Lux Spotlight
The Pace of Technology

Case Closed: Graphene Is the Next Carbon Nanotube

THE NEW YORKER

NEWS CULTURE BOOKS SCIENCE & TECH BUSINESS HUMOR CARTOONS MAGAZINE AUDIO VIDEO

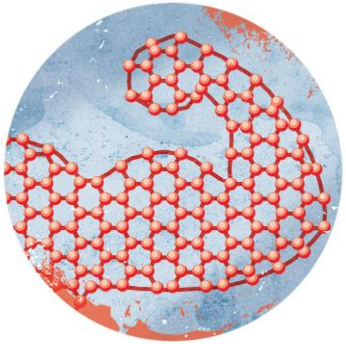
ANNALS OF INNOVATION | DECEMBER 22 & 29, 2014 ISSUE

MATERIAL QUESTION

*Graphene may be the most remarkable substance ever discovered. But what's it for?*

BY JOHN COLAPINTO

# Contamination is Graphene's Kryptonite




**Seyed Hamed Aboutalebi**

**Condensed Matter National Laboratory (CMNL)**


**Is Graphene the Next Silicon ... Or Just the Next Carbon Nanotube?**

December 18, 2012 | State of the Market Report

# Outline

1

A brief history

2

The coming age of supermaterials

3

The case of Carbon Nanotubes

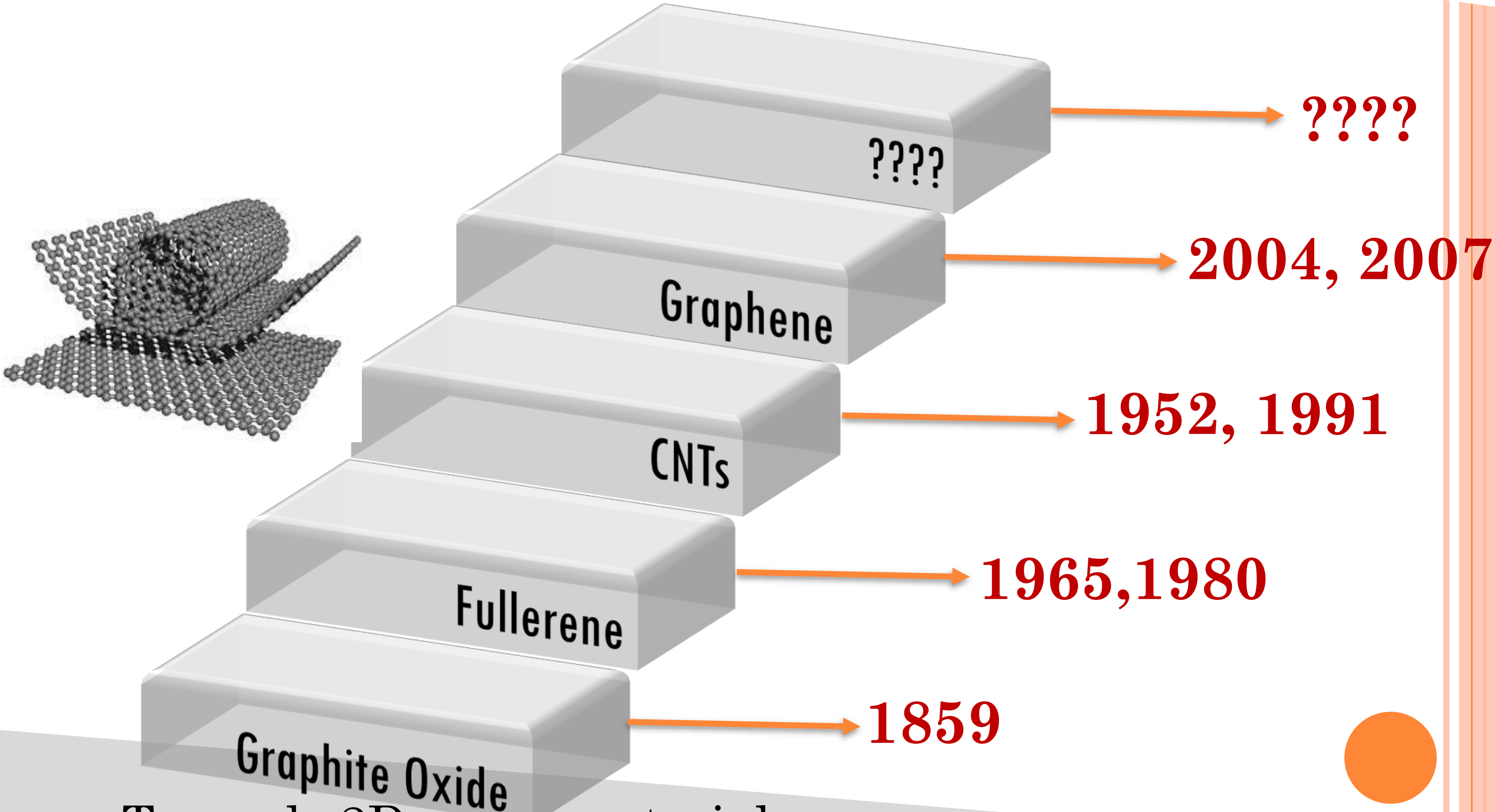
3

Challenges and Opportunities


# The coming age of super materials

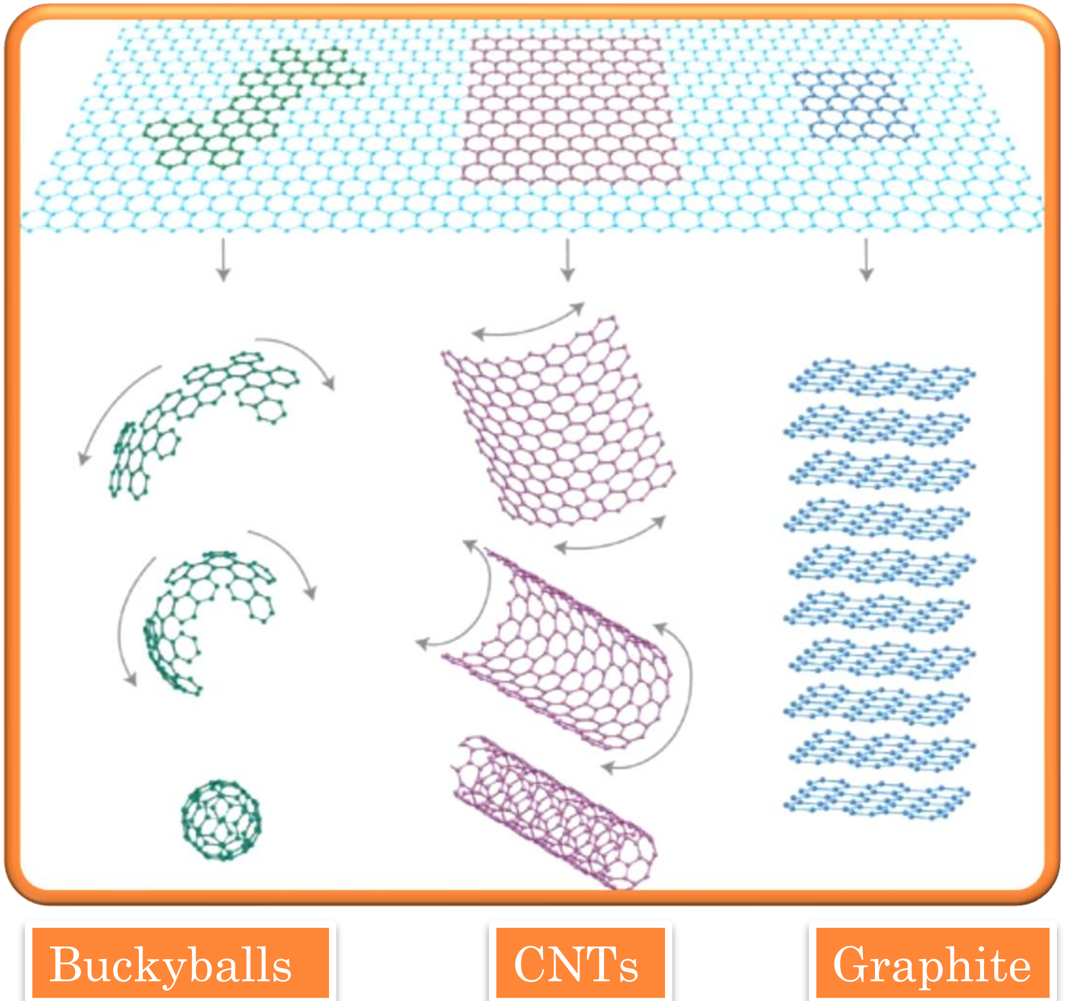
Or is it???

# Super Materials: Candidates




Towards 2D super materials

# Graphene




*A. K. Geim,& K. S. Novoselov* **The rise of Graphene,** *Nat. Mater.* 2007, **6** , 183.

# Graphene Vibe

nature International weekly journal of science

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*NATURE* | NEWS FEATURE

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## Graphene: The quest for supercarbon

**Graphene's dazzling properties promise a technological revolution, but Europe may have to spend a billion euros to overcome some fundamental problems.**

**Mark Peplow**

20 November 2013

nature International weekly journal of science

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Archive > Volume 493 > Issue 7434 > News > Article

*NATURE* | NEWS

## Research prize boost for Europe

**Graphene and virtual brain win billion-euro competition.**

**Alison Abbott** & **Quirin Schiermeier**

29 January 2013

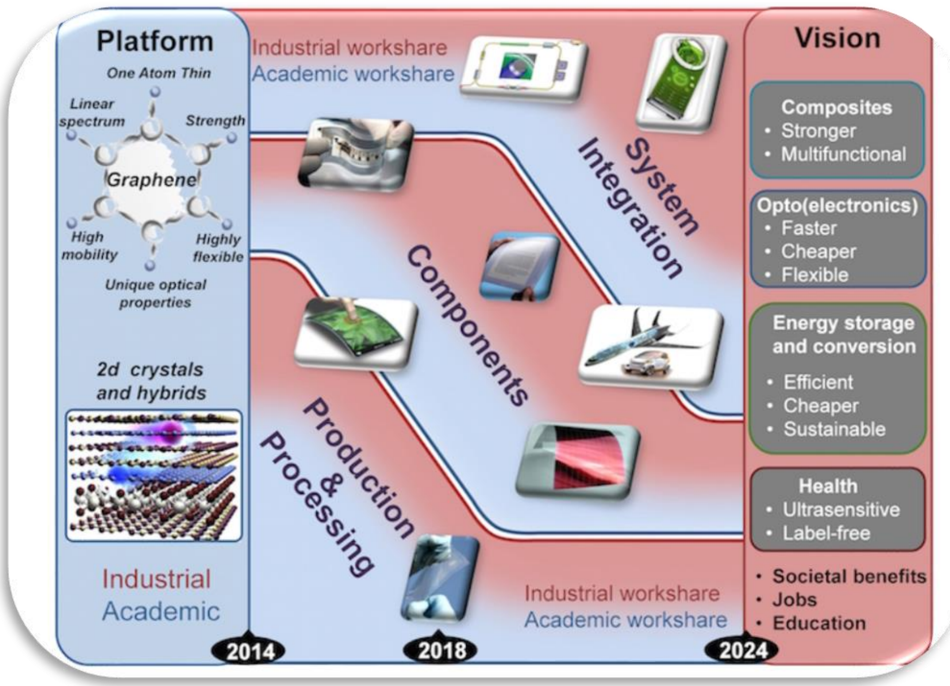


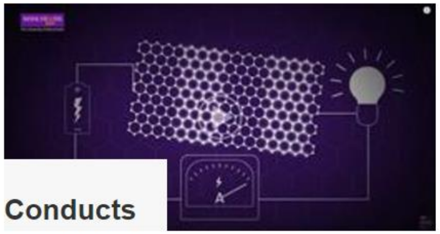

Image credit: Graphene Flagship Project

# Graphene Hype


Graphene's flexibility could be used in emerging technologies such as rollerball computers, heat sensitive clothing and flexible phones.


Graphene is transparent, meaning that we could see TV's built into windows and Sat Navs built into car windscreens in the future of electronics.


Graphene is the strongest material known to man. It is over 200 times stronger than steel. The strength of graphene could be used in composites...



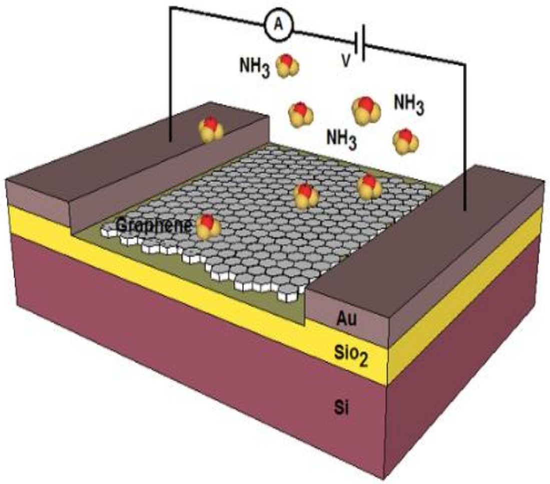

Graphene can conduct electricity even better than copper and this gives graphene endless applications including conductive paints and inks, next generation electronics and more efficient batteries.

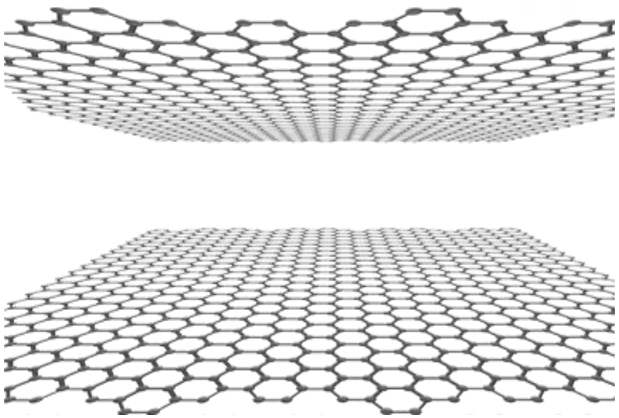

One of graphene's most dynamic properties is its remarkable thinness. At just one atom thick, graphene is one million times thinner than the diameter of a human hair.

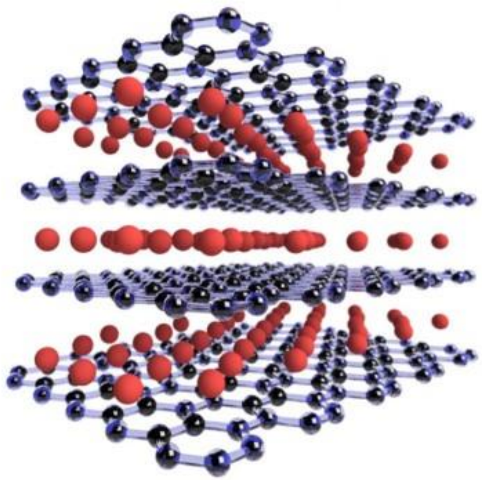

Graphene has the highest thermal conductivity known to man. But how can we harness this and what can it be used for?

Source: Graphene Flagship

# Why 2D?



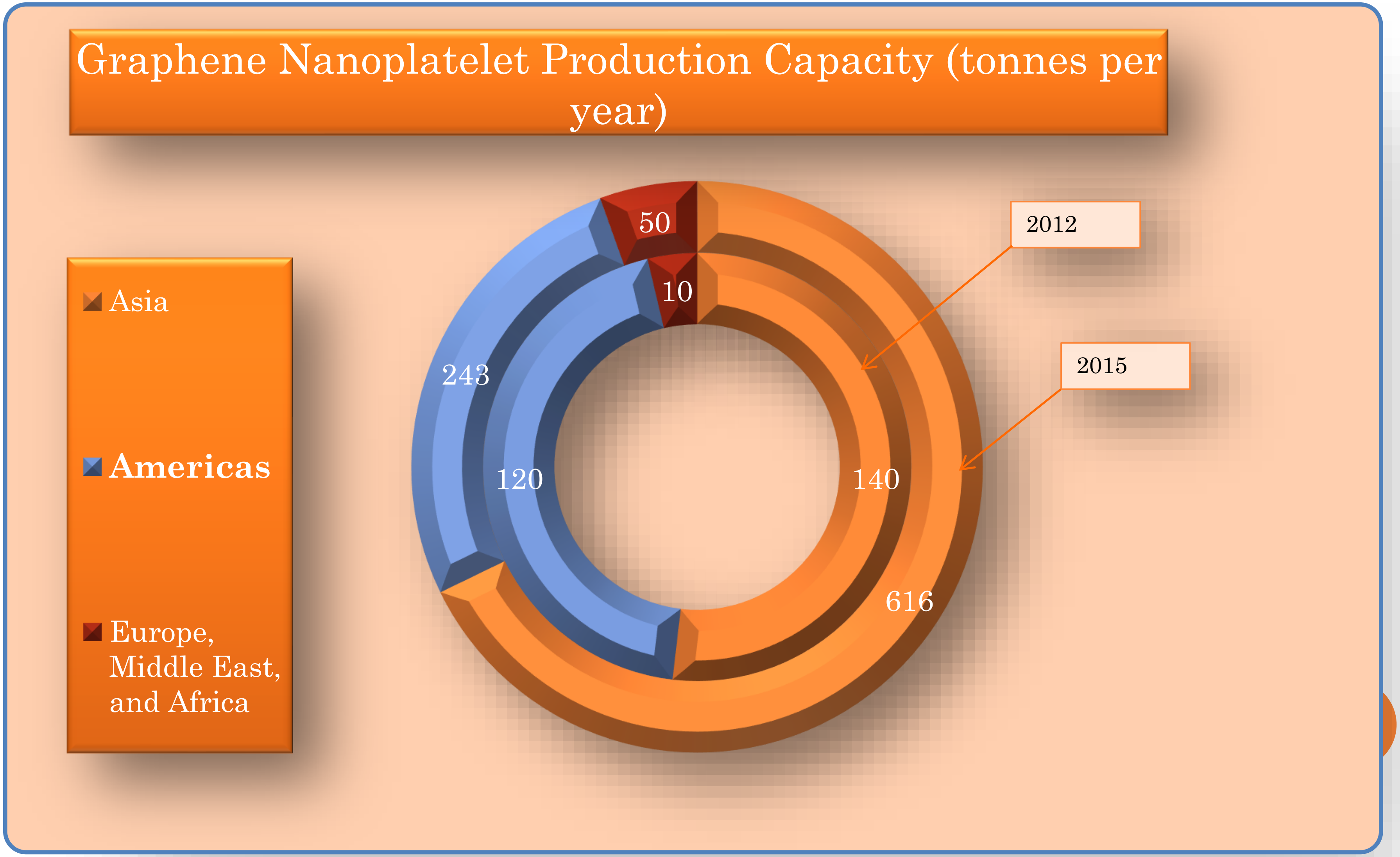


Flat, conductive, transparent, high surface area: Dream material for Sensing and energy application

Graphene: Its all surface

Why do both chemists and material scientists like it??? **HUGE surface area**

# Graphene: The Interest



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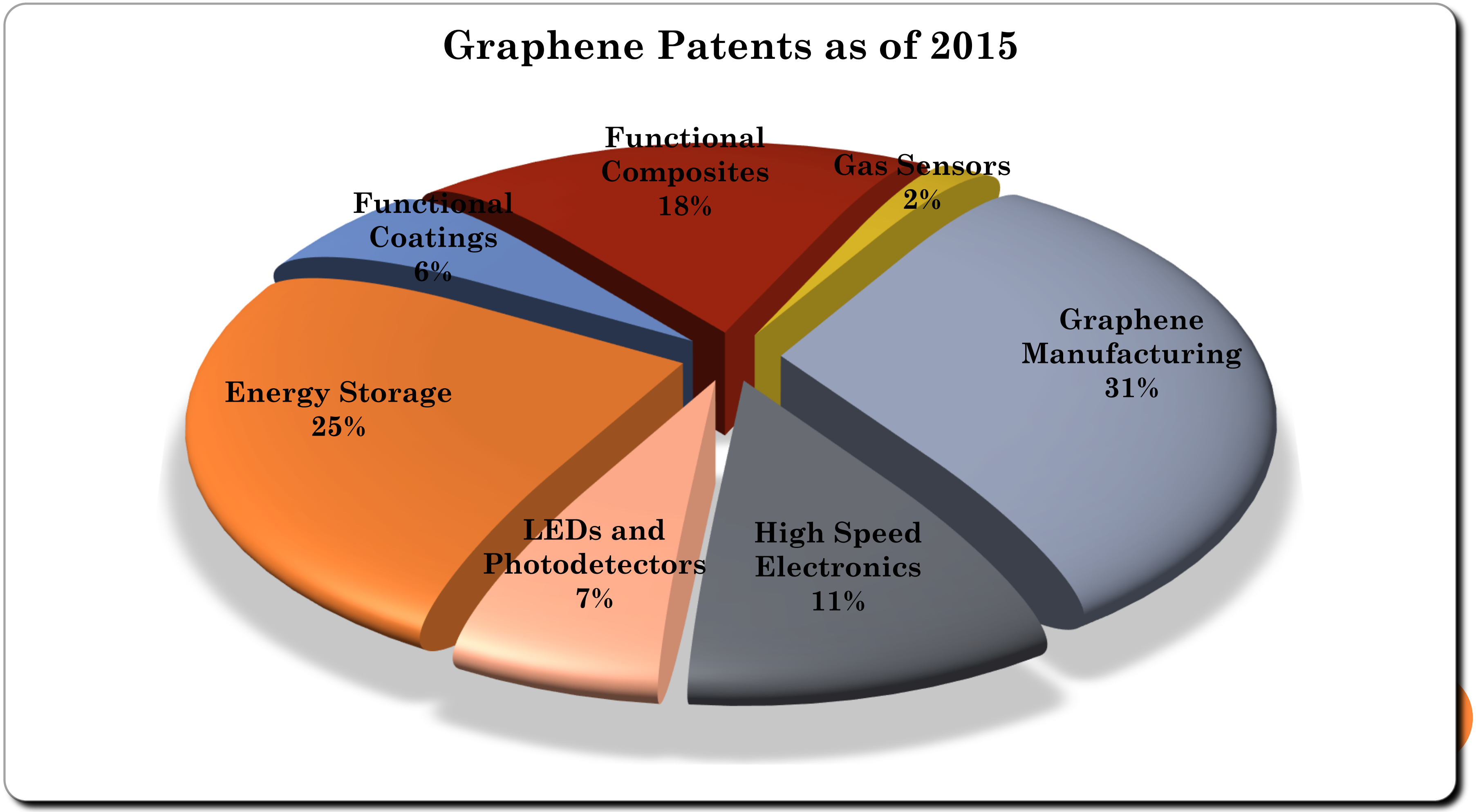
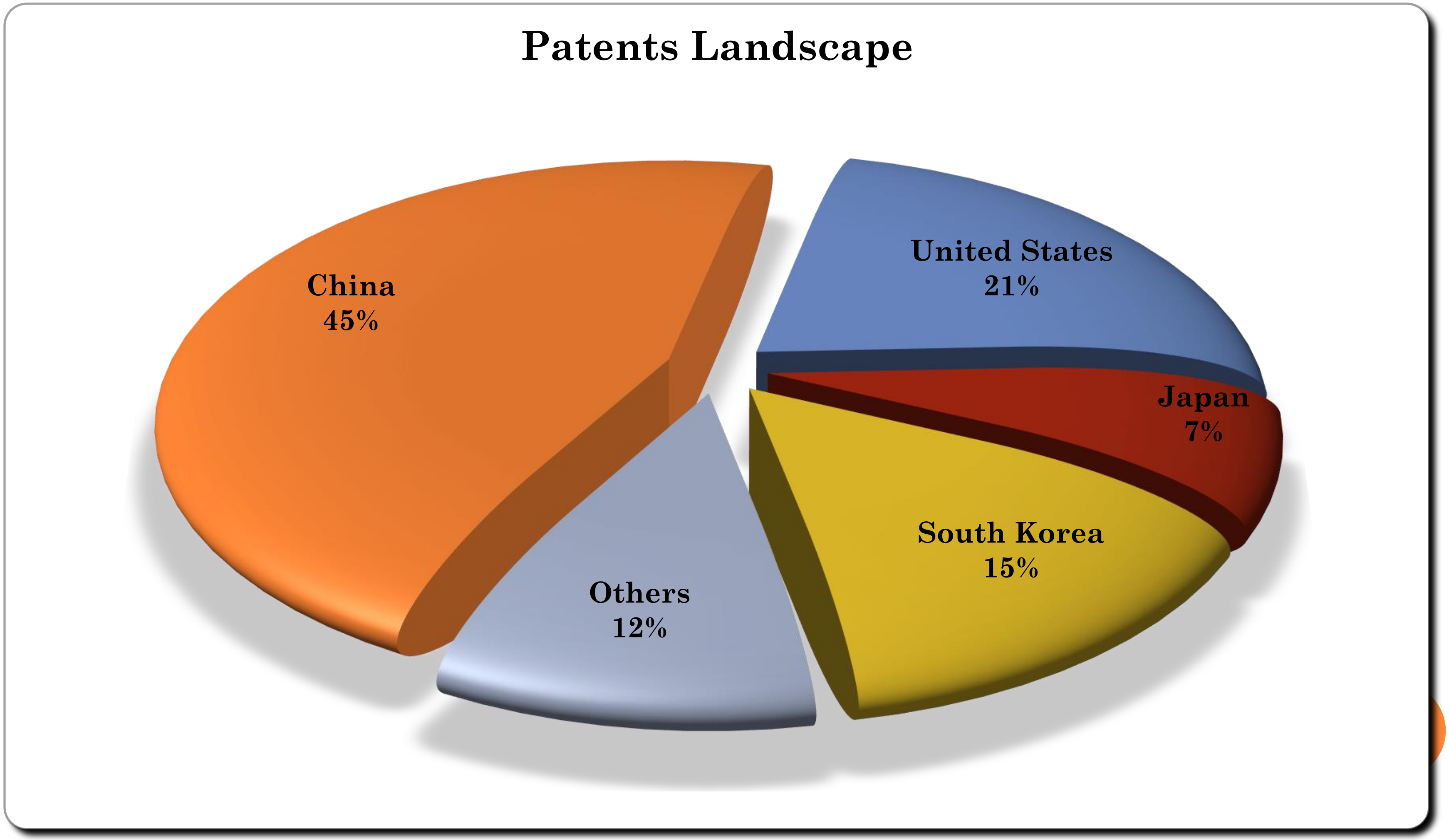


# Graphene: The Interest



# Graphene HYPE

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*NATURE* | NEWS

## UK graphene inquiry reveals commercial struggles

**Concerns about the University of Manchester's National Graphene Institute reflect a broader decline in industrial research and development.**

Mark Peplow

nature International weekly journal of science

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## Graphene booms in factories but lacks a killer app

**Although the wonder material is being made in record volume, commercial success is elusive.**

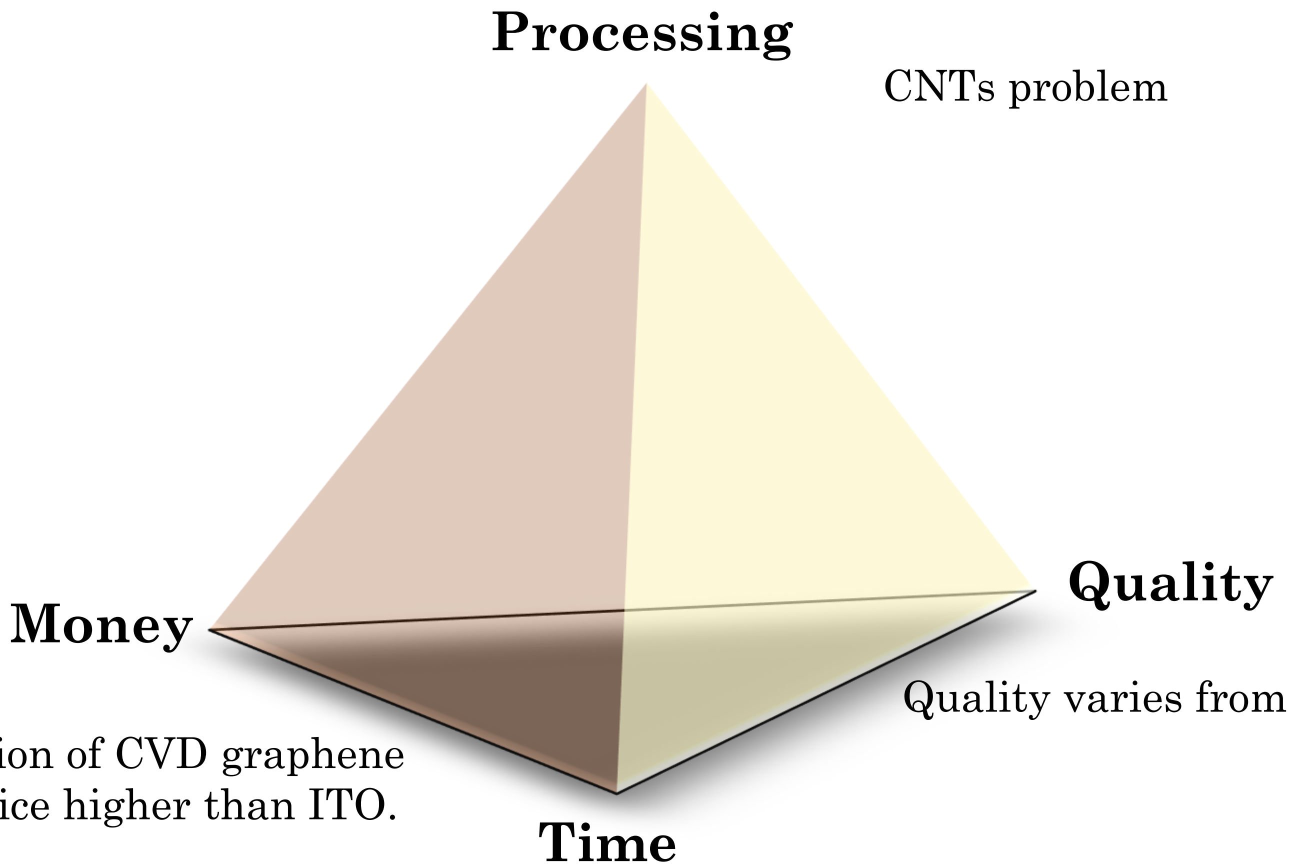
Mark Peplow

17 June 2015

## UK's National Graphene Institute in Revolt After Foreign Tech Grab

By Dexter Johnson
Posted 15 Mar 2016 | 19:33 GMT

# The Problem




CNTs problem

Quality varies from batch to batch

Production of CVD graphene costs twice higher than ITO.

Time consuming Processes

# The case of Carbon Nanotube: The Gold Rush

The end of gold rush!!!

A complete disaster!!!

Basically, nothing matched anything else!!!

History

2000-2005

Significant difference in CNT response

Extraordinary CNT properties

Unique electronic properties

The main Challange

# The case of Carbon Nanotube

The end of the golden age of CNT electrochemistry

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**Basal Plane Pyrolytic Graphite Modified Electrodes: Comparison of Carbon Nanotubes and Graphite Powder as Electrocatalysts**

Ryan R. Moore, Craig E. Banks and Richard G. Compton

View Author Information

Cite This: *Anal. Chem.* 2004, 76, 10, 2677-2682
Publication Date: April 20, 2004
https://doi.org/10.1021/ac040017q



Analytical Chemistry

Issue 16, 2004

Previous Article | Next Article


From the journal:
Chemical Communications

**Investigation of modified basal plane pyrolytic graphite electrodes: definitive evidence for the electrocatalytic properties of the ends of carbon nanotubes**

Craig E. Banks,[a] Ryan R. Moore,[a] Trevor J. Davies[a] and Richard G. Compton*[a]

# THE CASE OF CARBON NANOTUBE

It is all done with Metals!!!

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**Iron Oxide Particles Are the Active Sites for Hydrogen Peroxide Sensing at Multiwalled Carbon Nanotube Modified Electrodes**

Biljana Šljukić, Craig E. Banks and Richard G. Compton

Copper oxide nanoparticle impurities are responsible for the electroanalytical detection of glucose seen using multiwalled carbon nanotubes

Christopher Batchelor-McAuley [a], Gregory G. Wildgoose [a], Richard G. Compton [a], Lidong Shao [b], Malcolm L.H. Green [b]

**Carbon Nanotubes Contain Metal Impurities Which Are Responsible for the "Electrocatalysis" Seen at Some Nanotube-Modified Electrodes**

Craig E. Banks Dr., Alison Crossley Dr., Christopher Salter, Shelley J. Wilkins Dr., Richard G. Compton Prof. Dr.

Communication | Full Access

**Bioavailability of Nickel in Single-Wall Carbon Nanotubes†**

X. Liu, V. Gurel, D. Morris, D. W. Murray, A. Zhitkovich, A. B. Kane, R. H. Hurt



Angew Chem Int Ed 45 (16):2533

# The case of Carbon Nanotube

**Metallic impurities can be washed by $HNO_3$**

- Residual Metallic catalyst impurities cannot be washed out!!!

**Reduction of Hydrogen peroxide**

- Fe-based impurities are responsible!!!

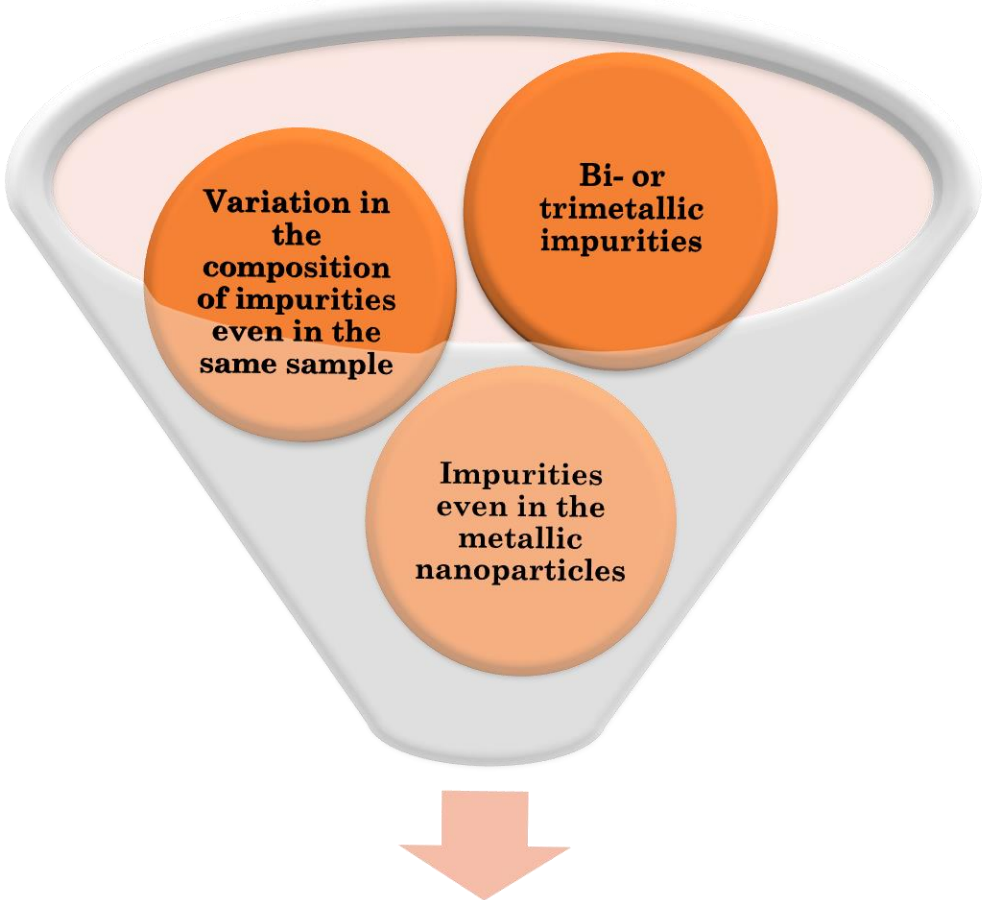
**Glucose Oxidation**

- Cu-based and Fe-based impurities are responsible!!!

**Electrocatalytic oxidation of amino acids, and sulfides**

- Ni-based impurities are responsible!!!

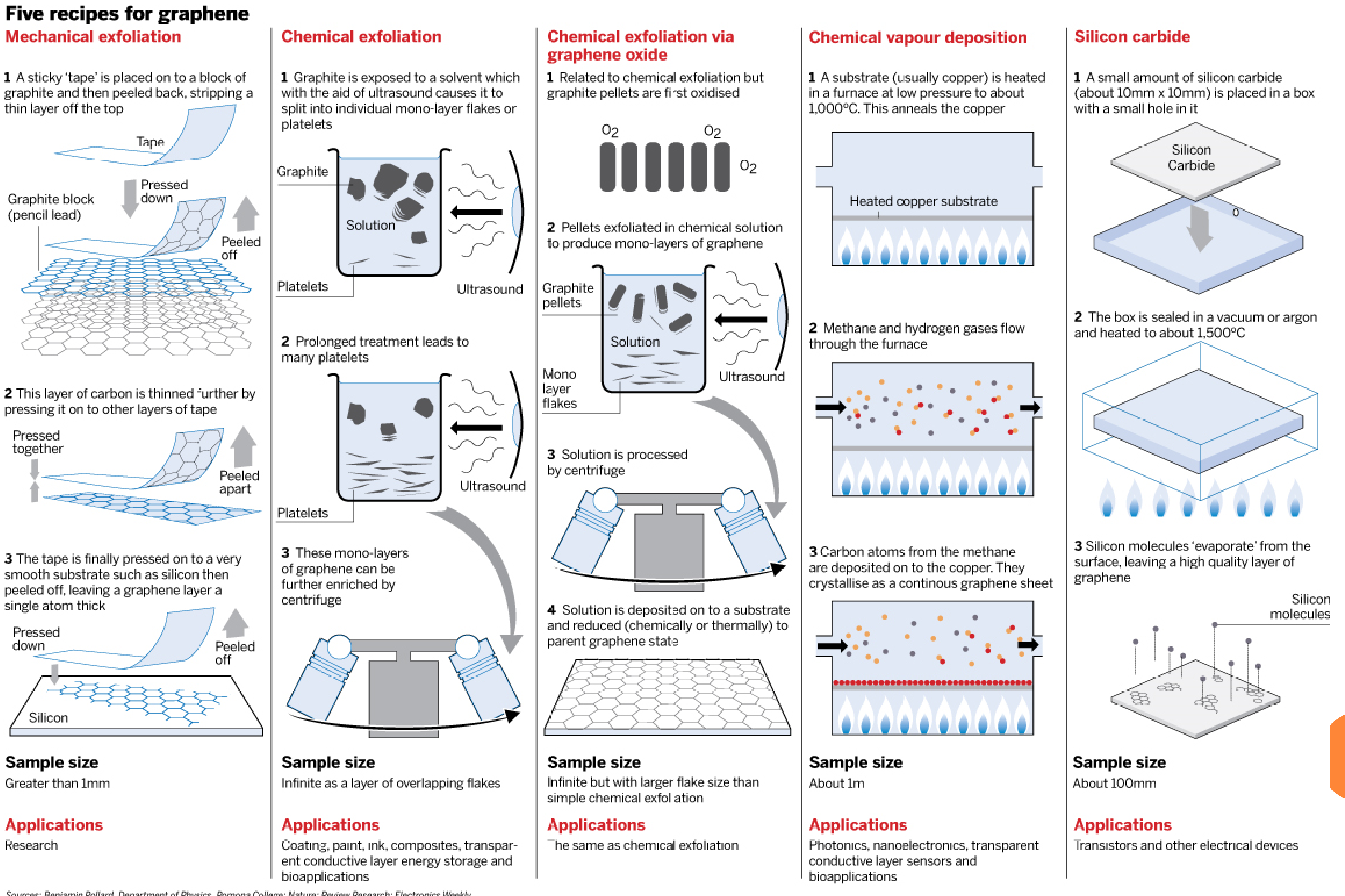
# The case of Carbon Nanotube: The biggest Challenge



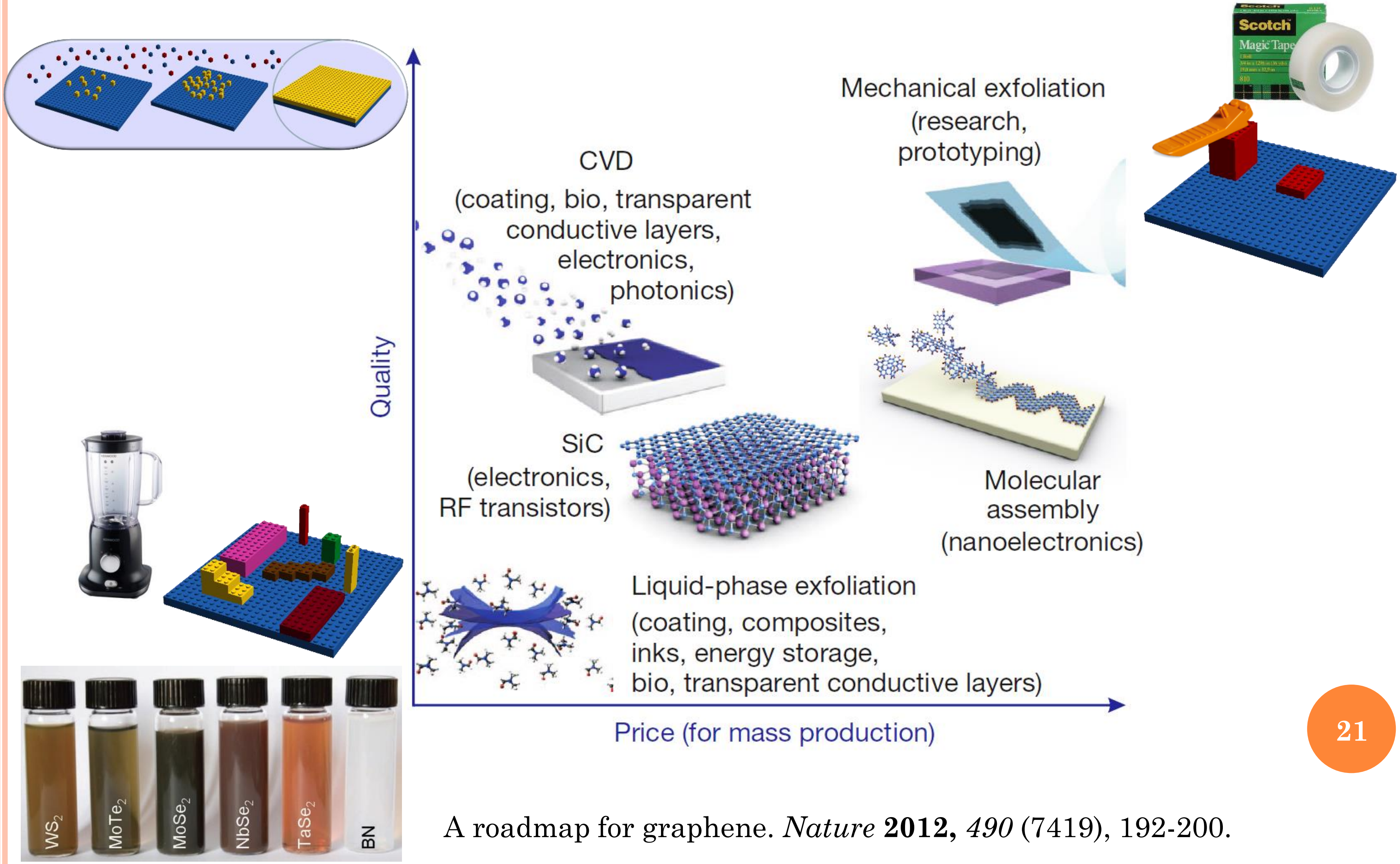

**There is no standard method recommended by IUPAC or any other authority for determining the amount of impurities!!!**


# What about Graphene???

# Graphene Production

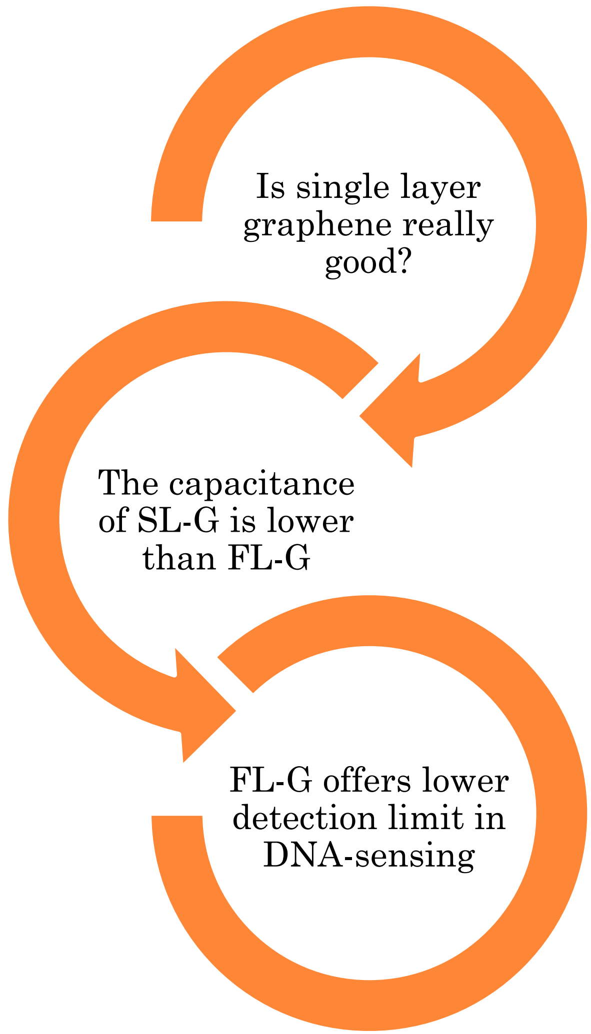


# 2D Materials Production




A roadmap for graphene. *Nature* **2012,** *490* (7419), 192-200.

# What about Graphene?

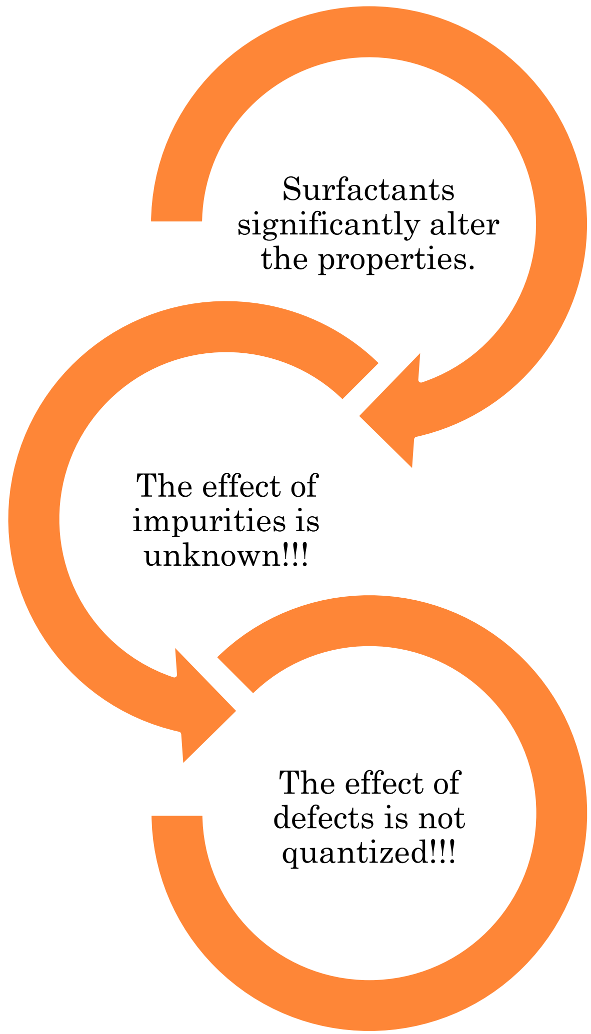





A. Bonanni, M. Pumera, *ACS Nano*2011, **5**, 2356.

M. S. Goh, M. Pumera, *Electrochem. Commun.* 2010, **12**, 1375.

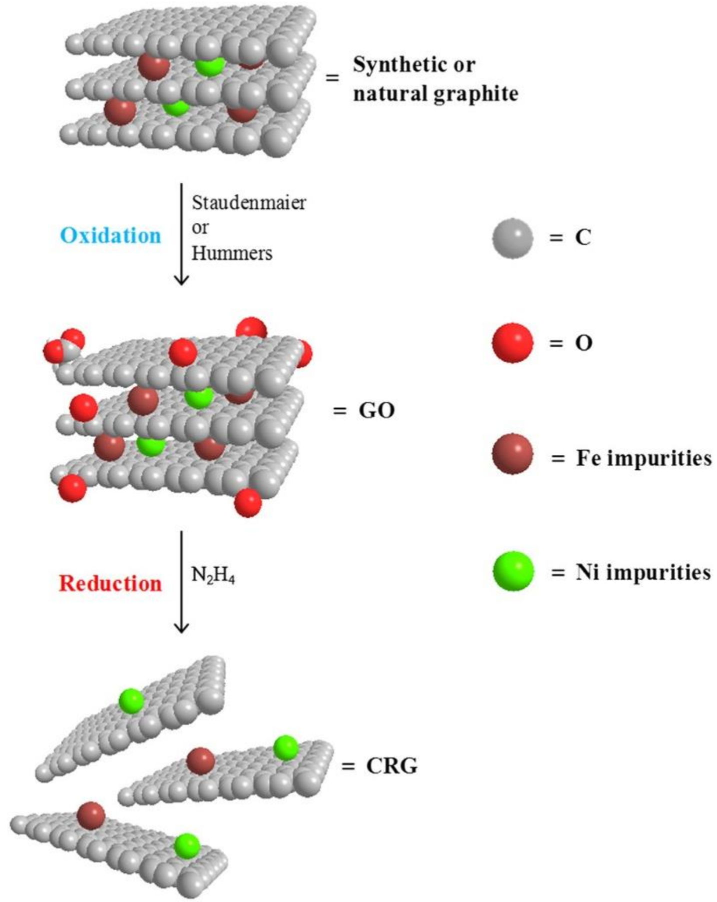
# What about Chemically modified Graphene?




A. Bonanni, M. Pumera, *ACS Nano*2011, **5**, 2356.

M. S. Goh, M. Pumera, *Electrochem. Commun.* 2010, **12**, 1375.

## Schematic for the preparation of chemically reduced graphene.

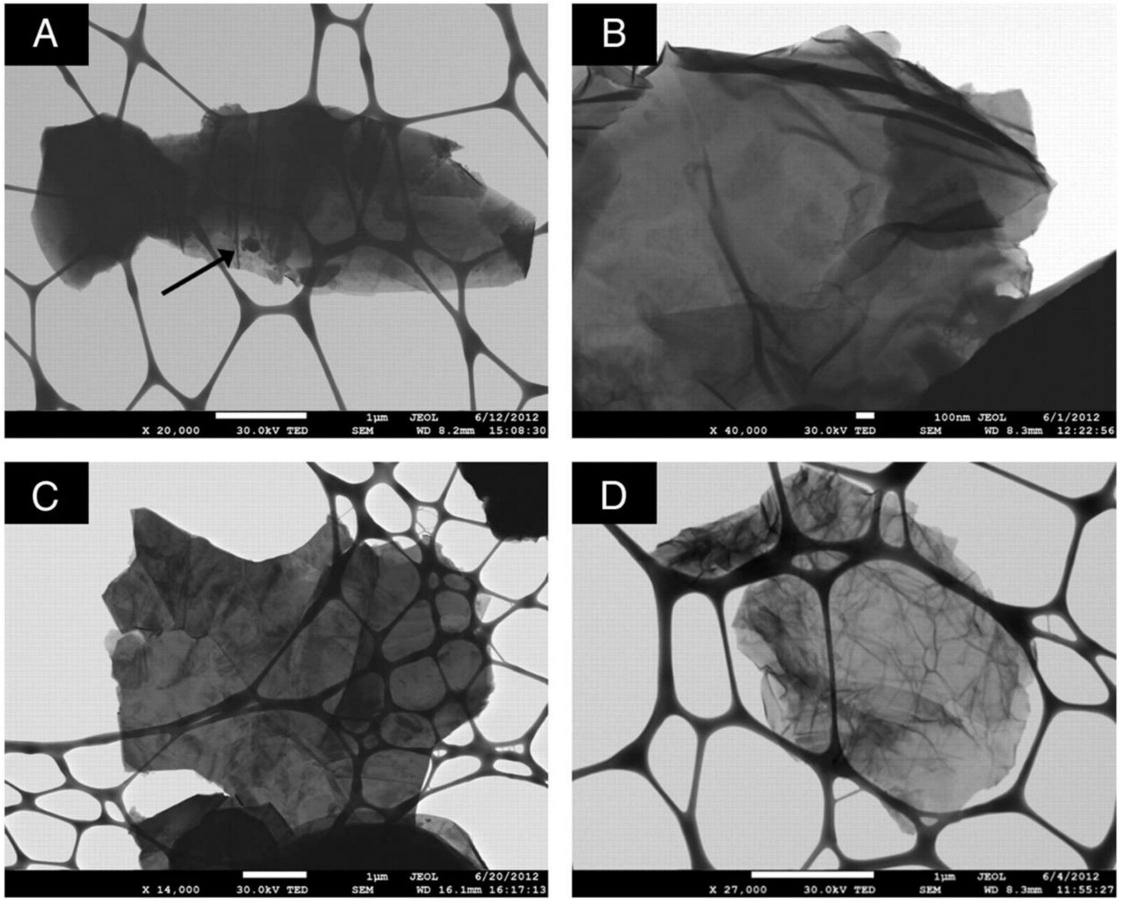



Adriano Ambrosi et al. PNAS 2012;109:32:12899-12904



PNAS

**STEM images of (A) natural graphite, (B) chemically reduced graphene produced from natural graphite, (C) synthetic graphite, and (D) chemically reduced graphene produced from synthetic graphite.**

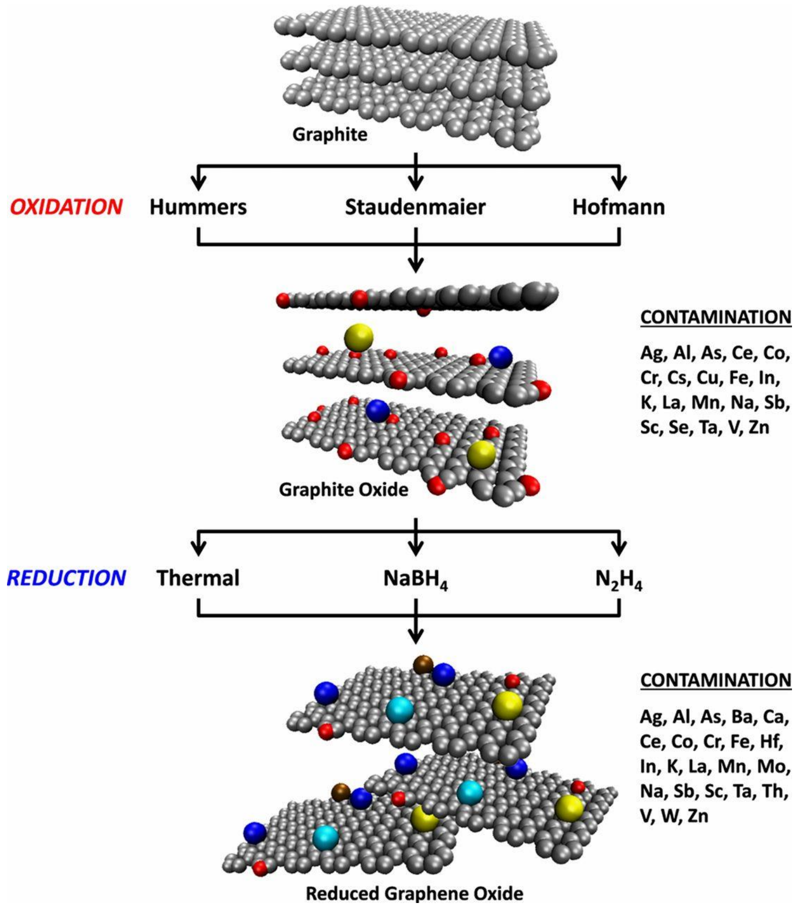



**Adriano Ambrosi et al. PNAS 2012;109:32:12899-12904**



PNAS

**Common synthesis methods for the preparation of RGOs using graphite as a starting material, which ultimately leads to varying contamination arising from impurities within the chemical agents used.**

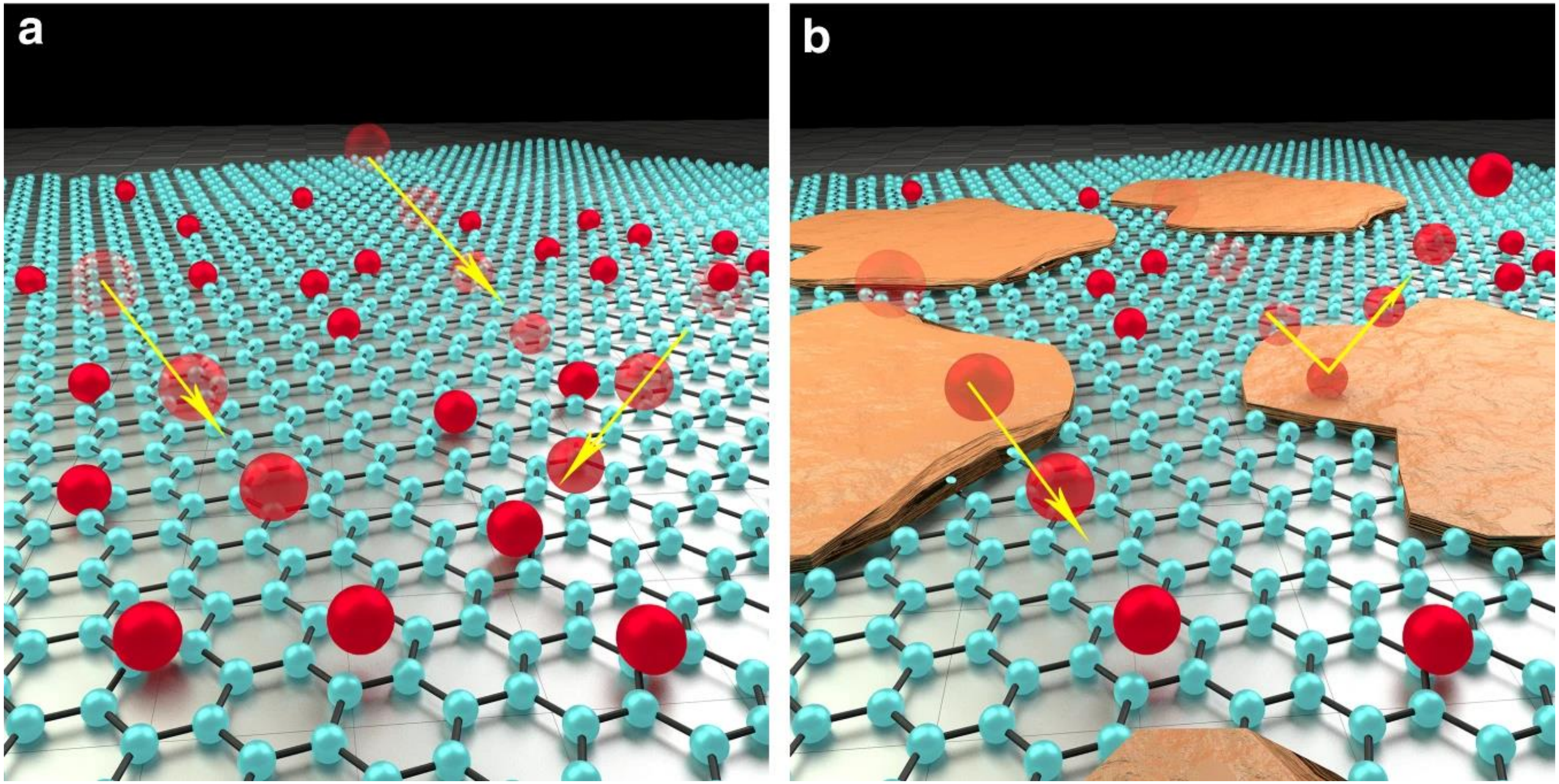



**Colin Hong An Wong et al. PNAS 2014;111:38:13774-13779**



PNAS

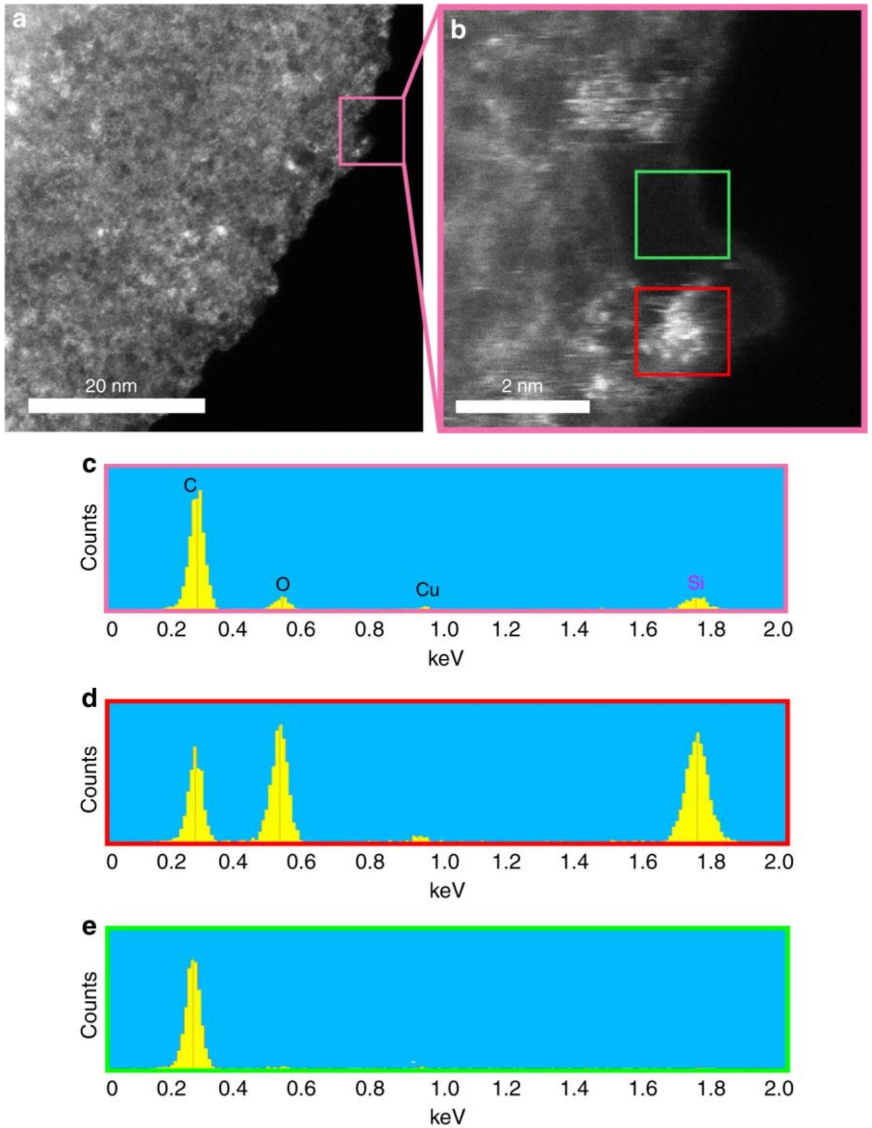
# THE CASE OF CHEMICALLY MODIFIED GRAPHENE





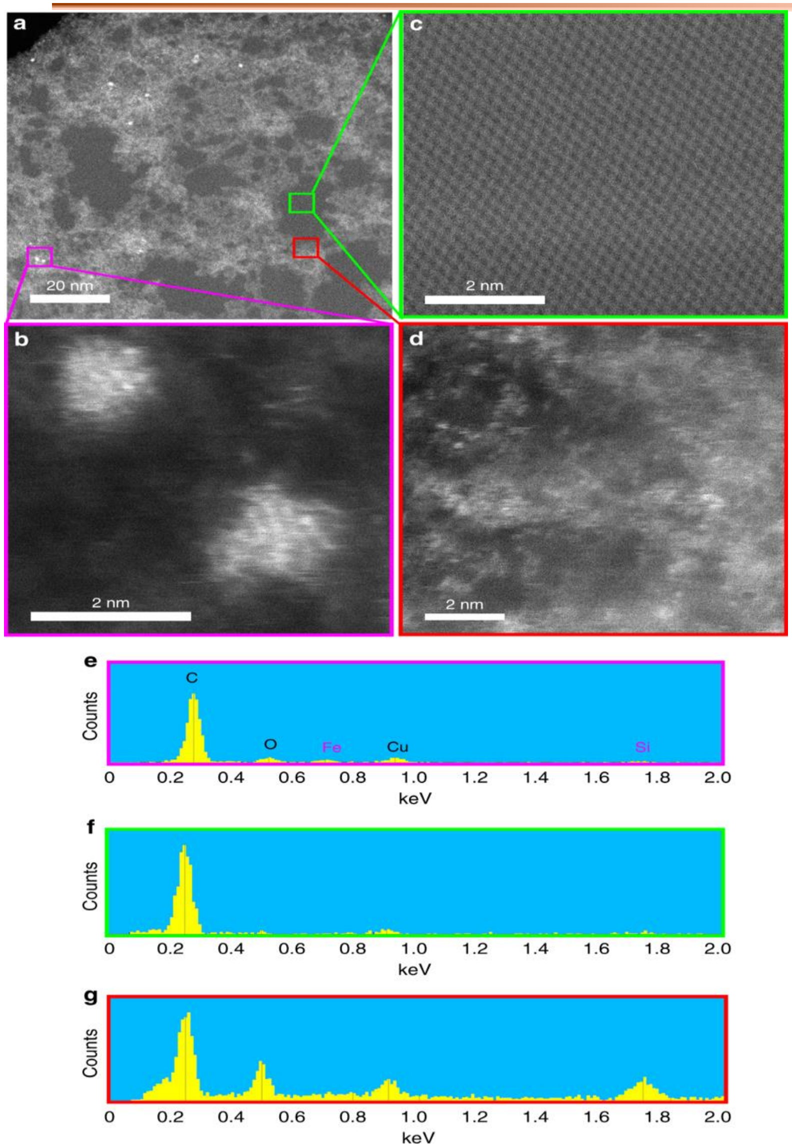

Schematic representation of the available surface area of graphene for molecular interaction. **a** Pure surface vs **b** contaminated surface. The red spheres represent molecules that can interact with the surface, while the orange rafts represent the contaminants

# THE CASE OF CHEMICALLY MODIFIED GRAPHENE



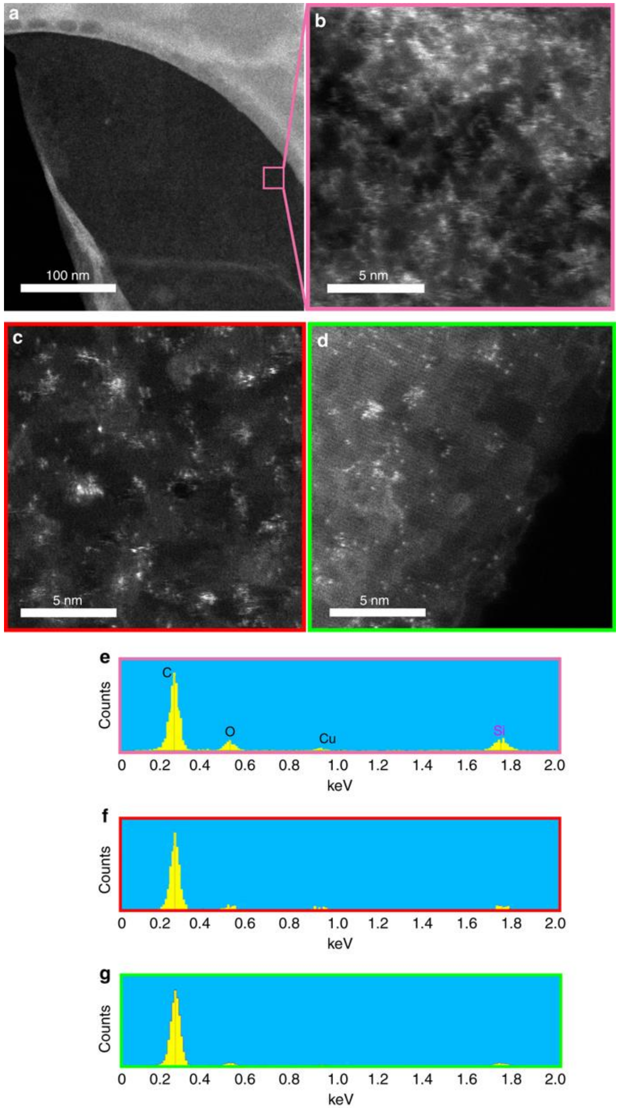

The extent of silicon contamination on the surface of typical solvent-exfoliated graphene derived from low-purity graphite (98% purity). **a** HAADF image of a typical graphene sheet. **b** Detail of HAADF image of the boxed region in **a**. **c** EDS spectrum of the boxed region in **a**.The strong Si peak at 1.739 keV confirms the presence of significant contamination. **d**, **e** A comparison of the EDS spectra of the contaminated area (**d**) and non-contaminated and monolayer area (**e**), which are marked as red and green boxes in **b**, respectively

# THE CASE OF CHEMICALLY MODIFIED GRAPHENE



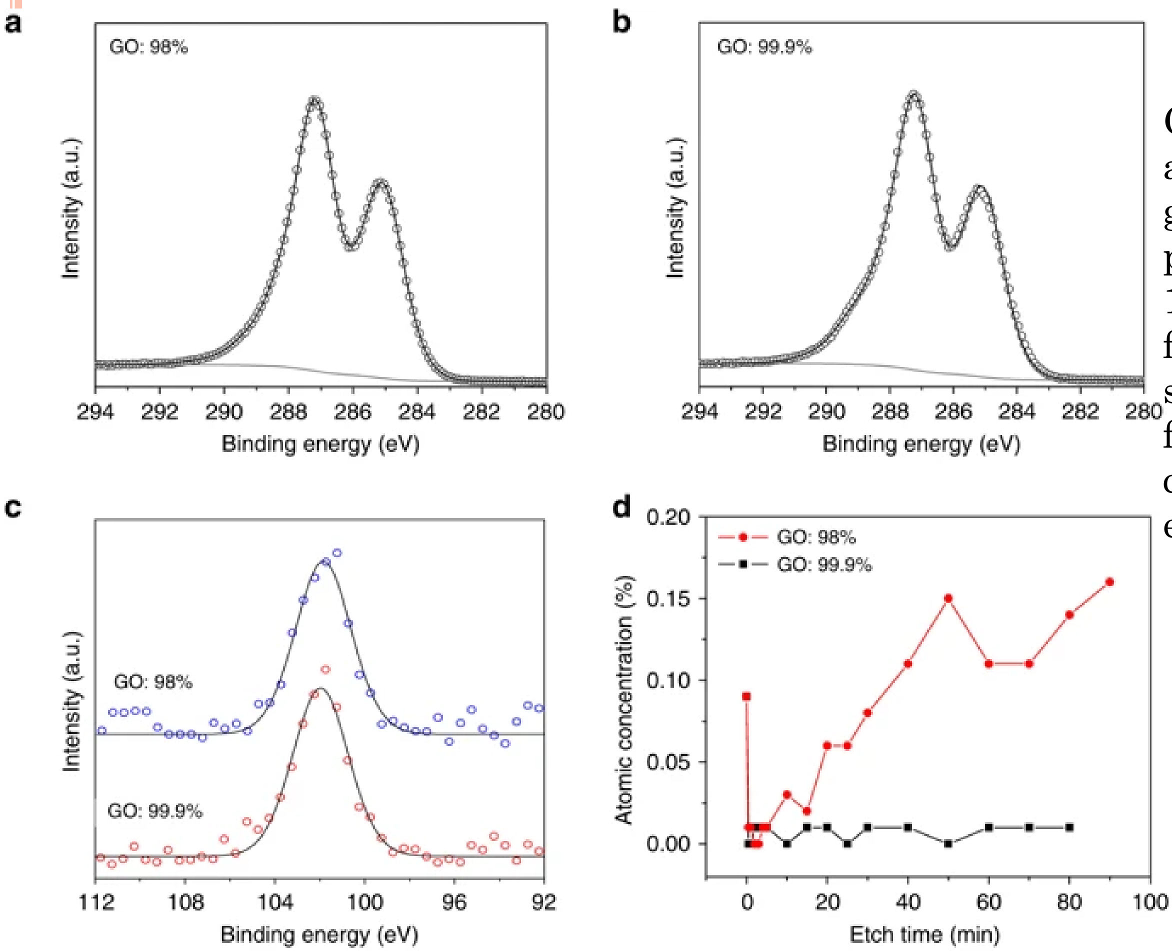

The extent of silicon contamination on the surface of typical low purity graphite (98% purity). **a** HAADF image of a typical graphite platelet. Details of the various boxed regions in **a** showing: **b** an iron contamination, **c** a clean area with a perfect graphitic lattice structure, and **d** a silicon contaminated area. **e**–**g** EDS spectra of **b**–**d**, respectively, showing iron contamination, clean graphene and silica contamination, respectively

# THE CASE OF CHEMICALLY MODIFIED GRAPHENE



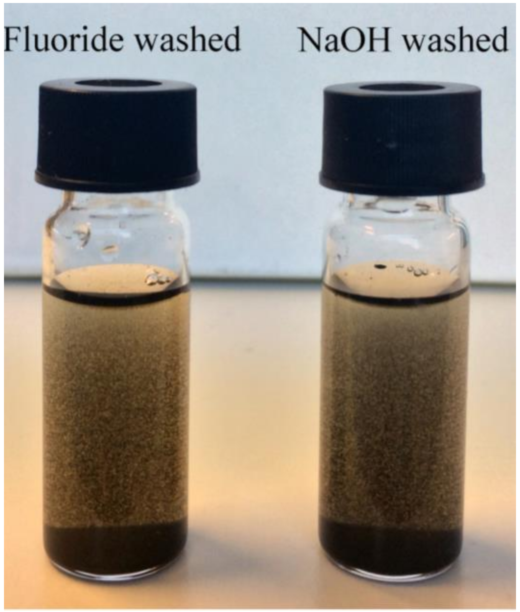

The effect of washing on typical graphene oxide derived from low-purity graphite (98% purity). **a**, **b** GO washed with 5 M NaOH at 120 °C. **a** Restacked GO sheets due to the basic washing. **b** Detail of the boxed region in **a** showing that the silicon-rich impurities have become more dispersed but have not been removed. **c** Chemically reduced GO showing the silicon-rich contamination. **d** $NH_4F$ washed GO. The surface appears cleaner, but this treatment also causes significant agglomeration and restacking of sheets. **e**–**g** A comparison of the EDS spectra of the NaOH washed, chemically reduced and $NH_4F$ washed GO in **b**–**d**, respectively

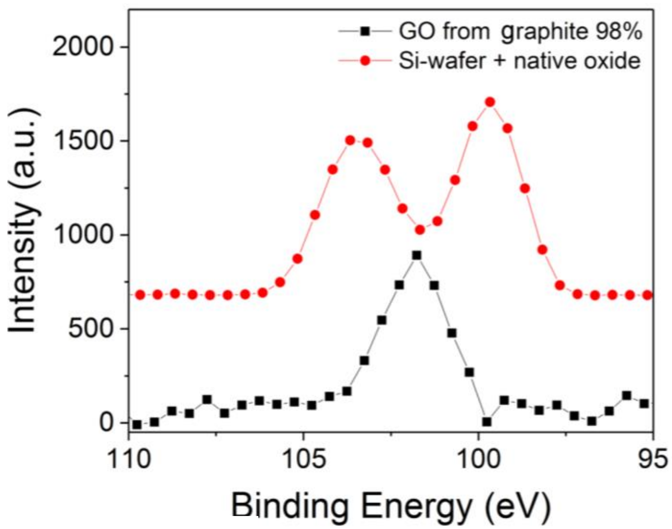
# The case of chemically modified graphene

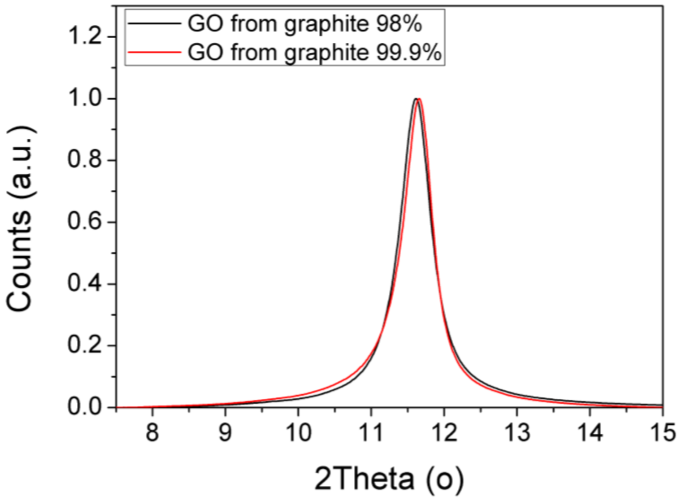



Characterisation of typical GO films and dispersions prepared from graphite feedstock of different purities. **a**, **b** Comparison of the XPS C 1s spectral region of GO films. **c** Comparison of the XPS Si 2p spectral region of GO films. **d** Comparison of the atomic concentration of silicon as a function of etching time.

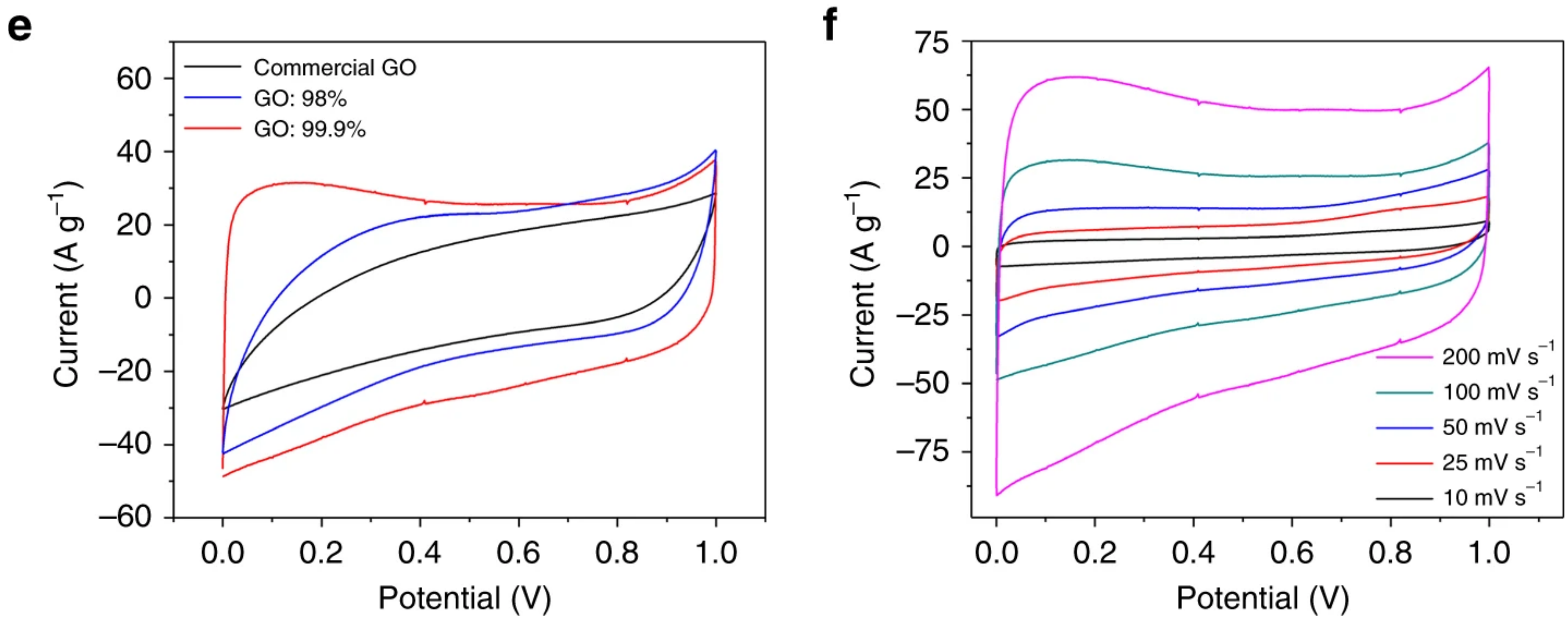
# THE CASE OF CHEMICALLY MODIFIED GRAPHENE



# The case of chemically modified graphene




**e** Double-layer supercapacitor performance of the reduced GO electrodes for the three different materials. The representative cyclic voltammograms (CVs) that were obtained using a two-electrode cell at 100 mV/s and using a 1 M $H_2SO_4$ electrolyte; **f** CV of the rGO electrode made from 99.9% purity graphite as a function of scan rates

# Current Research Trend on Graphene

- Can the oxygen on graphene oxide be removed completely, and yield perfect, high-quality graphene?
- Can liquid exfoliation give bigger sheets, and more routinely give only single layer graphene?
- Is there a way to transfer graphene perfectly, leaving no contaminants, wrinkles, or defects?
- Can we find a way to grow perfect graphene on any surface that we want?

# Conclusion

# Challenges slowing down the adoption

## Unrealistic Expectations

- Industrial processes need to be low cost
- Industrial processes need to be scalable

## Materials Consistency

- GNPs are a far cry from commercial-ready
- Agglomeration and Viscosity Issues are hurdles to handle

## Storage and Transport

- The decision to handle the material in dry or wet form
- Low Material Density

## Health and Safety

- Unreliable and contradictory data reagarding the safety
- Lack of Standardization

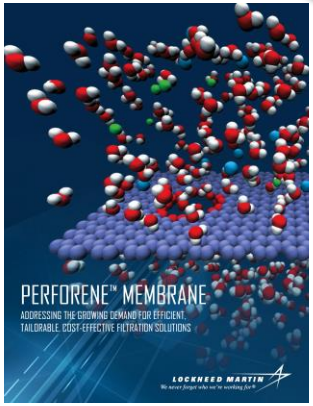


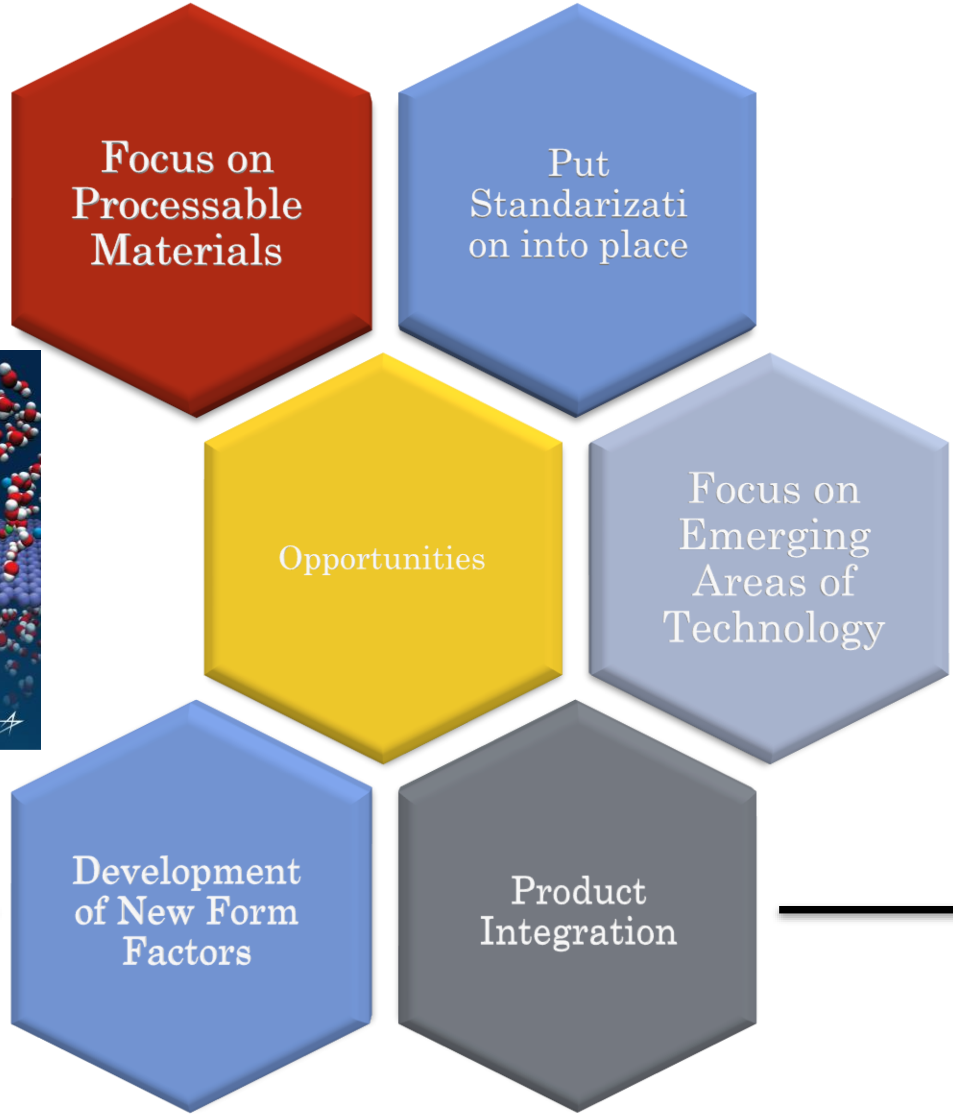
*Nature Nanotechnology* **9**, 730–734 (2014)

*Case Closed, graphene is the next carbon nanotube, LUX Research Report (2015)*

Graphene Oxide-Based Composite Materials, in Graphene Oxide: Fundamentals and Applications , John Wiley & Sons (2016)

# Opportunities




Water Desalination

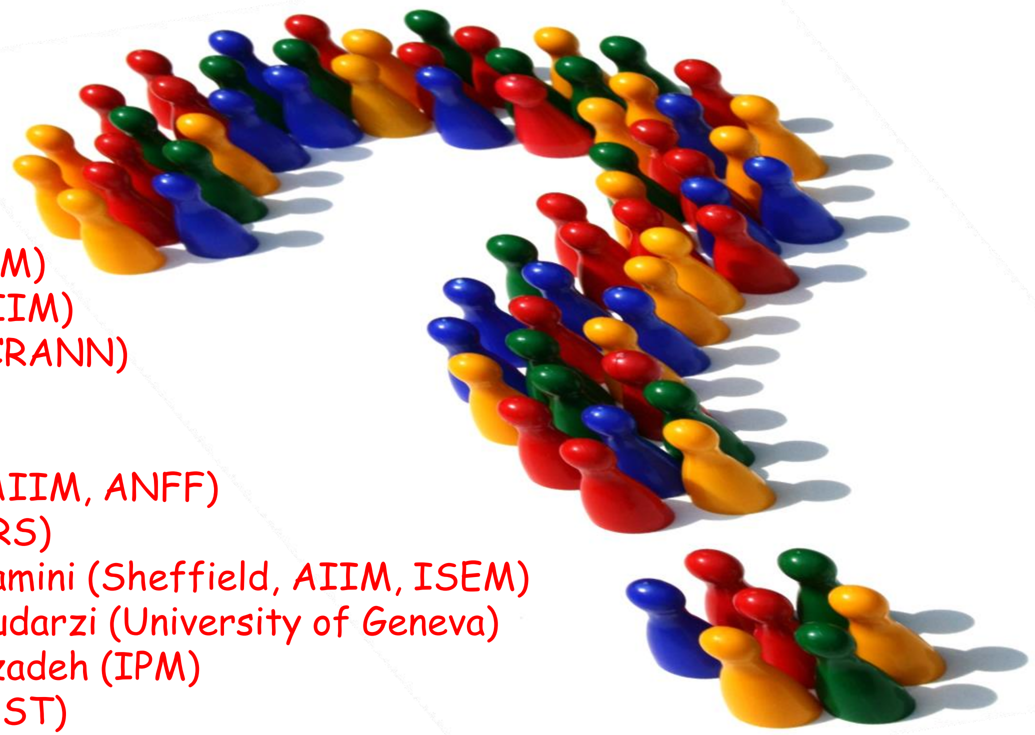
Energy Harvesting and Storage

Sensors, Bionic Devices

Fibers
Yarns
Tapes

Multifunctional Composites

# Thanks!!!



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Dr Konstantin Konstantinov (ISEM)
Wallace's Group
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# Aberration corrected scanning TEM