From Carbon nanotubes to Graphene

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Common Carbon-based materials

Diamond

Graphene layers

sp$^3$ hybridization

sp$^2$ hybridization
Formation of 0-dimensional fullerenes, 1-dimensional CNTs and 3-dimensional graphite from 2-dimensional graphene sheets
Carbon: a multi-dimensional story

1564 - Unknown

2004 - Geim Novoselov

1993 - Sumio Iijima

1985 - Kroto, Smalley, Curl

3D

2D

1D

0D
Carbon nanotubes

The original ‘Kataura plot’ of SWNTs showing relationships between the transition energies and diameters of different SWNTs

The Band Theory of Graphite

P. R. Wallace
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario
(Received December 19, 1946)

The structure of the electronic energy bands and Brillouin zones for graphite is developed using the “tight binding” approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for spins across the layers. The volume optical absorption is accounted for.
Massless Dirac Fermions

Continuum limit near the points $K$ and $K'$ (valley pseudospin $\pm 1$)

$$E = v_F \sigma \cdot \mathbf{p}$$

$$v_F = \frac{3ta}{2} \approx 10^6 \text{m/sec}$$

massless Dirac fermions!
2004: graphene is born

The first graphene

One million of a meter
Graphene superlatives

2010 Nobel Prize in Physics

- **Strongest Material**
  - 100 times tensile strength of steel
  - Young’s modulus = 1 TPa
  - Tensile strength = 80 GPa

- **Record Electronic Properties**
  - 60% higher conductivity than silver and copper; 1 million times the current density of copper
    - $e$ mobility $200 \times 10^5 \text{ cm}^2/\text{V s}$
    - Bulk resistivity = $10^{-6} \text{ } \Omega \text{ cm}$

- **Highest thermal conductivity**
  - 5 times that of copper, better than diamond
    - Thermal conductivity = 5000 W/mK

- **Highest Surface Area**
  - Superior to active carbon
    - $2630 \text{ m}^2/\text{g}$

- **Optically Transparent**
- **Completely Impermeable**

Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems *Nanoscale, 7* 4598 (2015)
Platform

Hybrid 2d structures

ICT
- Faster
- Cheaper
- Flexible
- Efficient
- Cost effective
- Renewable
- Sustainable

Health
- Cost effective
- Bio compatible

System Integration
- Plastic electronic
- Superfast optical communication
- Spin logic chips
- Self powered devices
- Automotive

Components
- Transistors
- Spin valves
- Flexible displays
- RF tags
- Ultra-light batteries
- Solar cells
- Ultrafast lasers
- Composite materials
- Prostheses
- Sensors
- 

Production techniques
- Large scale synthesis
- On demand growth
- Growth on flexible substrates
- Nanoribbons
- Inks
- Interfaces
- Doping
- Superstructures
- Toxicology
- 

Vision 2023 – 2033

Energy storage and conversion
- Efficient
- Cost effective
- Renewable
- Sustainable

Industrial workshare
- Academic workshare

Academic
- Industrial

2013 2016 2023

Societal benefits
- Jobs
- Education

System Integration
- Plastic electronic
- Superfast optical communication
- Spin logic chips
- Self powered devices
- Automotive

Energy storage and conversion
- Efficient
- Cost effective
- Renewable
- Sustainable

Health
- Cost effective
- Bio compatible

Graphene
- One Atom Thin
- Linear spectrum
- Strength
- High mobility
- Highly stretchable
- Unique optical properties

Industrial workshare
- Academic workshare

Academic
- Industrial
Graphene production


G Graphene quality
C cost aspect
S scalability
P purity
Y yield
Liquid phase exfoliation method

2D bulk materials → Ultrasonication → Ultracentrifugation

Graphene, Bi$_2$Te$_3$, WSe$_2$, WS$_2$, MoS$_2$, BN
Graphene production

Surface tension (γ) of the solvent must be similar to the surface free energy of the material
High-yield production of 2D crystals by wet-jet milling


Patent
WO2017089987A1
FLG flakes have tunable lateral size 1μm-300 nm and down ~1.3 nm in thickness.
CURIOSITY AND IMAGINATION WILL TAKE YOU FURTHER

We offer unique and customized solutions to improve and innovate the performance of our customers’ products, shaping the material through the use of two-dimensional crystals and the application of our know-how with scientific method.
Supply chain

DEVELOPMENT OF INNOVATIVE SOLUTIONS

2D materials included compounds with high performances and multifunctionalities

High quality 2D materials

PRODUCTION

Specific products
What is the killer application?

Alluminum’s legacy
Humphry Davy 1808
Aluminium can be produced from electrolytic reduction from alumina

Hans Christian Ørsted 1825
First isolation of Aluminium

Friedrich Woehler 1827
First Aluminium
30g production

Henri Sainte-Claire Deville 1856
First industrial production
Few Tons per year

First applications:
ornaments and luxury items
There is nothing harder than to make people use a new metal. Luxury items and ornaments cannot be the only sphere of its application. I hope the time will come when aluminium will serve to satisfy the daily needs.

Sainte-Claire Deville
Paul Héroult & Charles Hall 1886
New method of production.
Scale-up in Swiss and USA up to hundreds of tons per year

1889
Karl Benz
Sport car

1903
Wright airplane with Aluminium engine
graphene

2004 isolation
2019 production available

50 years compressed into 15 years...
A battery is a device that converts chemical energy into electrical energy and vice versa.

Alessandro Volta 1799
Battery: basic facts

The primary components of Li-ion batteries are the anode, cathode, electrolyte (LiPF₆ in EC/DMC) and separator.

(cathode) reduction reaction : \( \text{CoO}_2 + \text{Li}^+ + e^- \rightarrow \text{LiCoO}_2 \)  
160 mAh/g

(anode) oxidation reaction : \( \text{LiC}_6 \rightarrow \text{Li}^+ + C_6 + e^- \)  
372 mAh/g

One Li ion for six Carbon atoms

Energy density  
150–250Wh/kg
“Prices on electric cars will continue to drop until they’re within the reach of the average family”

Washington Post   1915

EV adoption is limited primarily due to the cost and inadequate storage capacity of today’s batteries
Need for high-energy density batteries

1 liter of gasoline
6000Wh/Kg

1kg of Li-ion
150-250 Wh/Kg

A 20-30 time gap!

Tesla model S → 100Wh → >700-1000kg
The future of Lithium batteries

Lithium Ion Battery,
Cathode - LiCoO$_2$
150 mAh g$^{-1}$

Lithium Ion Battery,
Anode - Si / carbon
1000 mAh g$^{-1}$

Lithium Ion Battery,
Cathode - NMC
200 mAh g$^{-1}$

Lithium Sulfur Battery,
Cathode - Sulfur Carbon
1675 mAh g$^{-1}$

Lithium Oxygen Battery,
Cathode - Oxygen, Carbon
3500 mAh g$^{-1}$

400 Wh kg$^{-1}$ → 500 Wh Kg$^{-1}$

1000 Wh kg$^{-1}$ → 3000 Wh Kg$^{-1}$
The future of Lithium batteries

- New functionalities
- New materials
- New chemistries
- Industrially-scalable and cost effective approaches
  - <100$/kWh on cell level
  - <120$/KWh on module level
  - 30$/Kg on active material
The future of Lithium batteries

Is the killer application of graphene in energy storage?

• Mechanical flexibility
• Electrical Conductivity
• Tunable morphological properties
• Functionalization
• Price compatible with market requirements (?)
Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage

F. Bonaccorso, V. Pellegrini

Material Matters, Sigma-Aldrich Merk

2016
Silicon-based anodes for Li-ion batteries

**PLUS**

Silicon expected capacity at room temperature:
~ 3597 mAh/g (Li$_{15}$Si$_4$)

**MINUS**

Large volume expansion (300%) $\rightarrow$ large irreversible capacity
(cracks and pulverization)

Poor electrical conductivity
Silicon capacity fading

Li / LP30 / Si-C(PAA)
10h 25Hz
500mA g⁻¹

Specific Capacity / mAh g⁻¹
Efficiency / %

Cycle number

(a) Traditional

1st Li⁺ insertion
As synthesized
Volume expansion
Li⁺ extraction

Broken electric contacts

non-conductive binder
Si-Graphene–NMC full cell

Graphene as additive outperforms both SuperP and r-GO

- NMC with a nominal capacity of 2.25mAh/cm².
- Anode and cathode masses balanced → anode reversible capacity (2300 mAh/g) → cathode reversible capacity (137mAh/g).
- 350-400 Wh/kg

A new method of production
Laminated structure

R. Maik, M. Loveridge, V. Pellegrini et al. submitted
Exceptional electrochemical behavior

450 cycles: capacity retention of 98%; columbic efficiency of 99.85% (under a current density of 358 mA g\textsuperscript{-1}).

R. Maik, M. Loverdige, V. Pellegrini et al. submitted
Stabilization of the electrode's structure

→ facilitate movement of Li+ ions throughout the bulk of the electrode material during cycling

Decrease in porosity:

- **Silicon 75%** after 200 cycles
- **Silicon/Graphene 15%** after 200 cycles
Silicon/Graphene - Prototyping

12 mm

5.4 mm

In-Ear Headset

Fitness Tracker

Smart Key

Insulin Patch
Silicon/Graphene - Prototyping

First prototypes from industrial production line
+25% of energy density vs market products
## Silicon/Graphene - Prototyping

### Format
- 12 mm diameter
- 5.4 mm thickness

### Application
- In-Car Headset
- Fitness Tracker
- Smart Key
- Insole Feather

### Current results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Capacity*</td>
<td>88 mAh (+35%**)</td>
</tr>
<tr>
<td>Total Energy*</td>
<td>300 mWh (+25%**)</td>
</tr>
<tr>
<td>Cyclability</td>
<td>tbd</td>
</tr>
</tbody>
</table>

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*0.1C Discharge
** compared to benchmark
Laura Silvestri
Stefano Palumbo
Lorenzo Carbone
Antonio Esau Del Rio Castillo
Alberto Ansaldo
Francesco Bonaccorso
Liberato Manna
Eugenio Greco
Haiyan Sun
Gianluca Longoni

Andrea Gamucci
Szabi Beke
Sulfur rich graphene-based cathode

• Graphene in cathodes in Li-S

\[ S_8 + 16\text{Li}^+ = 8\text{Li}_2S \]

1675 mAhg\(^{-1}\) → 3500 Whkg\(^{-1}\)
Li-S: Drawbacks

- Both sulfur and lithium sulfides are intrinsically insulated.
- The intermediate discharge products lithium polysulfides are soluble in the organic electrolyte → loss of active materials.
- The soluble polysulfide during the charge processes may migrate from the cathode to the anode, reacting on the anode surface producing an electrochemical short circuit well known as polysulfide shuttle effect.

Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_2$, Li$_2$S
Sulfur rich graphene-based cathode

Homogenous agglomerate of sulfur particles covered by graphene
Active material: 89% Sulfur 10% graphene
Sulfur mass loading of 1.5mg(S) cm⁻²
S-Graphene cathode

Patent submitted
L. Carbone et al. ChemSusChem (accepted)
Graphene

- Mechanical flexibility
- Electrical Conductivity
- Tunable morphological properties
- Functionalization
- Price compatible with market requirements (?)

Li-ion anodes

Li-rich layered oxides

Li-S cathodes

Aluminum-ion cathodes
ABS-graphene: role of quality

E. Lago et al., submitted
Graphene Silicon composite for anodes

Different approaches:

• Dispersion/sonication/annealing @ 700°

$\text{Si/G:SP:PAA} = 80:10:10$

LP30+FEC as electrolyte

Si-Graphene anode: stability

Silicon/Graphene:PAA:SP (80:10:10)  
LP30 + 10% FEC, 400mA/g, Coin cell, Annealed at 750 °C

Graphene as additive outperforms both SuperP and r-GO

The first ten producers of graphite in the world

China has the 66% of the world graphite production and the 35% of consumption

(Investing News Report 23/10/2017)

* data from US Geological Survey (2017)
Li-ion: can Graphene replace graphite?

- Marginal improvement vs graphite
- Irreversible processes
- Cost

J. Hassoun et al., NanoLetters 14, 4901 (2014)

(anode) oxidation reaction: \( \text{Li}_2\text{C}_6 \rightarrow 2\text{Li}^+ + \text{C}_6 + 2\text{e}^- \)  
744 mAh/g

\[ \text{Li}_2\text{C}_6 \rightarrow 2\text{Li}^+ + \text{C}_6 + 2\text{e}^- \]