New Directions in Materials Science and Technology: Two-Dimensional Crystals

Antonio H. Castro Neto
Graphene Research Centre

National University of Singapore

Worldwide investment in Graphene

European Union ~ USD$ 1,400 Million (?)	~ 500 Million souls (2.8)
USA ~ USD$ 50 Million	~ 300 Million souls (0.2)
United Kingdom ~ USD$ 80 Million	~ 60 Million souls (1.3)
South Korea ~ USD$ 300 Million	~ 50 Million souls (6)
Singapore ~ USD$ 100 Million	~ 5 Million souls (20)

GRAPHENE RESEARCH CENTRE

S$ 100 Million ~ USD$ 80 Million - in 5 years

NATIONAL RESEARCH FOUNDATION

Prime Minister's Office, Republic of Singapore

GC

NUS

National University of Singapore

GRAPHENE RESEARCH CENTRE

Visit:
www.graphenecenter.org

People

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ST Kinetics

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Lay-lay Chua
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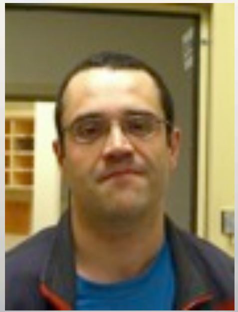
Yu Ting
Physics, NTU

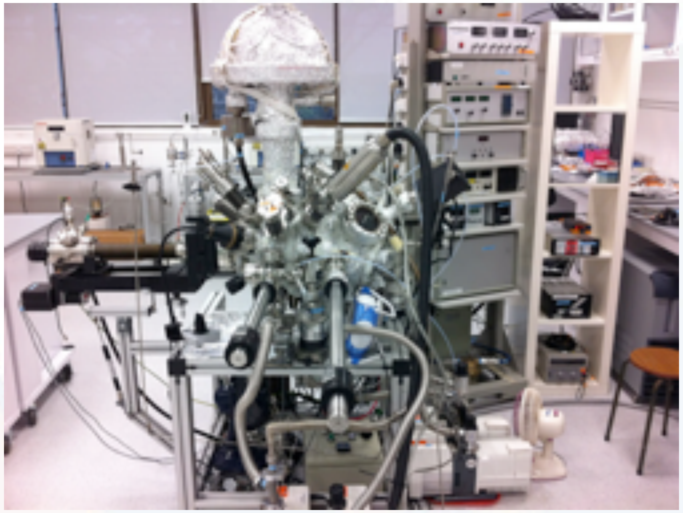


Miguel Cazallila
NUS, Physics

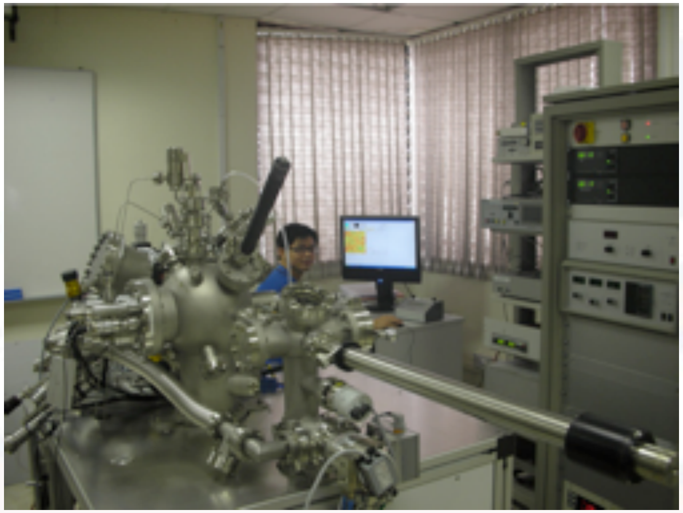
Vitor Pereira
Physics, NUS

1,000 sqm of lab space
600 sqm, Class 100/1000 Clean Room

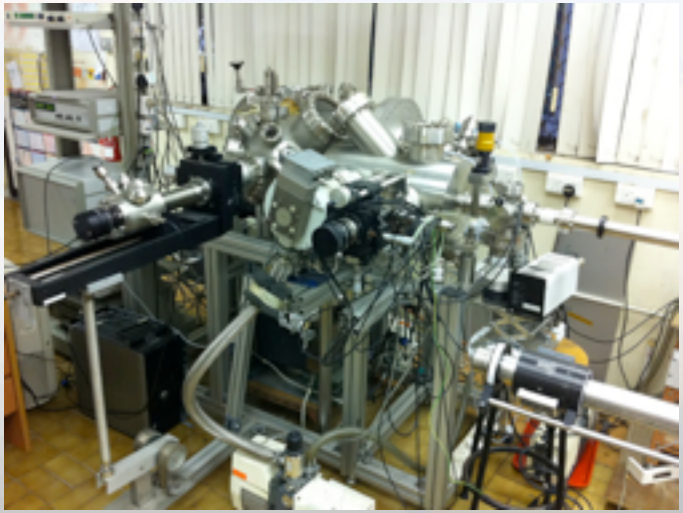
EQUIPMENT



XPS/UPS



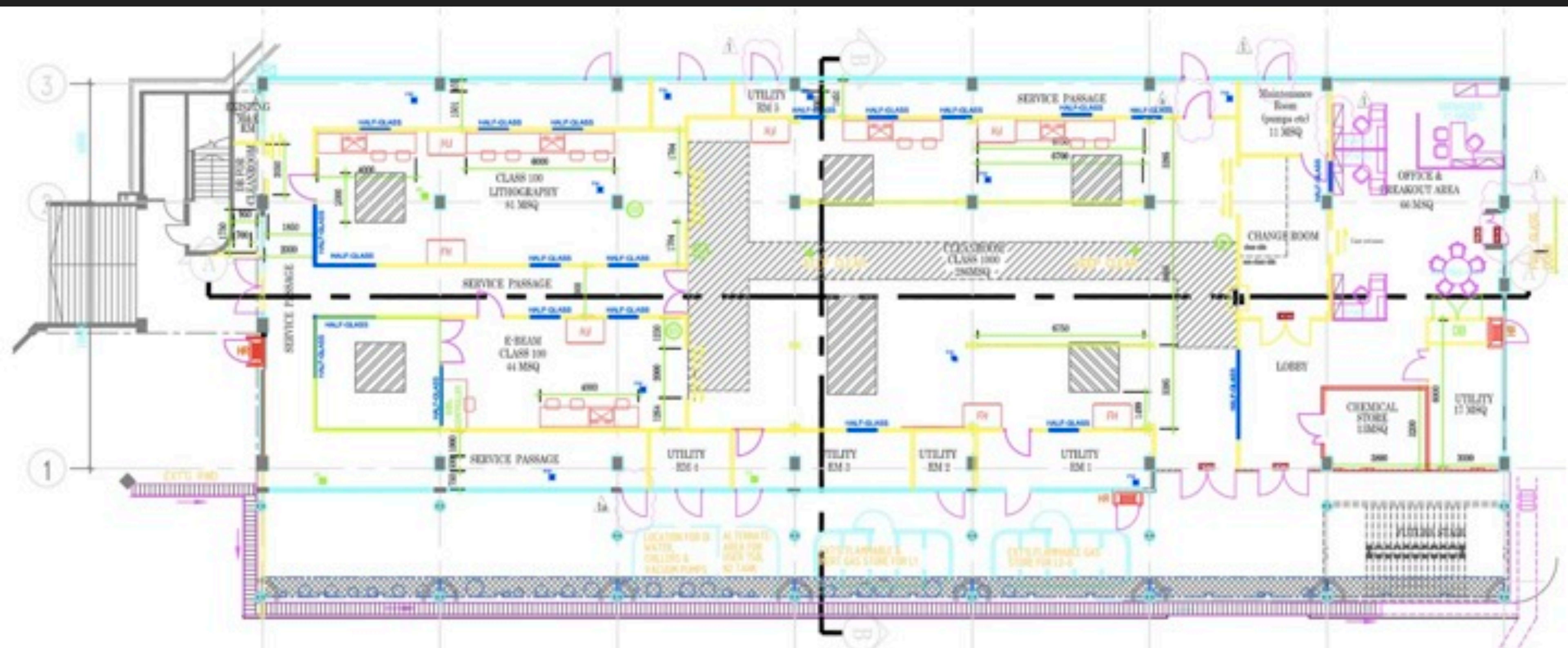
UHV-STM



HREELS

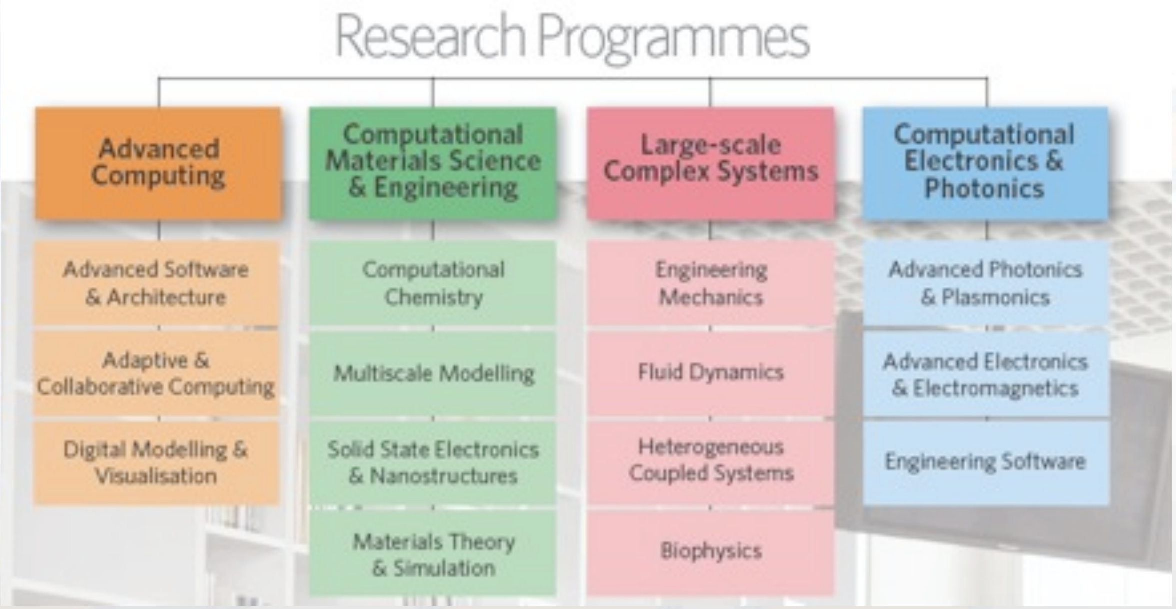
GLOVE BOX

Clean Room Class 100/1000



Modeling and Simulation of Structural and Electronic Properties of 2D-Crystals

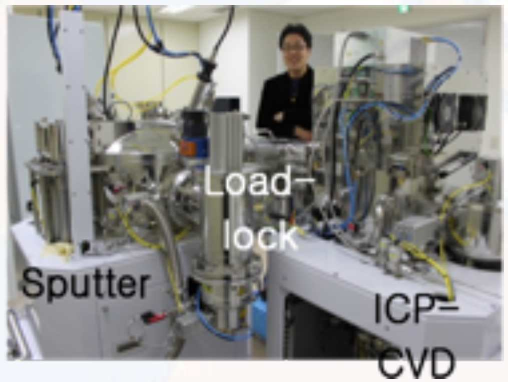
800 nodes IBM Computer Cluster

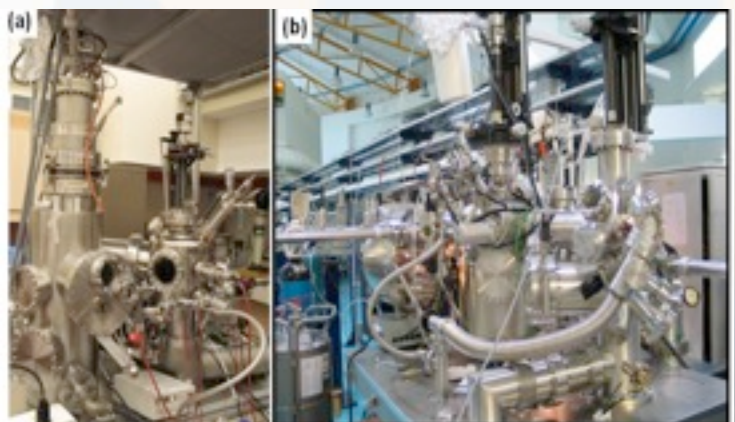


Research Lines and Collaborative Framework

Experiment

- Magneto-transport
- Optics
- Raman
- ARPES (SSLS)
- TEM
- STM
- SEM
- AFM





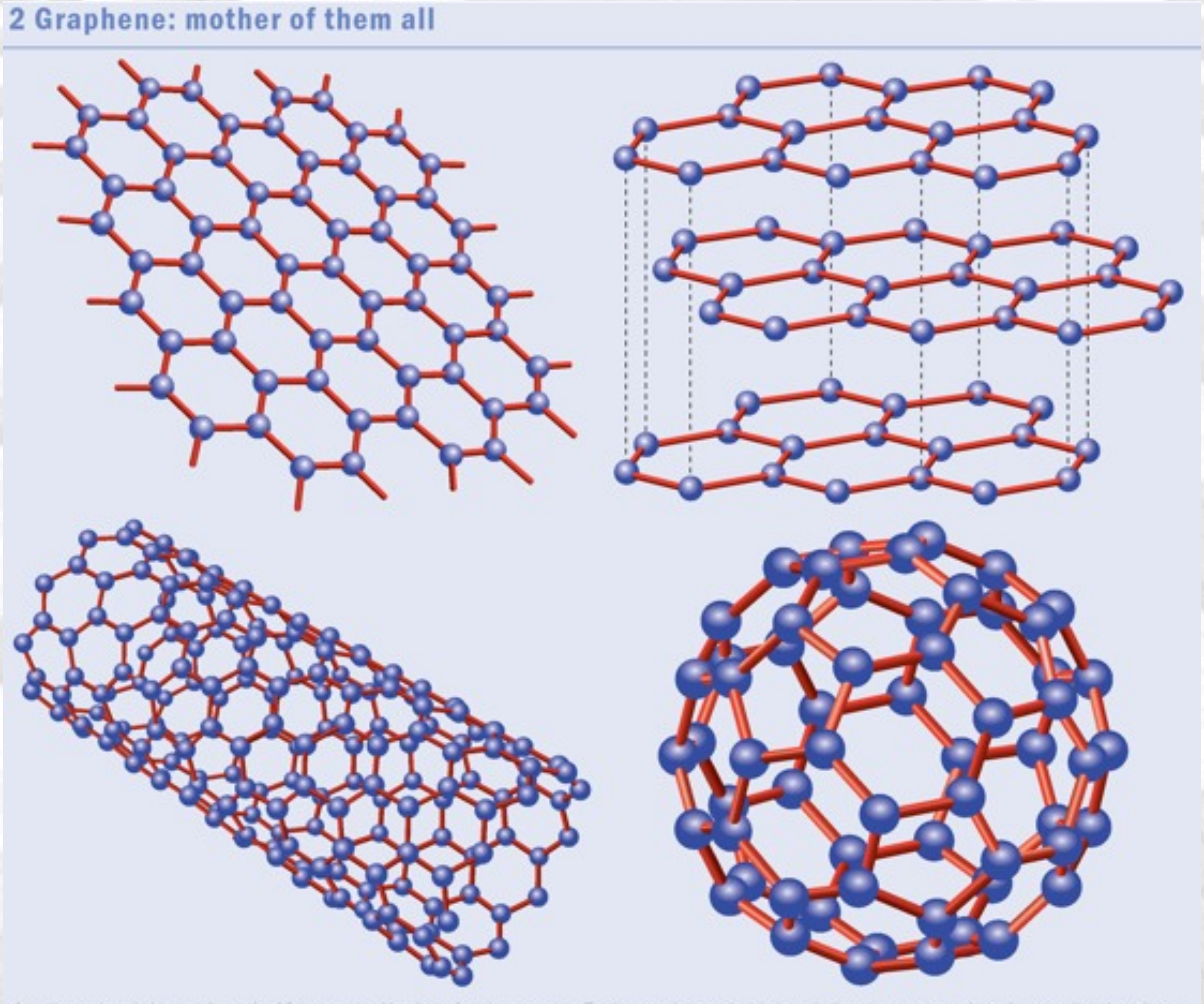
Theory

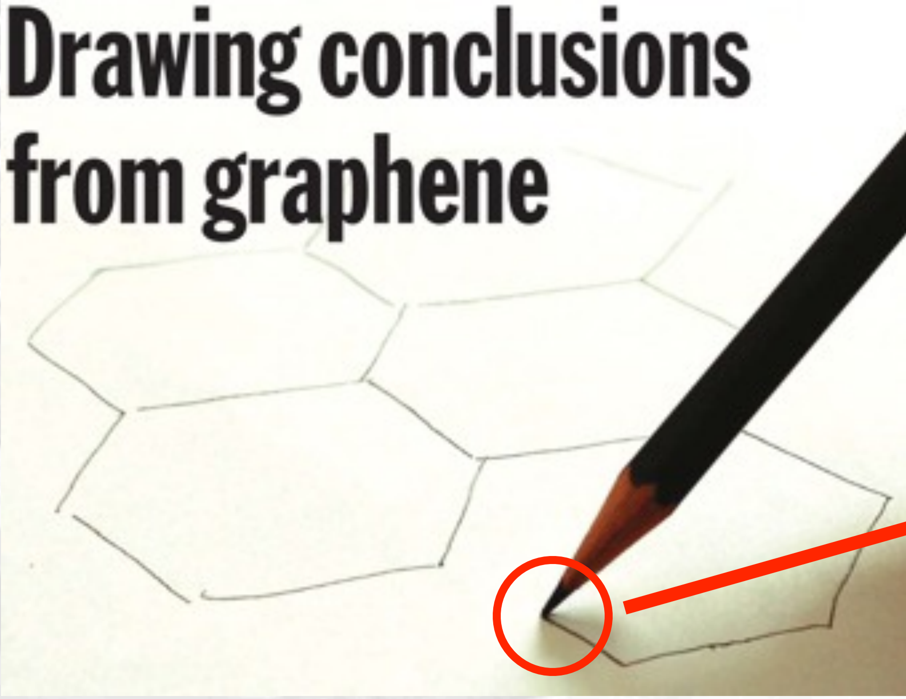
- Modeling
- Ab-initio
- Molecular Dynamics
- In-house HPC cluster

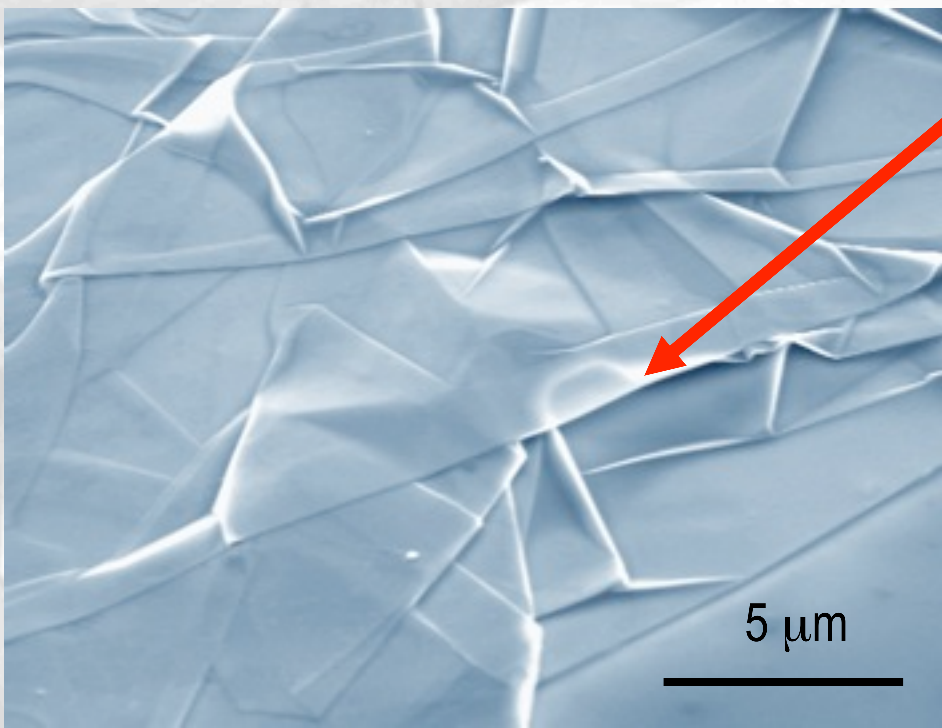
Applications & Devices

- Growth (CVD, MBE)
- Micro-fabrication
- Patterning
- Assembly

What about Graphene ?







Graphene has been produced since the pencil was invented in England in 1564 !

Human beings have been making money with Graphene since the 16th century !

From 1564 to 2004 !

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

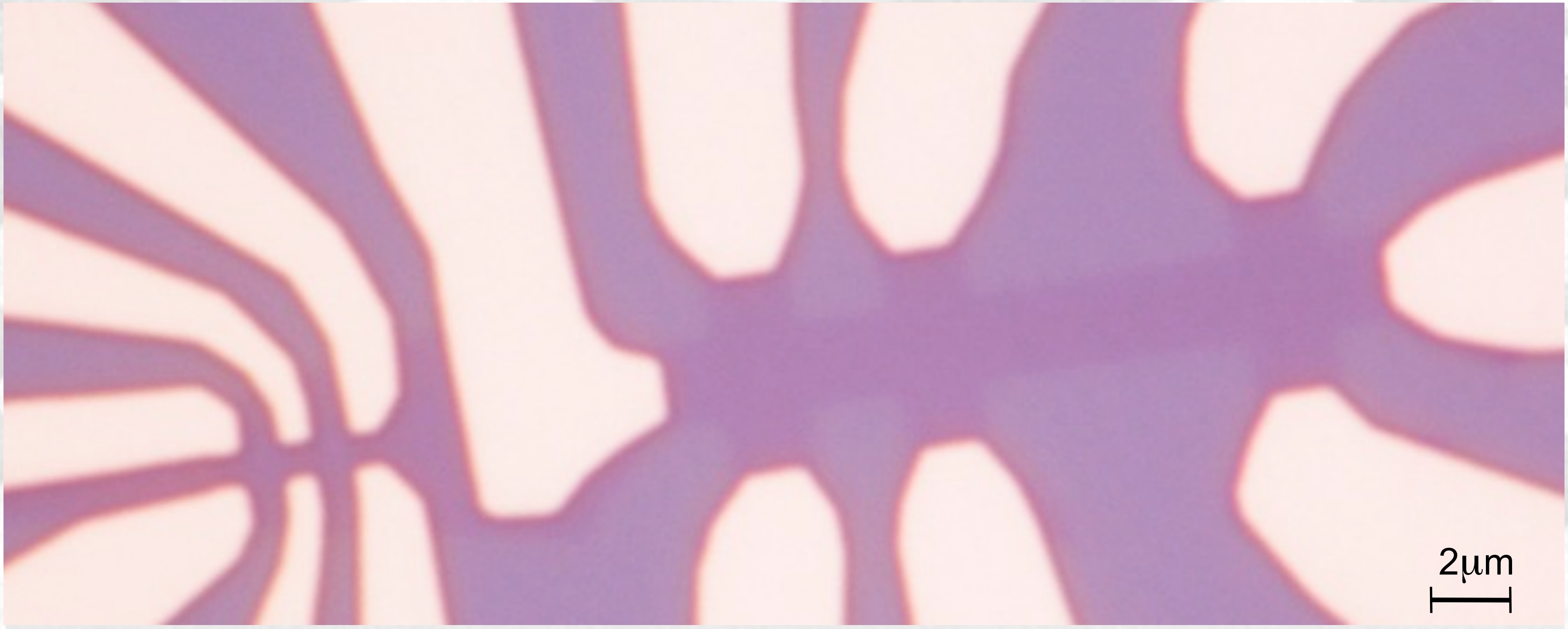
The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (*1*) and carbon nanotubes (*2*). It has long been tempting to extend the use of the field effect to metals [e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies than traditional semiconducting devices (*3*)]. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances (<1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable (>1%) field effect (*4*).

We report the observation of the electric field effect in a naturally occurring two-dimensional (2D) material referred to as few-layer graphene (FLG). Graphene is the name given to a single layer of carbon atoms densely packed into a benzene-ring structure, and is widely used to describe properties of many carbon-based materials, including graphite, large fullerenes, nanotubes, etc. (e.g., carbon nanotubes are usually thought of as graphene sheets rolled up into nanometer-sized cylinders) (*5*–*7*). Planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes (*5*–*14*).

[1]Department of Physics, University of Manchester, Manchester M13 9PL, UK. [2]Institute for Microelectronics Technology, 142432 Chernogolovka, Russia.

*To whom correspondence should be addressed. E-mail: geim@man.ac.uk

Plus some nanotechnology…

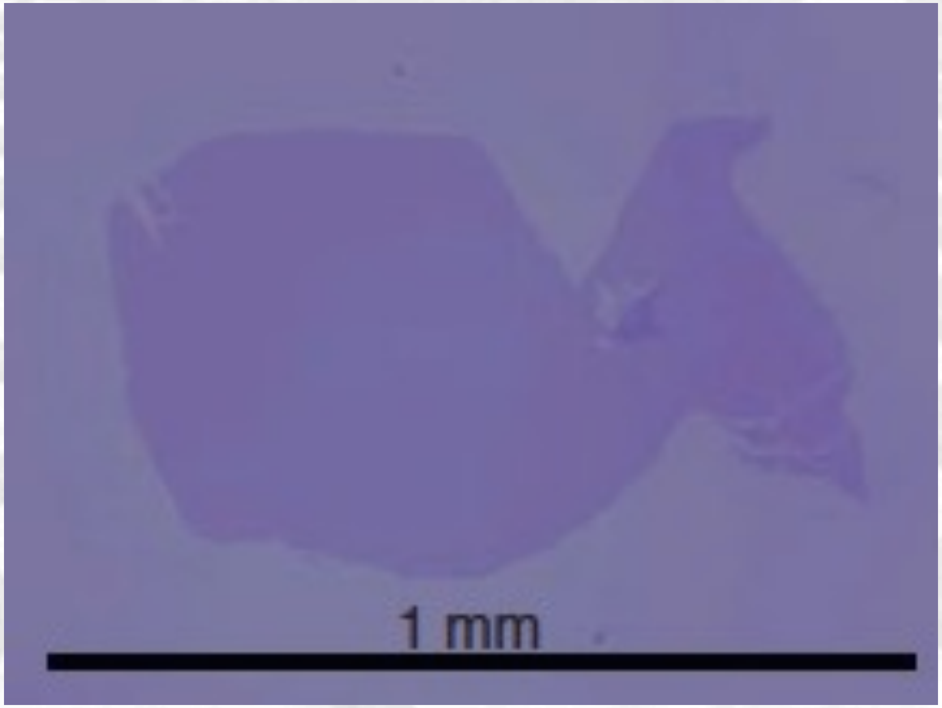


- optical image
- SEM image
- design
- contacts and mesa

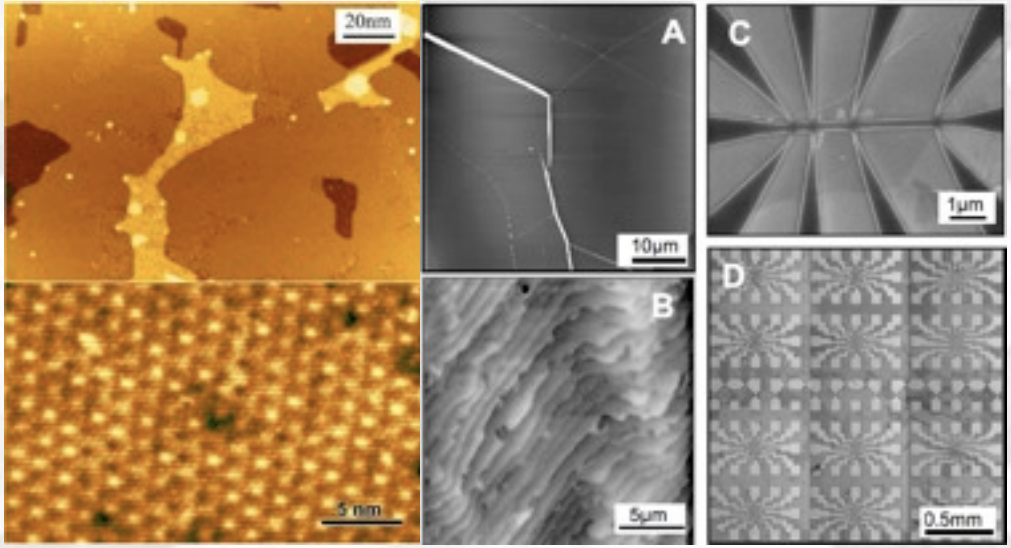
Graphene: leading the way in material science and technology

The 2010 Nobel Prize in Physics

Exfoliation



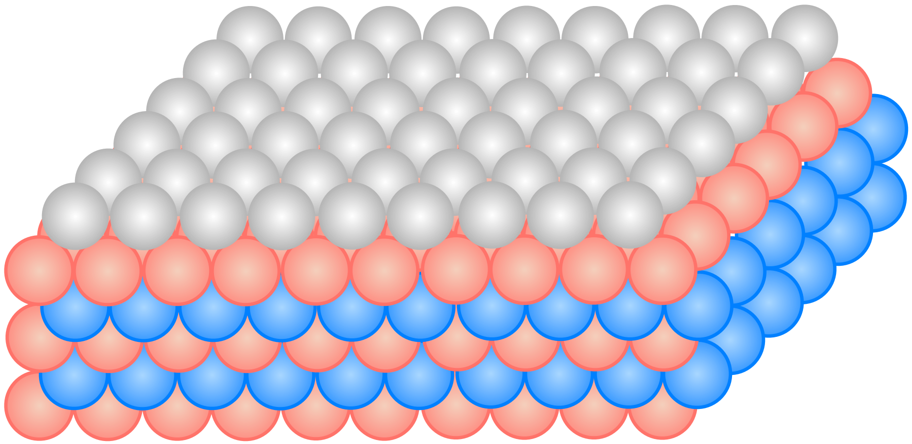
Growth on SiC



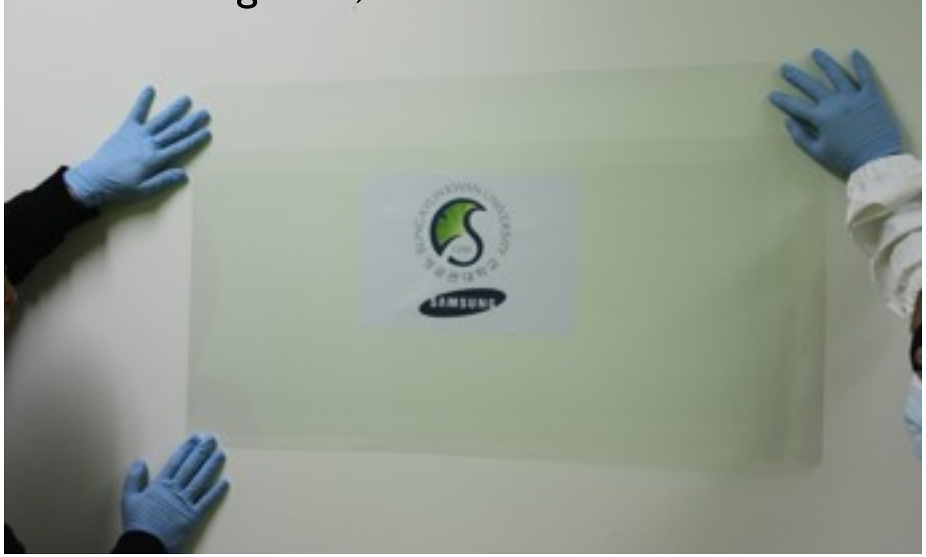
Berger et al., J. Phys. Chem. B, 2004, 108 (52)

CHEMICAL EXTRACTION

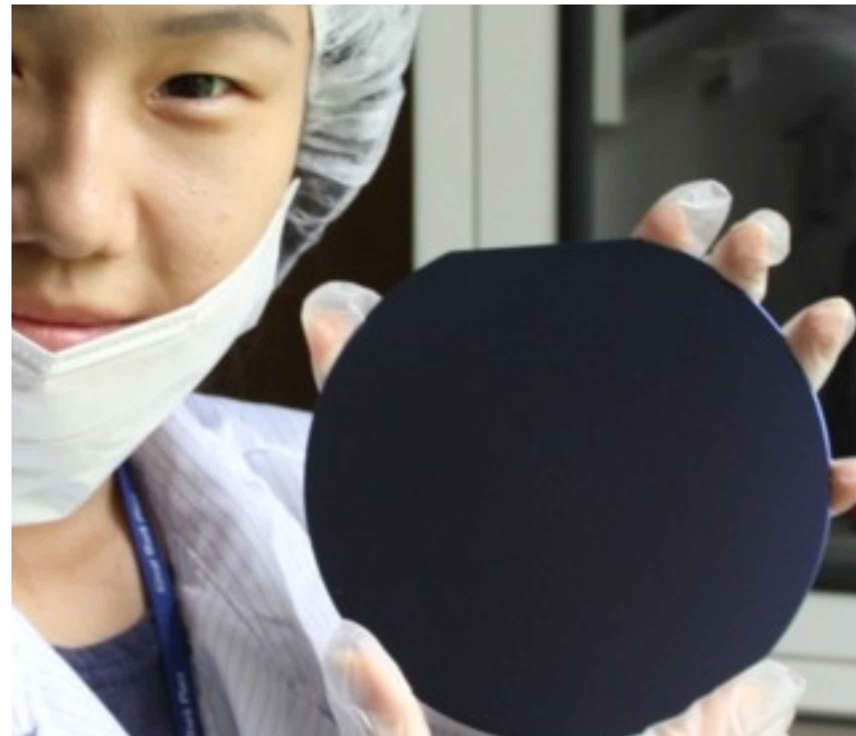
epitaxially grown monolayers



chemically remove the substrate



B. H. Hong et al, Nature Nanotech. 2010



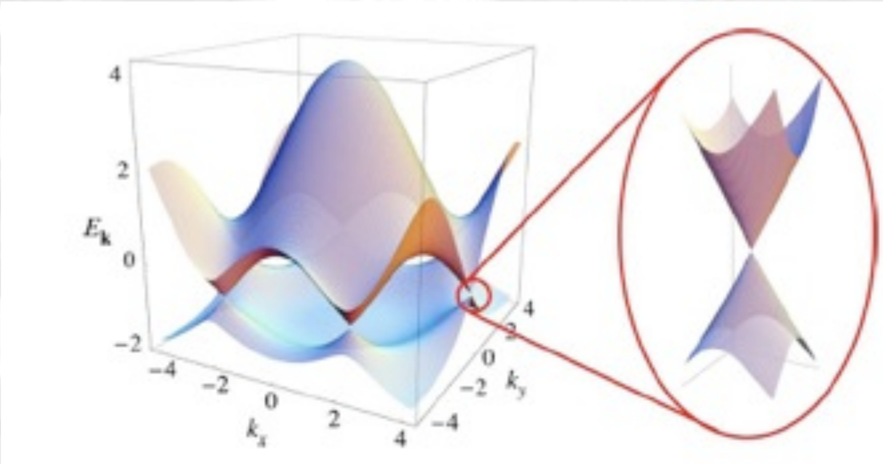
S. Seo (*Samsung* 2010)

FIRST DEMONSTRATED

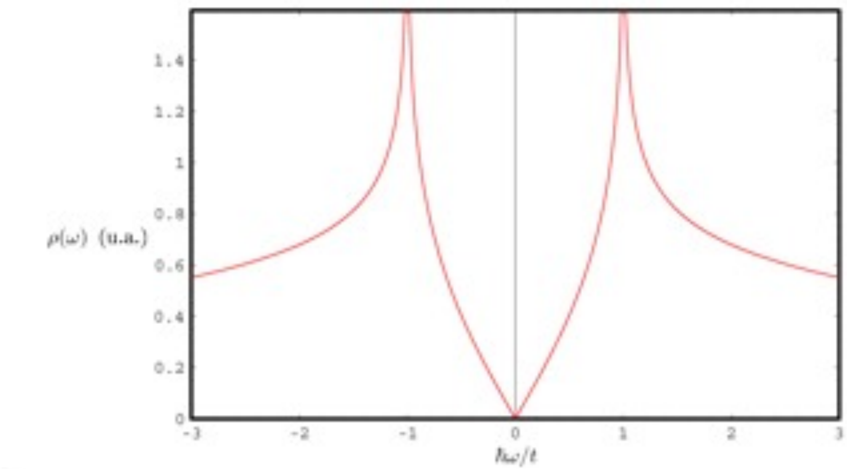
graphene-on-Si wafers

uniform; no multilayer regions;
few cracks; μ >5,000 cm^2/Vs

Summary of Electronic and Structural Properties



Dirac electrons



Semi-metal

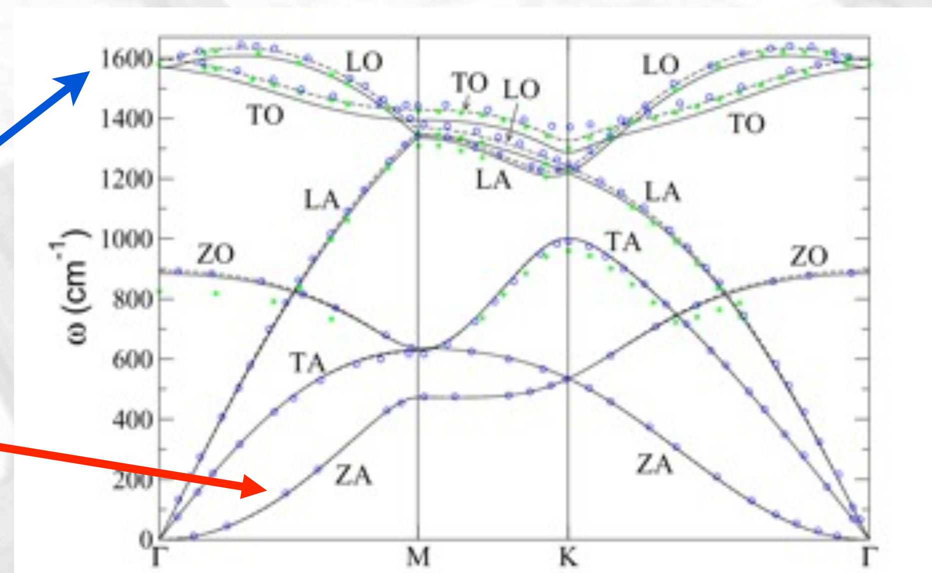
High optical phonon frequencies

K = Spring constant ~ 50 eV/A^2

Flexural modes

$$\omega \propto \sqrt{\kappa}\; q^2$$

κ = bending rigidity ~1 eV



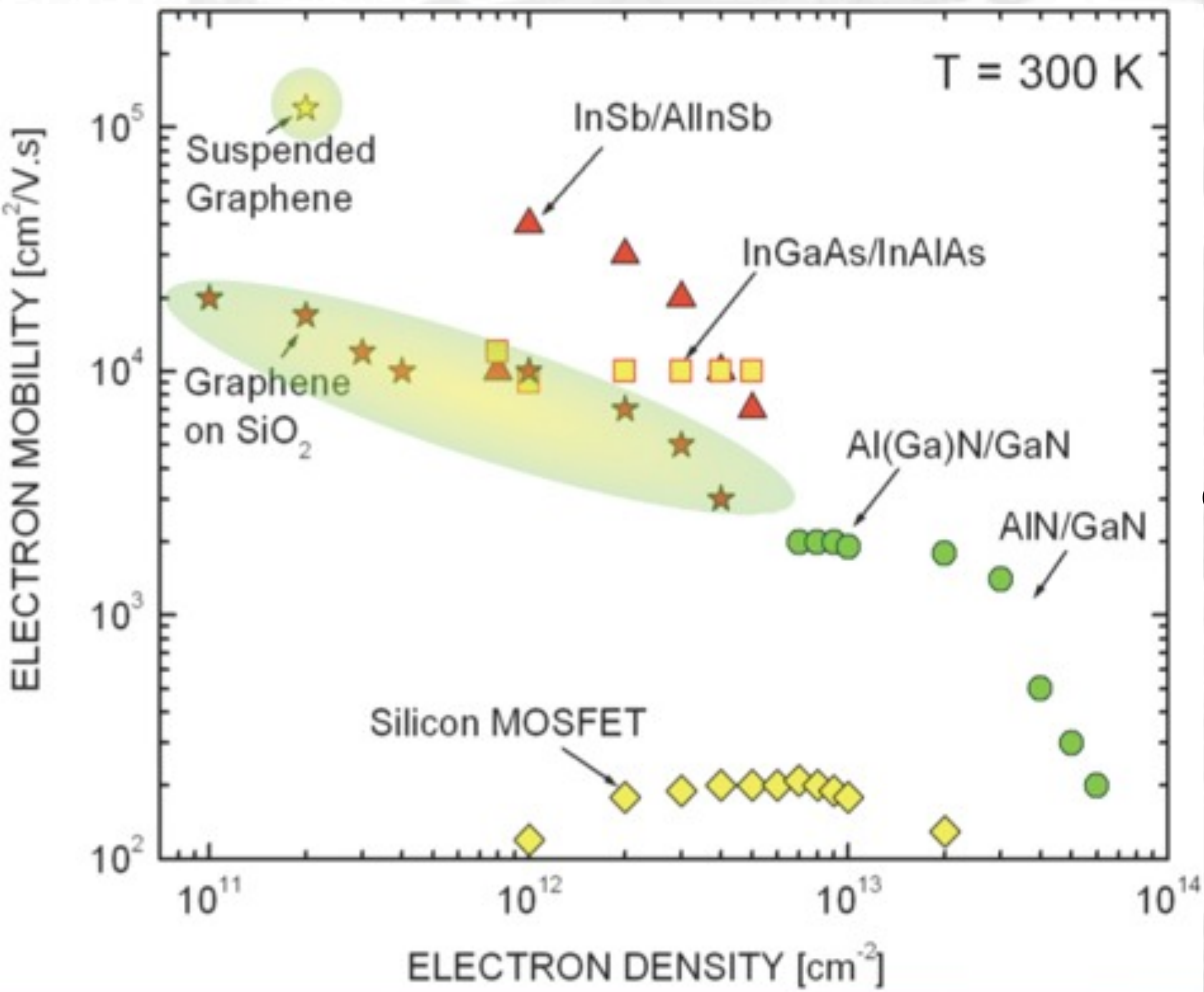
Phonons

Superlative Properties of Graphene

- ✓ Thinnest material sheet imaginable…yet the strongest! (5 times stronger than steel and much lighter!)
- ✓ Graphene is a semimetal
- ✓ Superb heat conductor
- ✓ Very high current densities (~10^9 A/cm^2)
- ✓ Easily transferrable to any substrate

Characterisitic	**Silicon**	**AlGaAs/ InGaAs**	**InAlAs/ InGaAs**	**SiC**	**AlGaN/ GaN**	**Graphene**
Electron mobility at 300K ($cm^2/V \cdot s$)	1500	8500	5400	700	1500-2200	> 100,000
Peak electron velocity ($\times 10^7$ cm/s)	1.0 (1.0)	1.3 (2.1)	1.0 (2.3)	2.0 (2.0)	1.3 (2.1)	5-7
Thermal conductivity (W/cm·K)	1.5	0.5	0.7	4.5	>1.5	48.4-53

Graphene: Unprecedented transport properties



Graphene shows the highest carrier mobility of any known material

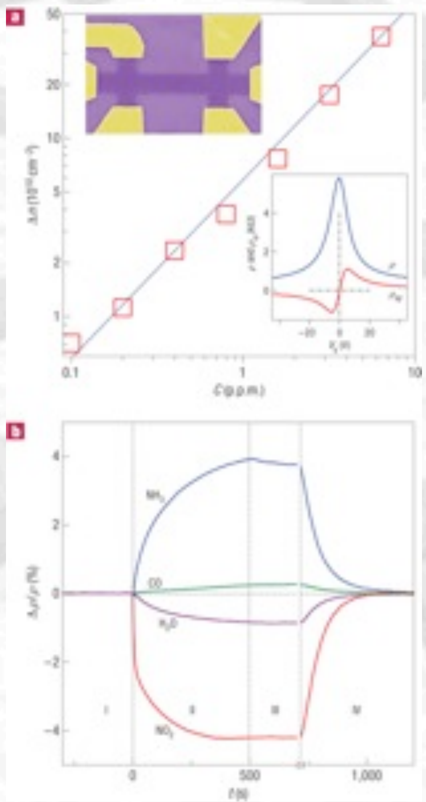
Unprecedented carrier mean free paths (~μm's at room temperature) enable new device architectures

Hype or Hope ?

Detection of individual gas molecules adsorbed on graphene

F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson & K. S. Novoselov

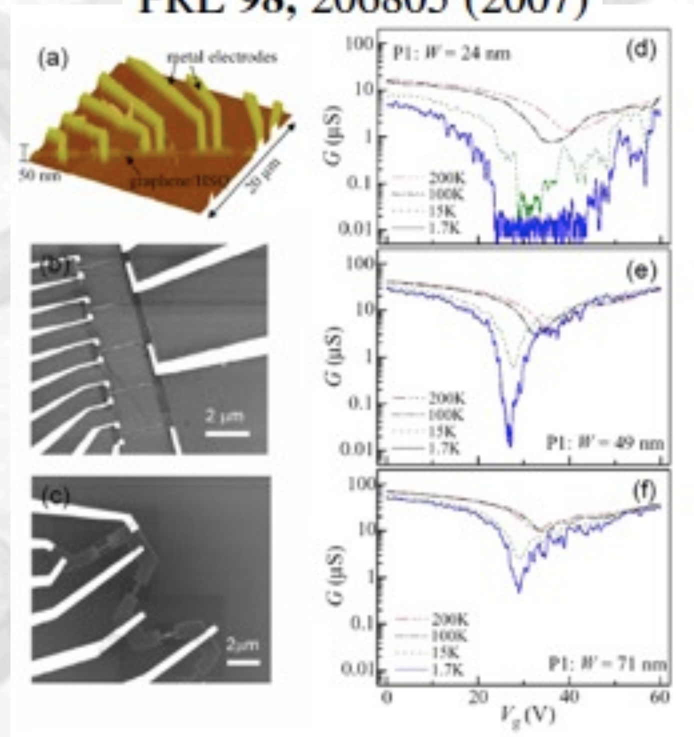
Nature Mater **6** (9): 652–655.



Energy Band-Gap Engineering of Graphene Nanoribbons

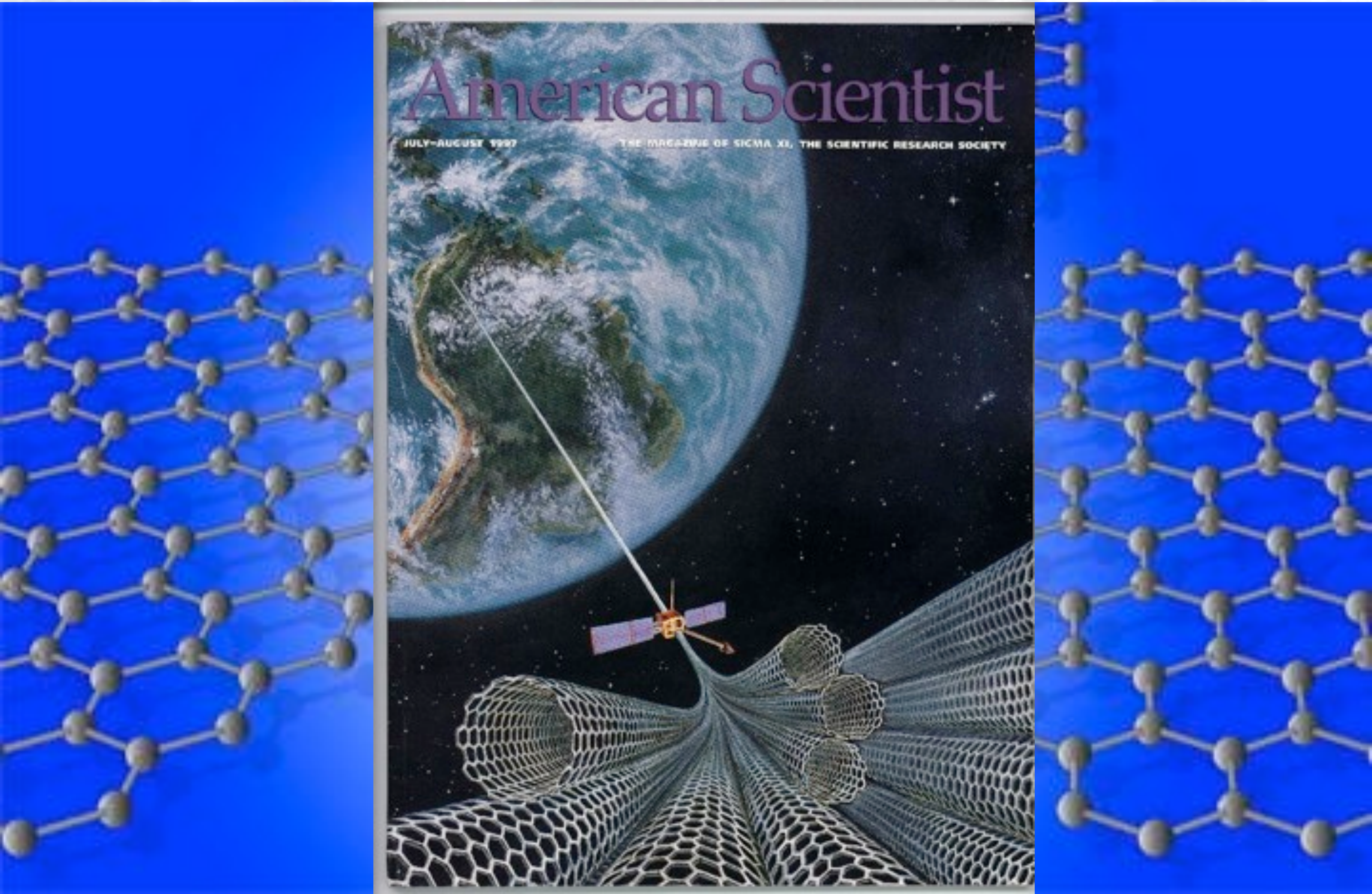
Melinda Y. Han,[1] Barbaros Özyilmaz,[2] Yuanbo Zhang,[2] and Philip Kim[2]

PRL **98,** 206805 (2007)



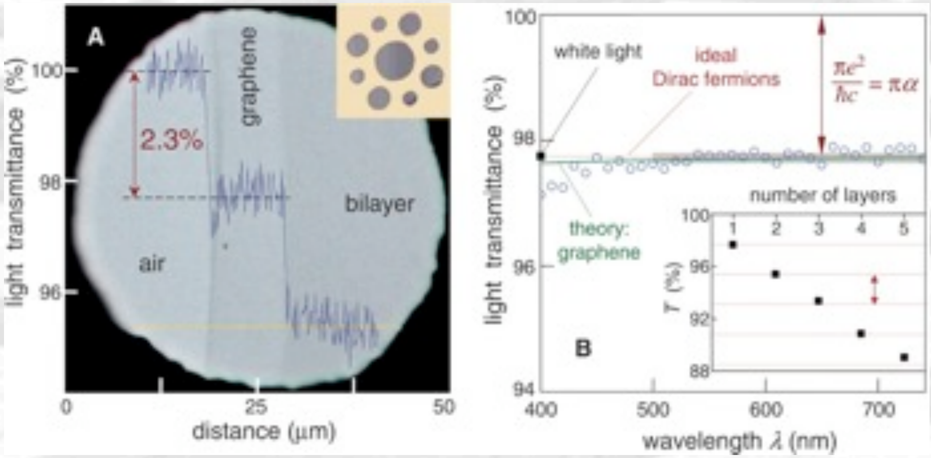
Miniaturization down to 1 nm : a few benzene rings

Graphene Quantum Dots



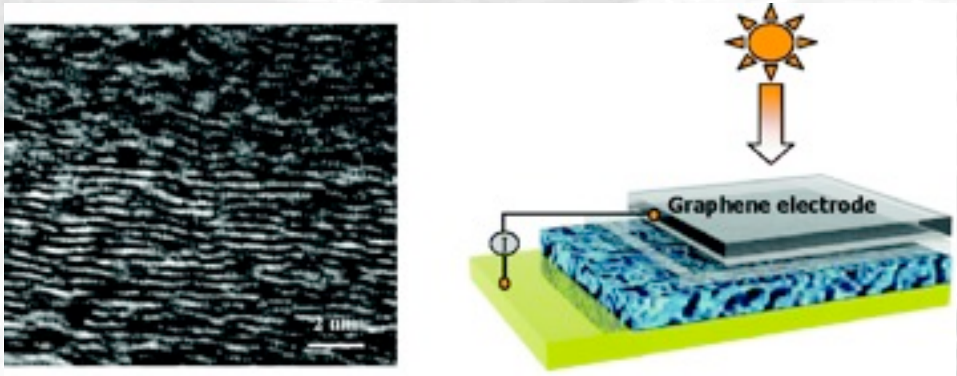
Fine Structure Constant Defines Visual Transparency of Graphene

R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim
Science **320**: 1308.



Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells

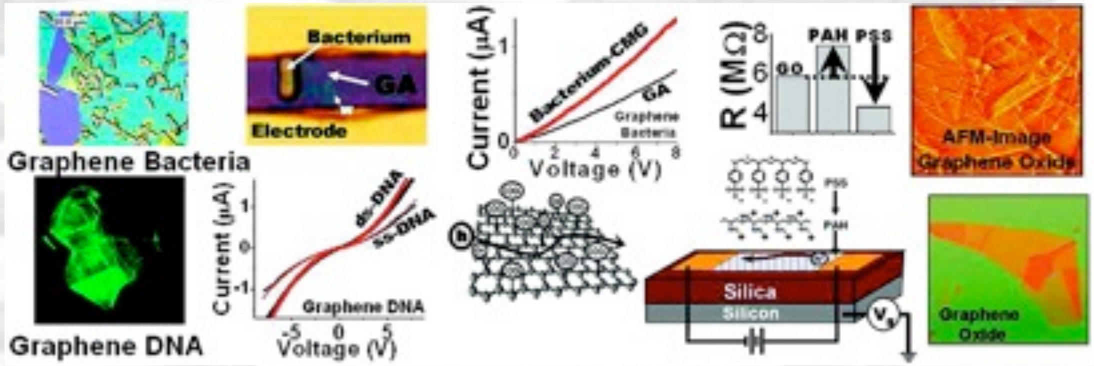
Xuan Wang, Linjie Zhi, and Klaus Müllen
Nano Letters **8** (1): 323.



Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale and Microscale Biocomponents

Nihar Mohanty and Vikas Berry

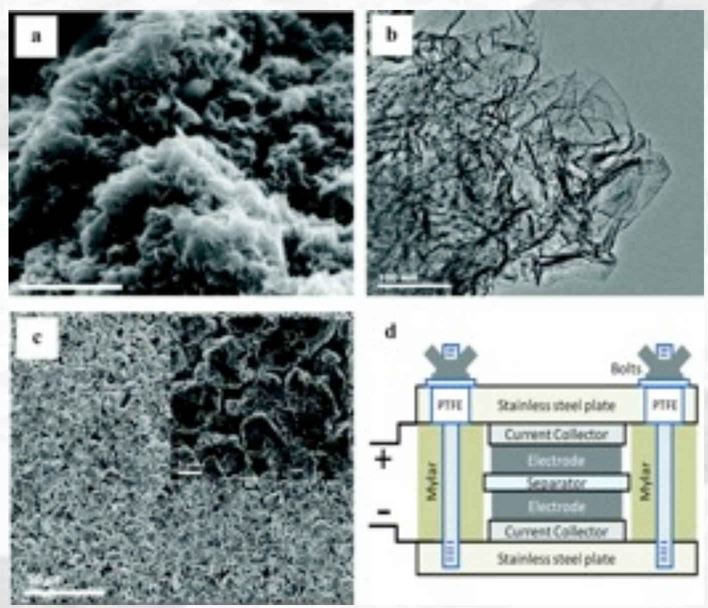
Nano Letters **8**: 4469–76



Graphene-Based Ultracapacitors

Meryl D. Stoller, Sungjin Park, Yanwu Zhu, Jinho An and Rodney S. Ruof

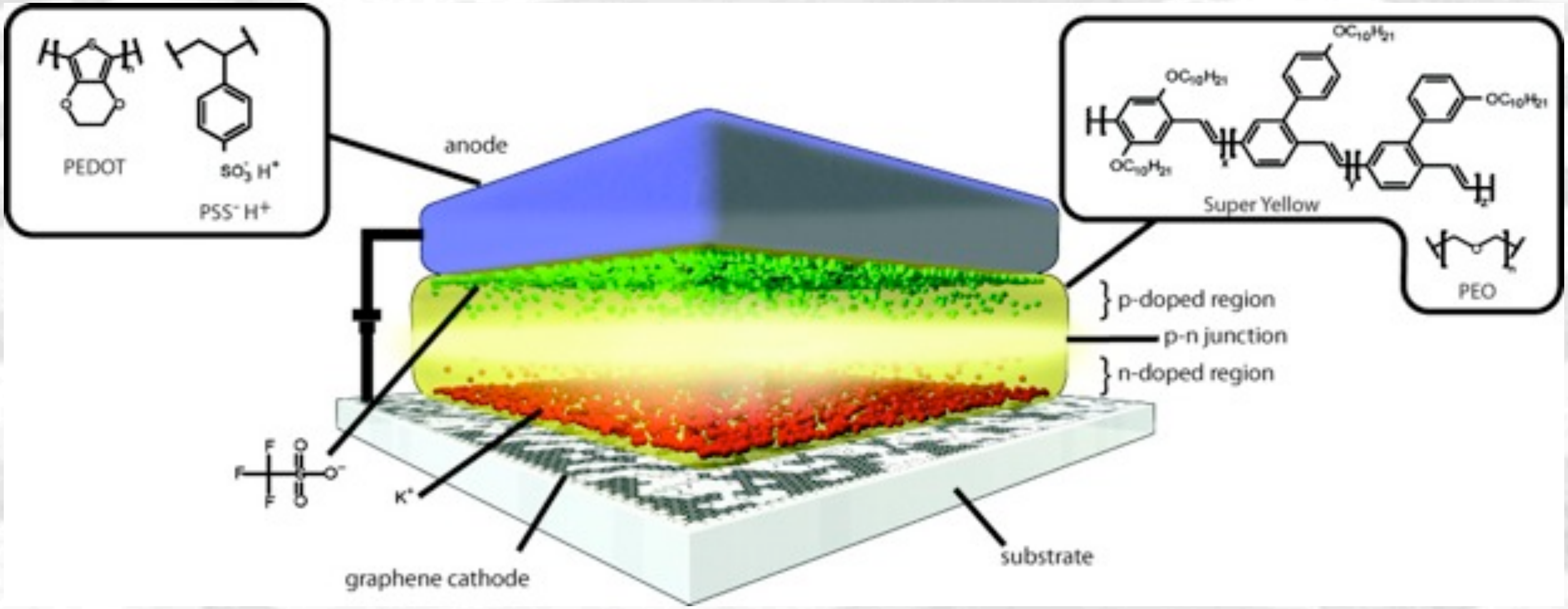
Nano Lett **8** (10): 3498.



Graphene and Mobile Ions: The Key to All-Plastic, Solution-Processed Light-Emitting Devices

Piotr Matyba, Hisato Yamaguchi, Goki Eda, Manish Chhowalla, Ludvig Edman and Nathaniel D. Robinson

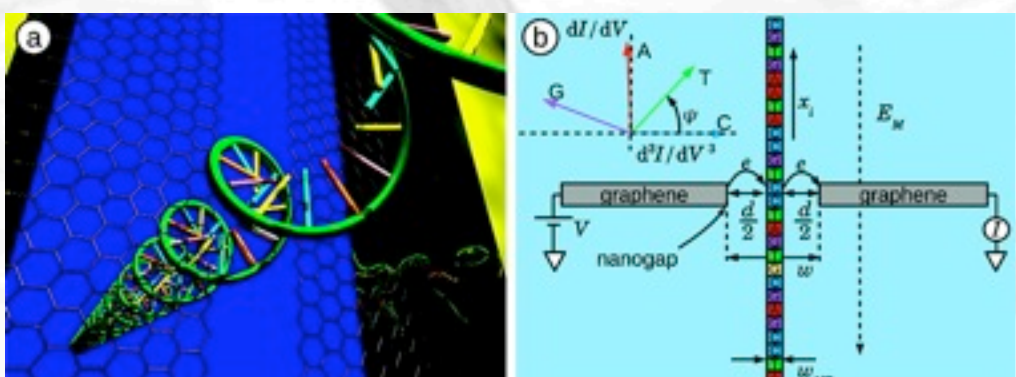
ACS Nano, 2010, 4 (2), pp 637–642



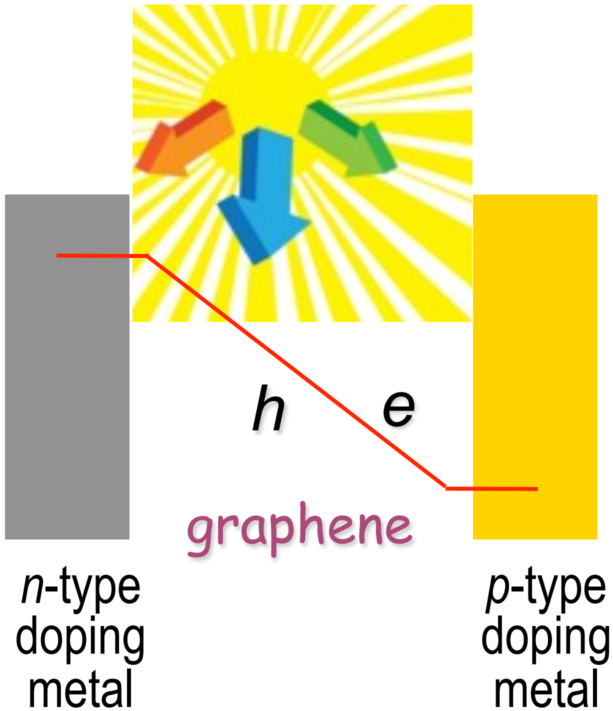
Rapid Sequencing of Individual DNA Molecules in Graphene Nanogaps

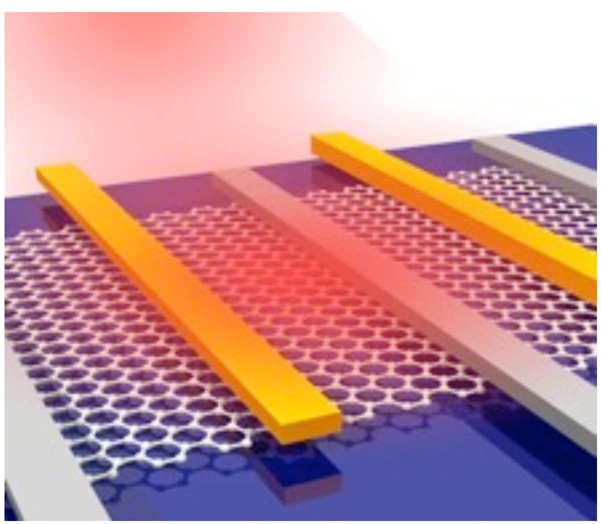
Henk W. Ch. Postma

Nano Lett., 2010, 10 (2), pp 420–425

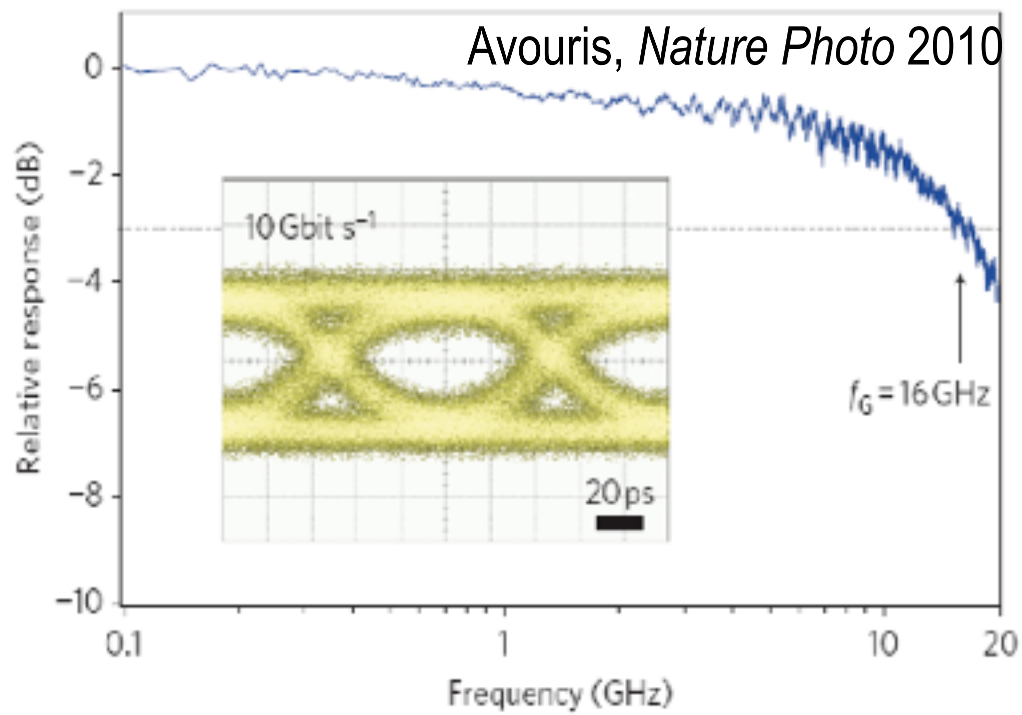


ULTRAFAST PHOTODETECTORS





ballistic transport
of photo-generated carriers
in built-in electric field



~2% conversion
due to high transparency of graphene

SUBSTITUTE FOR ITO

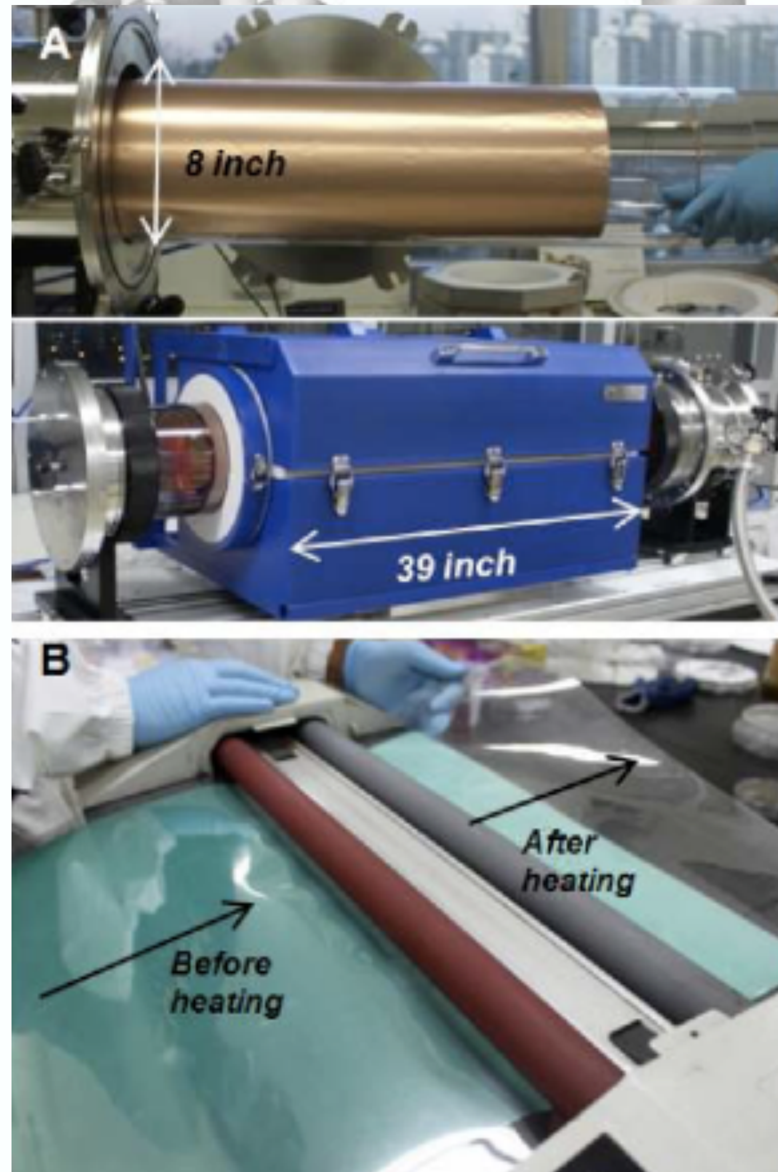
GRAPHENE:
conductive & transparent

ρ ~40Ω/□ transparency ~90%

μ ~5,000 cm^2/Vs

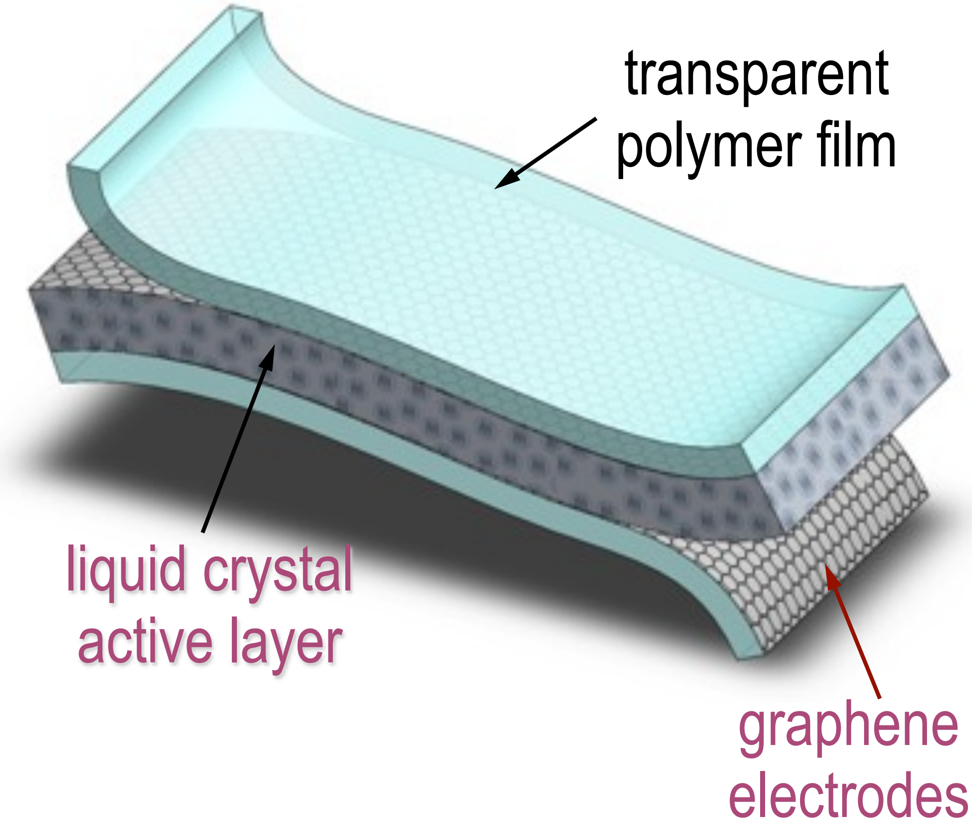
Hong, Nature 2009; Nature Nanotech. 2010

flexible:
sustains strain >10%



TOUCH SCREENS

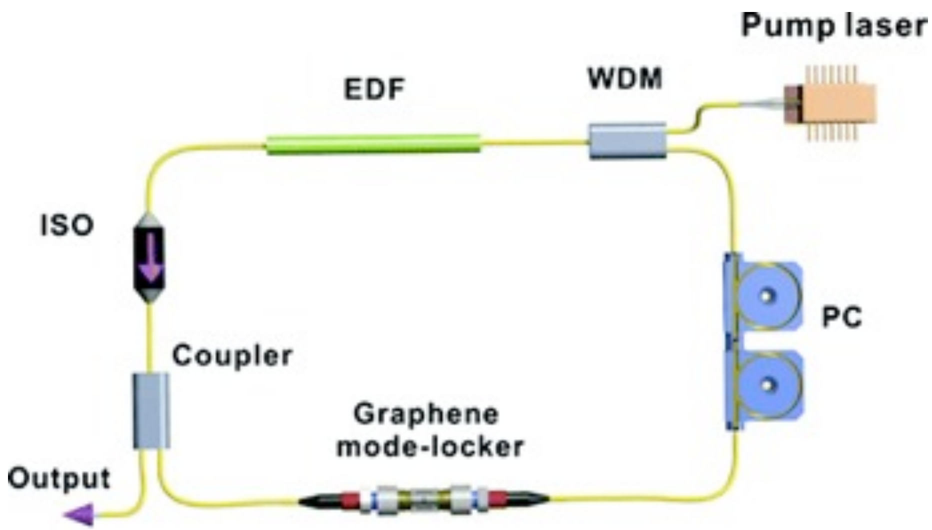
bendable & wearable

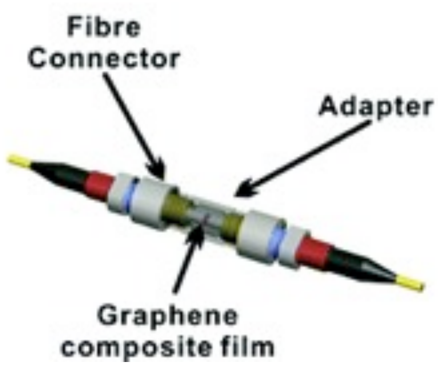


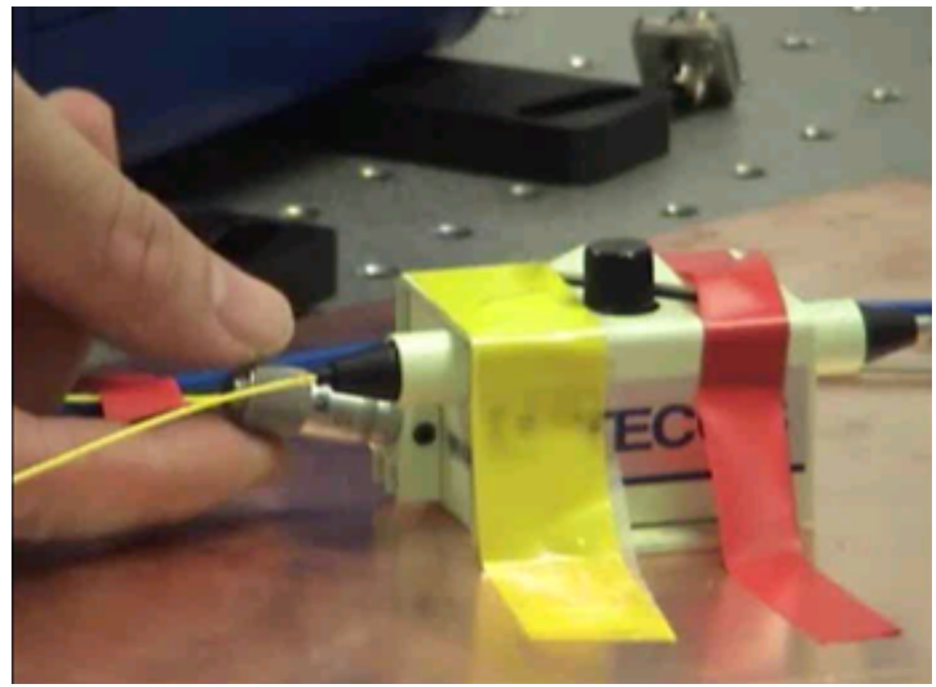
SKKU-Samsung 2010

BROADBAND SATURABLE ABSORBERS

non-linear opacity:
graphene is more
transparent at high powers



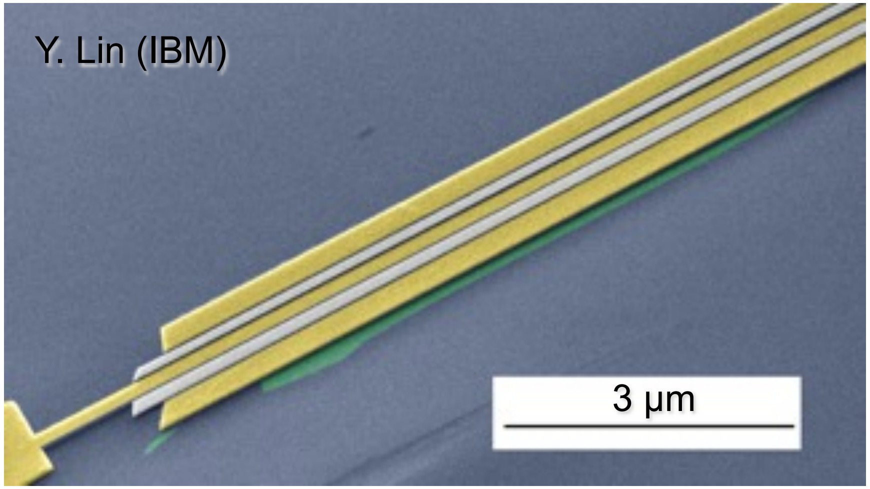


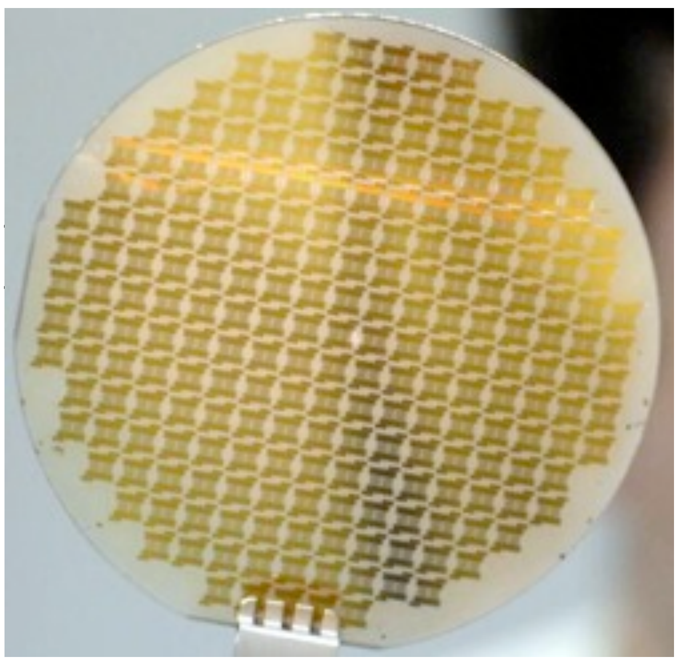


STARTUPS
@ Singapore & Cambridge

from far-infrared to UV
~10 fs response

THz Transistors





ballistic transport
on submicron scale,
high velocity,
great electrostatics,
scales to nm sizes

ultra high-f
analogue transistors;
HEMT design

Manchester, *Science* '04

US military programs:
500 GHz transistors
on sale by 2013 years

demonstrated (IBM & HRL 2009):
~100 GHz even for low μ & long channels

ANY APPLICATION
WHERE
CARBON NANOTUBES
OR GRAPHITE
ARE CONSIDERED

BUT can be BETTER

- both sides bind
- monolayers cannot cleave any further

production within 3 years: from 0 to >100 ton pa
low-quality graphene (multilayers)

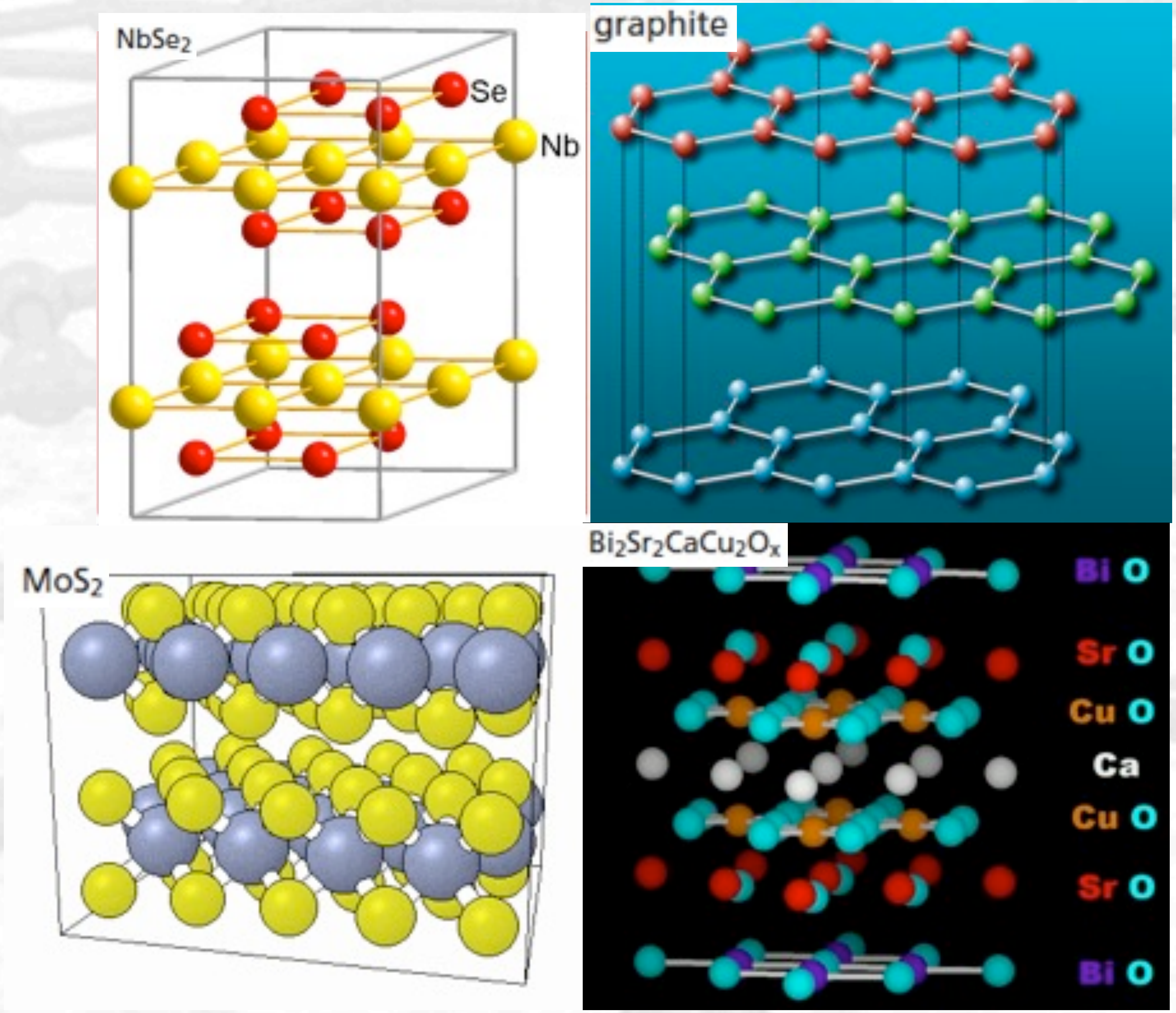
Take home lesson

Graphene

is NOT the end of the road !

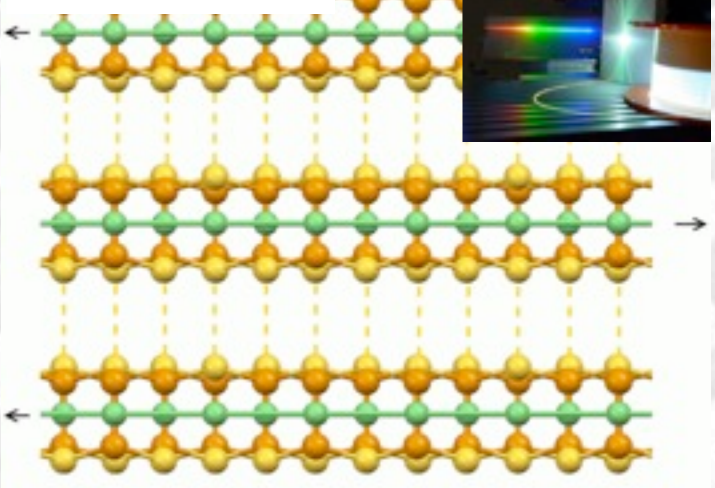
Take home lesson

Graphene
is the beginning of an exploration!

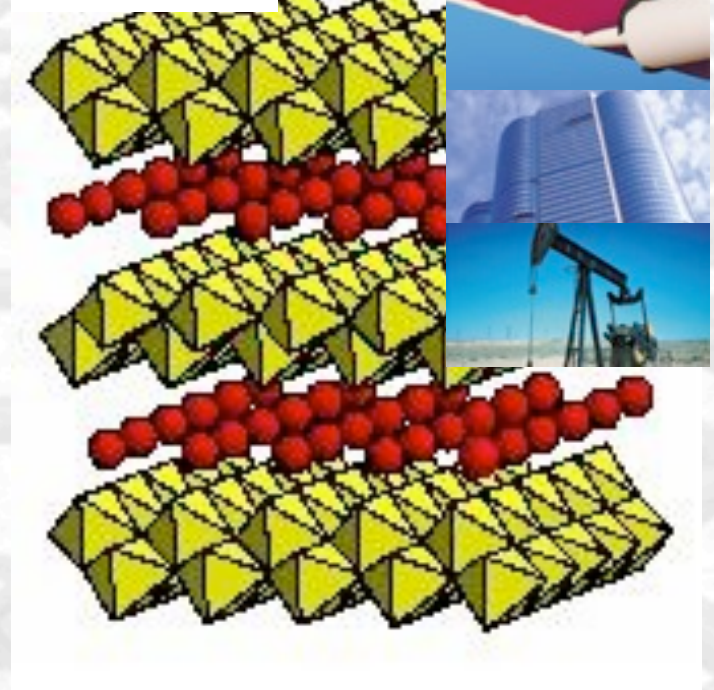


K.S. *Novoselov*, D. Jiang, T. Booth, V.V. Khotkevich, S. V. Morozov, & A.K. *Geim*. *Two Dimensional Atomic Crystals*. *PNAS* 102, 10451-10453 (2005).

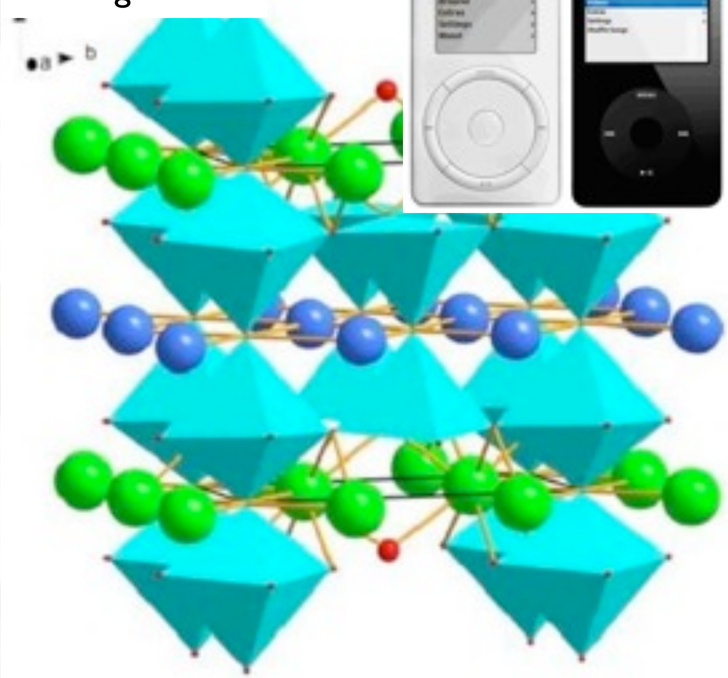
Phosphonates $FePS_3$



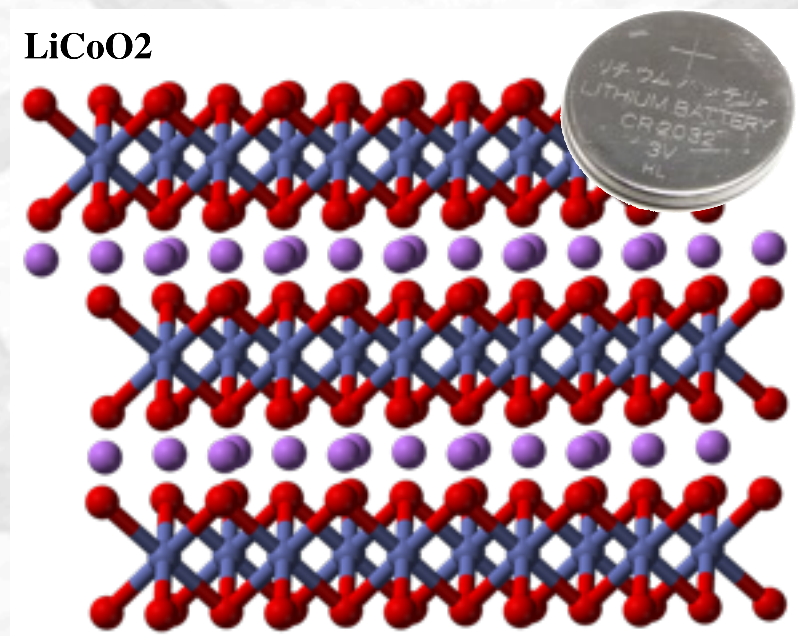
Titanates



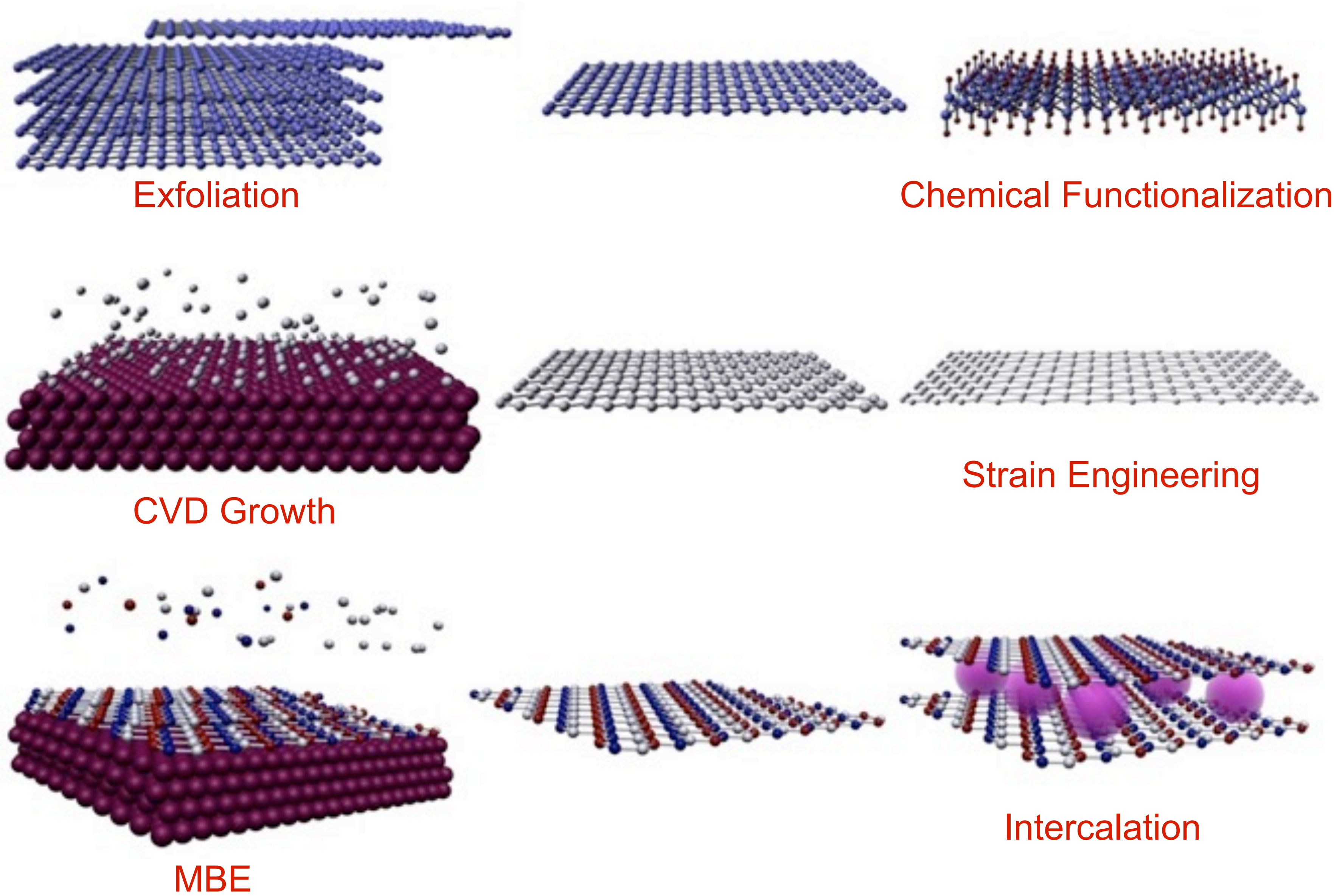
Manganites



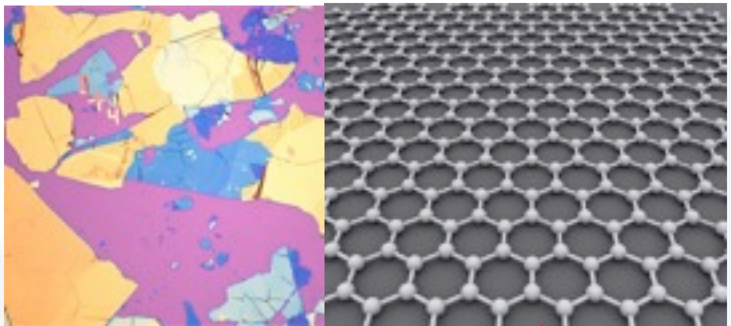
$LiCoO_2$



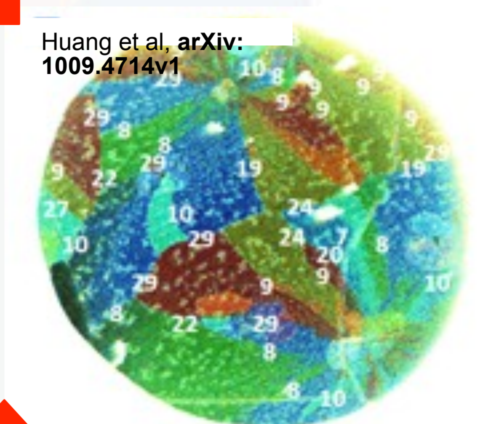
New Routes for 2D Crystal Growth and Tailoring



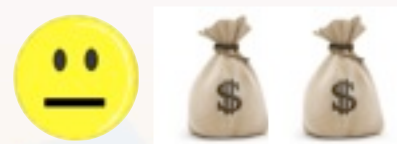
Platforms

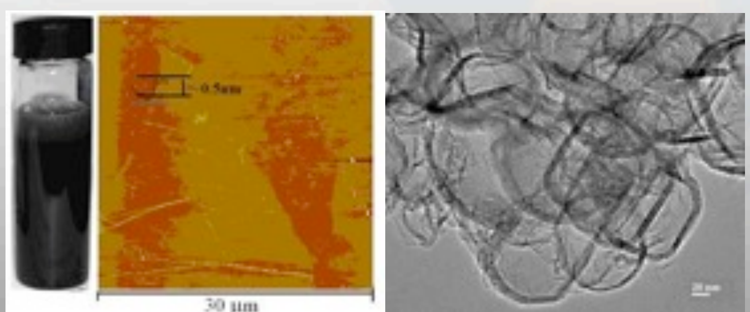


Single Crystal Graphene
- *Electronically great; Structurally great*
- *Mass Production Cost: ?*
- *High End Electronics*

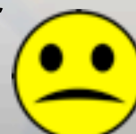


CVD Graphene : growth on metal
- *Electronically OK ; Structurally OK*
- *Mass Production Cost: Medium Price*
- *Flexible Electronics*

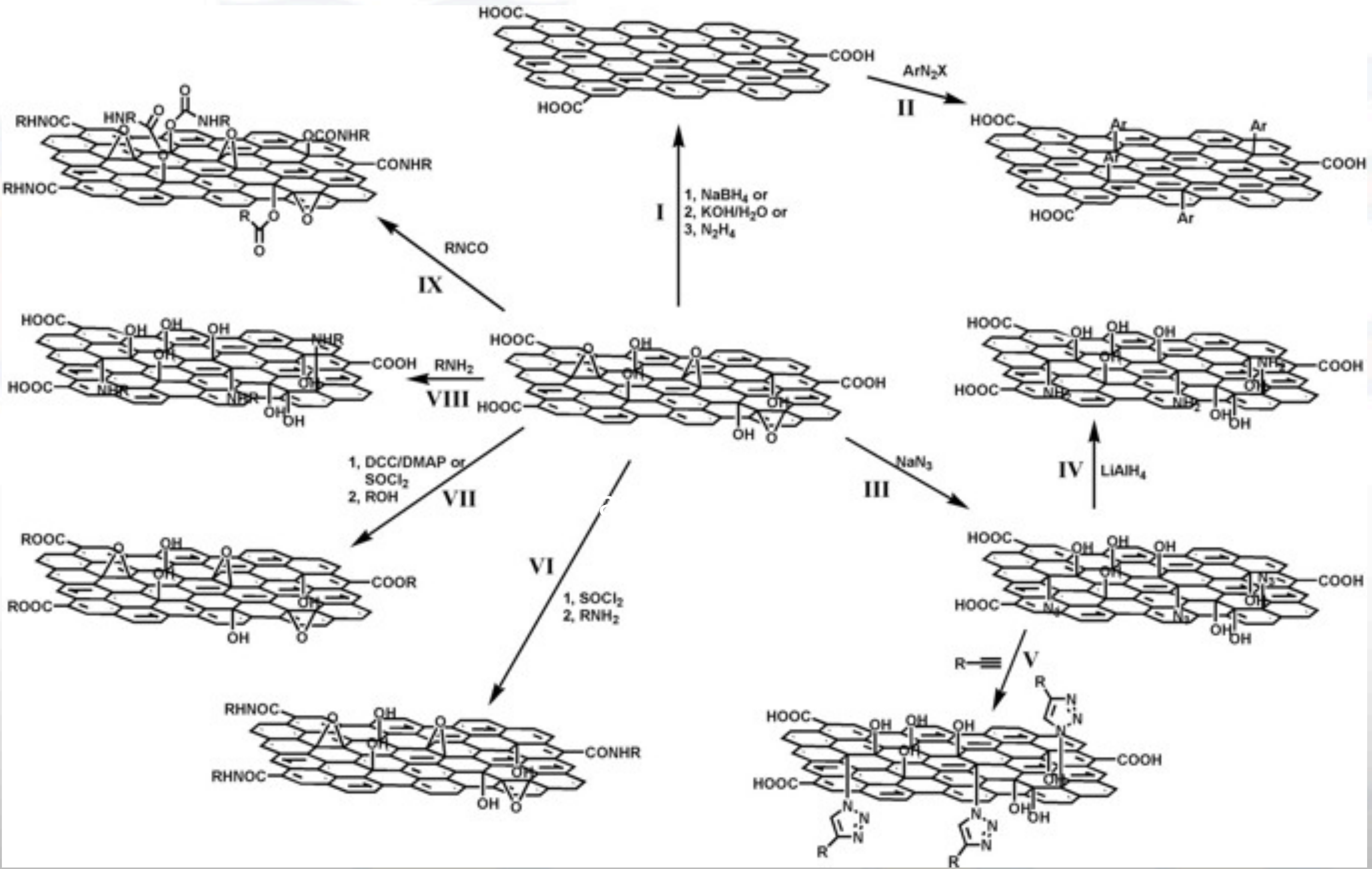




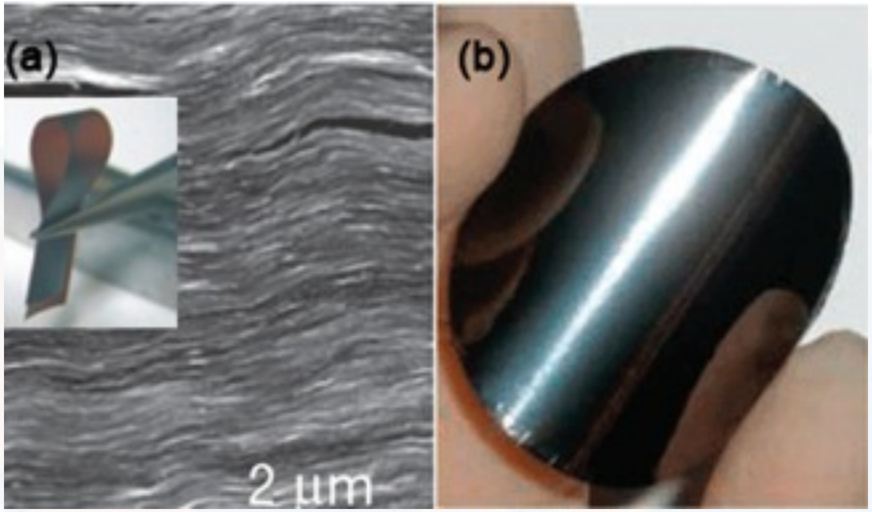
Graphene suspension obtained from sonication of graphite
- *Electronically dirty; Structurally poor*
- *Mass Production Cost: Low*
- *Printed Electronics*



TAILOR MADE CHEMISTRY ON GIANT POLYAROMATIC PLATFORM (GRAPHENE OXIDE)

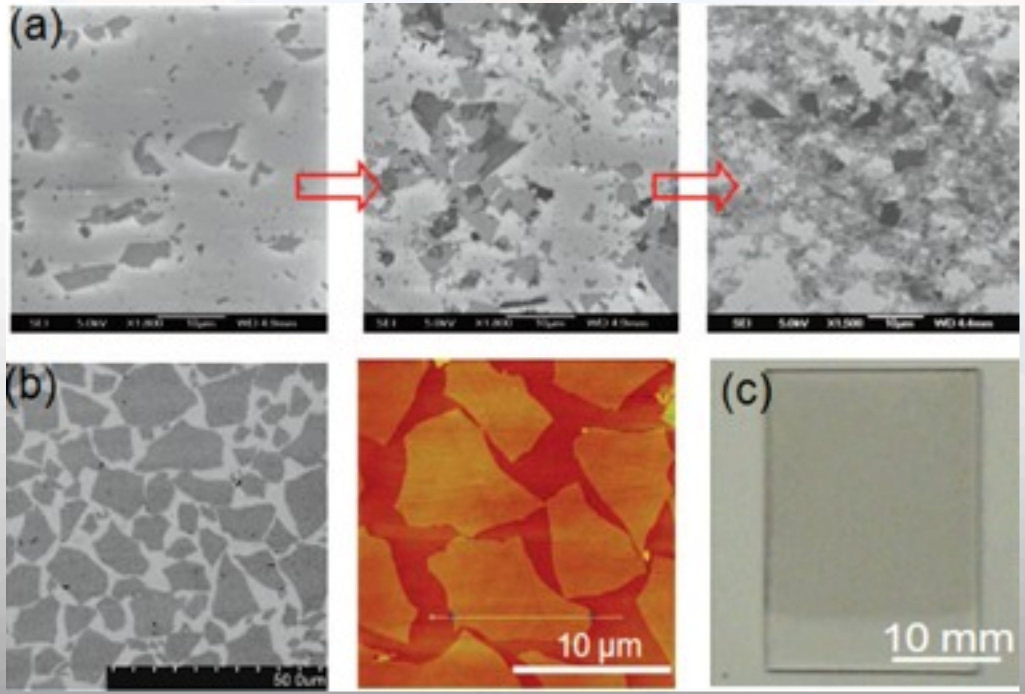


Atomically Thin Films (ATF)



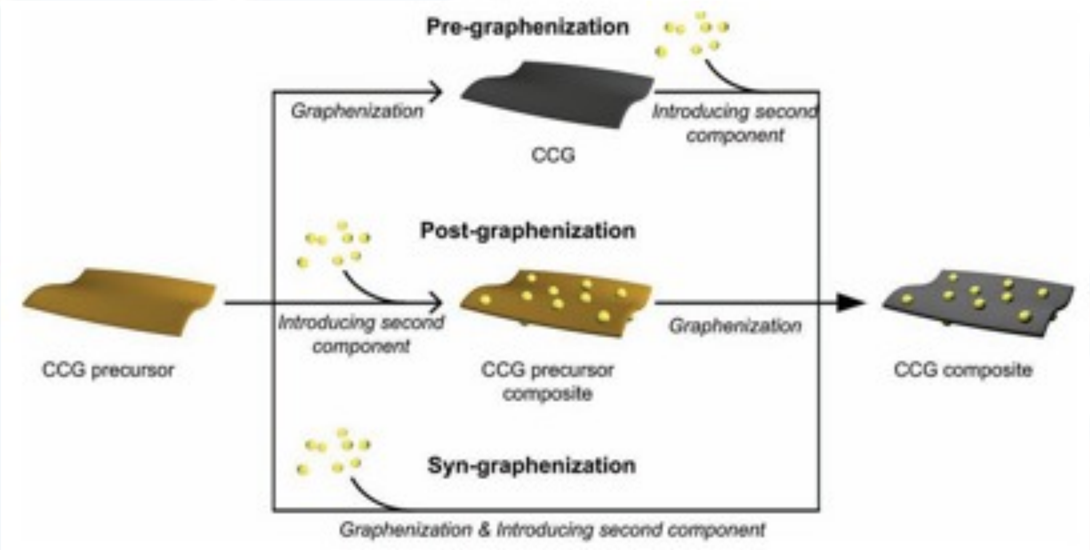
Free-standing graphene films

Solution process → density control

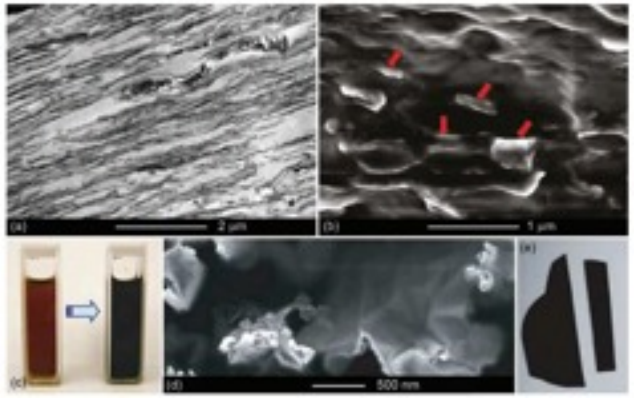


GO film by Langmuir-Blodgett assembly

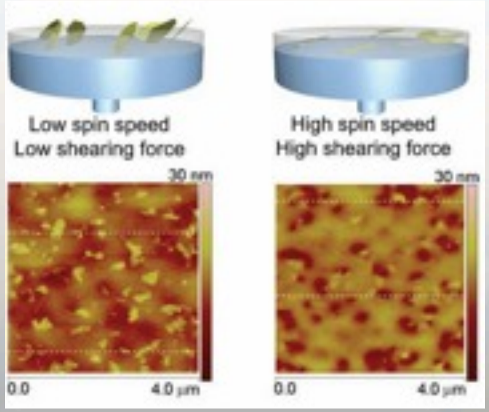
Composites



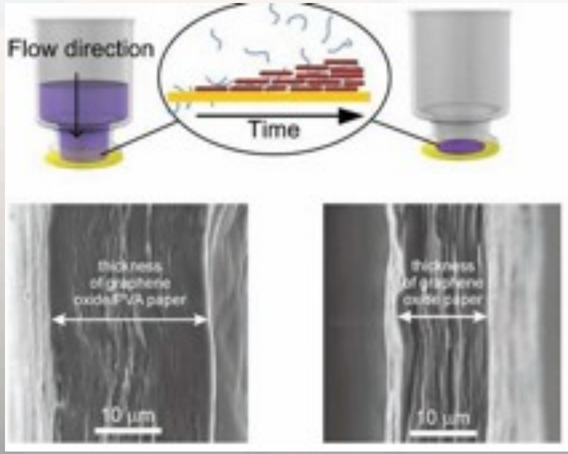
Casting G/Nafion



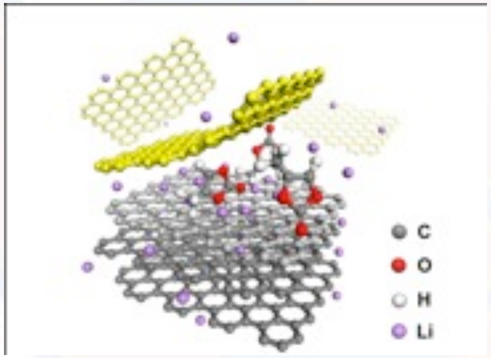
Spin-coating G film

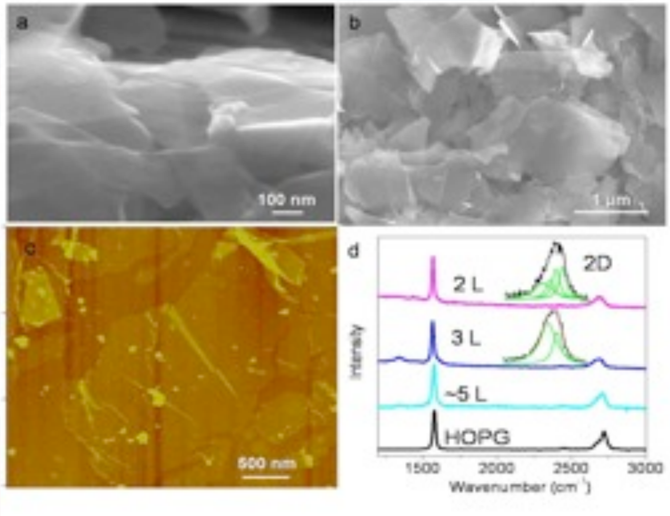


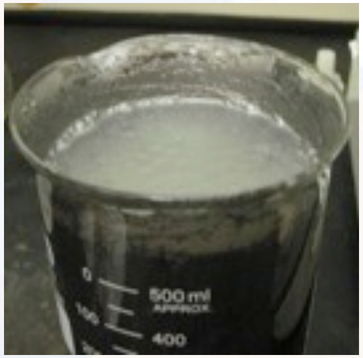
Vacuum filtration



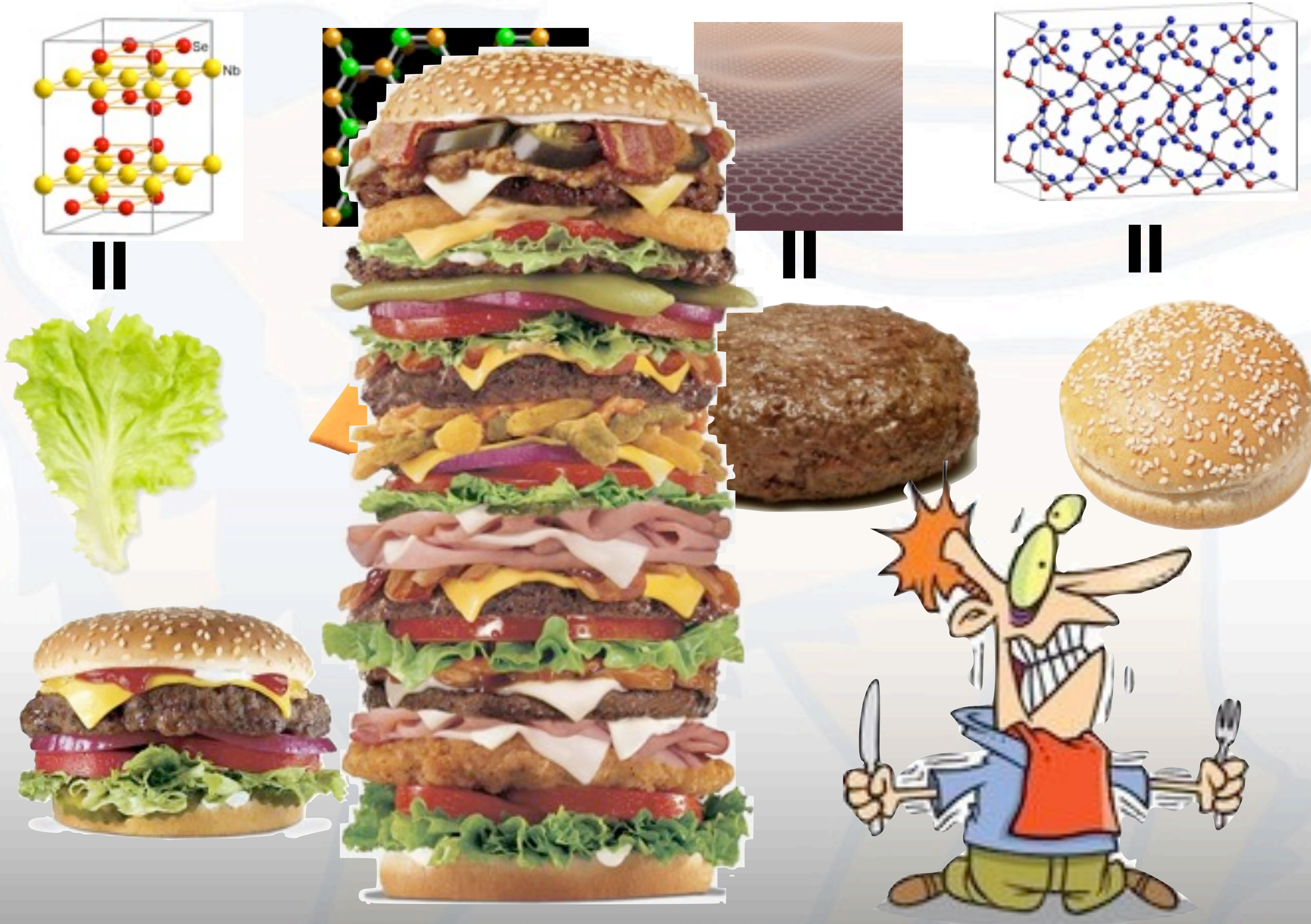
Large Scale Production: From Graphite to Graphene



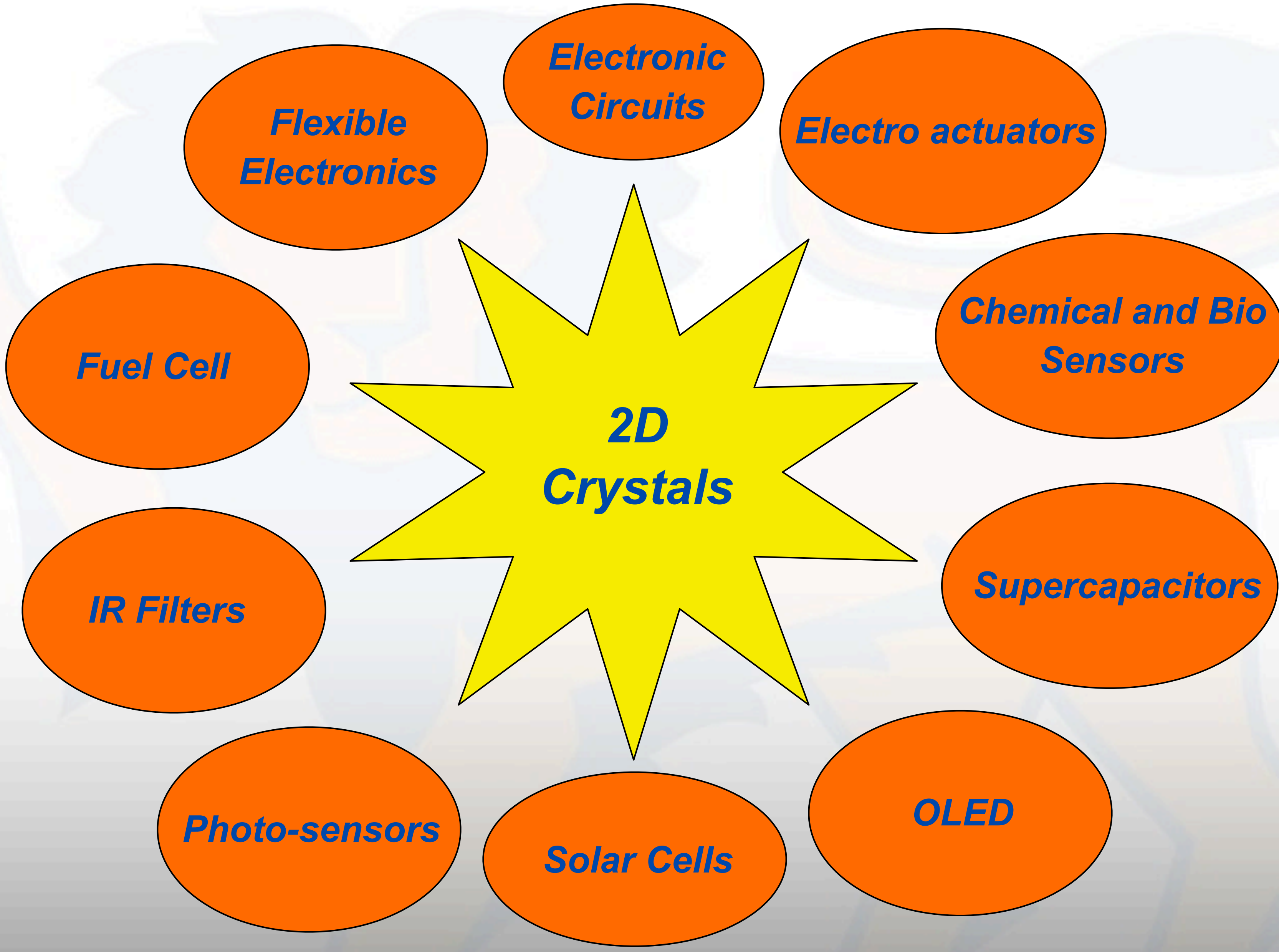




Our "gastronomy"...



Platform for Applications



Summary

- ***Paraphrasing Isaac Newton we can say that we are still in the infancy of a broad field and diverting ourselves with graphene, a material that looks more interesting than ordinary, whilst a great field of 2D crystals lay all undiscovered before us.***

Thank you !

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October, 2012, Beijing, China

Local Organization Chair:
Prof. Hong-Jun GAO, CAS (hjgao@iphy.ac.cn)