NanoNuclear Workshop
Nanotubes and Graphene
February 28, 2012

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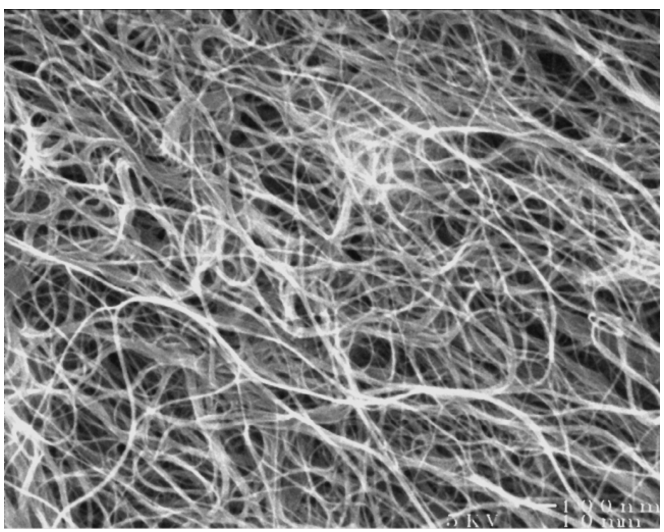
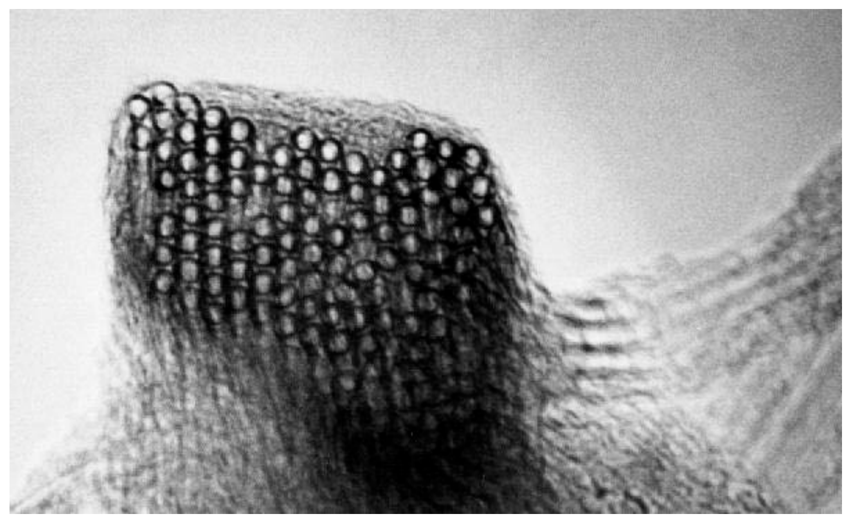
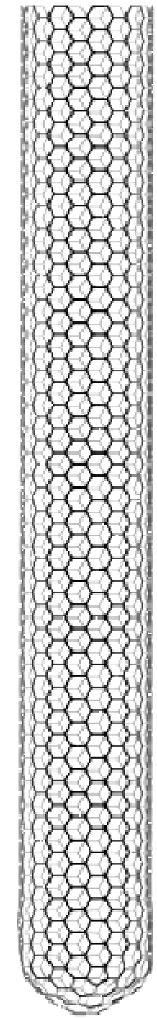
Single-Wall Nanotubes (SWNTs)

MOLECULAR PERFECTION & EXTREME PERFORMANCE

- The Strongest Polymer Possible
- Electrical Conductivity of Copper
- Carrier Mobility Surpasses InSb & GaAs
- Thermal Conductivity of Diamond
- The Unique Chemistry of Carbon
- Versatile Engineering Material



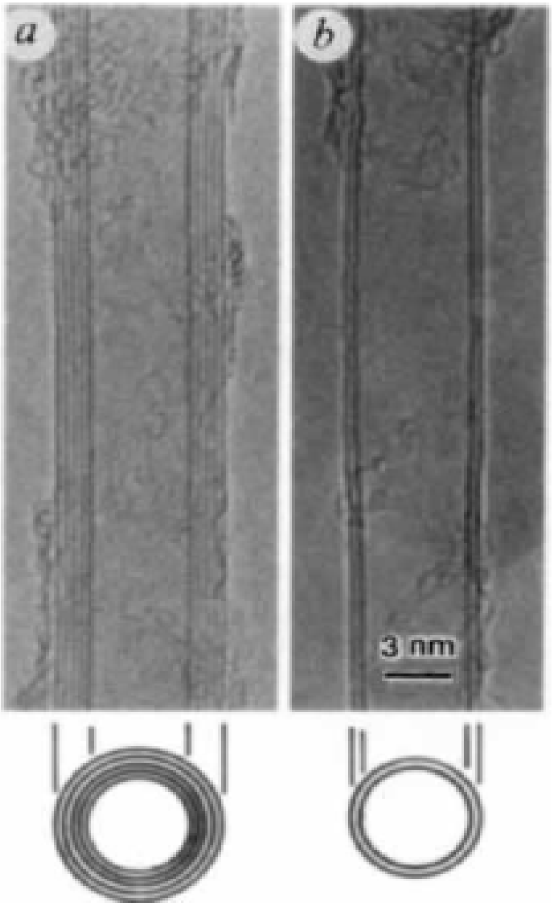


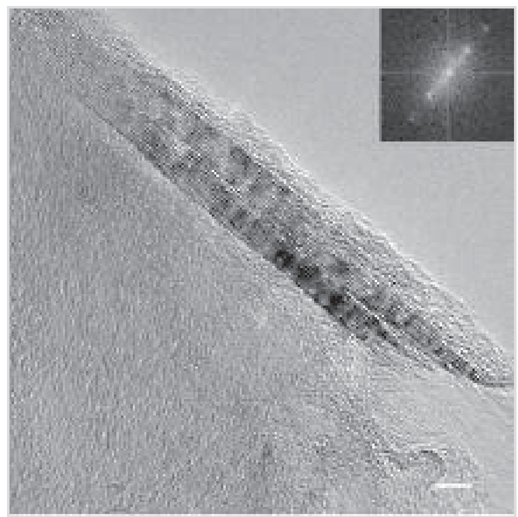


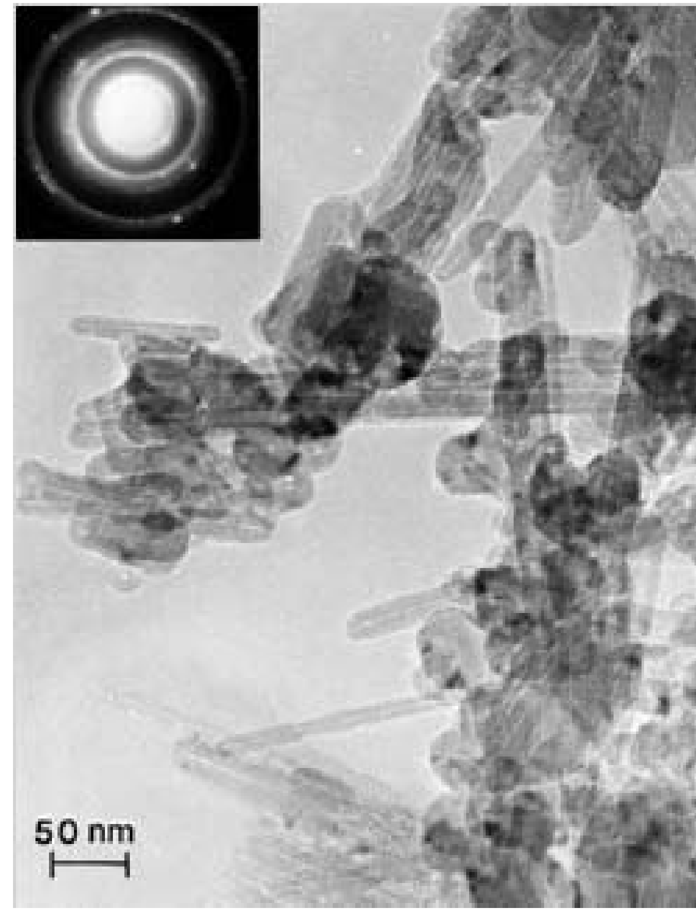
General Characteristics of SWNTs

- A tube-shaped form of carbon
- A few nanometers in diameter
- On the order of a micron long
- Structure is similar to a rolled graphite sheet
- Possess a yield strength of 45 ± 7 GPa, cf. with 20 GPa for graphite whiskers.
- SWNTs behave as conductors ($\rho \sim 10^5 - 10^6$) or semiconductors ($\rho \sim 10^{-1}$)
- Heat conduction of 17.5 W cm^{-1} K to 58 W cm^{-1} K (on the order of diamond)
- 20 µm/sec growth = 1000 C atoms/millisec

When were CNTs first prepared? Brief History



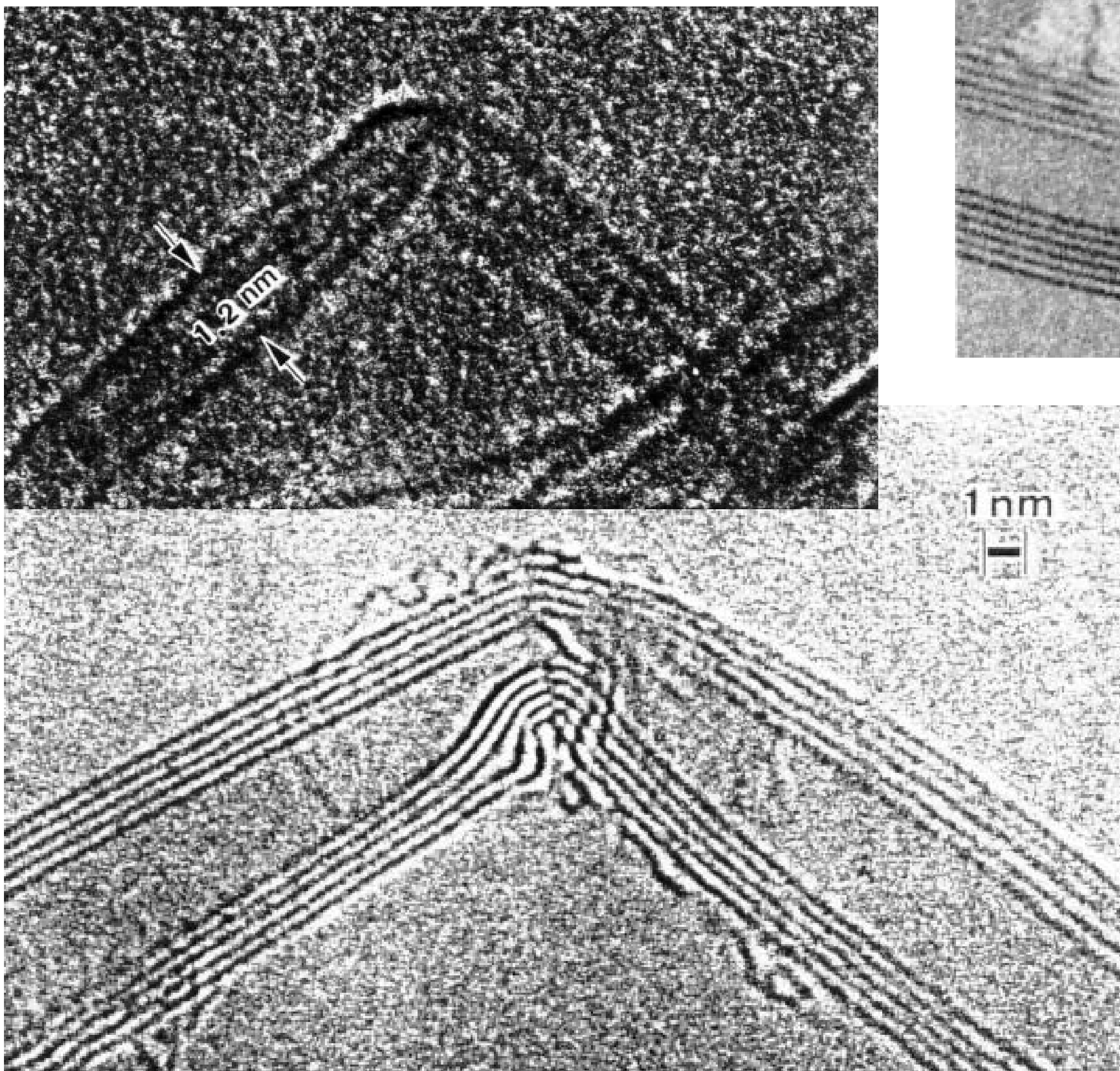


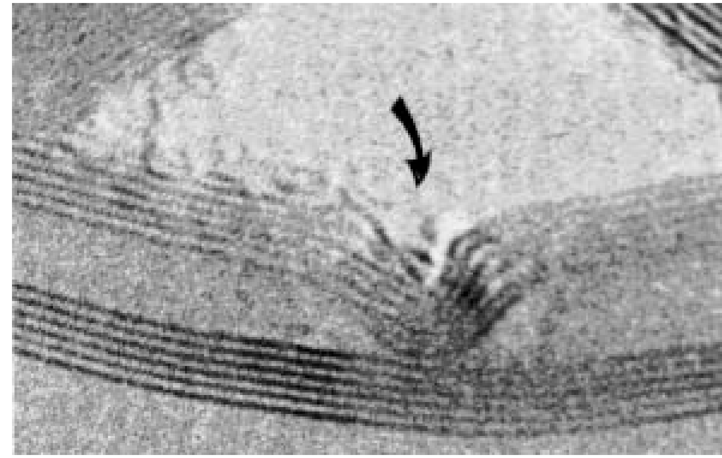


Carbon microtubules: Ijima, S., Nature 1991; 354; 56-58
Carbon filaments: Oberlin, et al., J. of Crystal Growth 1976; 32; 335-349
Graphite whiskers: Bacon, R. J. App. Phys. 1960; 31: 283-290
Raduskevich, et al., Surn Fisisc Chim 1952; 26: 88-95
CNTs on ancient Damascus sword (17th century):Reibold et al. Nature 444, 286
CNTs in the environment (10 K years-old ice core): Murr et al., JOM; June; 28-31

Mechanical Resilience

Iijima

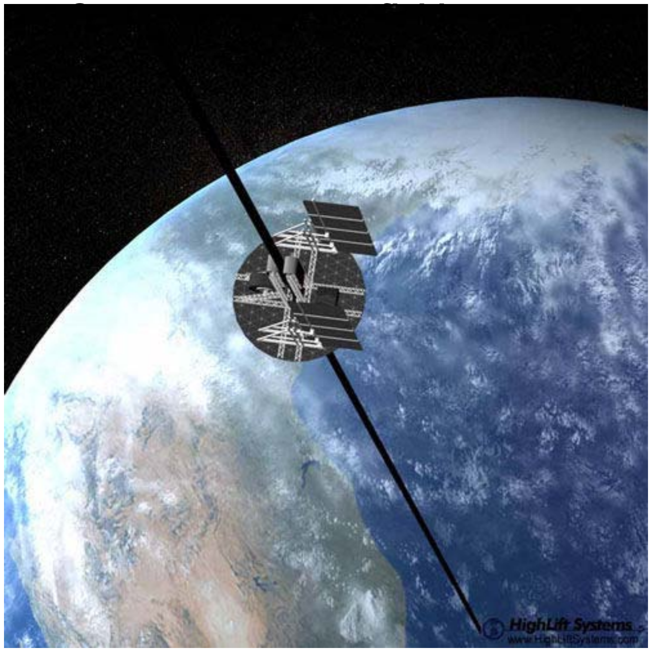




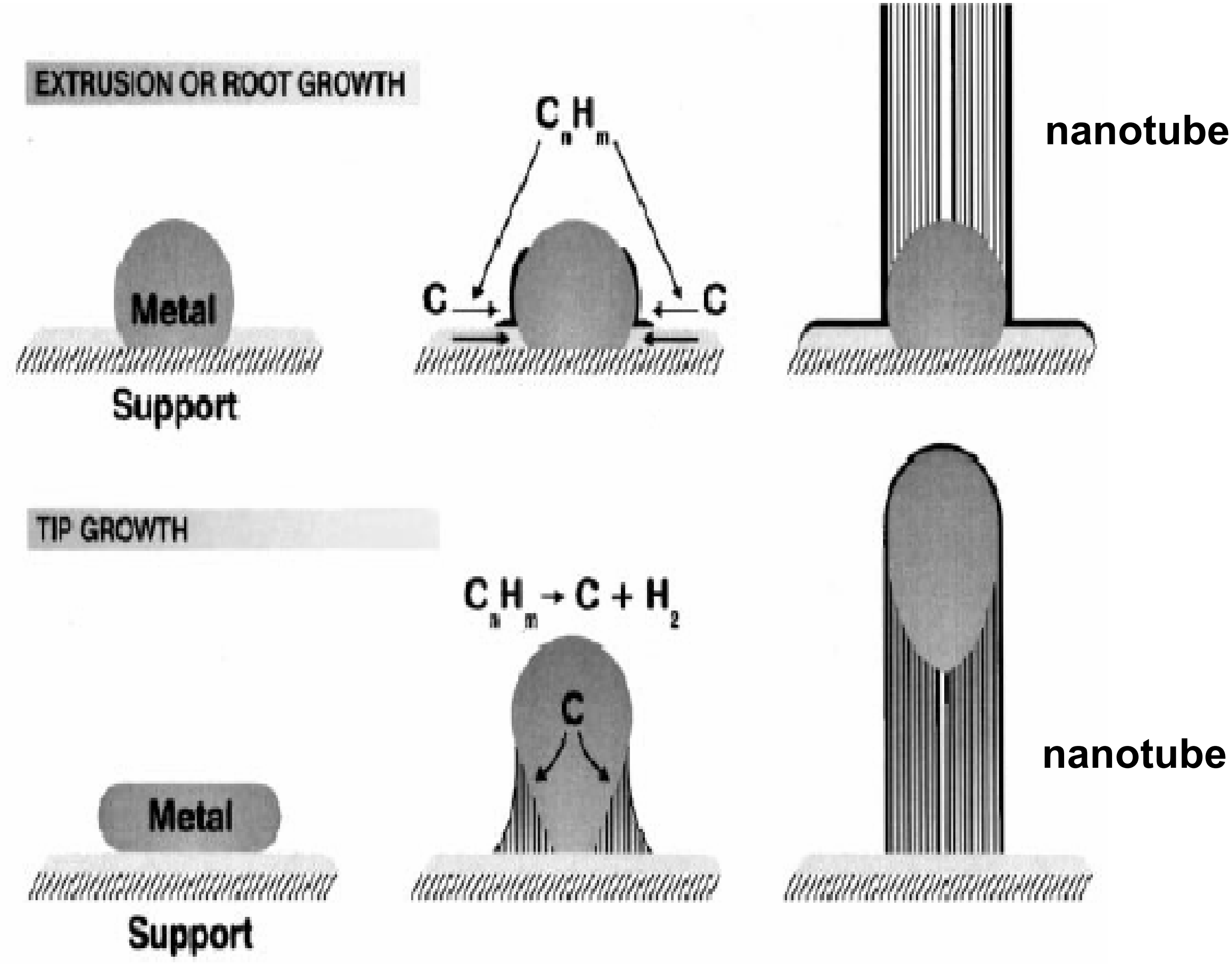
Despres *et al*

Uses of CNTs

- Field emission devices
- Supercapacitors & batteries
- Electronics devices and interconnects
- Nanoscale sensors
- Composite materials, conducting Composites
- Electromechanical actuators
- Computer display thin films
- Optoelectronics, optical activity
- Catalysis
- Mechanical strength.
- Gas separation membranes
- Data storage
- Controlled Drug Delivery/release
- Energy Storage: Hydrogen storage
- Armchair Quantum Wire
- Nanocoolants

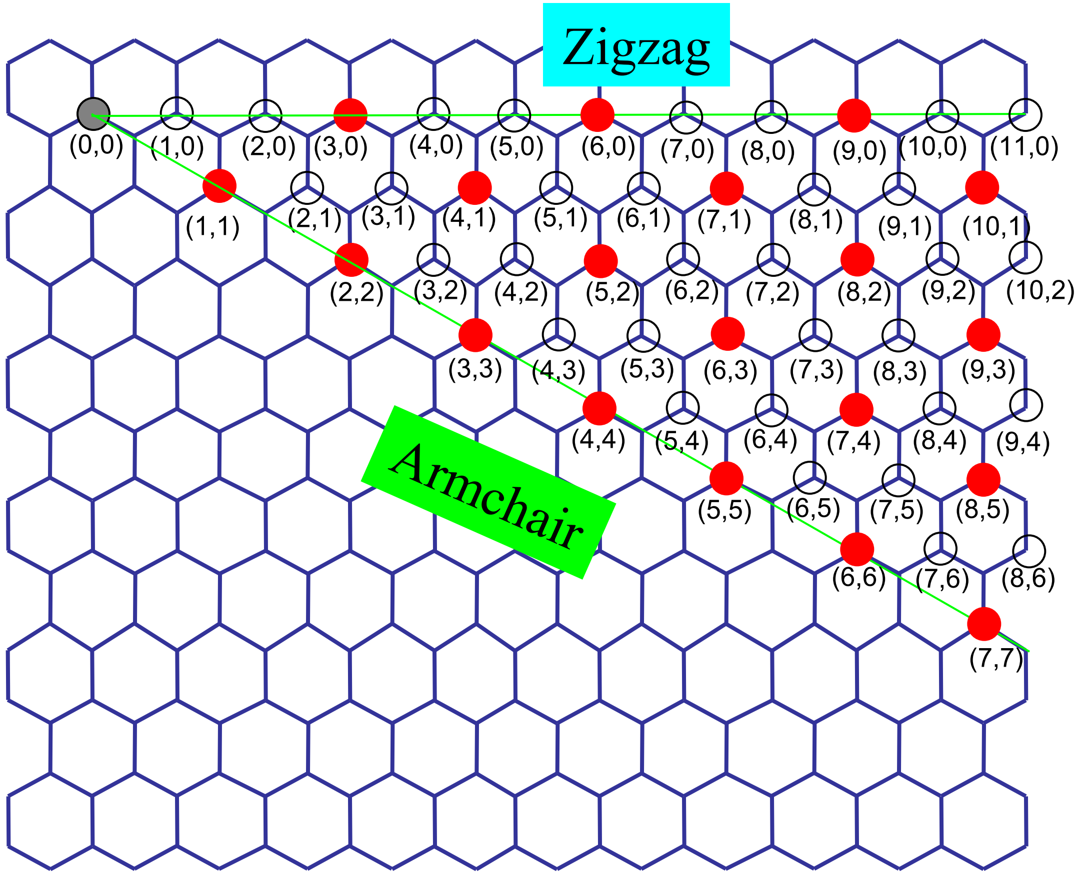


Growth Mechanism



Sinnot et al., Chem. Phys. Lett. 1999; 315; 25-30

Hexagonal Lattice (n,m) nanotubes



A) ”Zig-zag” – semiconductor

B) “ Chiral” – Semiconductor

C) ”Armchair” – metal-like conductivity

- Electrical conductivity higher than copper.
- Thermal conductivity as high as diamond.
- Superconductivity has been observed at very low temperatures.

$n - m = 3q$ (q: integer): metallic

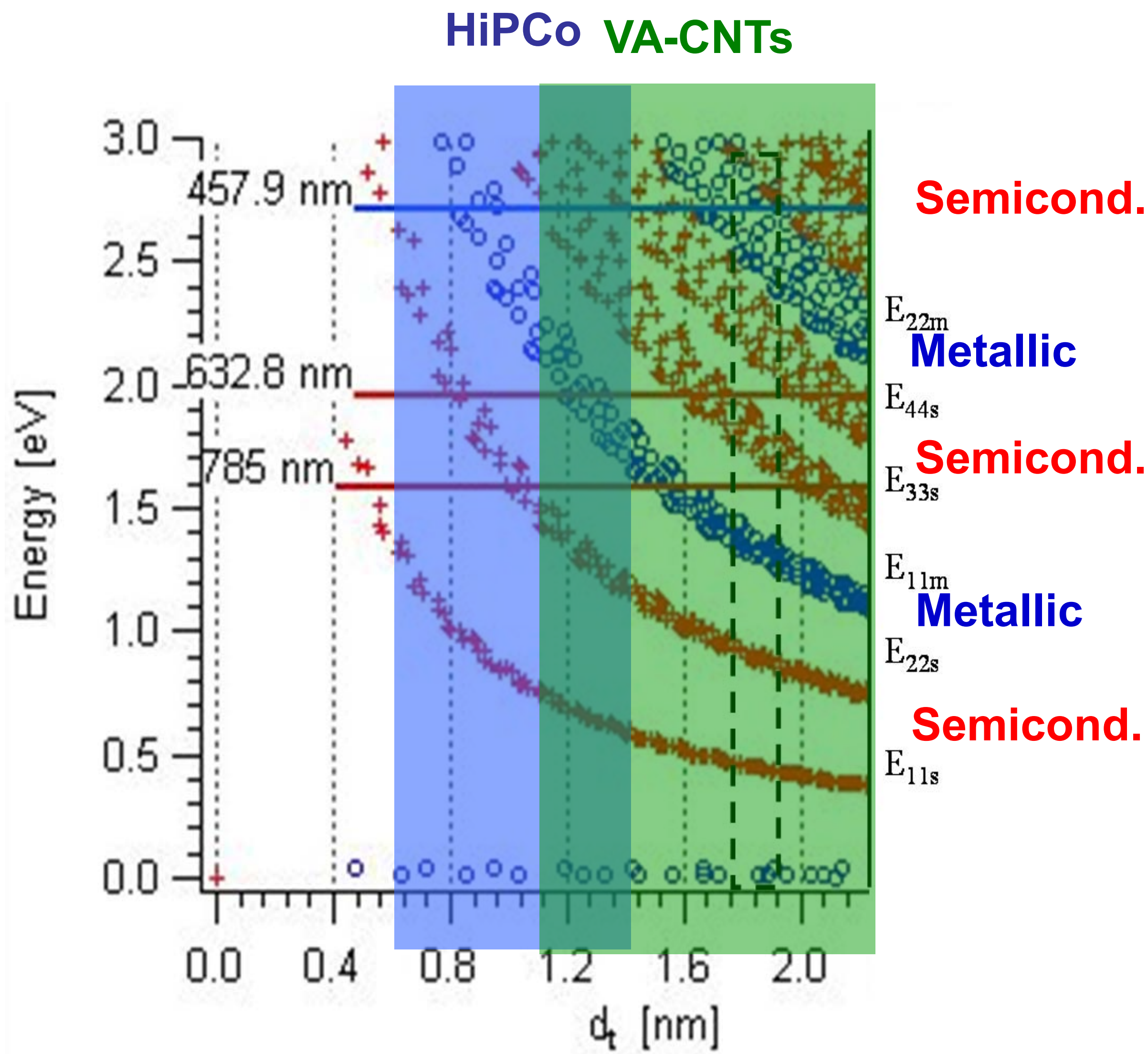
$n - m \neq 3q$ (q: integer): semiconductor

http://www.photon.t.u-tokyo.ac.jp/~maruyama/nanotube.html

Variety of CNTs: Raman of Carbon nanotubes

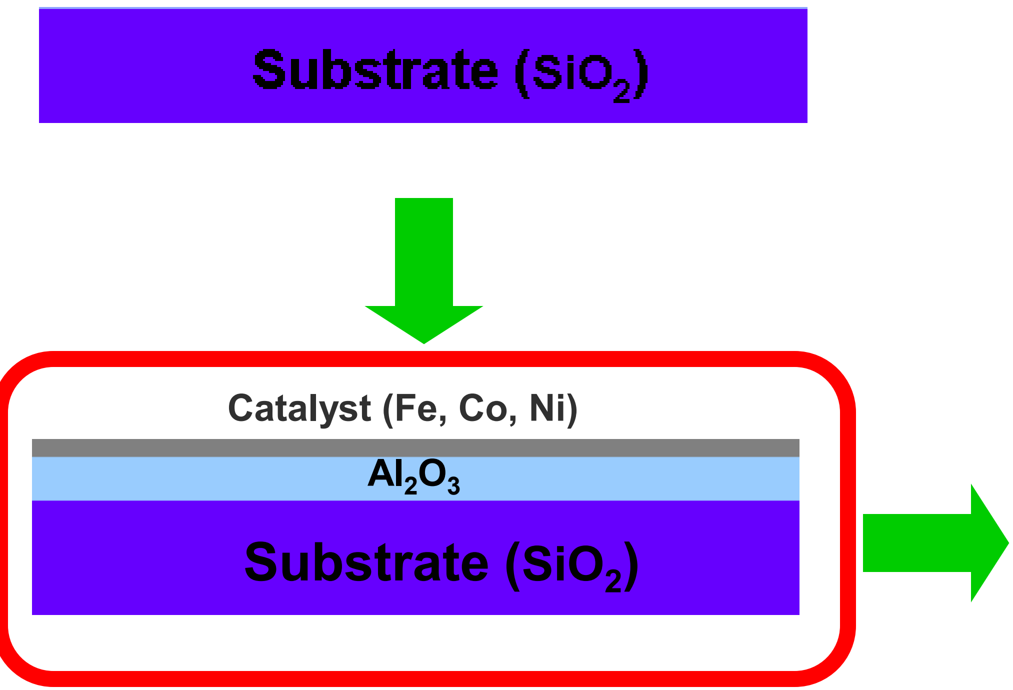
Hipco:
- diameter 0.6-1.4 nm
- Suitable for conventional optical spectroscopy techniques

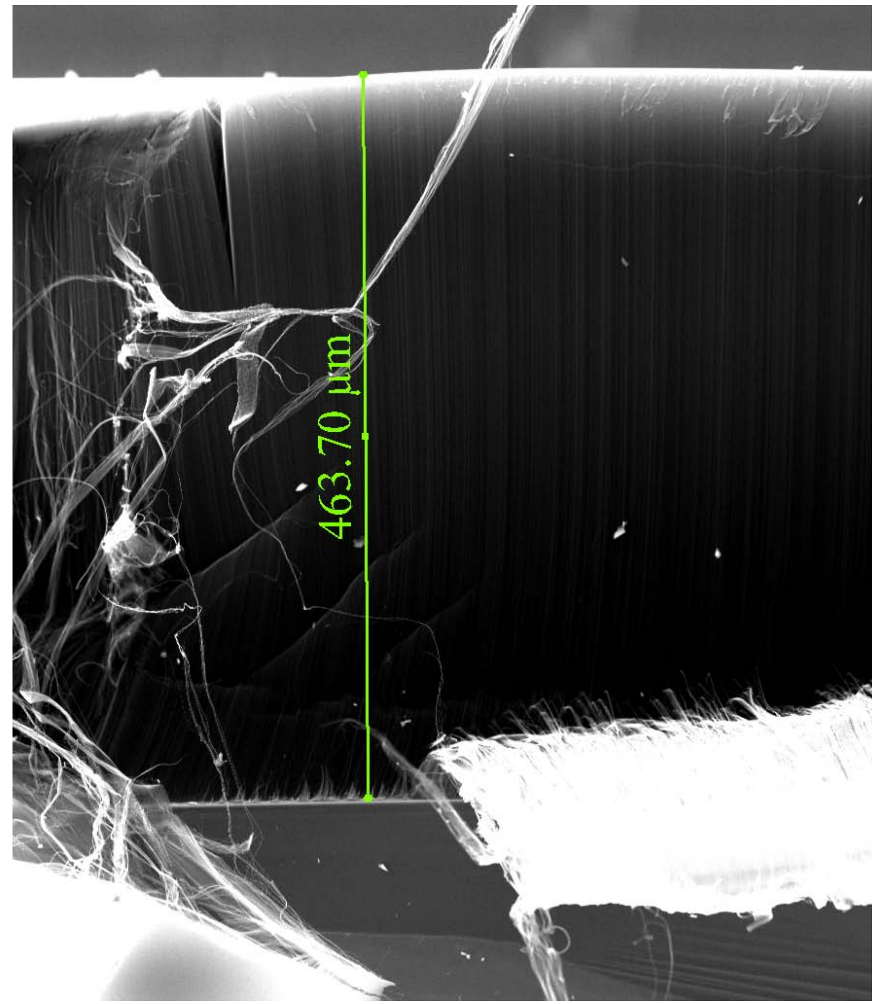
VA-CNTs
- Average diameter 2-3 nm
- Higher Raman complexity
- Most conventional spectroscopy no longer suitable



Kataura et al., Proc. of the int. winter school on elect. prop. of novel Mat. 1999

Typical VA-SWCNT growth process:





Electron beam evaporation: P < 1x10^{-5} T

Al_2O_3 (10 nm); Fe (0.5 nm)

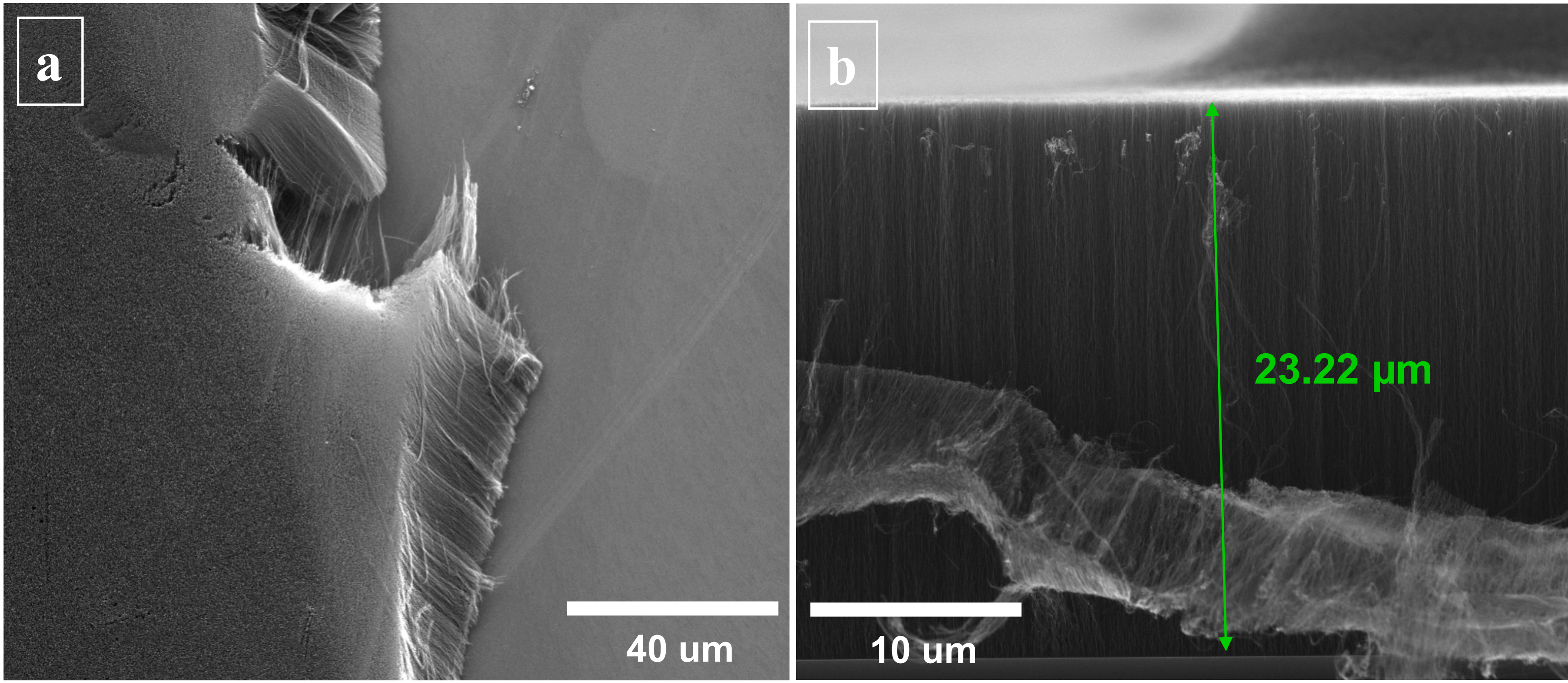
Typical growth conditions:

C source: C_2H_2

Temperature : 750 ºC

N. Alvarez

SEM: VA-CNTs grown from 4 nm Fe nanoparticles

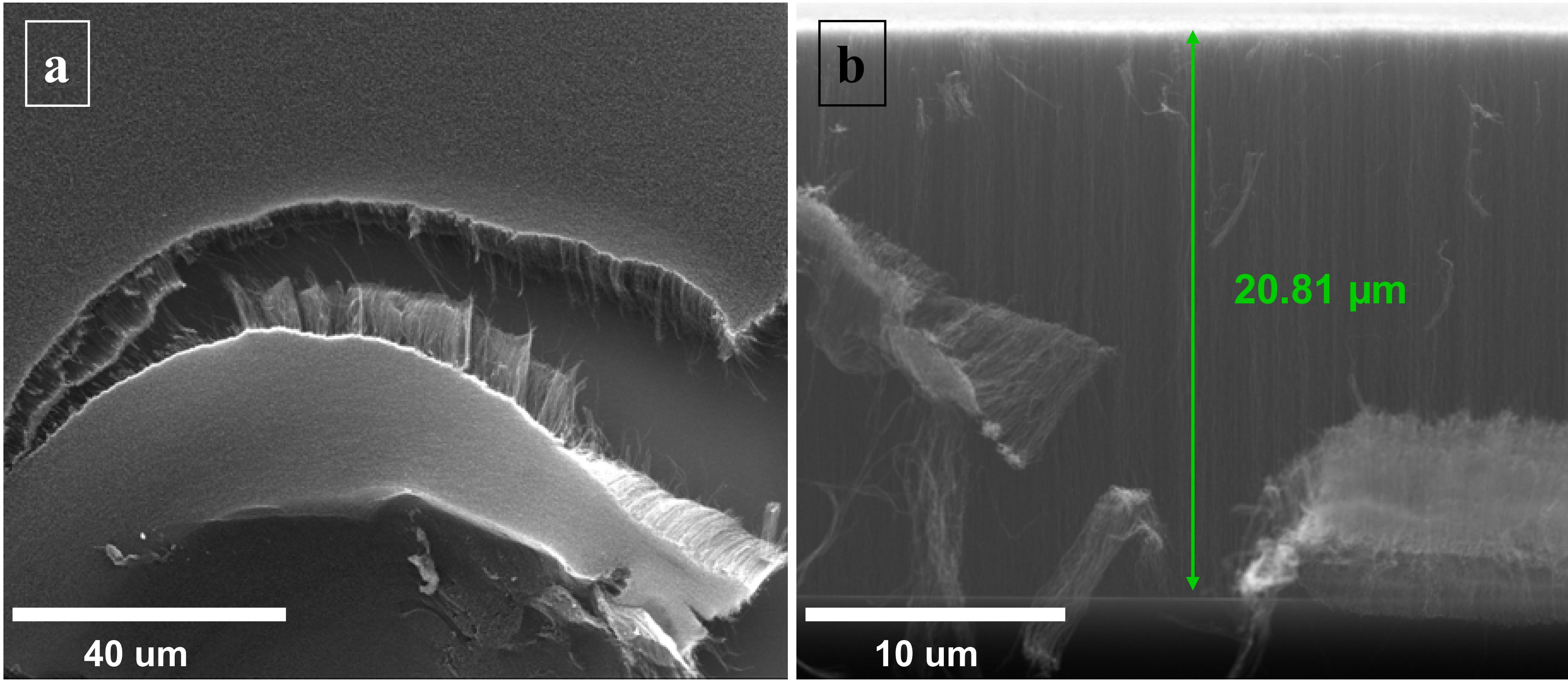


- Image taken on a CNT striped area
- Continuous and smooth top surface continuous CNT height covering all substrates
- 1 cm^2 substrate

CNT height image

N. Alvarez

SEM: VA-CNTs grown from 8 nm Fe nP

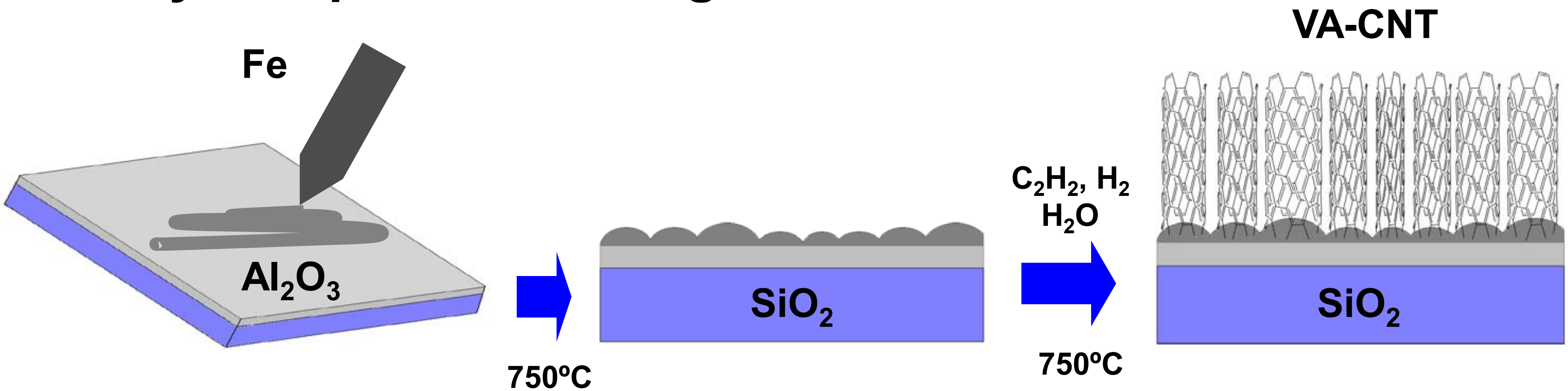


CNT height

- Image from open area
- Continuous and smooth top surface continuous CNT height covering all substrates
- Complete coverage of 1 cm^2

N. Alvarez

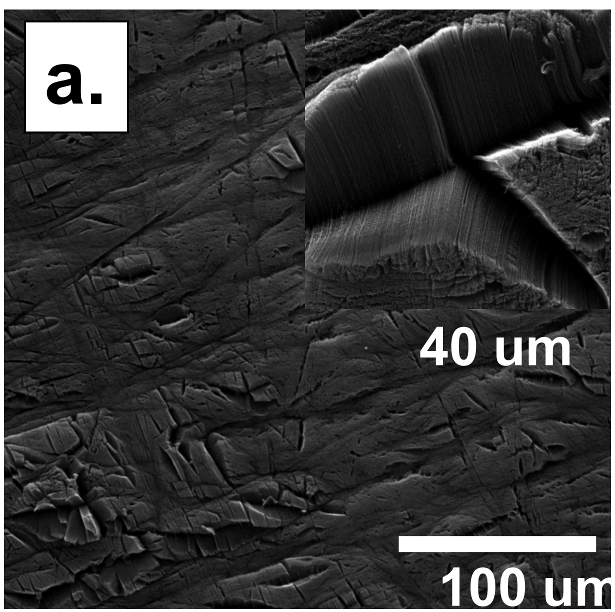
Catalyst Deposition through Abrasion



Fe Abrasion on Al_2O_3/SiO_2

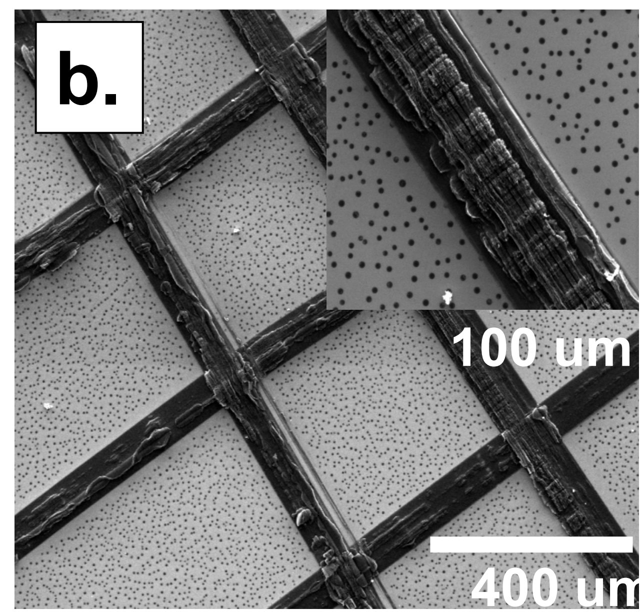
Abraded Fe Catalyst on Al_2O_3

CNT growth from abraded Fe



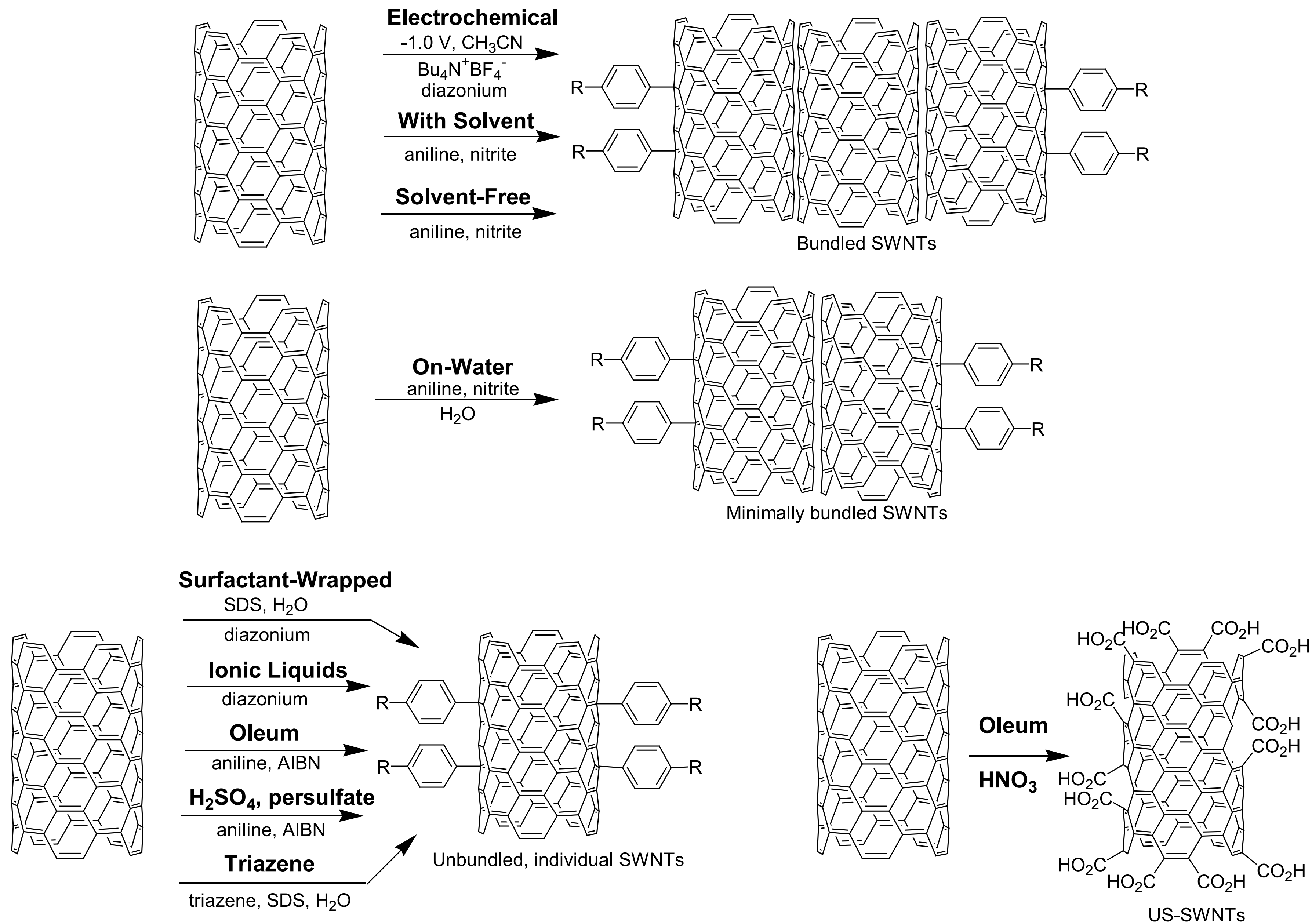
Large scale CNT production

Nano- and Micro-scale pattern making approach

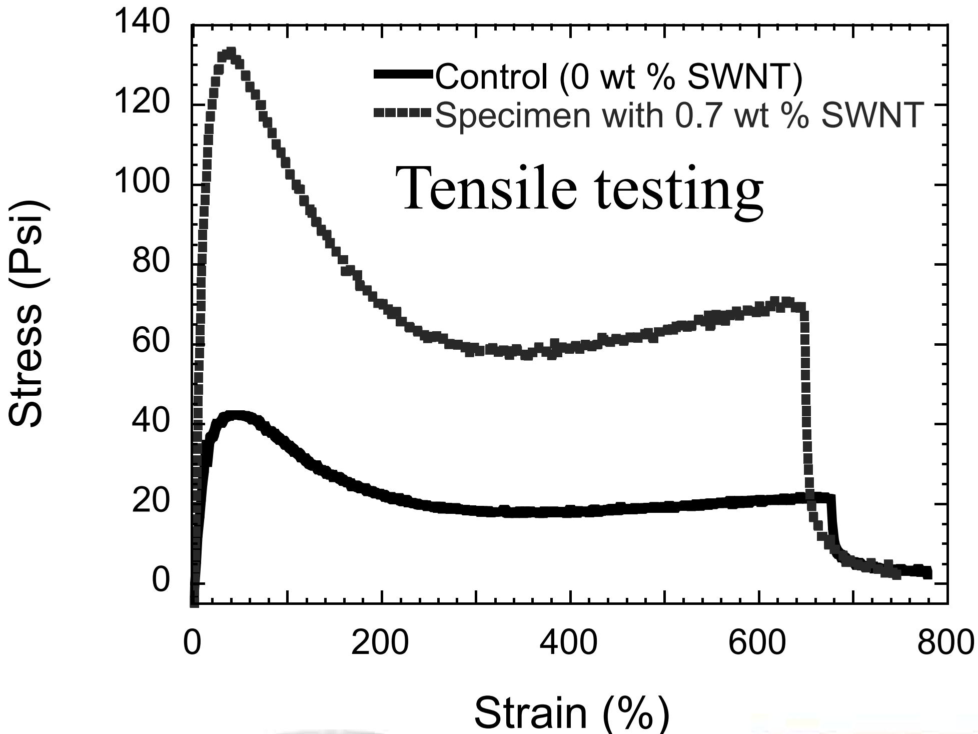


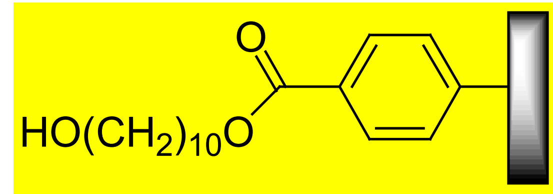
N. Alvarez

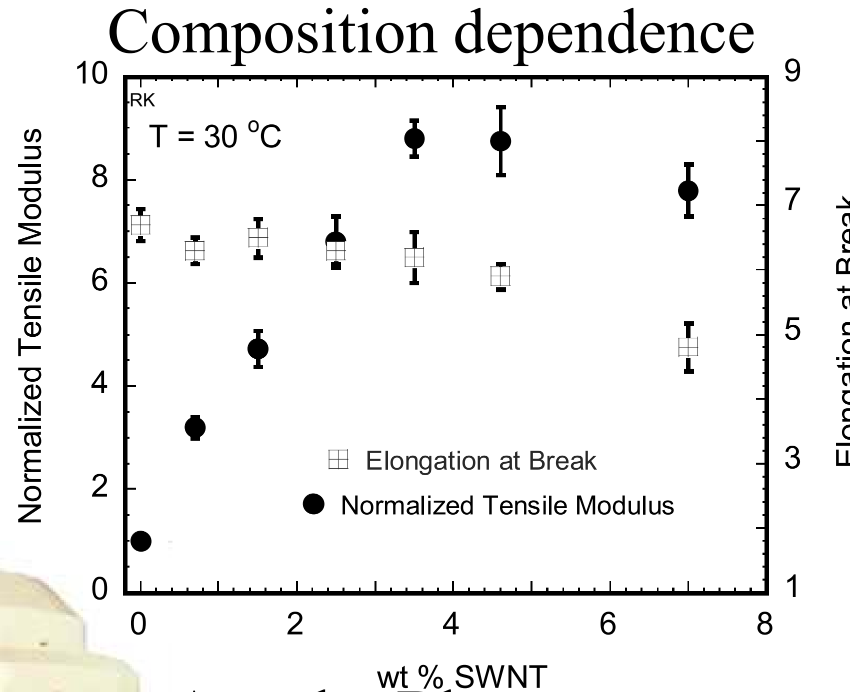
SWNT Functionalization Methods



Observed Elastomeric Reinforcement (Siloxane)





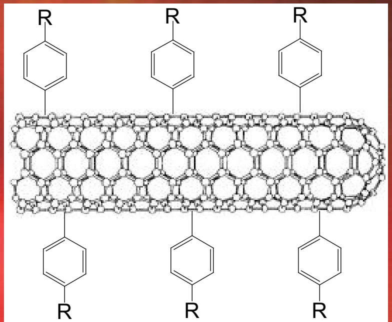


Annular Blowout Preventers (BOPs), elastomers enduring up to 20,000 psi with 90” ODs

C. Dyke
R. Krishnamoorti

THE NEXT, BIGGEST DEVELOPMENT IN ELASTOMERIC OILFIELD PRODUCTS

may be found at the center of this poster



Hydril products have long been found at the leading edge of what *works* while Hydril engineers have been developing what's *next*. That's why we have partnered with NanoComposites, Inc., with the goal of leveraging Rice University's patented technology for single-walled, carbon nanotubes into the next revolution in d products. Imagine elastomer "software" as durable as the magine if packers and seals simply didn't care how much eat, sand or fluids they encountered. What if an old annular nano-engineered packing unit could outperform newbuilds? nenting this revolution now.
the future for the O-ring shown above? Follow Hydril for ts as they become available.

O-ring testing results

Sample	Pressure (psi)	Extrusion Gap (in.)	Failure Temp. (°F)	Comments
Nano-Composites 1290	15K	0.017	**350**	Held pressure for one hour, no commercial material compares in performance
Std. HNBR1	15K	0.017	250	Unable to pressurize
Std. HNBR2	15K	0.017	250	Held for 15 sec.
Std. HNBR3	15K	0.011	250	Unable to pressurize
Std. HNBR4	15K	0.011	250	Held for 2 min
Std. HNBR3	15K	0.005	250	Held for 2 min 11 sec

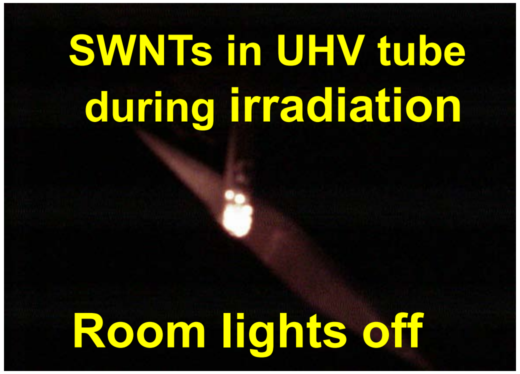
REDEFINING RELIABILITY™

HYDRIL

NanoComposites Inc.
Hydril

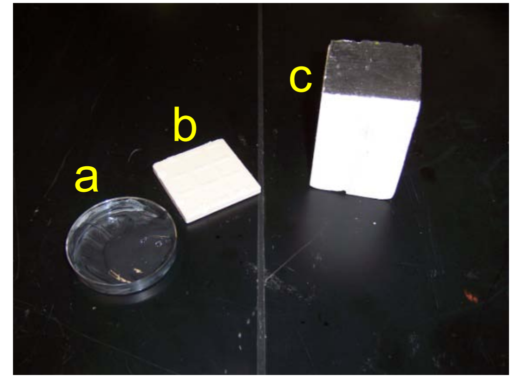
Remote Repair of Spacecraft

Nanotube RTV and NOAX Composites by Microwave Curing



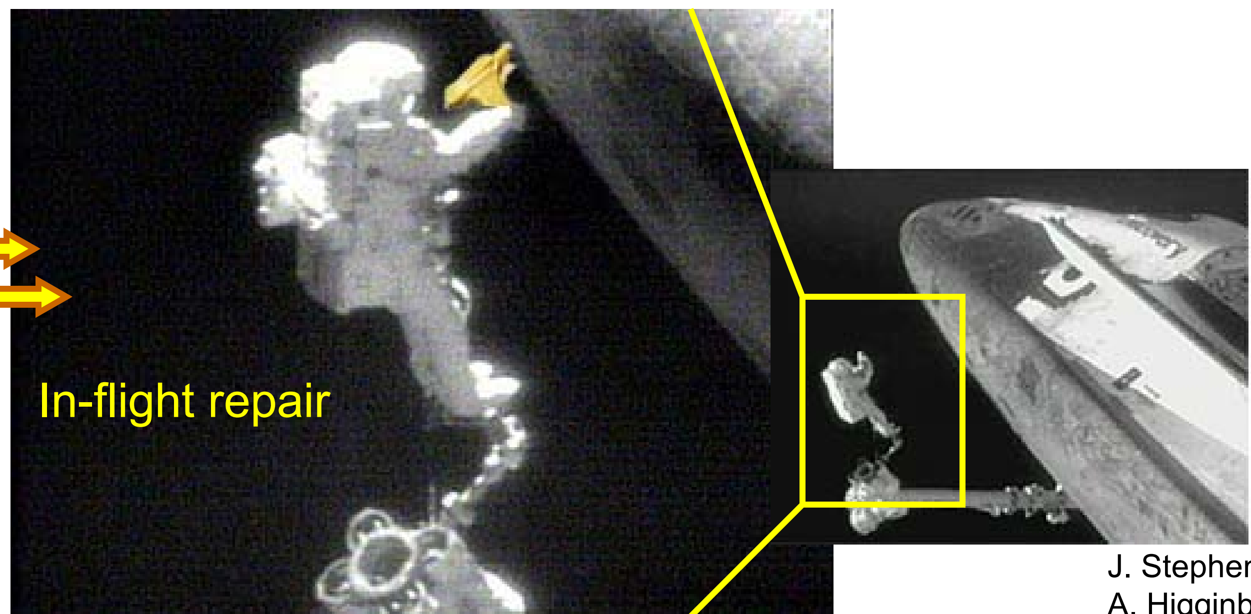
>2000°C in 1 sec @ 2.45 GHz, 750 W
~ 1:1 microwave to Δ

Shuttle tile



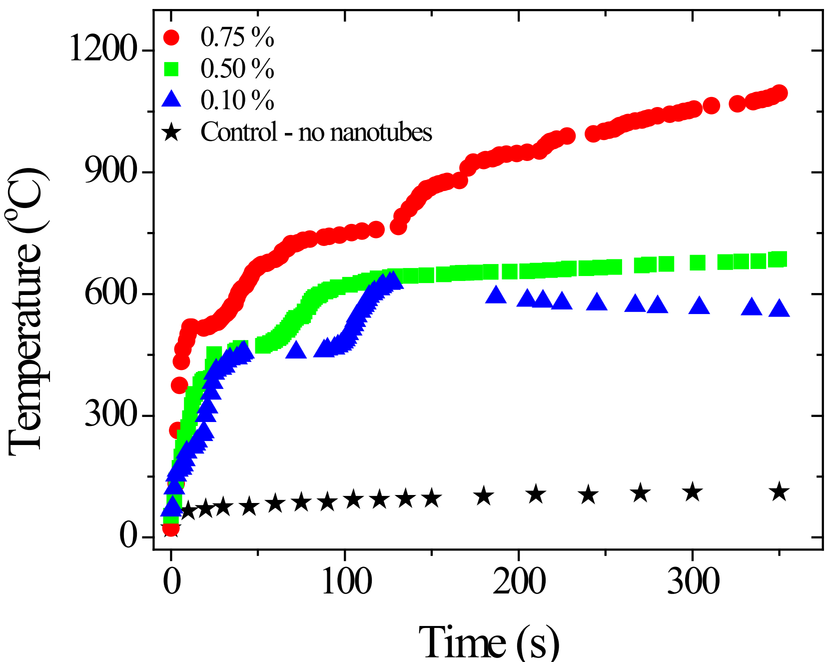
a. RTV 511 + 0.5 % CNTs
b. Ceramic tile
c. Diced shuttle tile

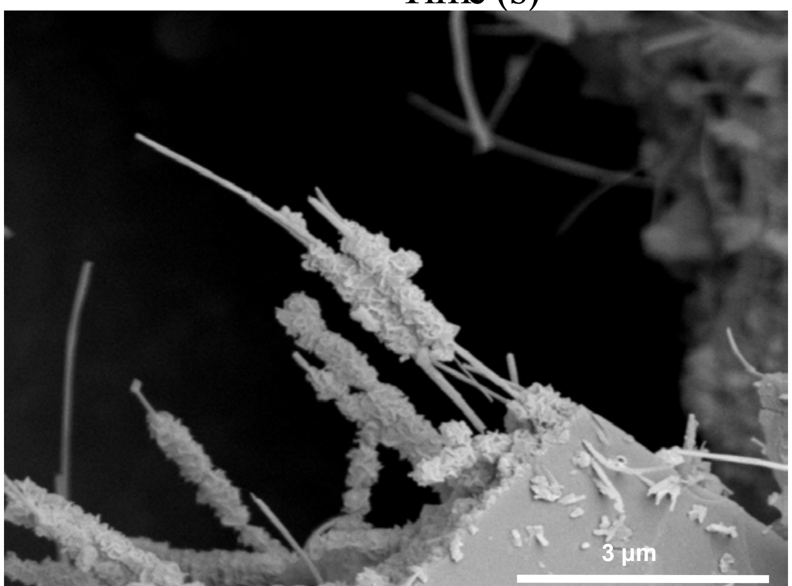
6 min cure at 90 W vs. 24 h cure



J. Stephenson
A. Higginbotham

Curing NOAX with MWNTs/SWNTs

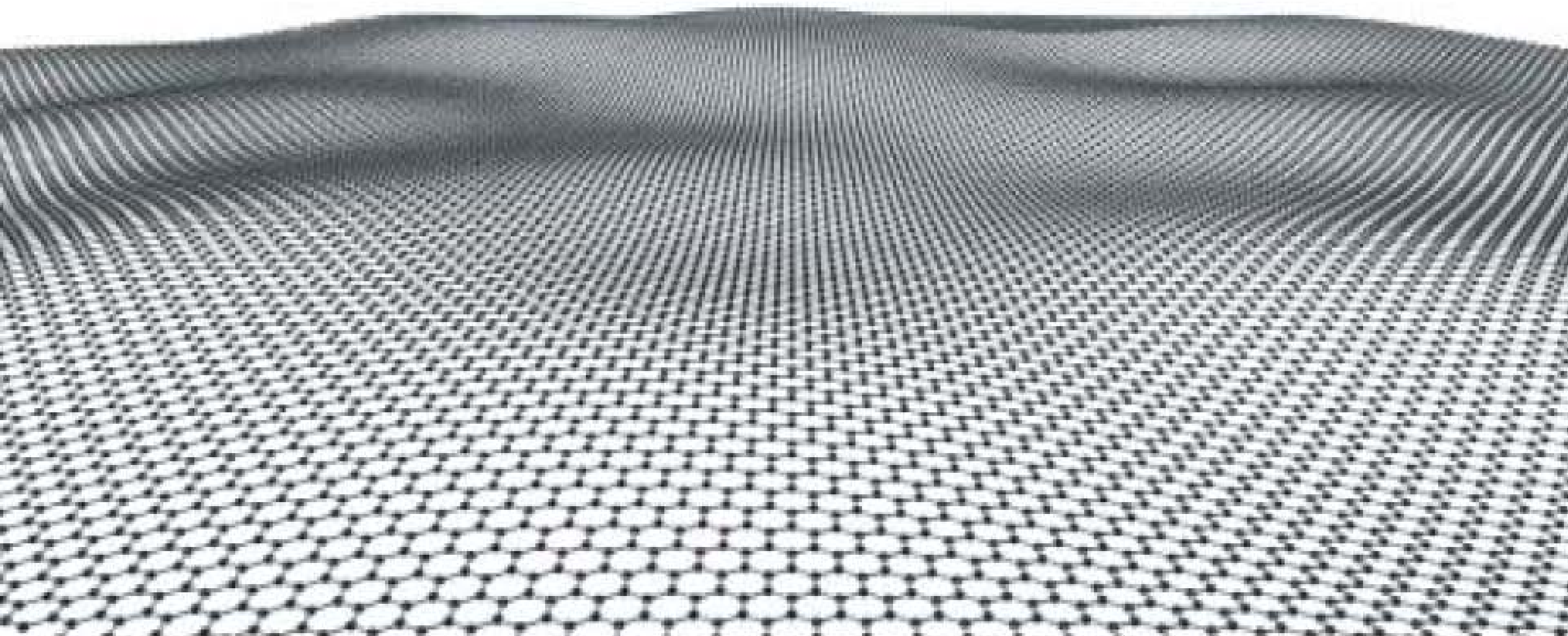




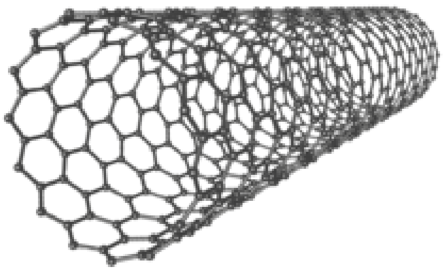
- Ceramic adhesive
- One-component, mainly silicon carbide (SiC)
- Short shelf-life
- Becomes fully ceramic at 850 to 1200 °C
- 0.75 wt % MWNTs at ca. 30 W cm^{-2} reaches >950 °C for curing of the composite

A. Higginbotham
P. Maloney

Graphene



Carbon materials for electronics

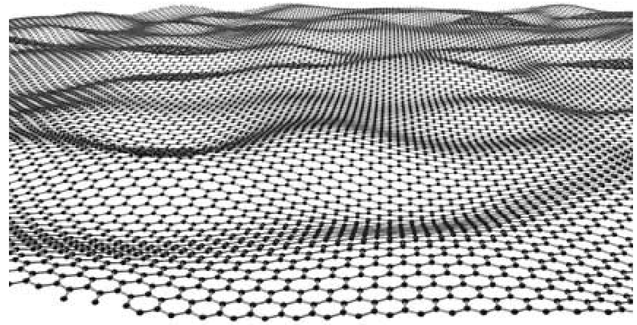


Carbon nanotubes

- pseudo 1D

- High mobility (up to 10,000 $cm^2V^{-1}s^{-1}$)

- High ON/OFF ratios (up to 10^6)



Graphene

- 2D

- High mobility (up to 200,000 $cm^2V^{-1}s^{-1}$)

- Low ON/OFF ratios

But must discuss mobility in terms of carrier density. G on SiO^2 has ~10^4 $cm^2V^{-1}s^{-1}$ at ~10^{10}-10^{11} cm^{-2} electron density which is near to InGaAs

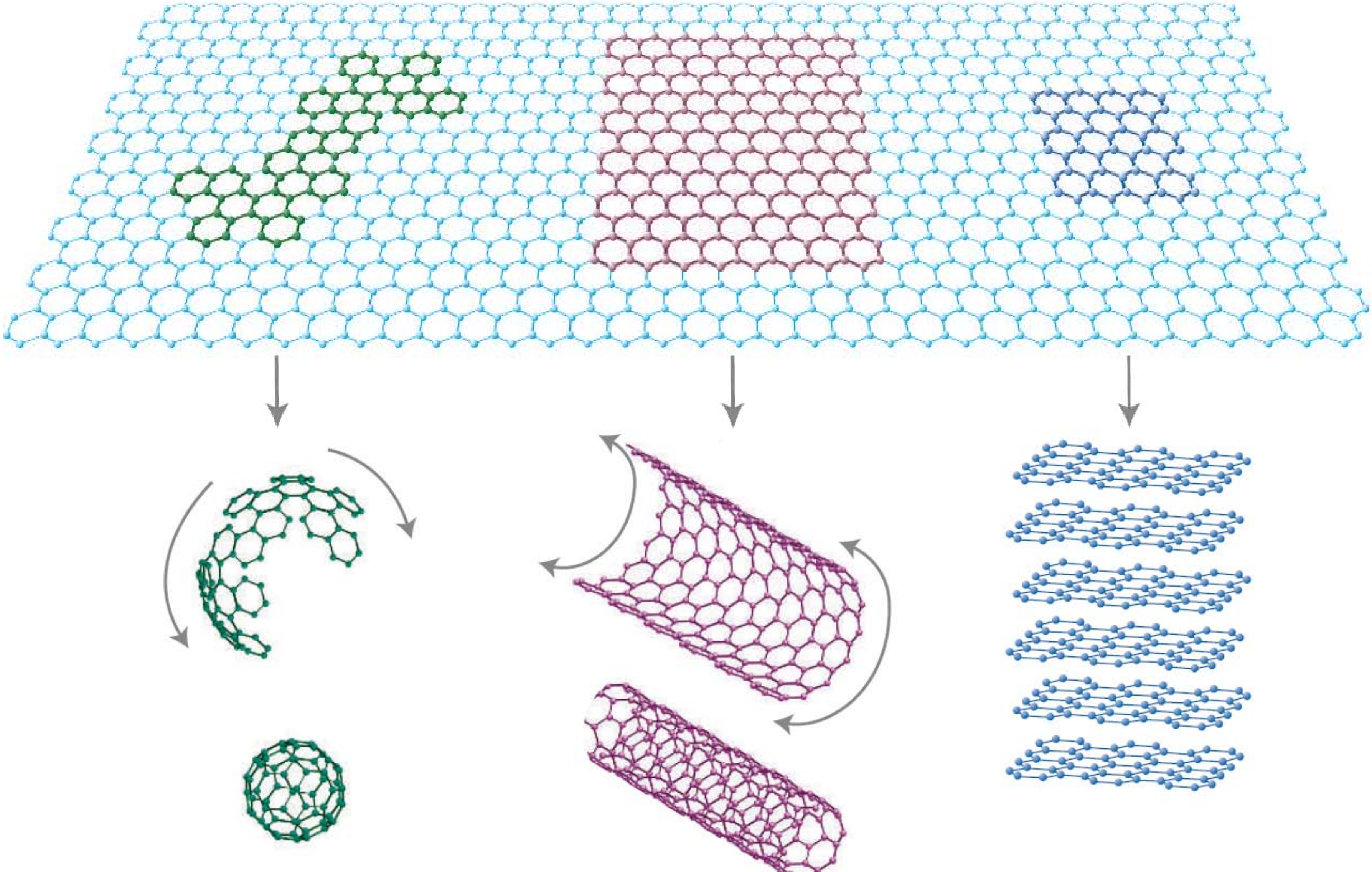
Graphene nanoribbons

- 1D

- High mobility (up to 200 $cm^2V^{-1}s^{-1}$)

- High ON/OFF ratios (up to 10^5)

Relationship with other carbon allotropes



For decades graphene was considered theoretically as an integral part of other graphitic materials, but was believed to be thermodynamically unstable and impossible to exist

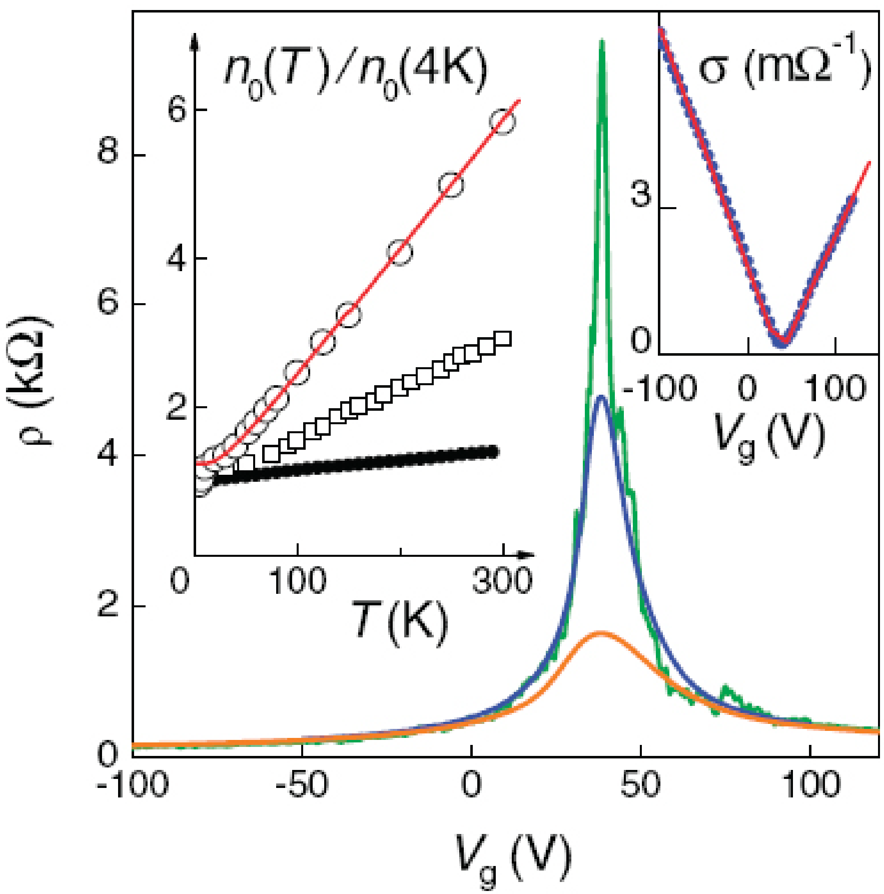
Image: A.K. Geim, K.S. Novoselov, *Nature Materials*, **2007**, *6*, 183

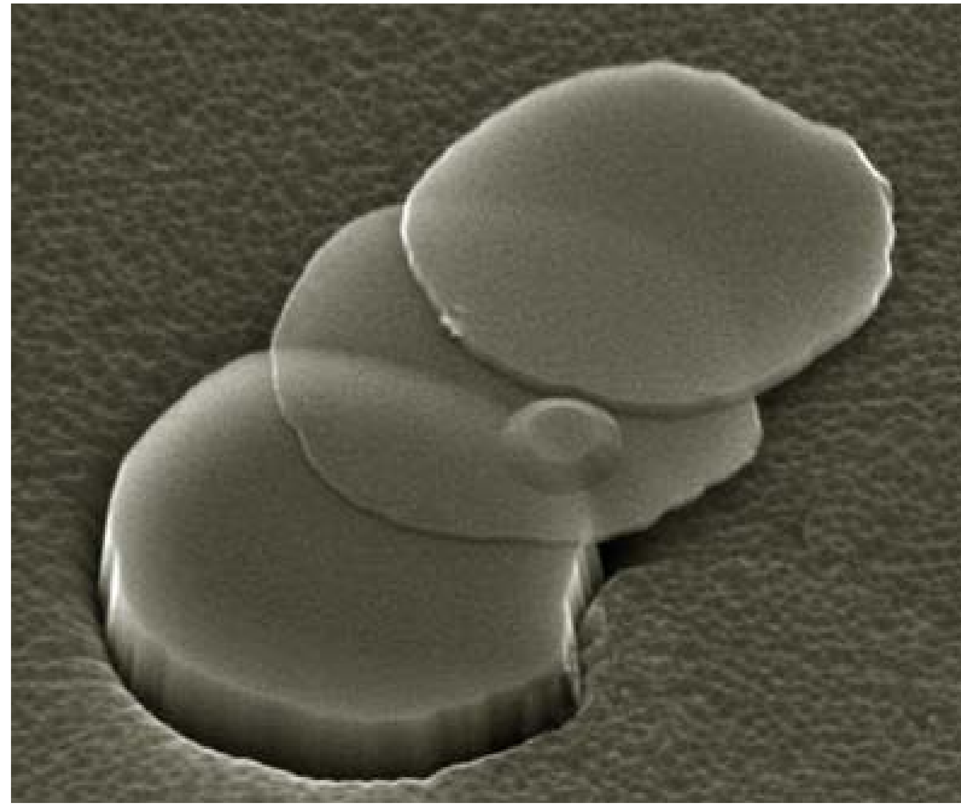
First isolation of graphene

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]

Science, **2004**, *306*, 666





Graphene was obtained by micromechanical exfolation of graphite (so-called "Scotch-tape technique")

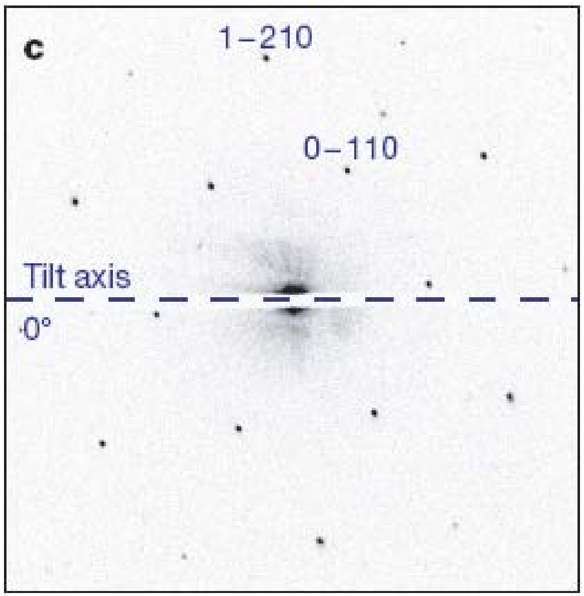
Graphene was shown to exhibit ambipolar electric field effect.

Why graphene is stable?

The structure of suspended graphene sheets

Jannik C. Meyer[1], A. K. Geim[2], M. I. Katsnelson[3], K. S. Novoselov[2], T. J. Booth[2] & S. Roth[1]

Vol 446 | 1 March 2007 | doi:10.1038/nature05545



Using electron diffraction it was shown that suspended graphene exhibits corrugation with an amplitude of ~ 1 nm. This ‘transition’ from truly 2D to quasi-3D crystal could be responsible for the stability of suspended graphene.

Single-layer graphene membrane on a TEM grid

Remarkable properties of graphene

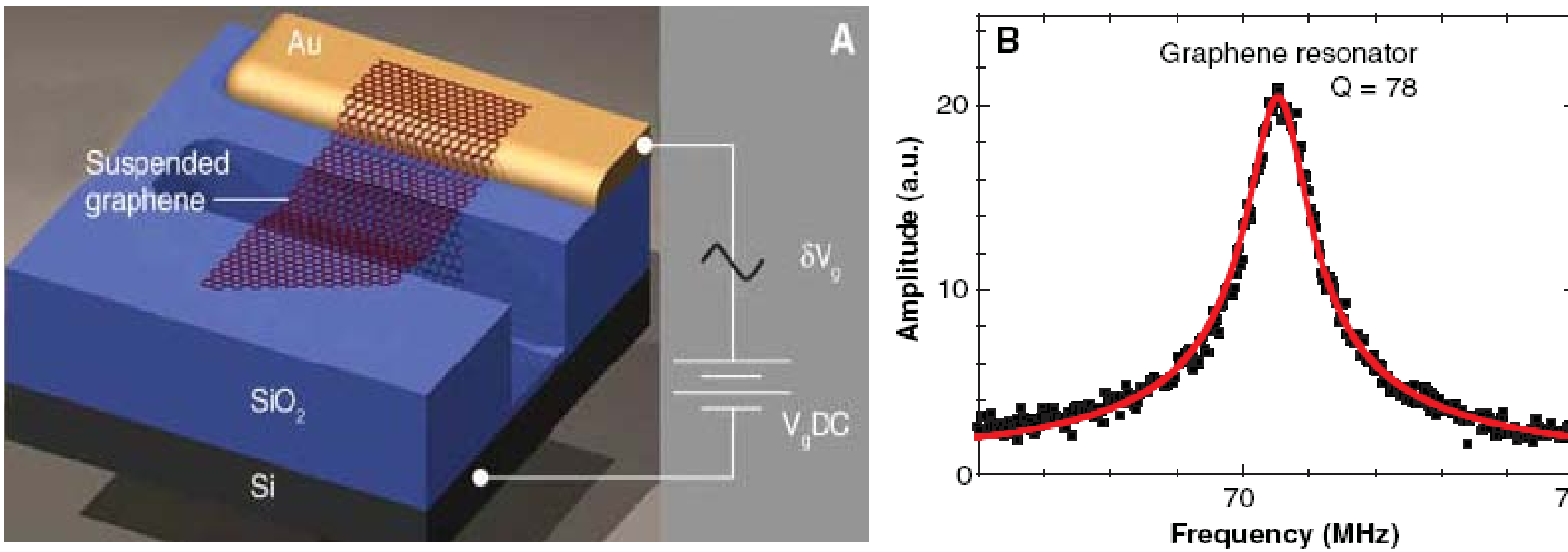
“Graphene is a wonder material with many superlatives to its name. It is the thinnest known material in the universe and the strongest ever measured. Its charge carriers exhibit giant intrinsic mobility, have zero effective mass, and can travel for micrometers without scattering at room temperature. Graphene can sustain current densities six orders of magnitude higher than that of copper, shows record thermal conductivity and stiffness, is impermeable to gases, and reconciles such conflicting qualities as brittleness and ductility. Electron transport in graphene is described by a Dirac-like equation, which allows the investigation of relativistic quantum phenomena in a benchtop experiment.”

A.K. Geim. **Graphene: Status and Prospects**

Sceince, **2009**, *324*, 1530

Mechanical properties of graphene

The thinnest resonator consists of a single suspended layer of atoms and represents the ultimate limit of two-dimensional nanoelectromechanical systems

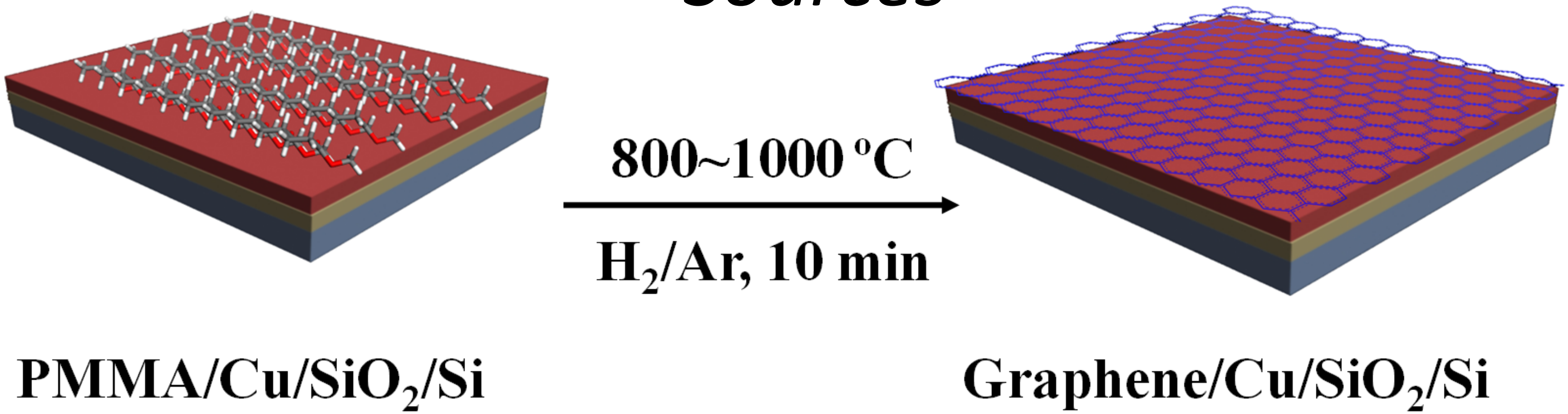


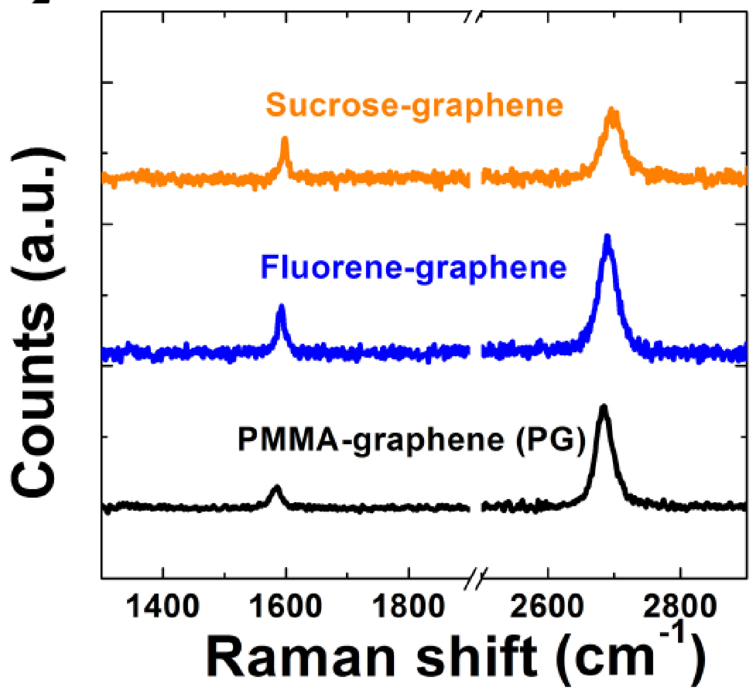
Schematic and an amplitude versus frequency dependence for the single-layer graphene resonator.

The high Young's modulus (~ 1 TPa) , extremely low mass, and large surface area make these resonators ideally suited for use as mass, force, and charge sensors.

J.C. Bunch, et al. *Science*, **2007**, *315*, 419

Growth of Graphene from Solid Carbon Sources

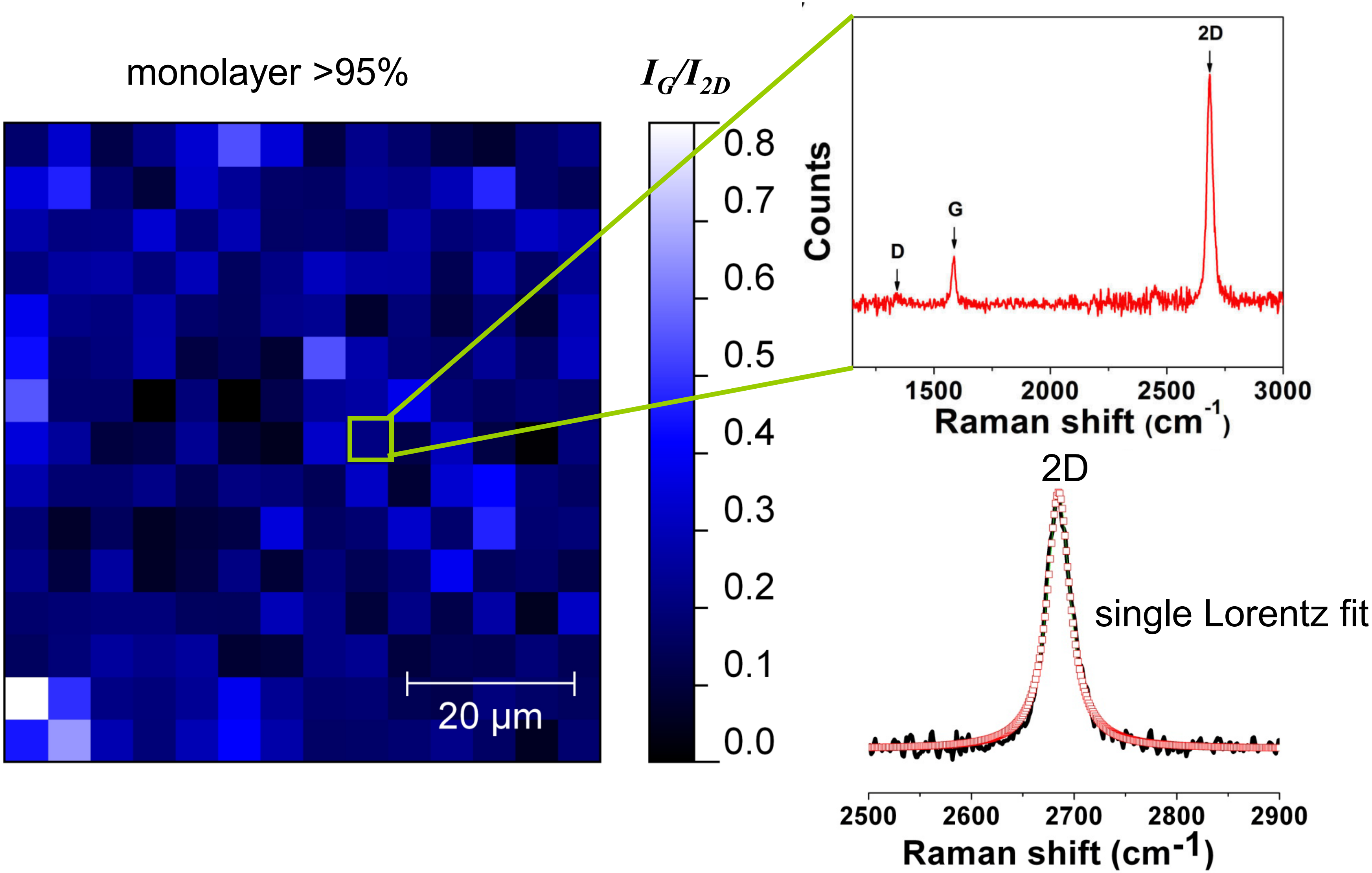




Polymer-derived graphene = PG

Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu

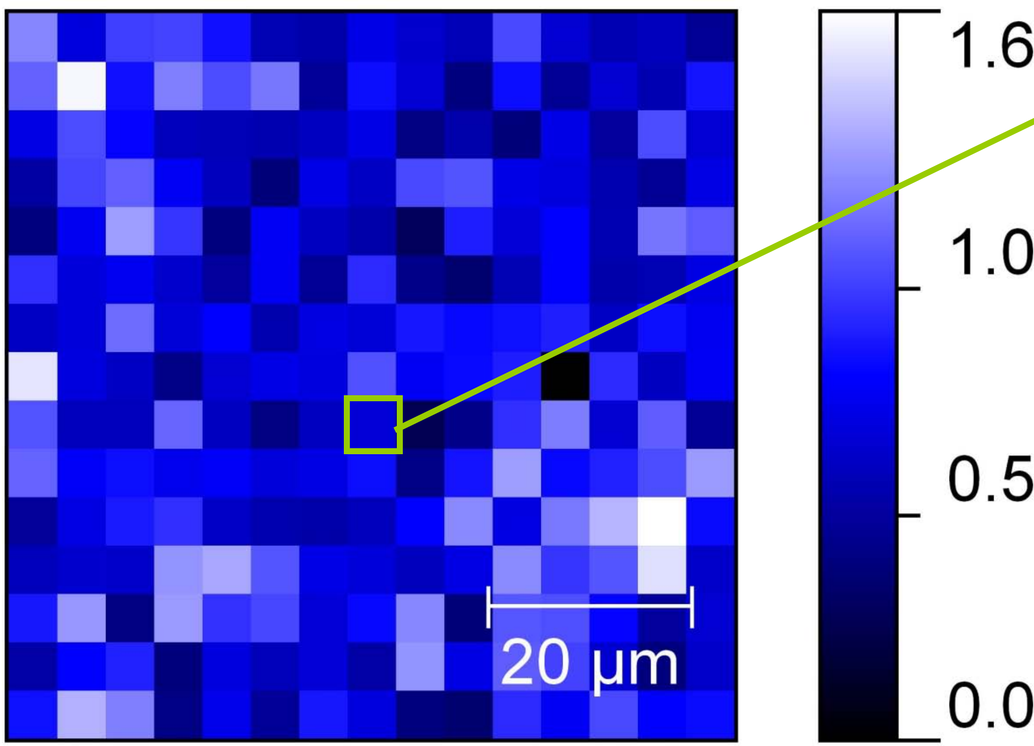
Raman of Monolayered PG

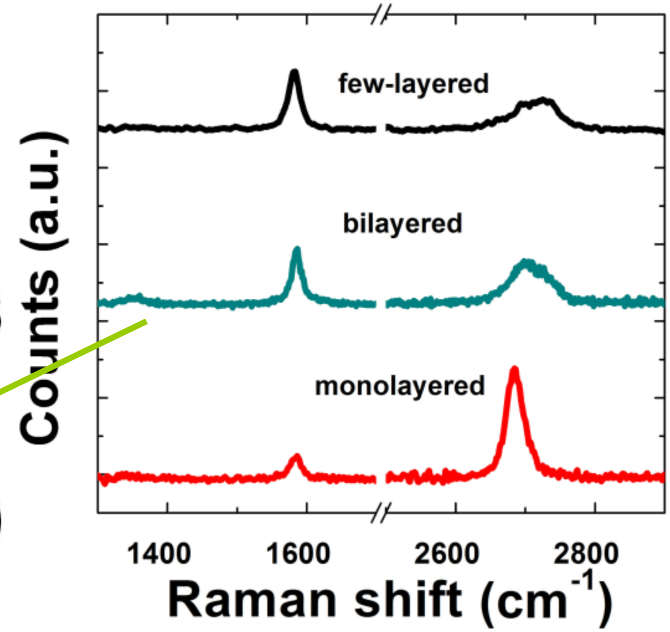


Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu

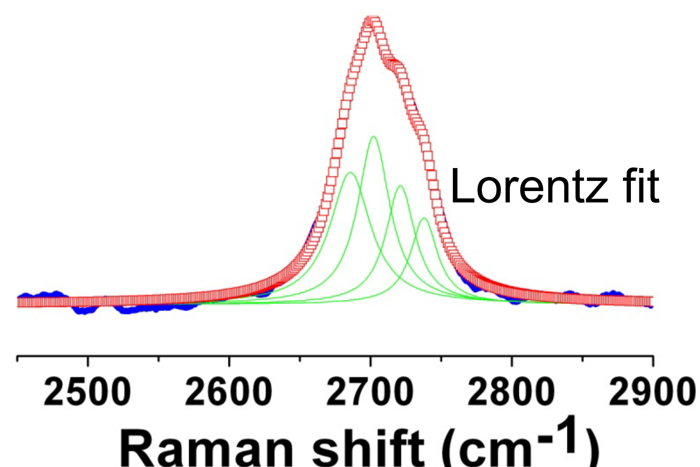
Raman of Bilayered PG

Bilayer >85%





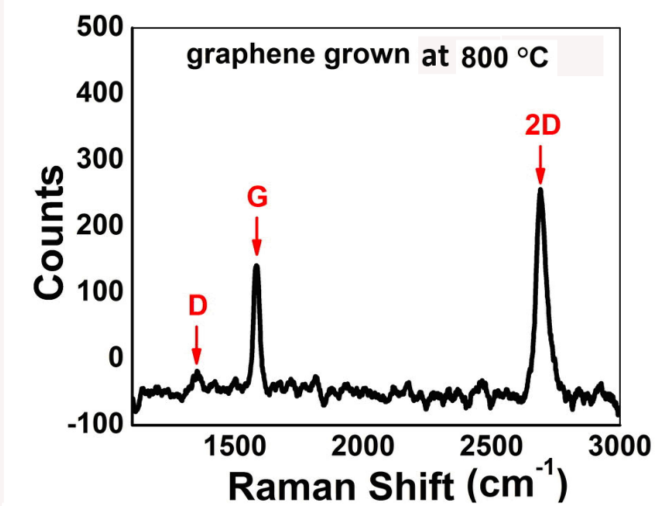
2D

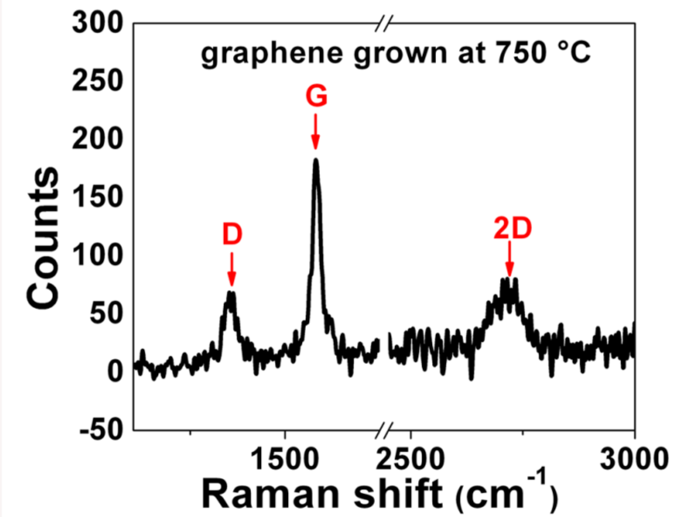


Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu

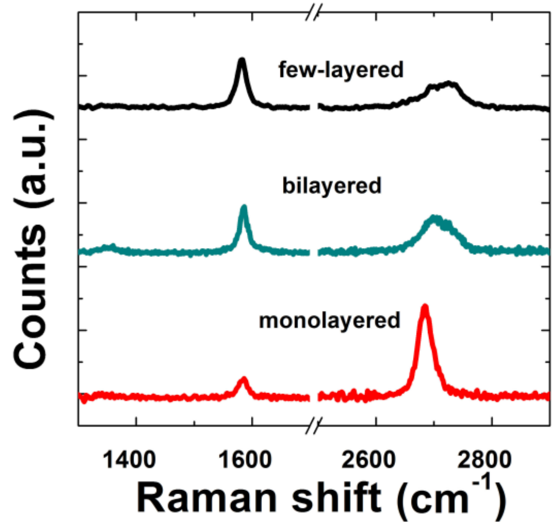
Characterization of PG

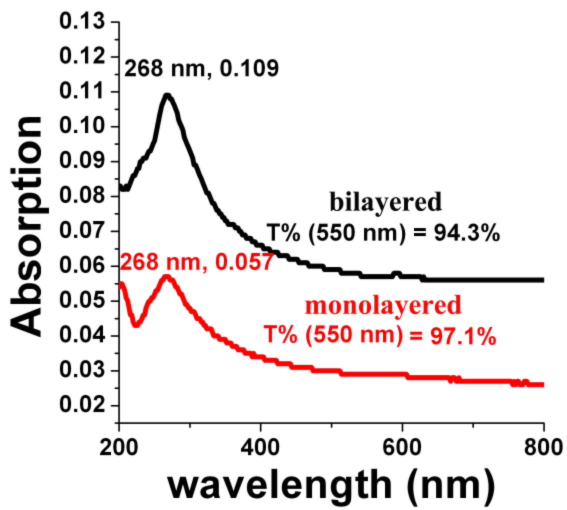
Low T growth



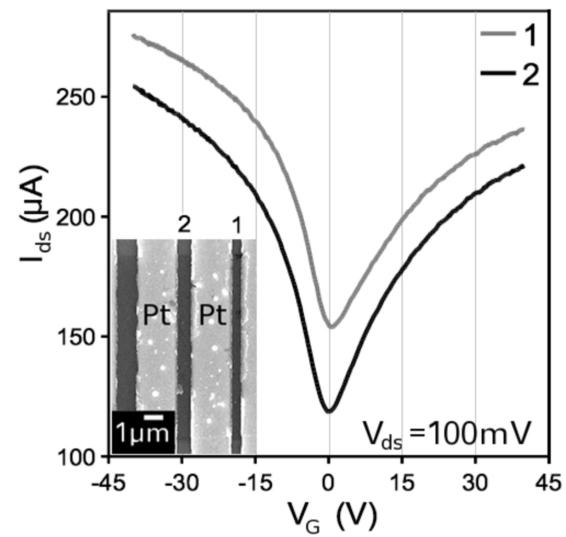


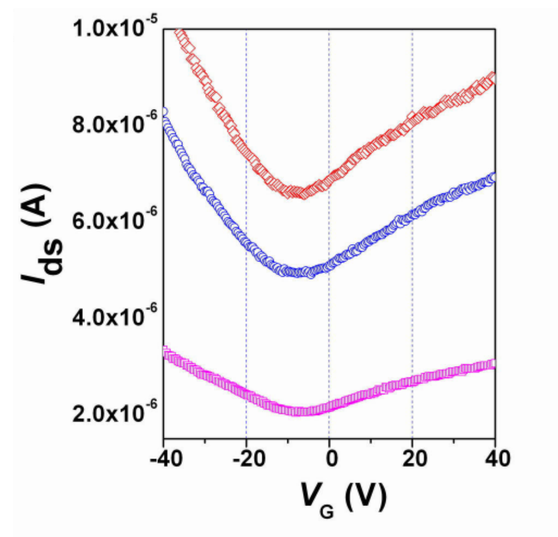
Thickness





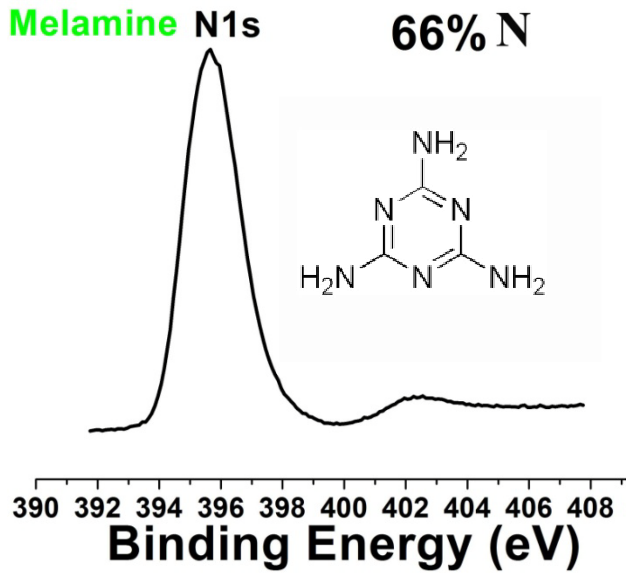
Electronics

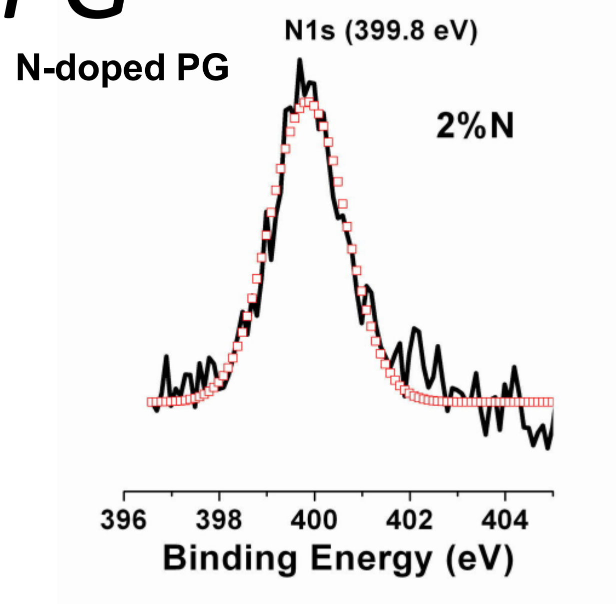


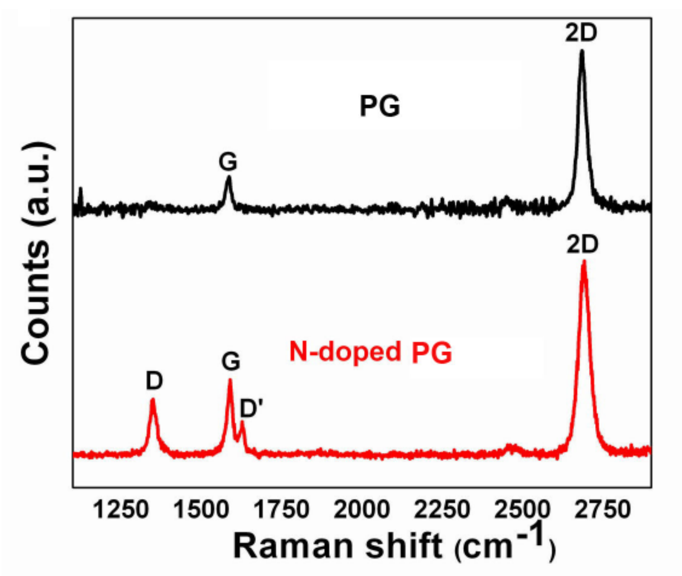


Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu

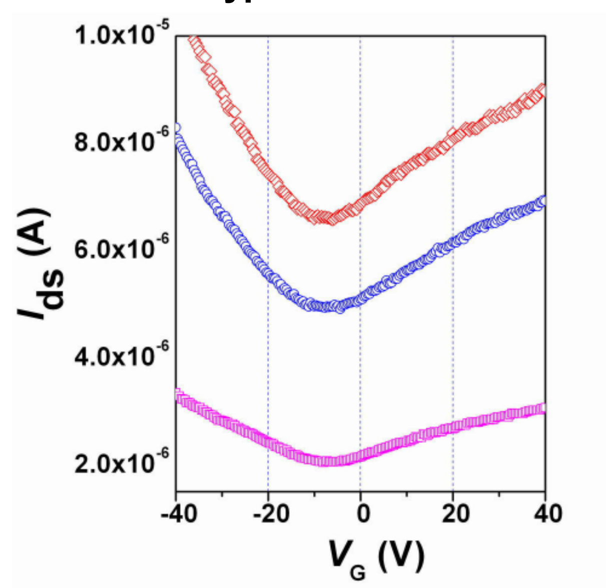
N-doped PG





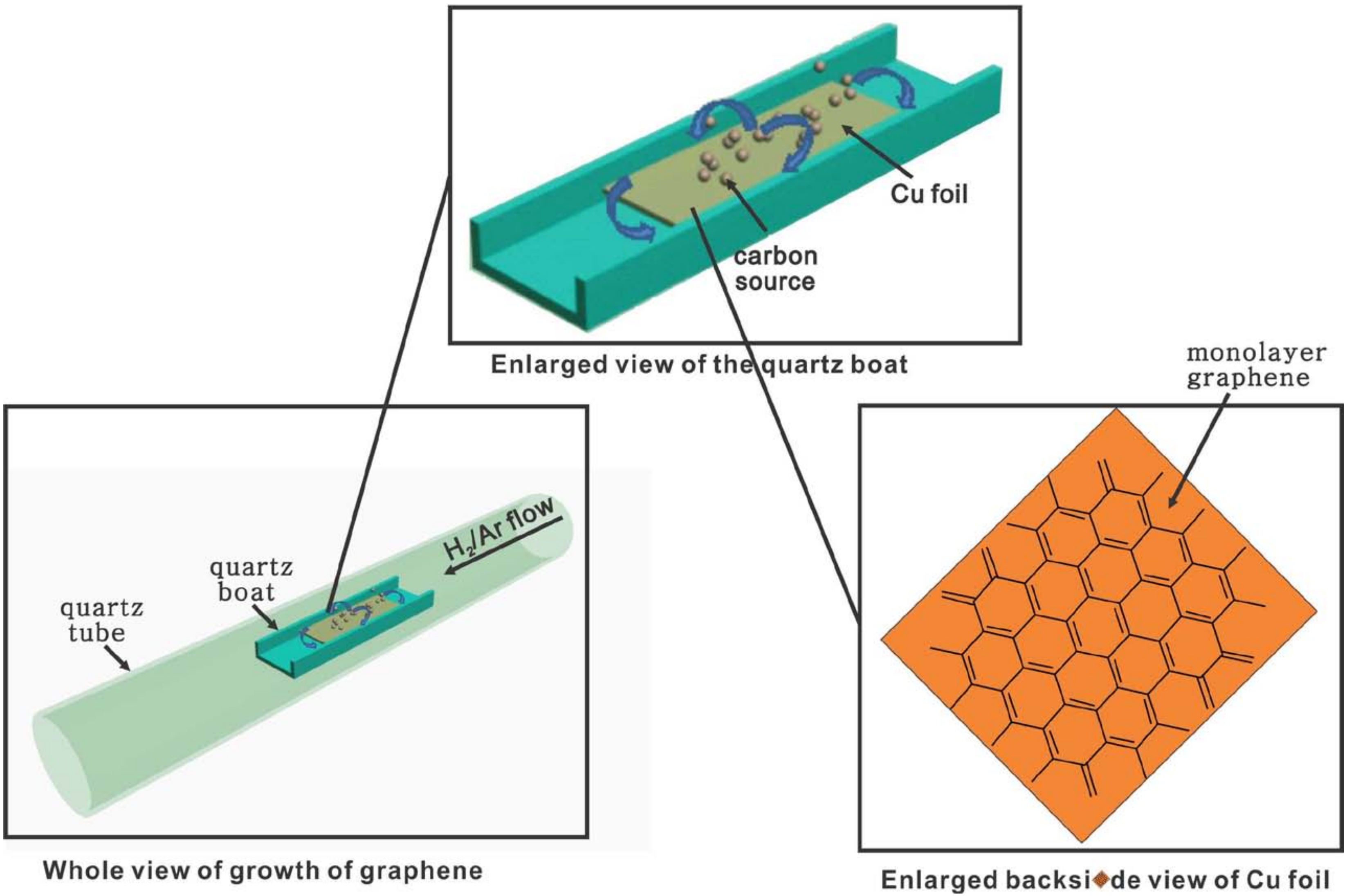


n-type FET behavior



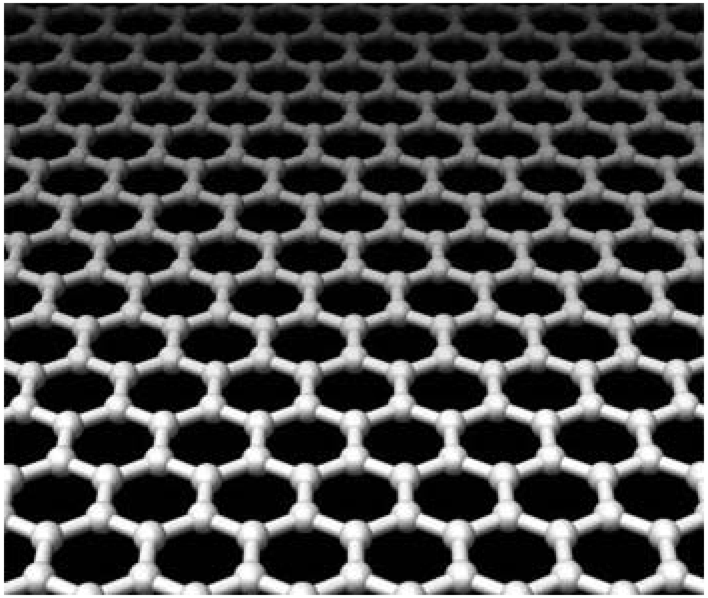
Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu

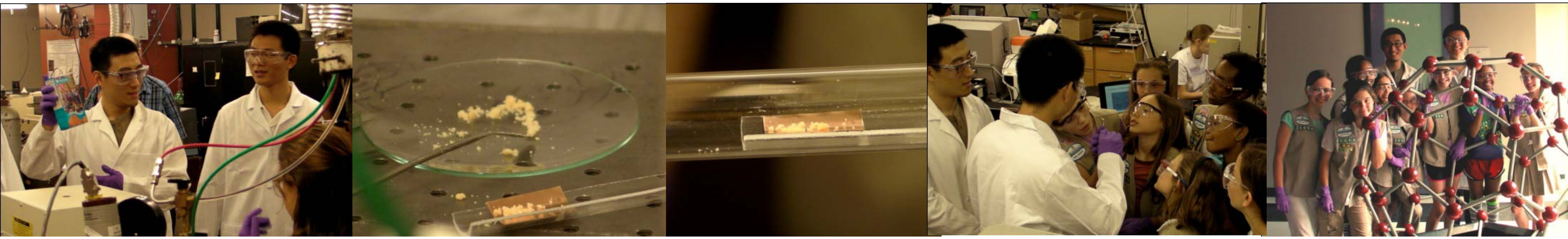
Growth of Graphene from any Carbon Source



Graphene from Girl Scout Cookies

Carbon



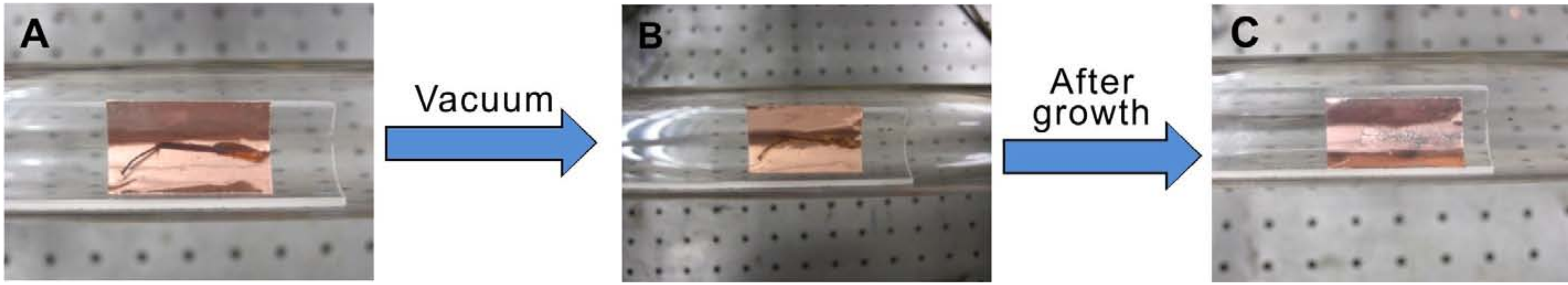


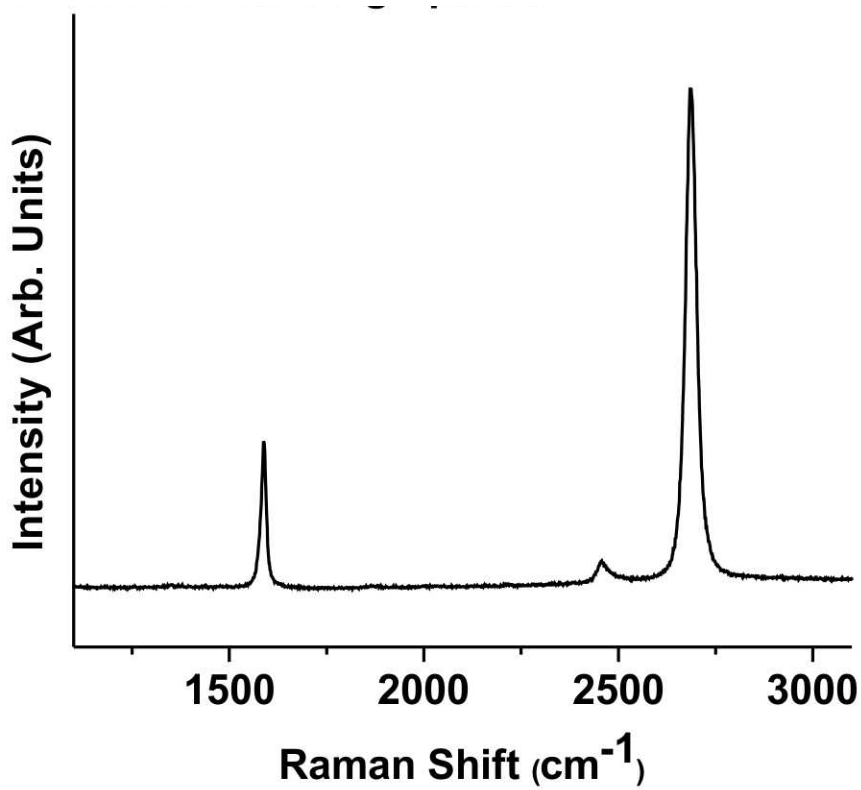
Some Interesting Value Facts

If all the graphene were used as touch screens in iPad2's, one box of Girl Scout cookies (255 grams) is enough to make 3,500,000 iPad2 screens.

The current value of the graphene derived from one box of Girl Scout cookies, if sold as 1-inch graphene squares, is $15 billion.

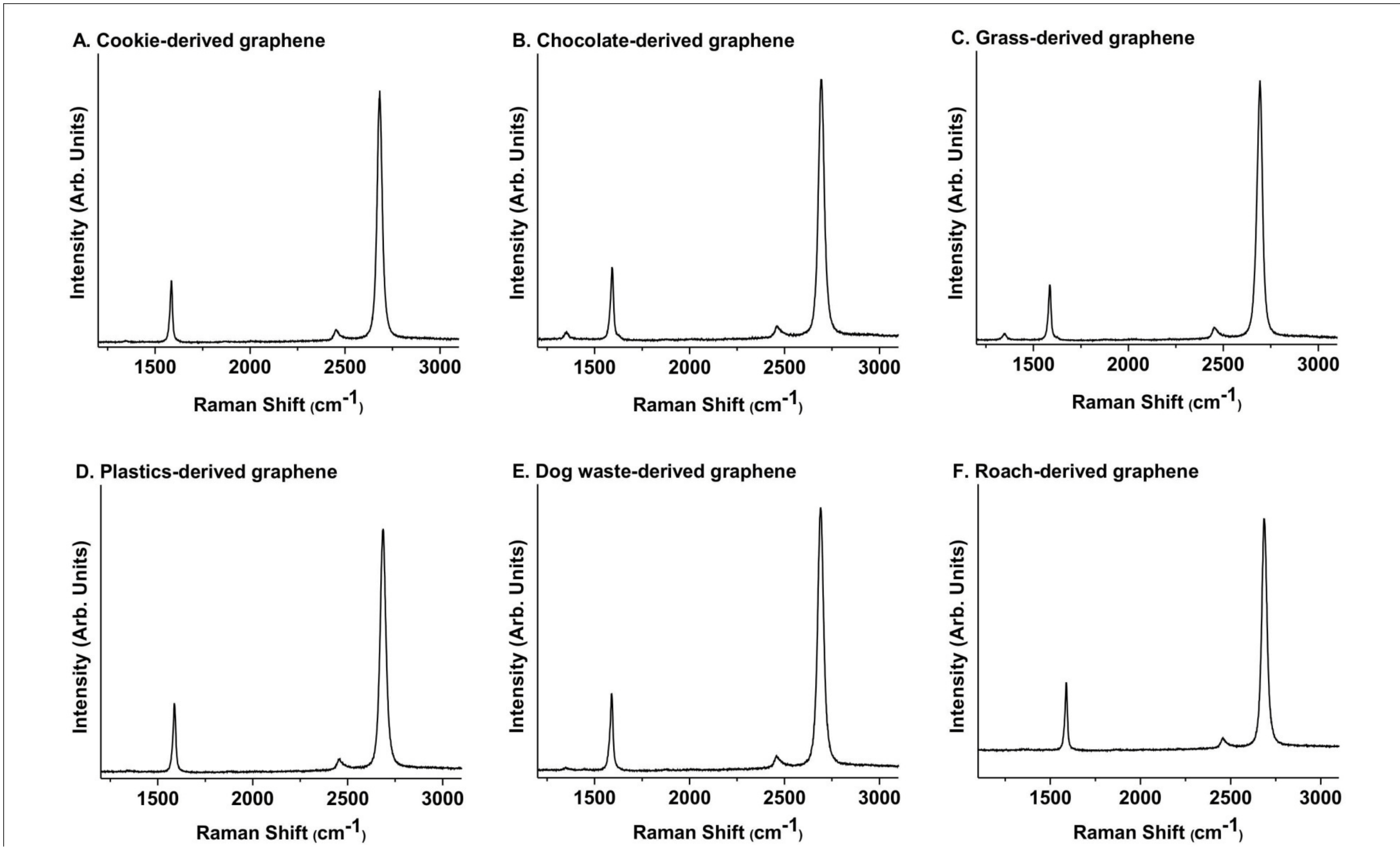
Graphene from a Roach Leg





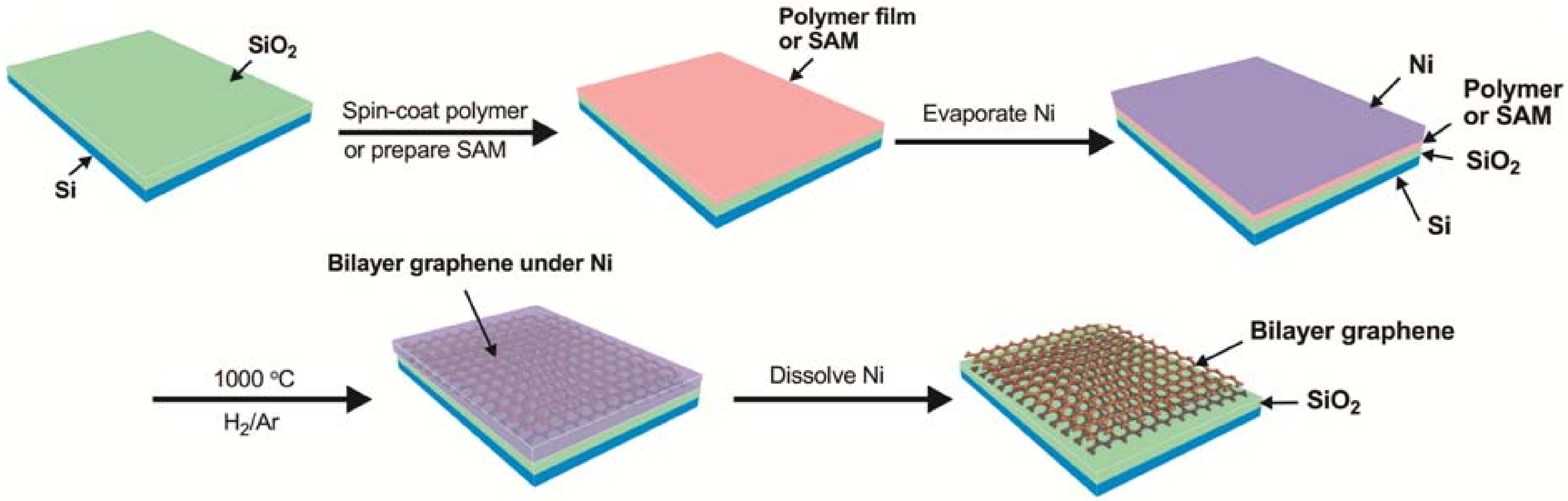
G. Ruan and Z. Sun

Raman Spectra of Graphene Derived from Six Carbon Sources



G. Ruan and Z. Sun

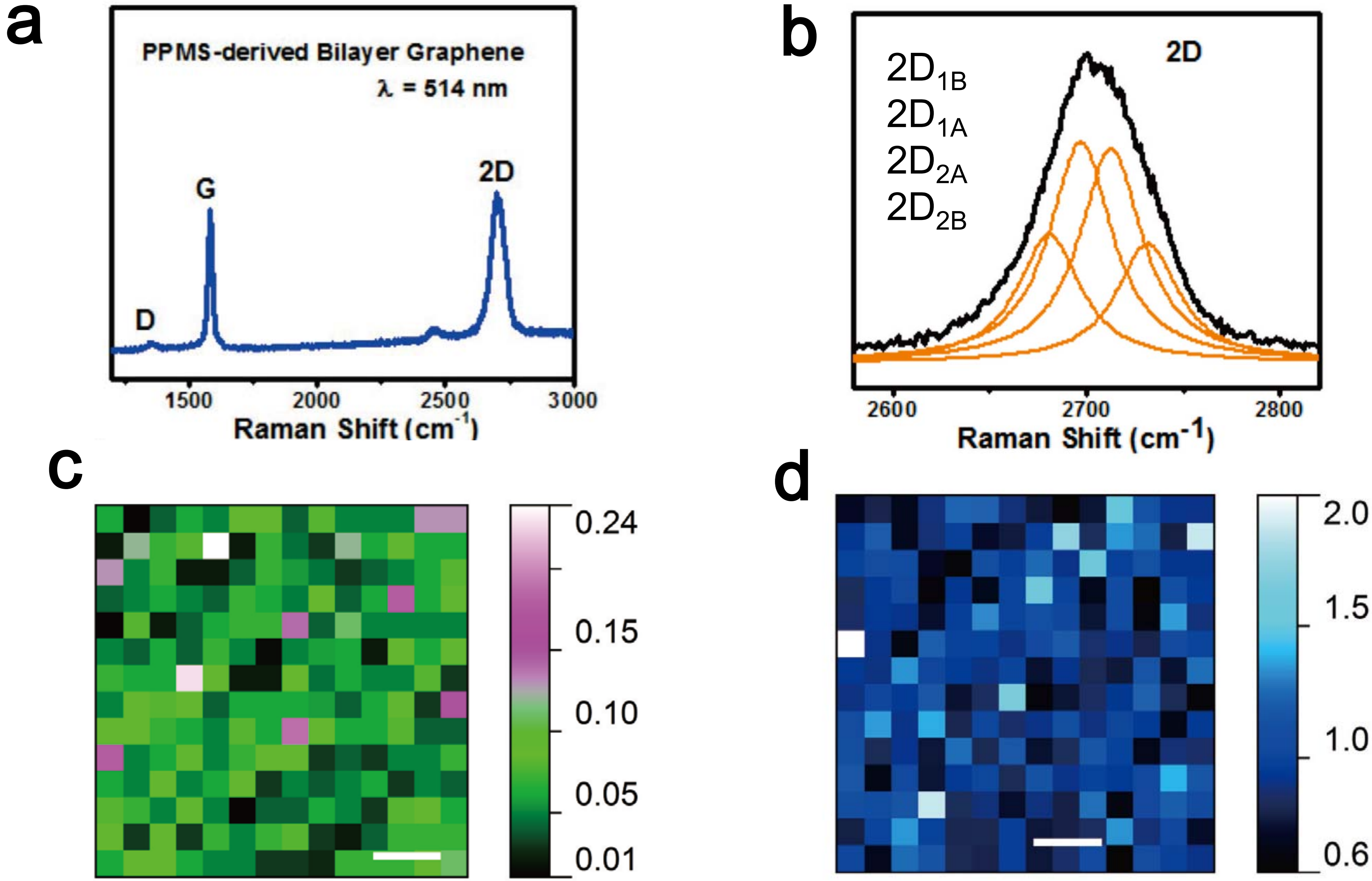
Growth of Bilayer Graphene on Insulating Substrates



Carbon sources:

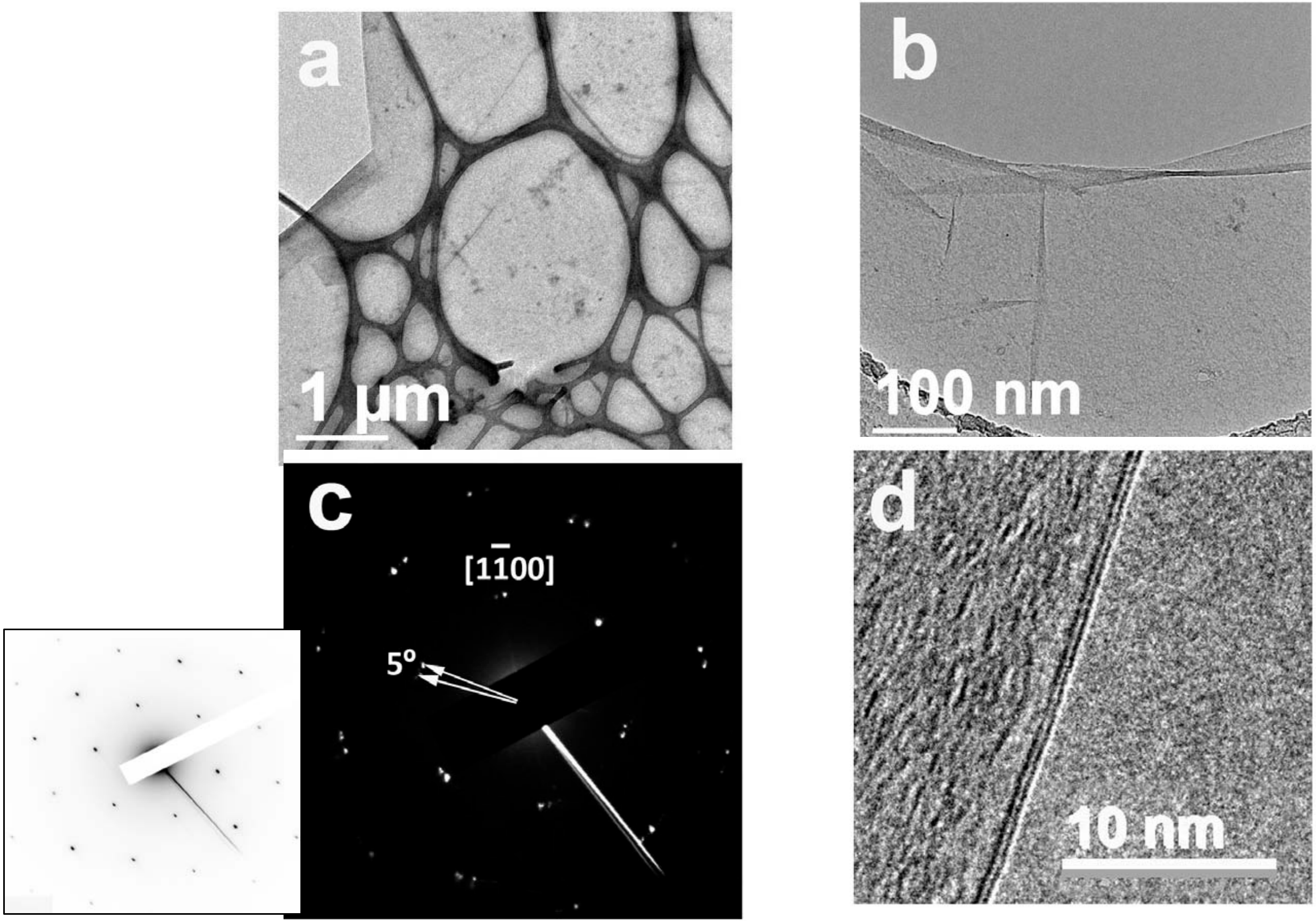
Insulating substrates: SiO_2, h-BN (Z. Liu & P. M. Ajayan), Si_3N_4 and Al_2O_3 (sapphire)

Z. Yan, Z. Peng, Z. Sun



c-d. Two-dimensional Raman (514 nm) mapping of bilayer graphene film (112 × 112 μm^2). The color gradient bar to the right of each map represents the D/G (< 0.1) (c) peak ratio, G/2D peak ratio (d) showing 90% bilayer. The scale bars are 20 μm.

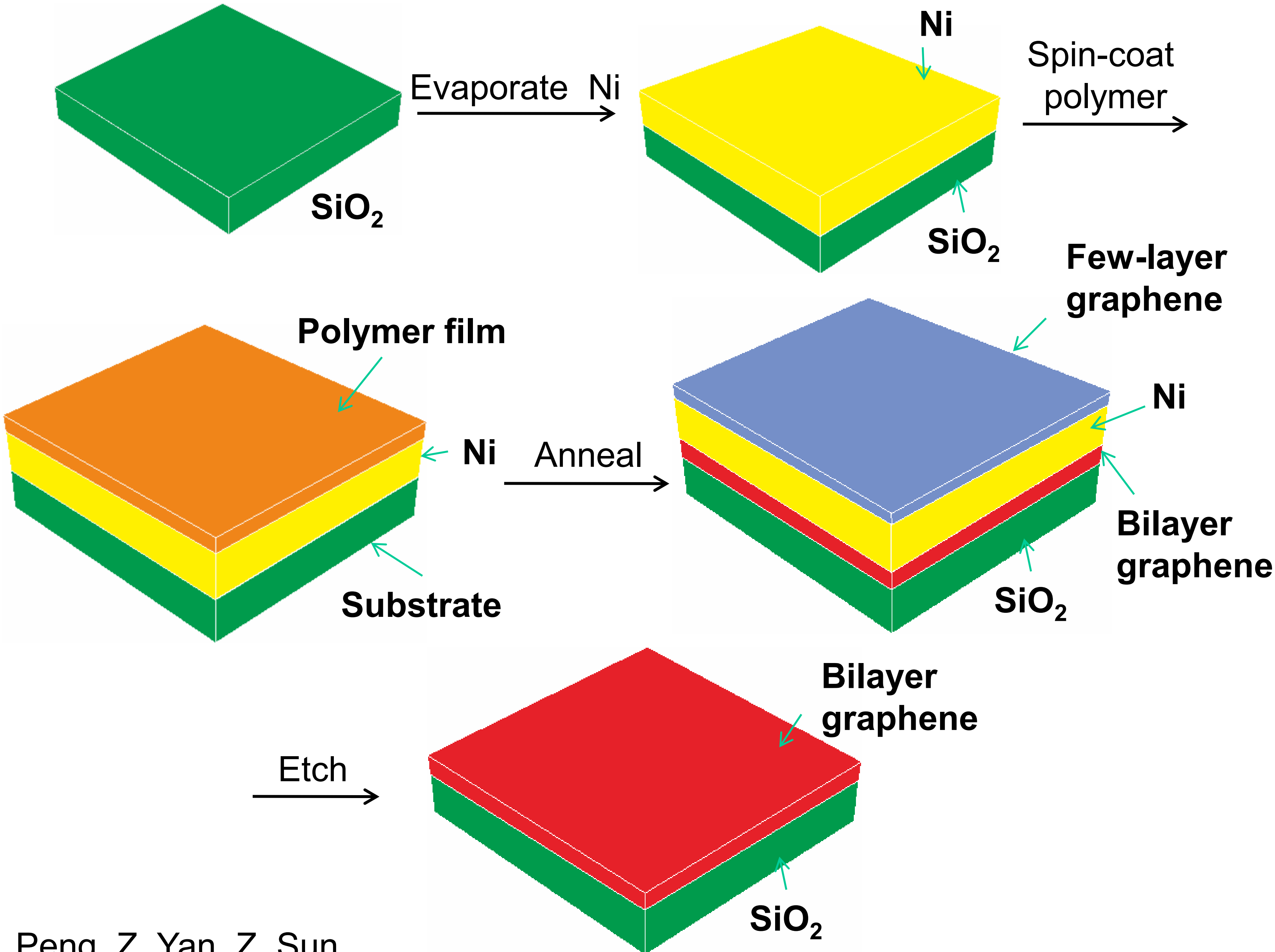
Z. Yan, Z. Peng, Z. Sun



a-b, Low-resolution TEM images showing bilayer graphene films suspended on a TEM grid. c, Hexagonal SAED pattern of the bilayer graphene with a rotation in stacking of 5º between the two layers (~5% Bernal, inset). d, HRTEM picture of PPMS-derived graphene edges. The PPMS-derived graphene was two layers thick at

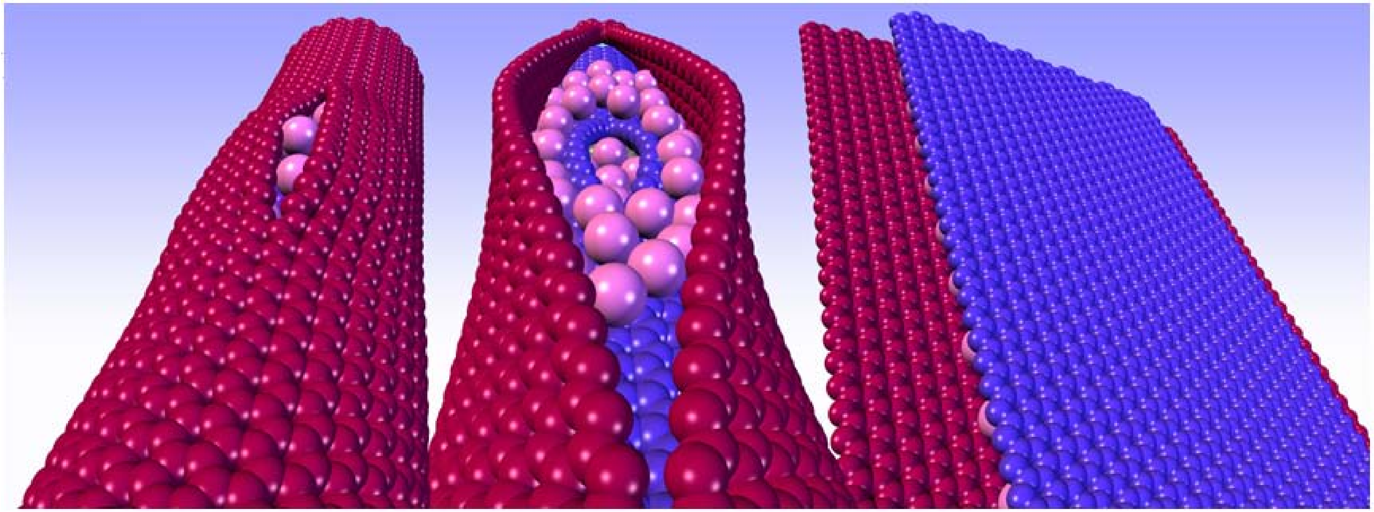
Z. Yan, Z. Peng, Z. S

Complementary Bilayer Growth Method– Top Down



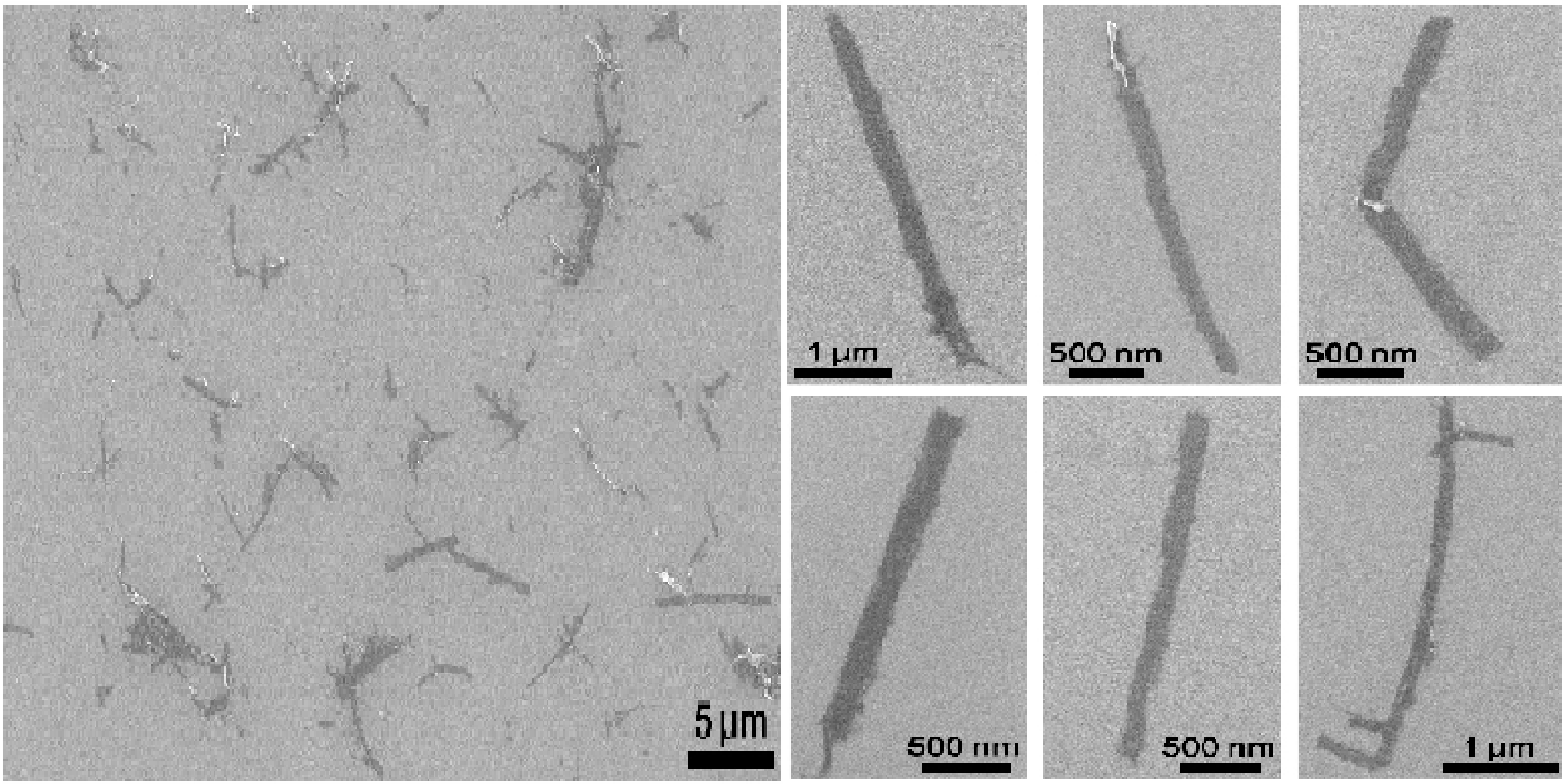
Z. Peng, Z. Yan, Z. Sun

K-Split MWCNTs to Form Graphene Nanoribbons



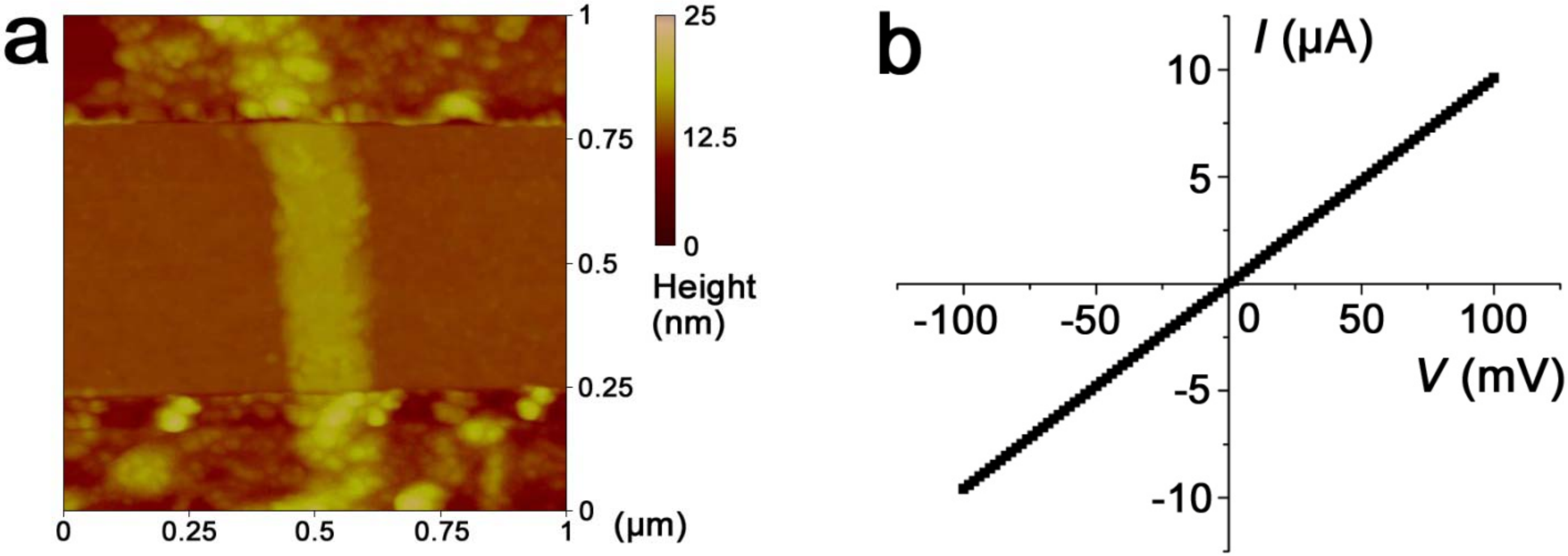
D. Kosynkin
W. Lu
G. Pera

K-Split MWCNTs to Form Graphene Nanoribbons



D. Kosynkin, W. Lu, A. Sinitskii

K-Split MWCNTs to Form Graphene Nanoribbons

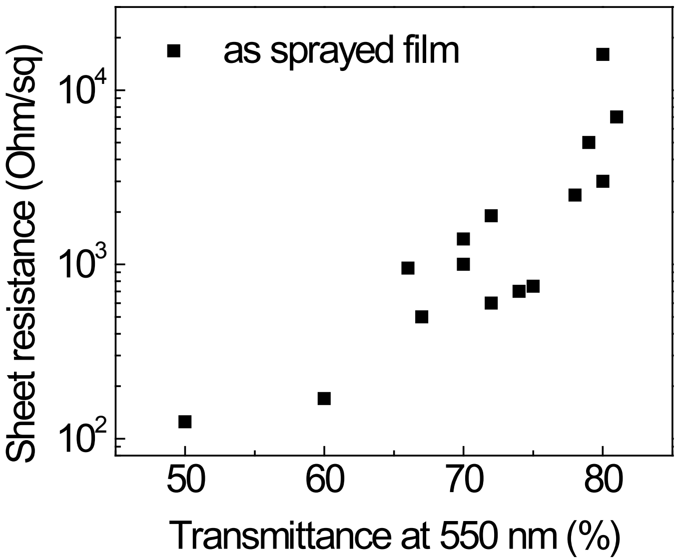


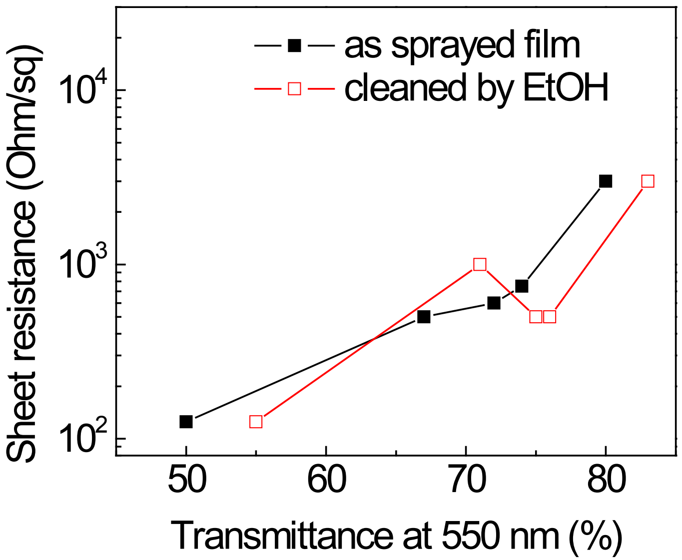
Appearance and electrical properties of a device made from a thin (3.8 nm) GNR stack. a, AFM image of a GNR (~5-layered) with 0.5-µm-spaced platinum electrodes shown spanning horizontally at top and bottom. b, Electrical properties (conductivity 800 S/cm) of the GNR shown in a.

D. Kosynkin, W. Lu, A. Sinitskii

Conducting Films from K-Split Ribbons

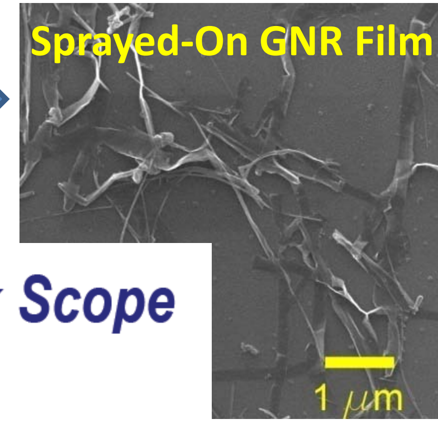
- Method: K-ribbons dispersed in *o*-dichlorobenzene and sprayed on glass substrate.
- Results: 76% transmittance with 500 Ohm/□ , 83% transmittance with 3000 Ohm/□

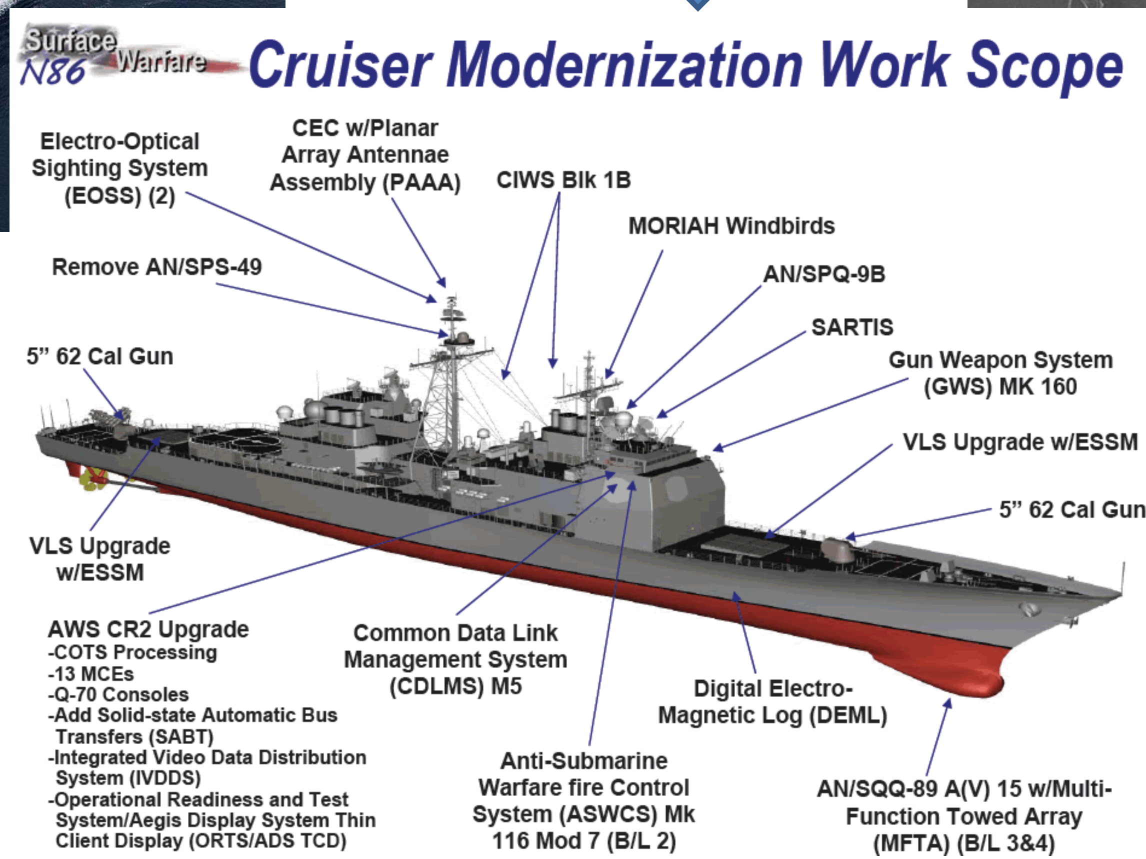




Y. Zhu, Z. Sun, D. Kosynkin

Application of Graphene Nanoribbon (GNR) Films to Aegis Cruiser Radome and Phased Array Antenna De-icing Circuits– a collaboration between Rice University and Lockheed Martin for the transition to Naval systems





10 grams of graphene nanoribbons per 10 m x 10 m antenna aperture/face. Cost is $10 in nanoribbon starting material = $40 per ship

http://en.wikipedia.org/wiki/File:USS_Lake_Champlain_%28CG-57%29.JPG
http://www.google.com/imgres?imgurl

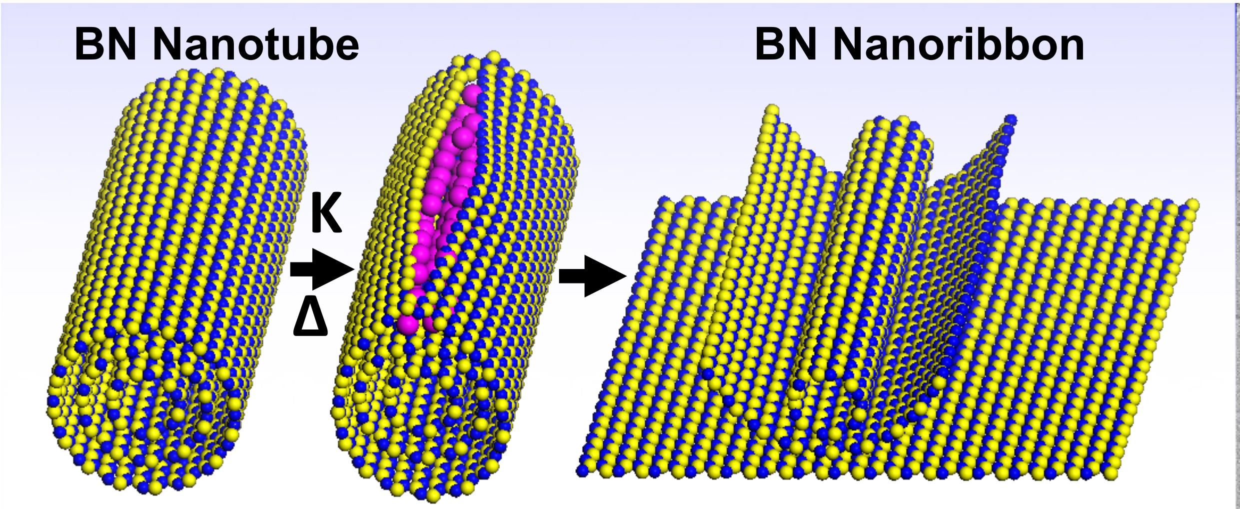
Y. Zhu; A. Raji; C. Kittrell; V. Volman

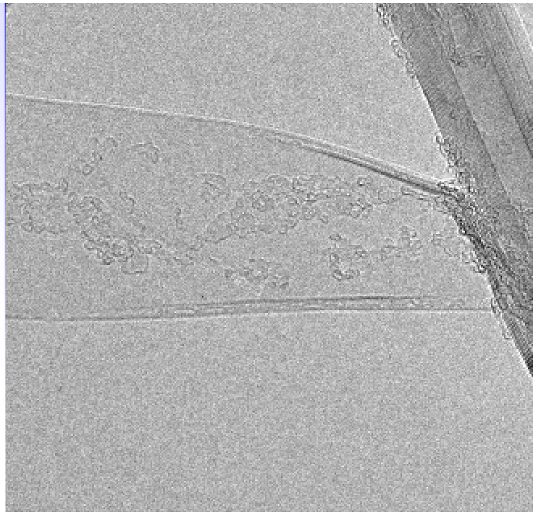
Hybrid Graphene Transparent Electrode Performance

Name	Grid size	Grid line width	Metal/Substrate	Sheet resistance (Transmittance) *
Hybrid TCE	100 µm × 100 µm	10 µm	Au/Glass	5 Ω/☐ (79%)
	200 µm × 200 µm	5 µm	Au/Glass	20 Ω/☐ (91%)
	100 µm × 100 µm	10 µm	Al/Glass	13 Ω/☐ (79%)
	200 µm × 200 µm	5 µm	Al/PET	60 Ω/☐ (91%)
	100 µm × 100 µm	10 µm	Cu/Glass	3 Ω/☐ (79%)
	200 µm × 200 µm	5 µm	Cu/PET	30 Ω/☐ (91%)
ITO			Glass	30-80 Ω/☐ (90%)
PEDOT/PSS			Glass/PET	100 Ω/☐ (with 5% DMSO)(90%)

Y. Zhu

BN Nanoribbons (BNNRs) using Potassium Metal at 300 °C

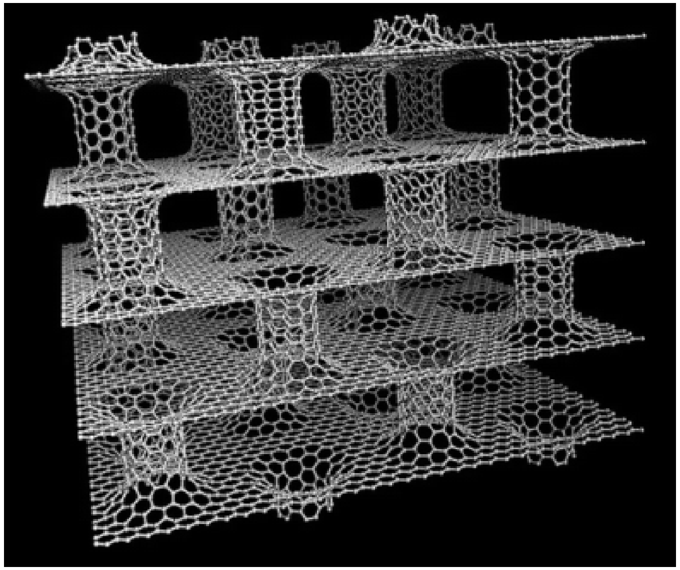




K. Erickson, A. Gibb, A. Sinitskii, M. Rousseas, N. Alem, A. Zettl

3D graphene/nanotube composite

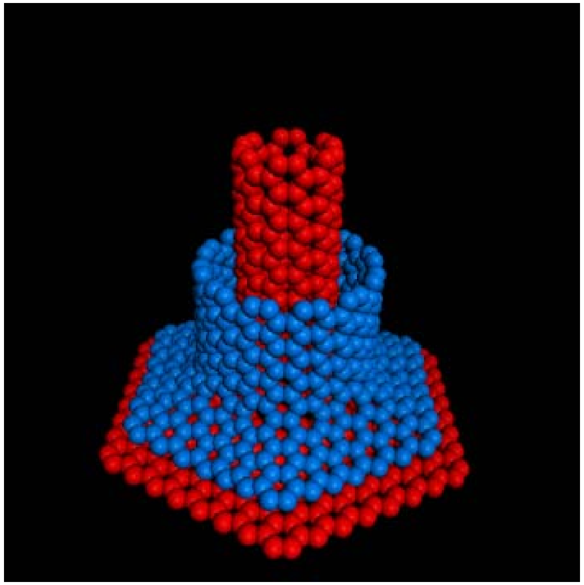
Fabrication procedure



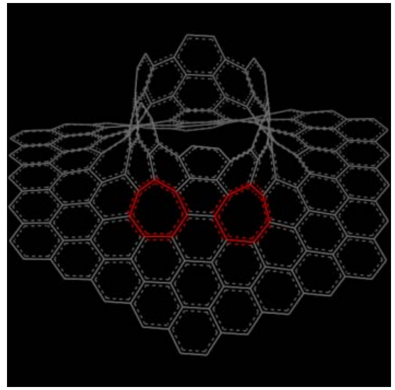
- 3D graphene-vertically aligned carbon nanotube structure have promising applications
  - Hydrogen storage
  - Supercapacitor
  - Li-Battery electrodes
- Practical problem
  - no method available so far that achieves both high surface area and good electrical junction between nanotube and graphene

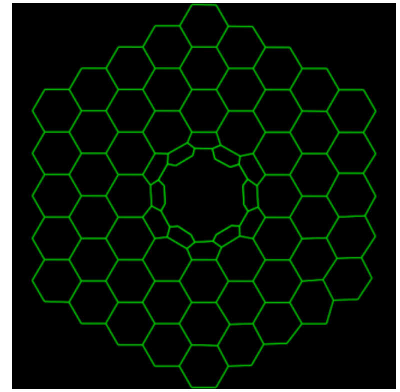
Y. Zhu, L. Li, C. Zhong

Explore the bonding status of CNT and graphene



Model of the CNT-graphene junction





Theoretical work suggested model
Nano Lett. **8**, 3166 (2008)
ACS Nano **4**, 7596 (2010)
ACS Nano **4**, 1153 (2010)

High-resolution STEM images show the structure of CNT-graphene junction

Y. Zhu, L. Li, C. Zhong

Application for supercapacitors

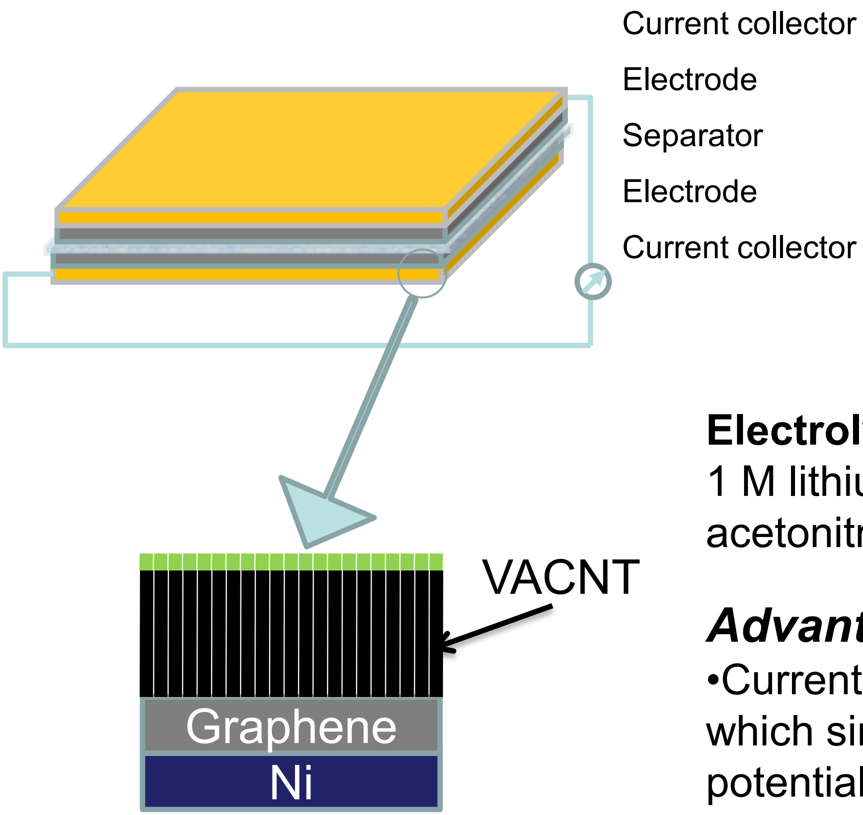


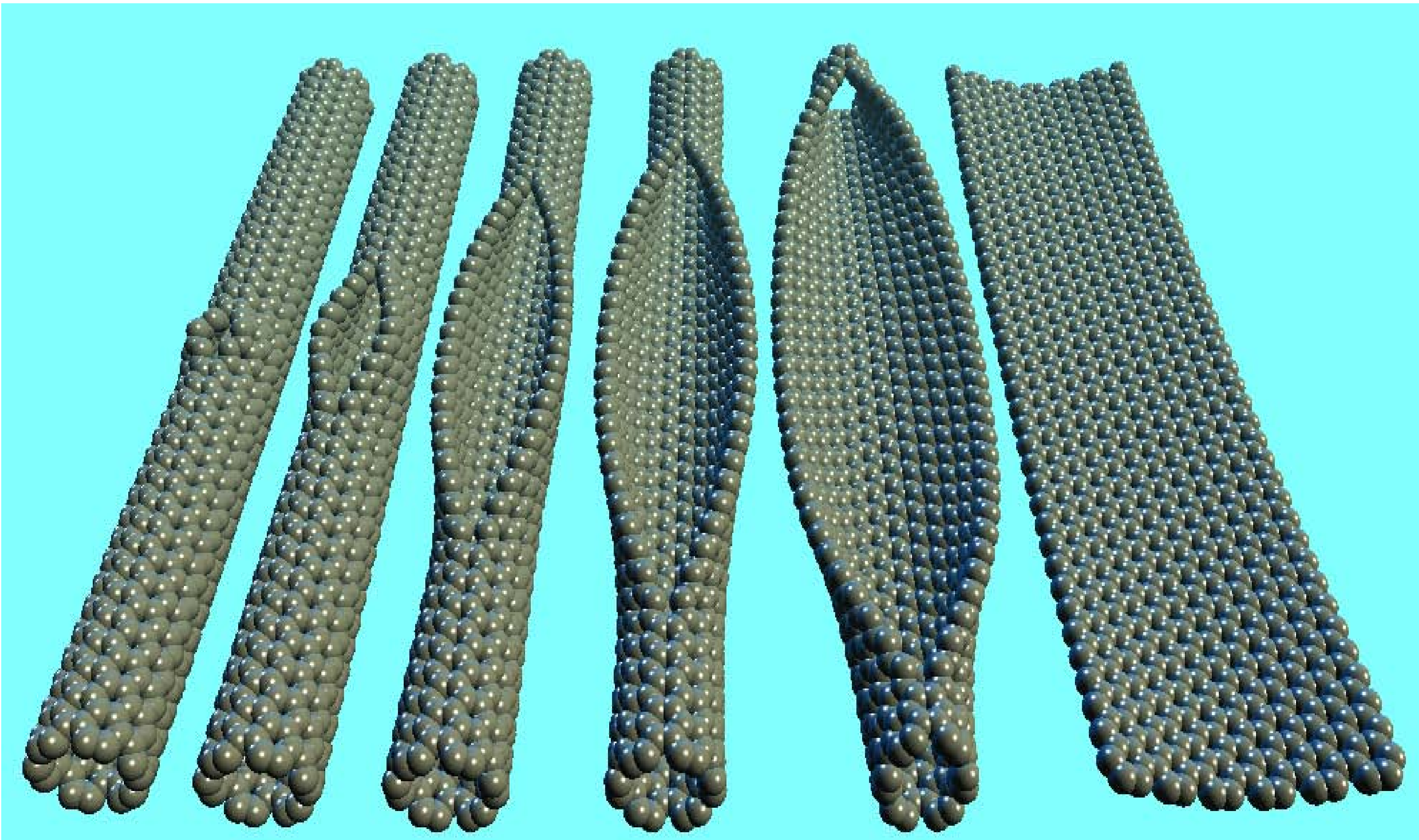
Photo of capacitor device

Electrolyte:
1 M lithium hexafluorophosphate in acetonitrile and BMIM BF_4 (1:1 volume ratio)

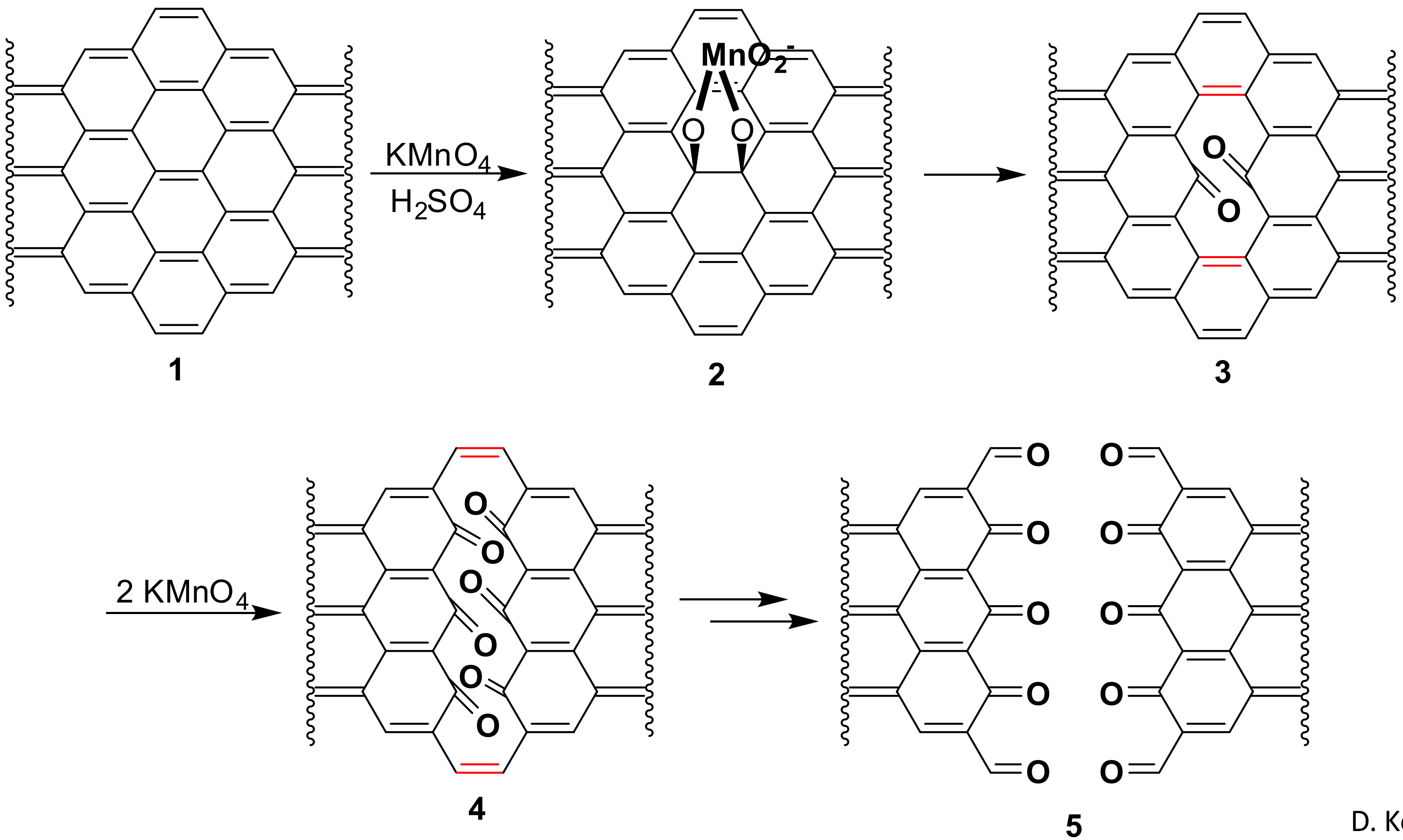
Advantages:

- Current collector and electrode are combined, which simplifies the fabrication procedure and potentially decreases the total weight of the devices
- Good electrical connection between the current collector and electrode

Longitudinal Unzipping of CNTs to Form Graphene Nanoribbons (GNRs)

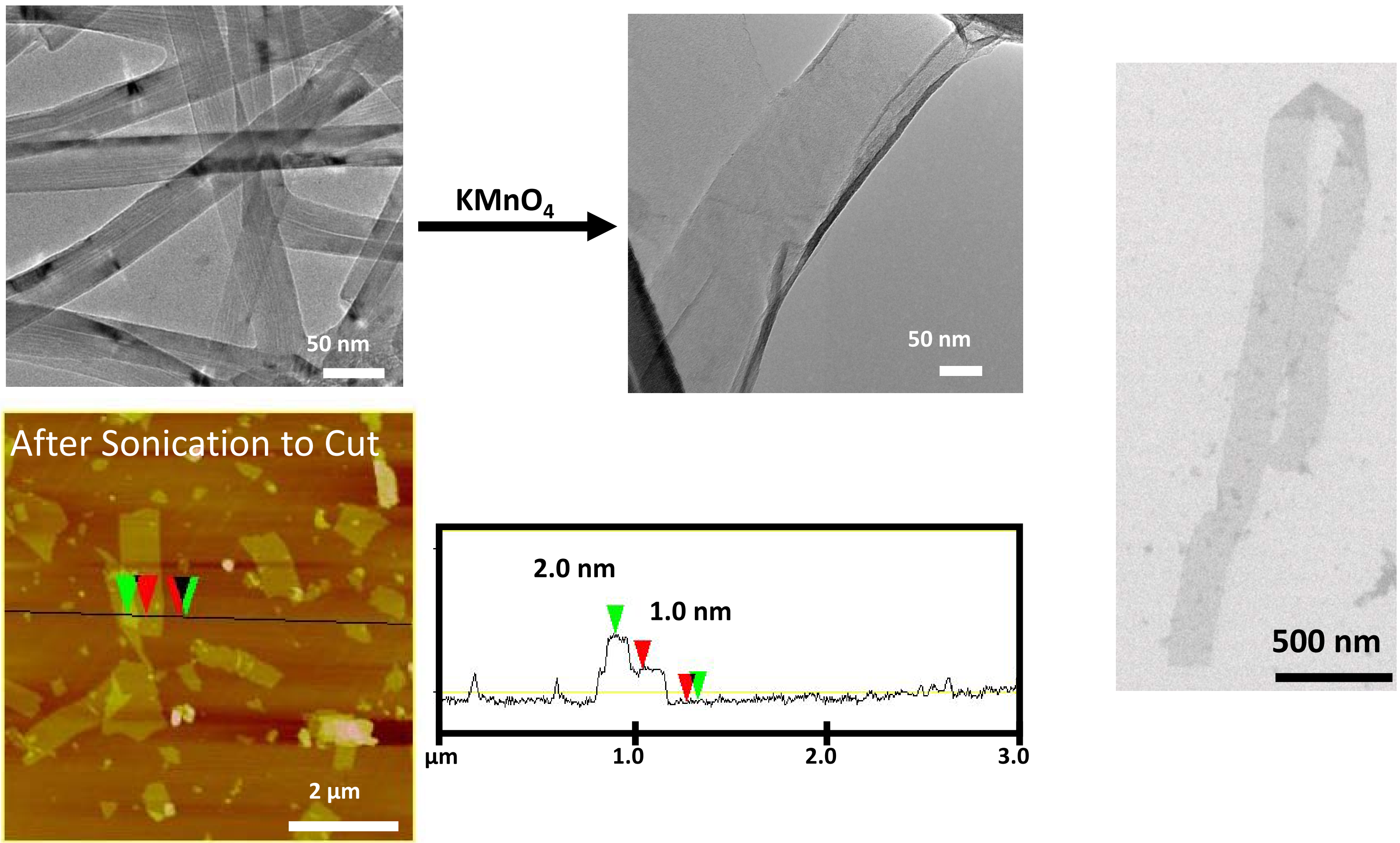


Bulk Chemical Method for Longitudinal Unzipping of CNTs to Form Graphene Nanoribbons (GNRs)



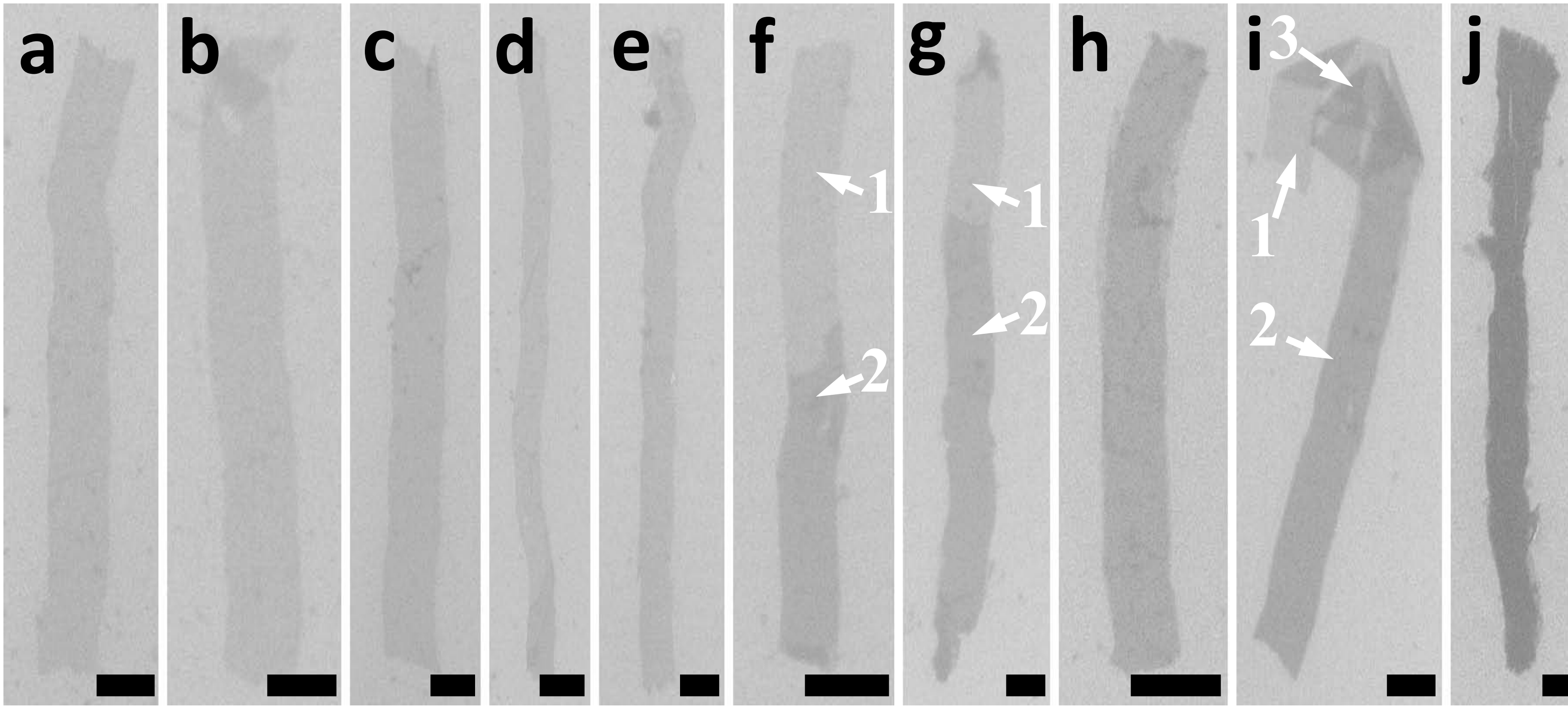
D. Kosynkin

Longitudinal Unzipping of CNTs to Form Graphene Oxide Nanoribbons (GONRs)



D. Kosynkin, A. Higginbotham, A. Sinitskii, A. Dimiev, J. Lomeda, B. K. Price

Alignment of Nanoribbons (no picture rotation)



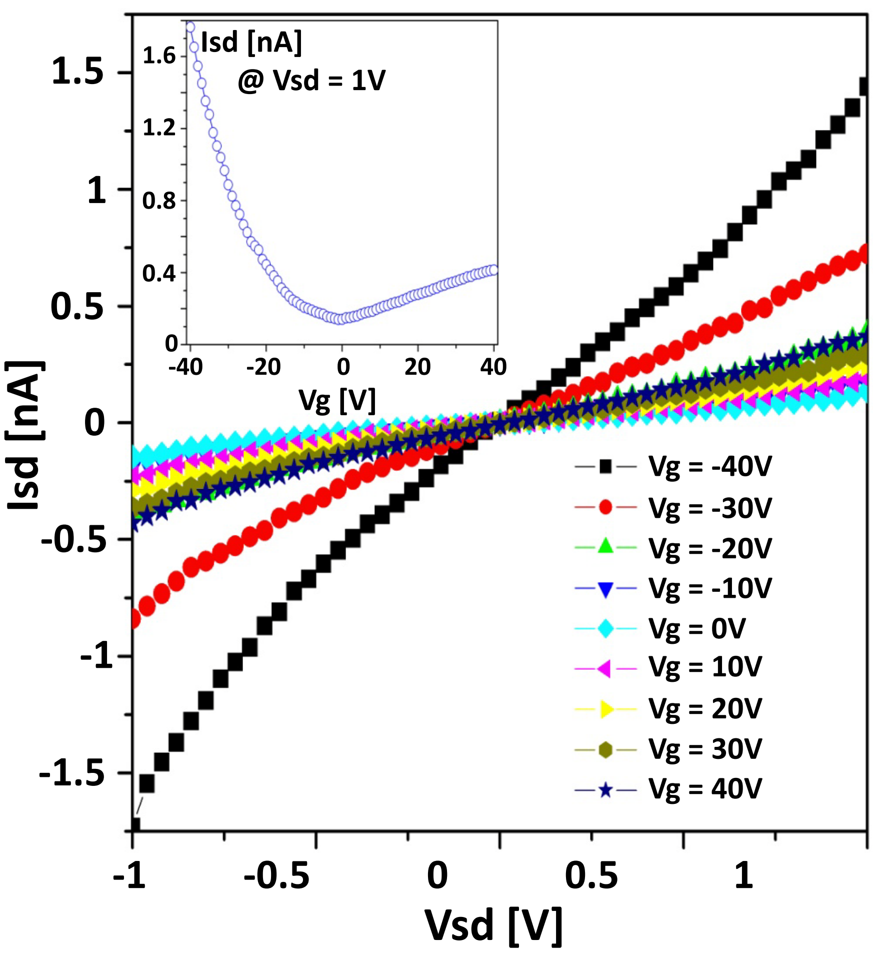
SEM images of **(a-e)** monolayer ribbons, **(f,g)** GNRs with coexisting mono- and bi-layer fragments, **(h,i)** bilayer ribbons, and **(k)** a multilayer stack of GNRs. All scale-bars in (a-j) are 250 nm, except for (d) at 500 nm. All GNRs have a width of 180-320 nm, they can be up to several µm long, as shown in (d) at 6.1 µm and (e) at 3.2 µm. All scale-bars are 250 nm except for (e) at 500 nm.

A. Sinitskii, A. Dimiev, D. Kosynkin

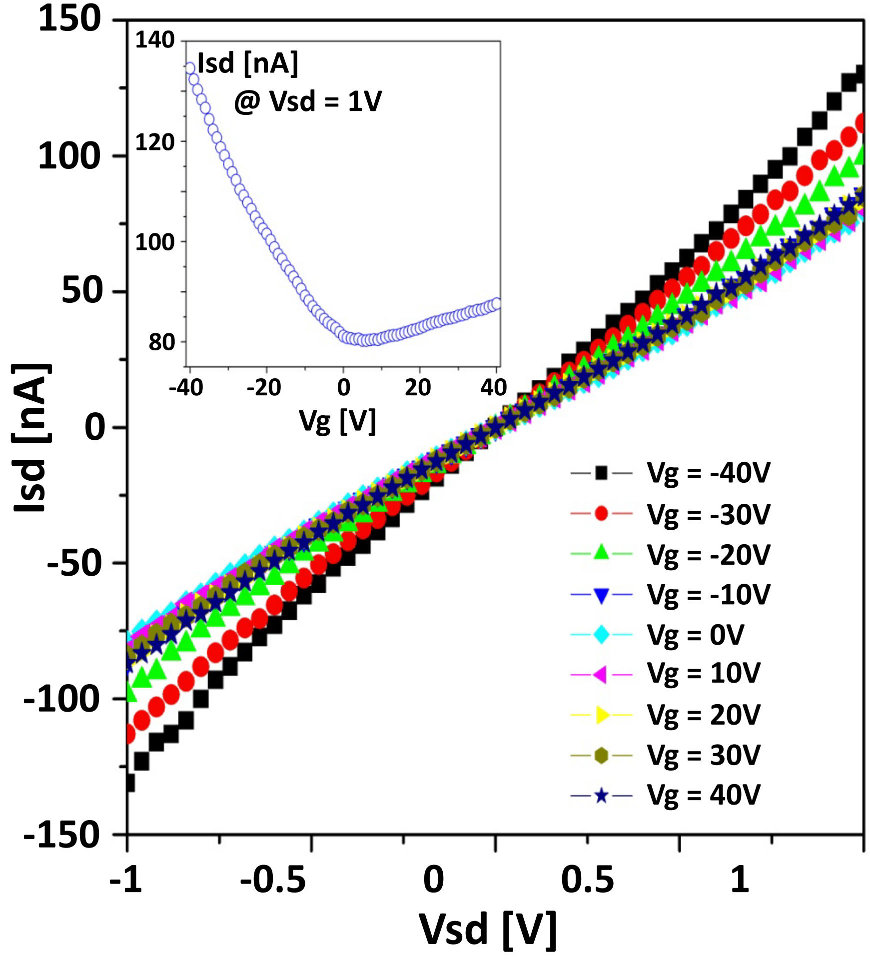
Reduction of the Ribbons

Electrical properties of the same device based on a N_2H_4-reduced single-layer ribbon

N_2H_4-reduced

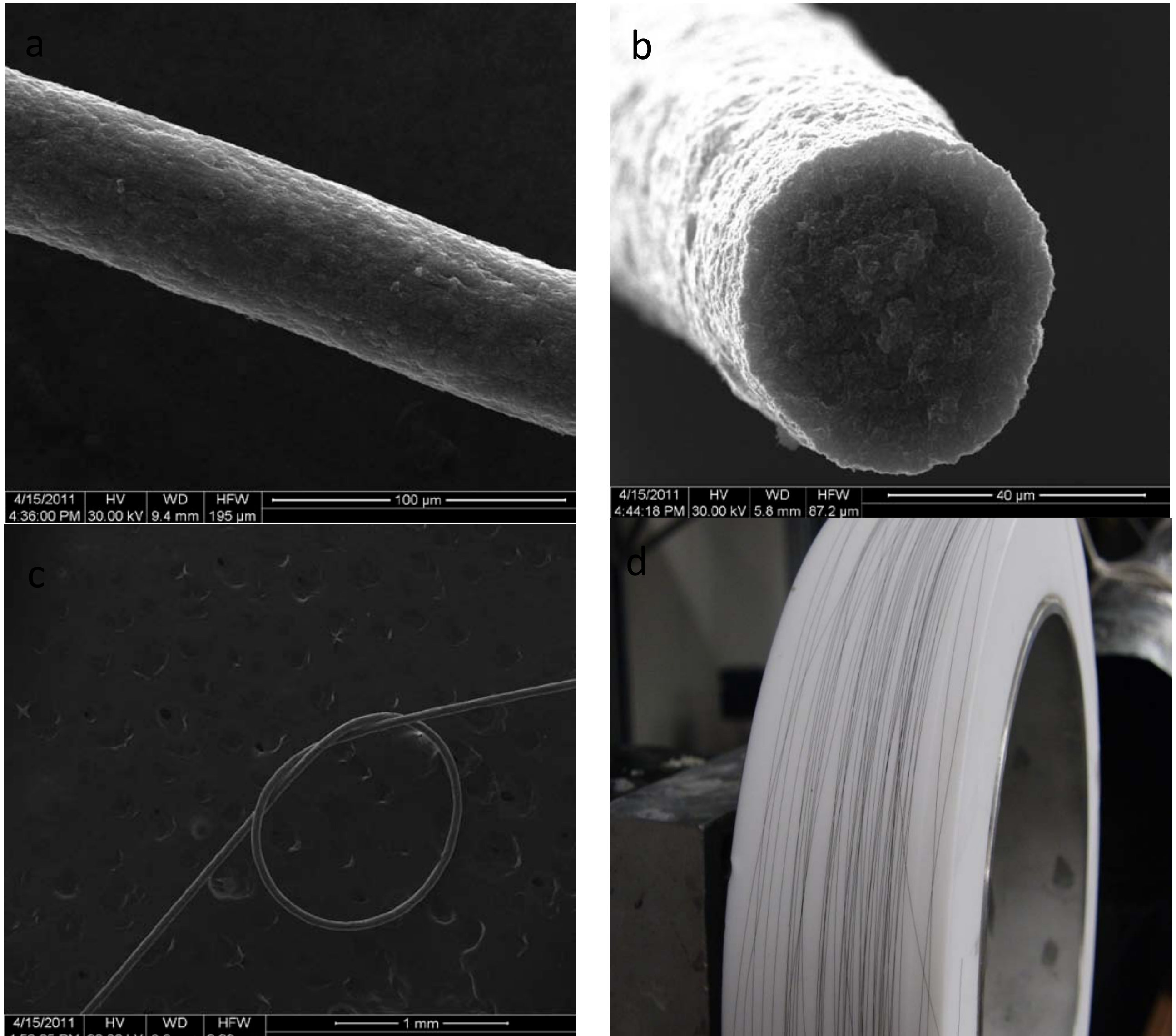


After annealing in H_2/Ar at 300 ^oC



A. Sinitskii, D. Kosynkin

As-Spun GONR Fibers



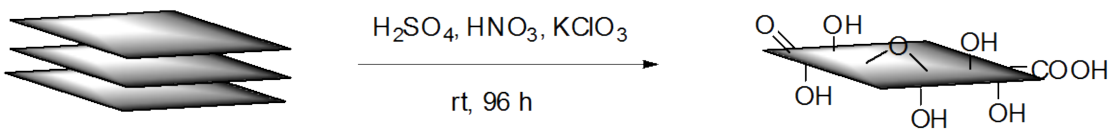
C. Xiang, N. Behabtu, M. Pasquali

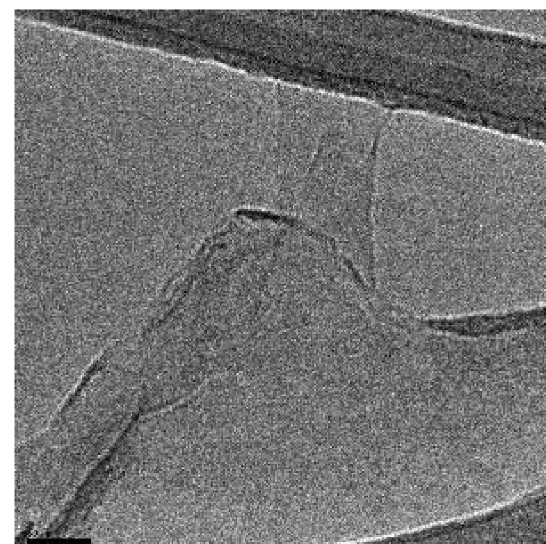
Graphene oxide

Graphite Oxidation

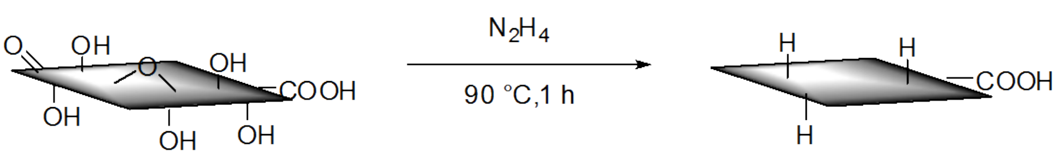
- $KClO_3$, 90% HNO_3 (Brodie, 1859)
- 98% H_2SO_4, HNO_3, $KClO_3$ (Staudenmaier, 1898)
- 98% H_2SO_4, $NaNO_3$, $KMnO_4$ (Hummers and Offeman, 1957)
- 98% H_2SO_4, H_3PO_4, $KMnO_4$ (Tour, 2010 → Commercial Partner)

Graphite oxidation

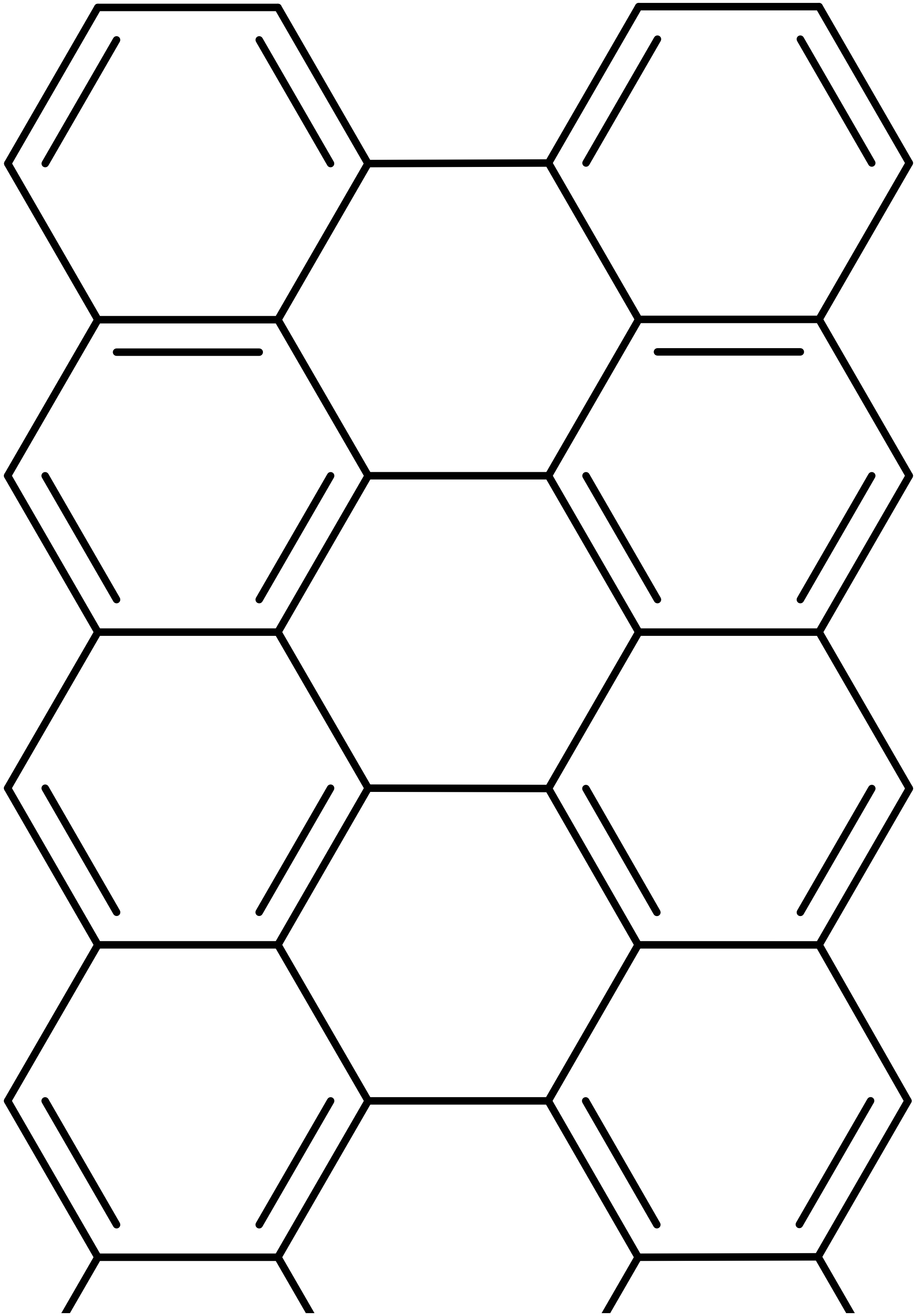




Graphite oxide reduction



"Improved" GONR (IGONR) Formation



Key step: *in situ* protection of vicinal diols by a second, weaker acid

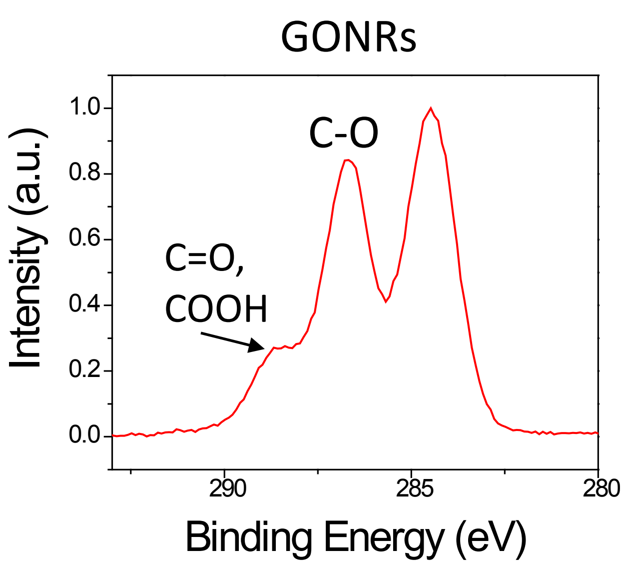
D. Kosynkin
A. Higginbotham

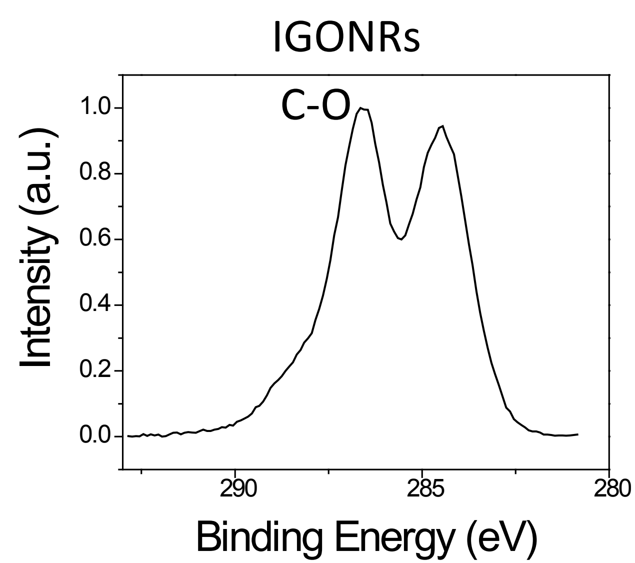
IGONR Properties

- Fewer defects/holes on basal plane
- Maintains narrow ribbons < 100 nm wide
- Maximizes ribbon aspect ratio
- 20% more oxygen-containing functional groups
  - Highly water soluble
  - Handles for further functionalization or polymerization
  - Larger proportion of oxygen present as –OH and fewer -C=O, -COOH
- Better quality ribbons upon chemical reduction of XGONRs
  - Higher conductivity measures
  - Less distortion of atomic lattice
  - Likely improved tensile strength (to be tested)

XPS C1s spectra:

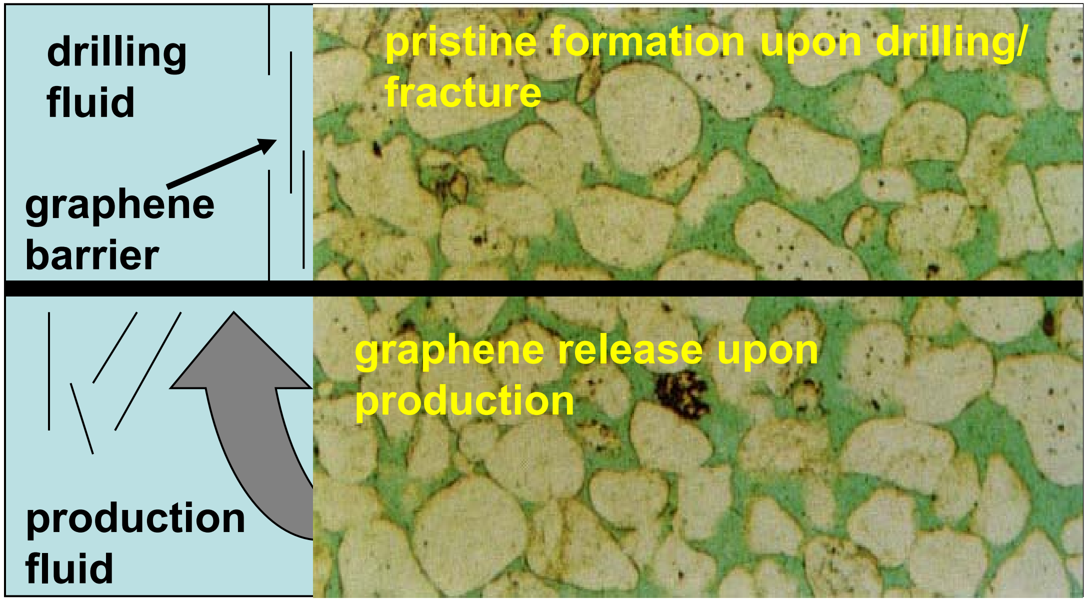
decreased intensity of -C=O, -COOH shoulder





D. Kosynkin
A. Higginbotham

Graphite Oxide for Drilling Fluids: Nanosheet Filtering Agents



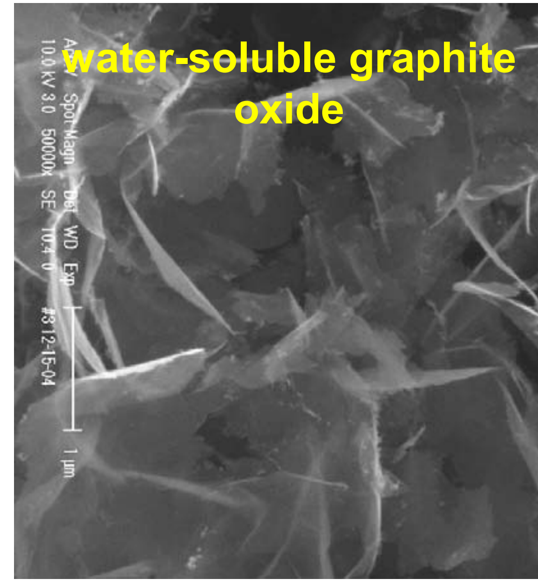


Table 1. API test results of GO solutions

Solution	Filtrate Volume (mL) (95% confidence)	Final Filtration Rate (mL/min)	Cake Thickness (mm)
2 g/L GO (75:25 mix)	10.8 ± 0.7	0.20	0.016
4 g/L GO (75:25 mix)	6.1 ± 0.5	0.10	0.021
SWACO Formula with PolyPAC UL	7.2 ± 0.4	0.14	0.255

Carbon Nanotubes and Graphene– Enhancing the Nuclear Program

Open to partnerships

James M. Tour

tour@rice.edu

www.jmtour.com


Acknowledgements: ARO, AFOSR, ONR, MI-SWACO, Alliance for NanoHealth-UTHSC, DoD-Army Medical Command, NSF, NASA, Navy Space and Naval Warfare Systems Command, NSF-CBEN, PrivaTran LLC, Mitsui Corp., Bayer Corp., Advanced Energy Consortium (BakerHughes, BP, ConocoPhillips, Halliburton, Marathon, OXY, Petrobras, Schlumberger, Shell, and TOTAL)
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