<tr>
<td>Siliphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40K</td>
<td>120.03</td>
<td>0.11 x 10^{-4}</td>
<td>0.03 x 10^{-4}</td>
</tr>
<tr>
<td>300K</td>
<td>94.75</td>
<td>0.09 x 10^{-4}</td>
<td>0.02 x 10^{-4}</td>
</tr>
</tbody>
</table>
Role of Oxygen Functional groups (C-O, O-C-OH, C-OH) of Graphene / Graphene Oxides: Magnetic behavior
Magnetic behavior of 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 \( \mu_B \) 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

(iii) Boukhvalov, D. W. et al. ACS Nano 2011, 5, 2440

GO is usually considered as an diamagnetic insulator / semiconductor material
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 \( \sim 150 \) Oe
Saturated field about \( 3000 \) Oe

Ferromagnetic behavior gradually decreases (paramagnetic behavior) for MrGO / HrGO on PT-reduction process.
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. [1]

*J. Phys. Chem. C 2009, 113, 18546–18551*
Fluorescent Carbon Nanoparticles for Bio-imaging probes

(Carbon Quantum DOTs: ≈ 2 – 6 nm)

Size of CQDs: ≈2-6 nm

Fluorescent CQDs

HRTEM

Under UV exposure

Ray et al., 113/43 (2009) 18546-51
Functionalized with Nano pores

- **Yellow**
- **Green**
- **Red**

**FCN**
- **FCN\text{yellow}**
- **FCN\text{green}**
- **FCN\text{red}**

**Absorption**
- **Wavelength (nm)**
- **Absorbance**
- **Emission Intensity (a.u.)**

**Microscopy Images**
- **FL**
  - 20 μm
- **BF**
  - 20 μm
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