About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

About OMICS Group Conferences

OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Scalable Production of Highly Sensitive Nanosensors Based on Graphene Functionalized with a Designed G Protein-Coupled Receptor

Dr. Mitchell Lerner

SPAWAR Systems Center Pacific – US Navy

Materials Science 2014

San Antonio, TX

Email: mitchell.lerner@navy.mil

Motivation

Nanomaterials research is attracting international attention:

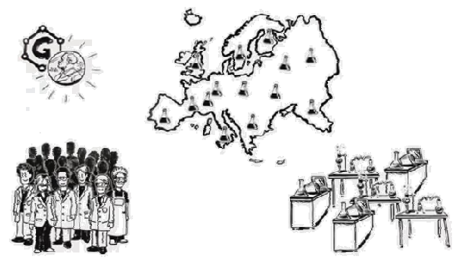
US DoD

Totals $15M/year, graphene research is near 1% of DoD annual basic research budget

- DARPA CERA Program, $30M
- 2 Air Force MURIs, $15M
- 3 Navy MURIs, $22M
- Army MURI, $8M

US holds 40% of graphene-related patents, trailing Asia (45%)

Patent landscape is rapidly shifting towards Asia



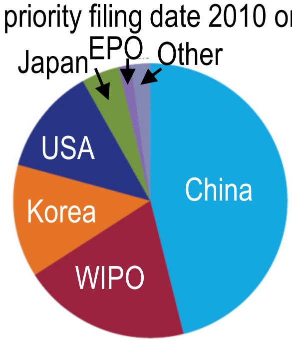
Europe – Graphene Flagship

Initiating biggest research initiative ever to increase graphene IP stake (12%)

→ **€1B ($1.38B) over 10 years**

Earliest priority filing date 2009 or earlier

Earliest priority filing date 2010 or later



Asia

China and Korea are rapidly becoming the pacesetters in terms of graphene manufacturing, packaging and integration.

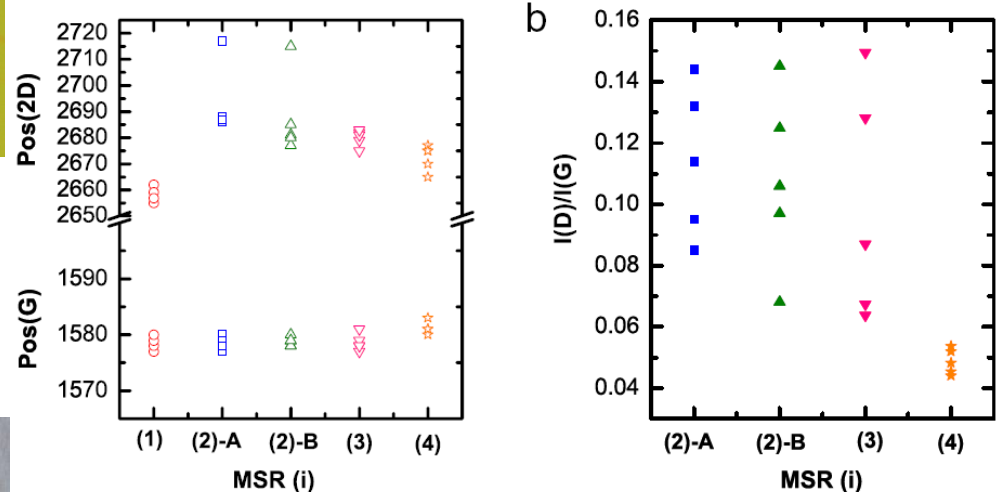
Basic research publications by China outnumber US 3:2

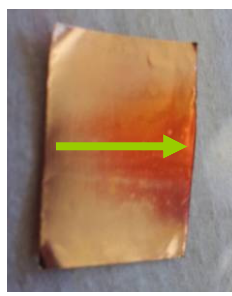
Motivation

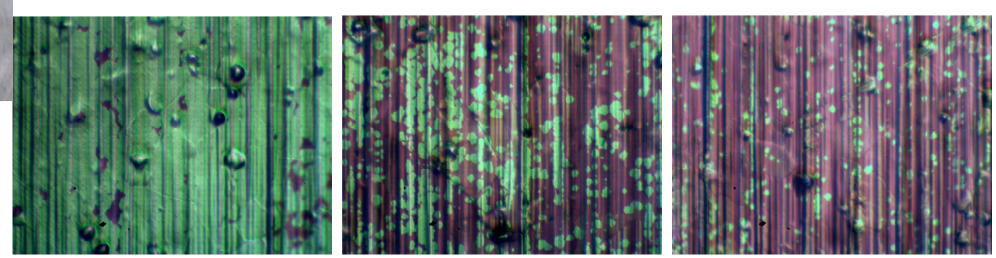
Are we maximizing our return on investment?

- **Devices fall short of theoretical performance limits** because of contamination issues
- There exists variation across a single sample and batch to batch variation
- Reproducibility and reliability are necessary for viable manufacturing process

Fan et al., Solid State Communications (2011)

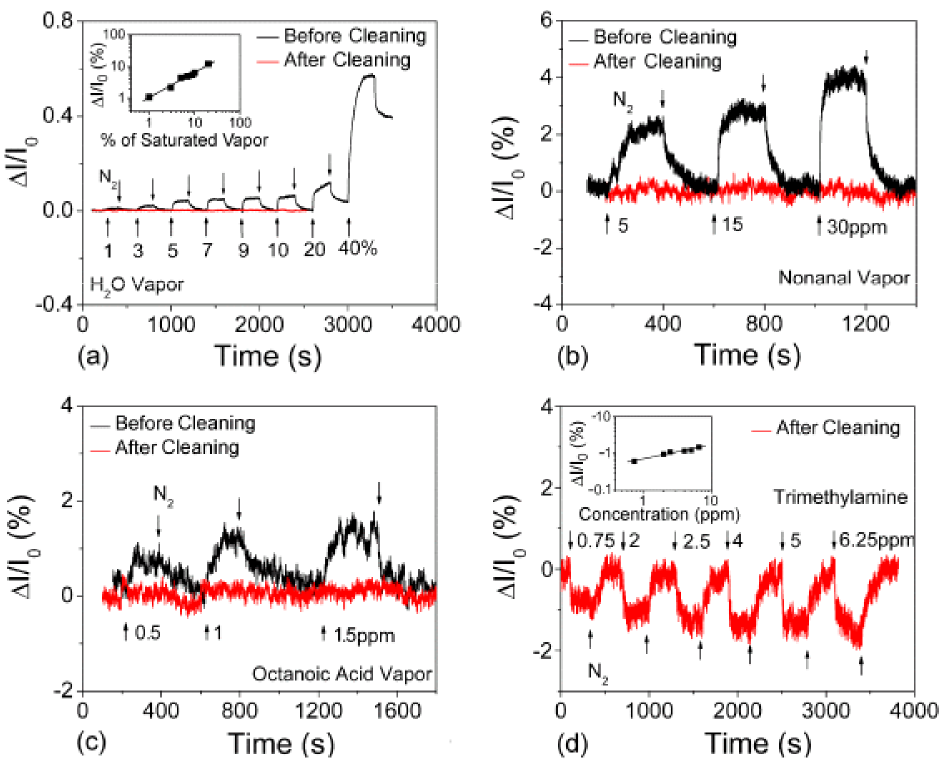




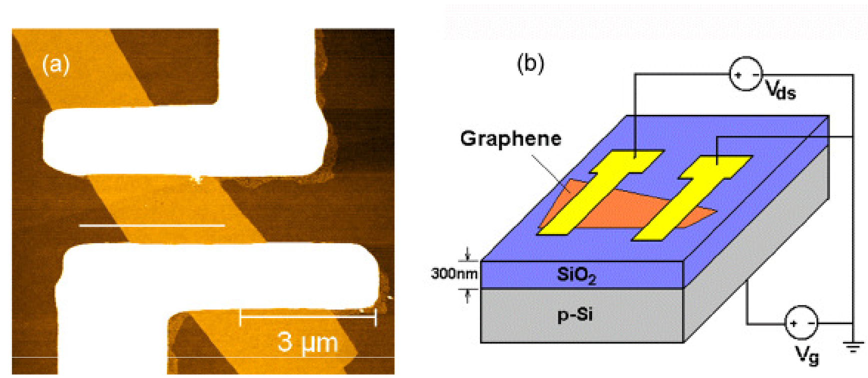


Motivation

Variability can have a dramatic impact on device properties

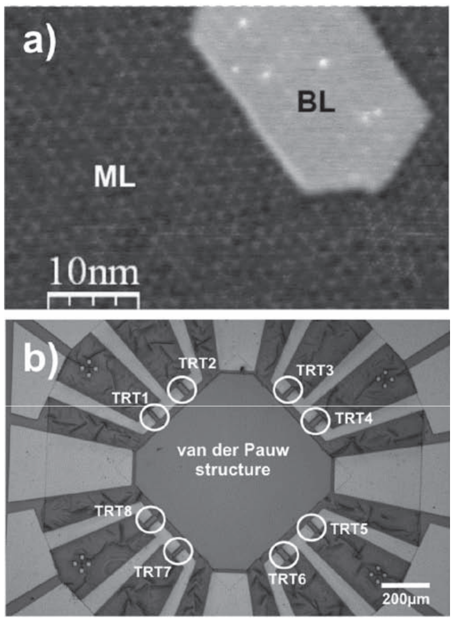


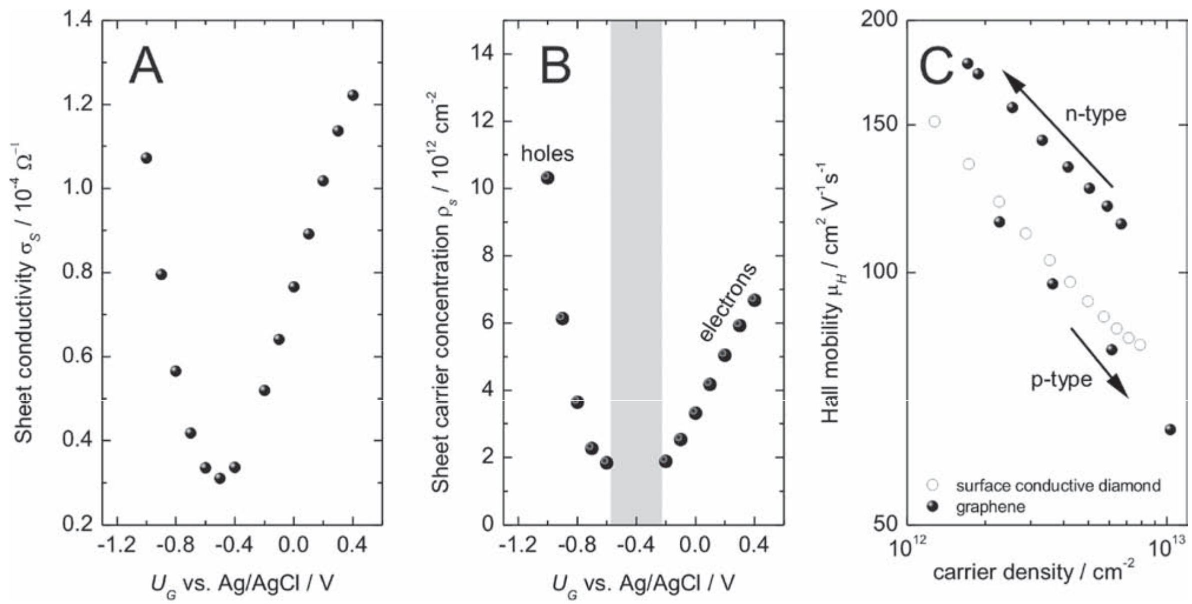
Dan et al., Nano Letters (2009)



- As an example, graphene devices used in chemical sensing applications demonstrate a **false response from resist residue**
- Clean devices do not sense well, and intentionally functionalized devices function more reliably

Towards Large Scale Device Manufacturing



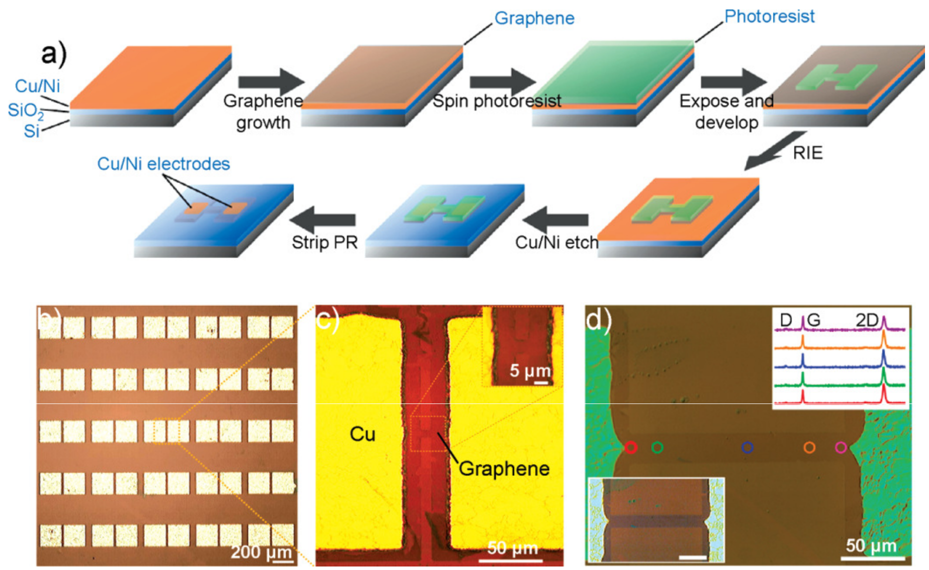


Dankerl et al., Advanced Functional Materials (2010)

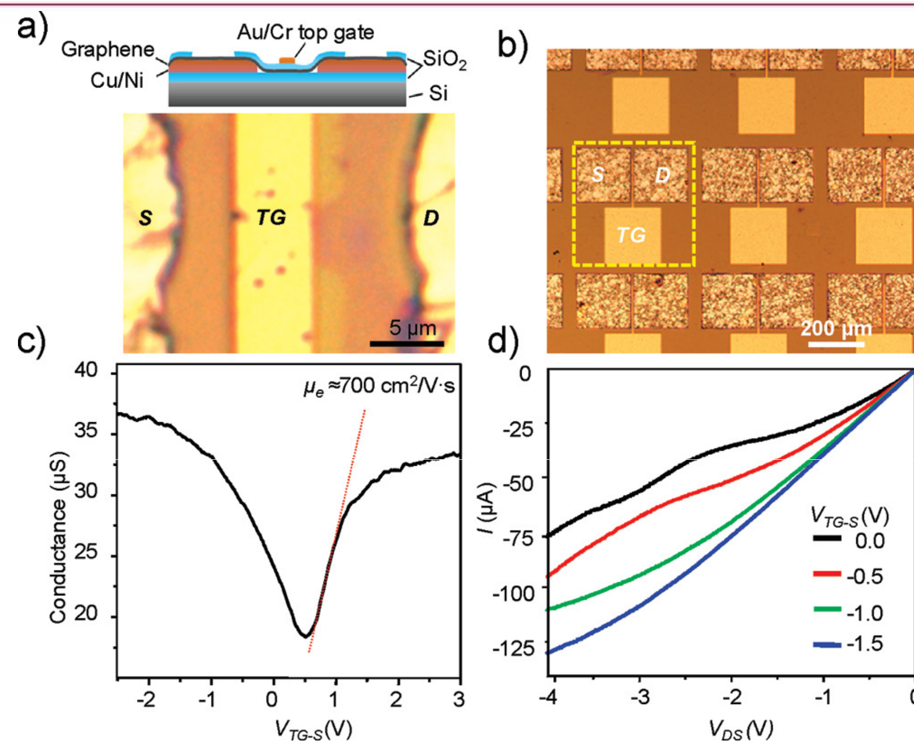
Epitaxial graphene, solution gated, mobility ~ 100-200 $cm^2\ V^{-1}\ s^{-1}$

- Only a handful of examples exist in the literature reporting large scale (hundreds or greater) arrays of graphene electronic devices.
- Success in maintaining the native graphene quality is limited.

Towards Large Scale Device Manufacturing



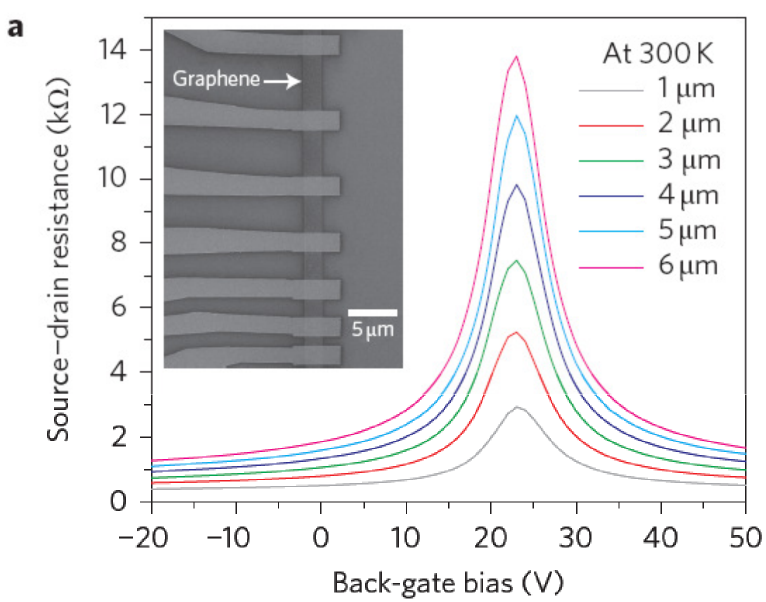
Levendorf et al., Nano Letters (2009)

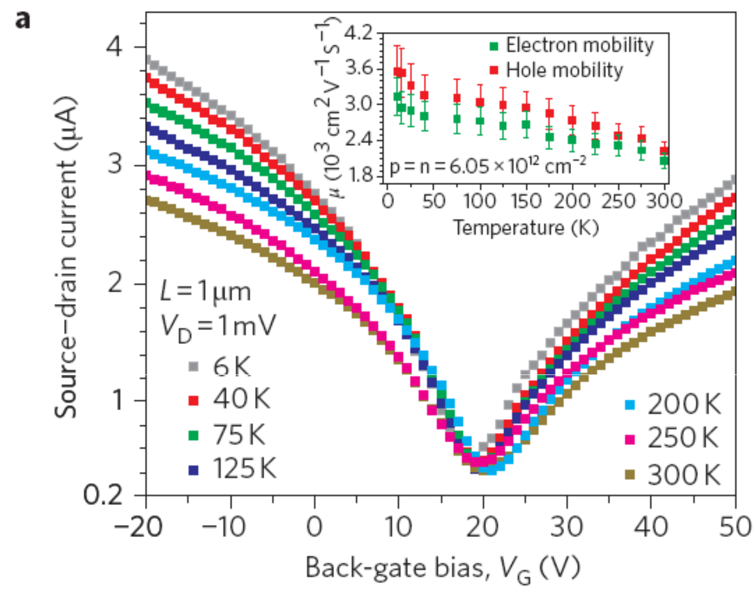


CVD graphene, back gated, mobility ~ 700 $cm^2 V^{-1} s^{-1}$

- Only a handful of examples exist in the literature reporting large scale (hundreds or greater) arrays of graphene electronic devices.
- Success in maintaining the native graphene quality is limited.

Towards Large Scale Device Manufacturing





Xia et al., Nature Nanotechnology (2011)

Exfoliated graphene, back gated, mobility ~ 2000 cm^2 V^{-1} s^{-1}

- Only a handful of examples exist in the literature reporting large scale (hundreds or greater) arrays of graphene electronic devices.
- Success in maintaining the native graphene quality is limited.

Motivation: Better Diagnostics

- Clinical immunoassays have limitations:
  1) Costly
  2) Significant processing time
  3) Specific for a particular analyte

- Environmental Monitoring sensors are inflexible
  - One sensor, one analyte
- Best sensor available is not technologically matched

PSA ELISA kit

Chemical Detection Platform: NanoCarbon Transistors

Goal: Develop a modular chemical detection platform adaptable to any vapor or liquid target with high sensitivity and selectivity

NanoCarbon Platform:

Transistor devices based on carbon nanotubes and graphene can be fabricated into large arrays and then functionalized with biochemical agents for tailored detection of molecules of interest.

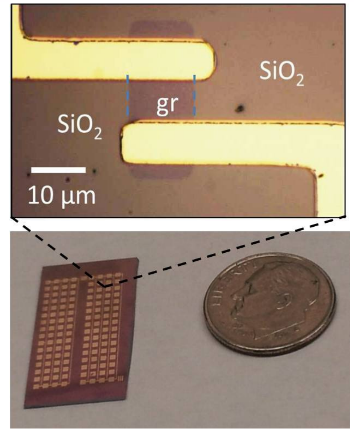
Scalable: 100 sensors on a dime

Modular: Generic chemistry can be easily modified to detect any molecule

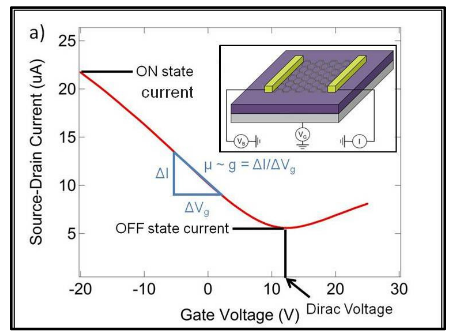
Low cost: Materials cost <$0.10 per sensor

Rapid detection: Minutes

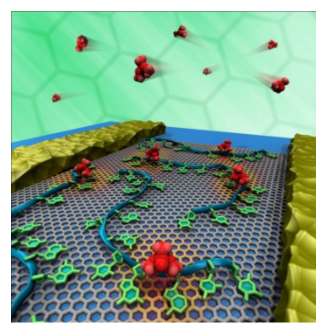
Robust to possible interfering compounds



Sensor Fabrication: High yield process (>98%) for making large arrays of transistors at a small size scale [1]



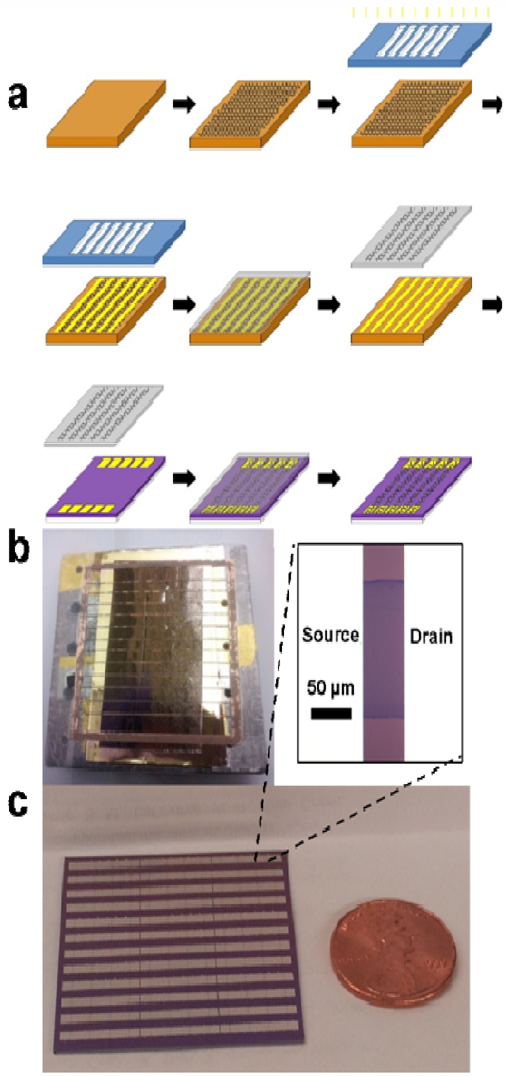
Sensor Operation: Electrical characterization of the devices produces several parameters for chemical detection, hence a multidimensional feature vector [2]



Sensor Functionalization: Transistors are chemically modified to detect molecules of interest [3]

[1] Kybert, **Lerner**, et al. *ACS Nano* (2013) [2] **Lerner** et al. *AIP Advances* (2011) [3] Lu, **Lerner** et al. *Applied Physics Letters* (2011)

Device Fabrication



Graphene field effect transistor (GFET) fabrication process:

- Graphene patterned by conventional lithography is contaminated by resist residue
- Need a method to **pattern graphene during transfer**
- Gold is evaporated onto the graphene using a shadow mask
- Gold/Cu foil covered in PMMA
- PMMA removed by bubble transfer technique

→ Uncovered graphene is removed preferentially

- Graphene strips are transferred to Pd electrodes
- **Yield is >99%**

[1]Lerner et al., Nano Letters (2014)

Device Fabrication

GRAPHENE TRANSFER

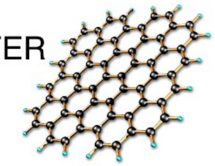


Figure .1

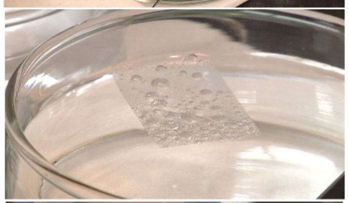


Figure .2

Figure .3

Figure .4

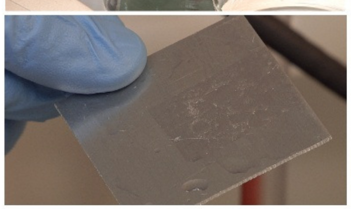


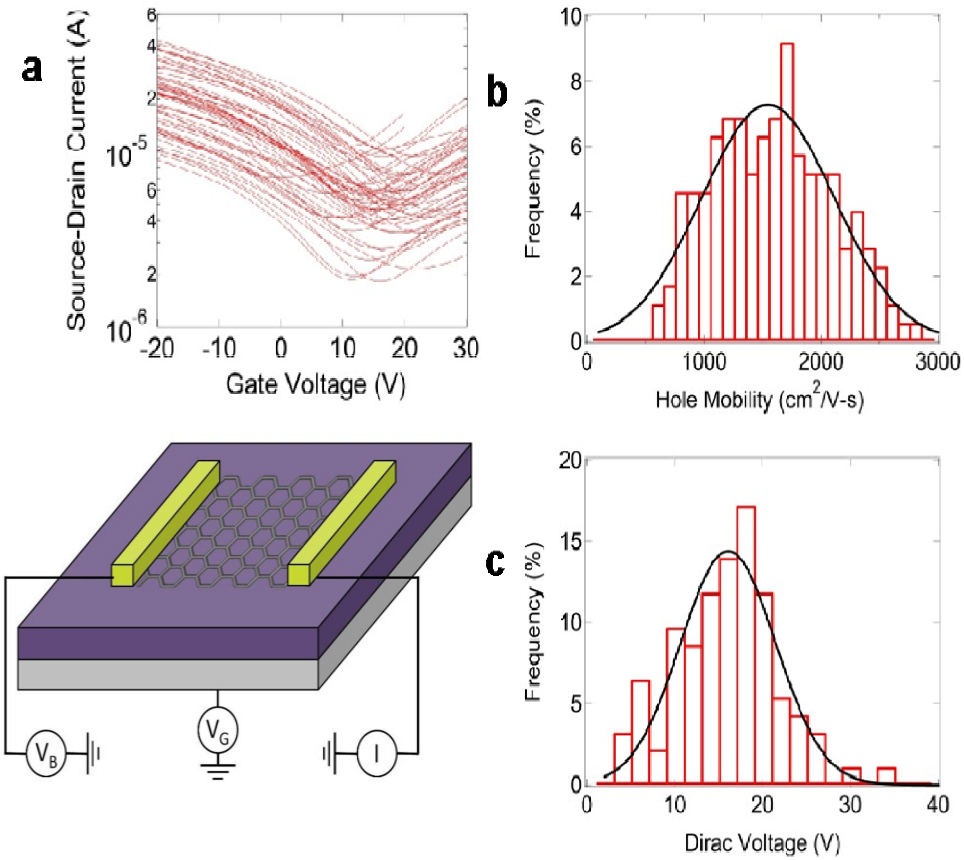
Figure .5

Bubble transfer:

- Cu/Graphene/PMMA stack is lowered into a solution of NaOH
- There is a potential difference maintained between the copper foil and the solution
- Electrochemically drives the formation of hydrogen and oxygen bubbles at the electrodes
- **Bubbles gently lift graphene/PMMA from the copper**

Gao et al., Nature Communications (2012)

Electrical Characterization of Transistor Array



Performance characteristics of GFETs:

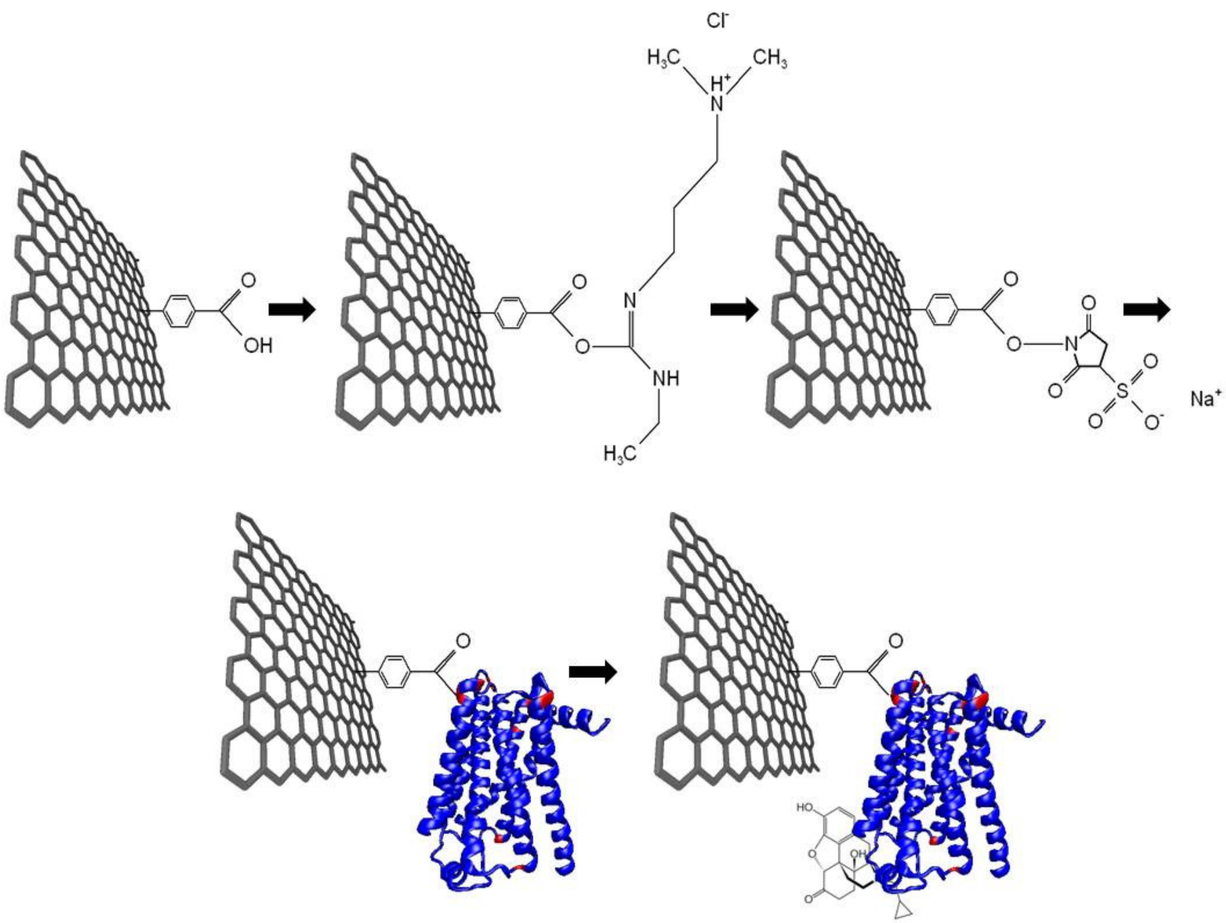
a) Representative set of 50 highly uniform I-V_g curves along with graphene FET schematic

b) Histogram of GFET mobility
   - **Average at 1500 $cm^2 V^{-1} s^{-1}$**

c) Histogram of GFET Dirac Voltage
   - **Average at 15 V**

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Opioid Functionalization

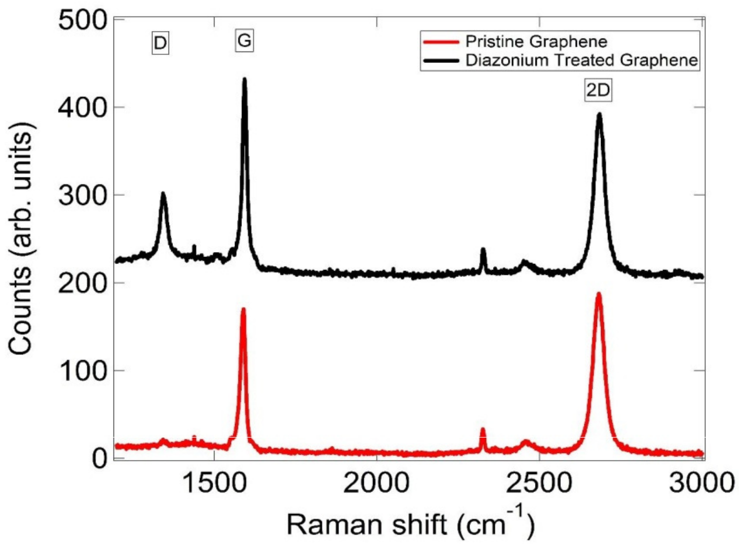


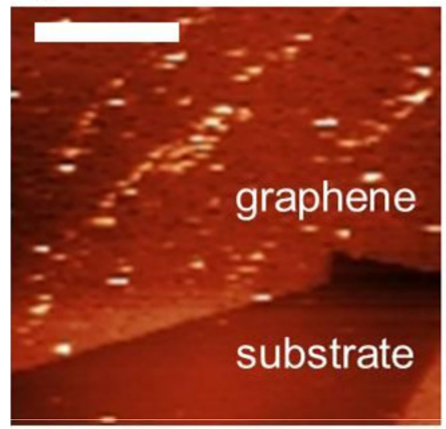
Tailored chemical detection of opioids:

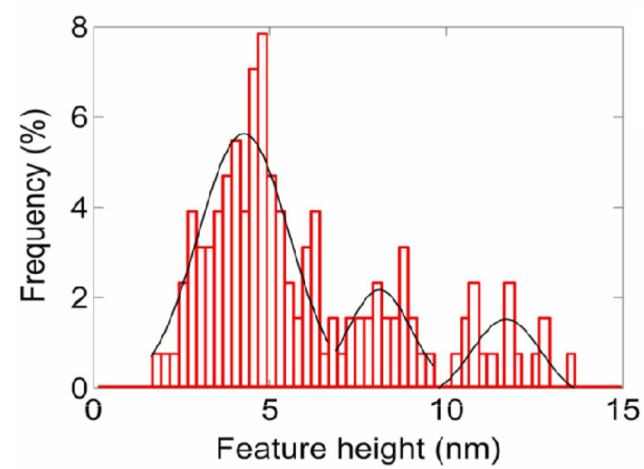
a) Diazonium-based approach to chemical functionalization
b) Activation and stabilization with EDC/sNHS
c) Mu opioid receptor (GPCR) displaces sNHS at lysine residues
d) Mu receptor binds target naltrexone

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Opioid Functionalization







Characterization by Raman spectroscopy and Atomic Force Microscopy:

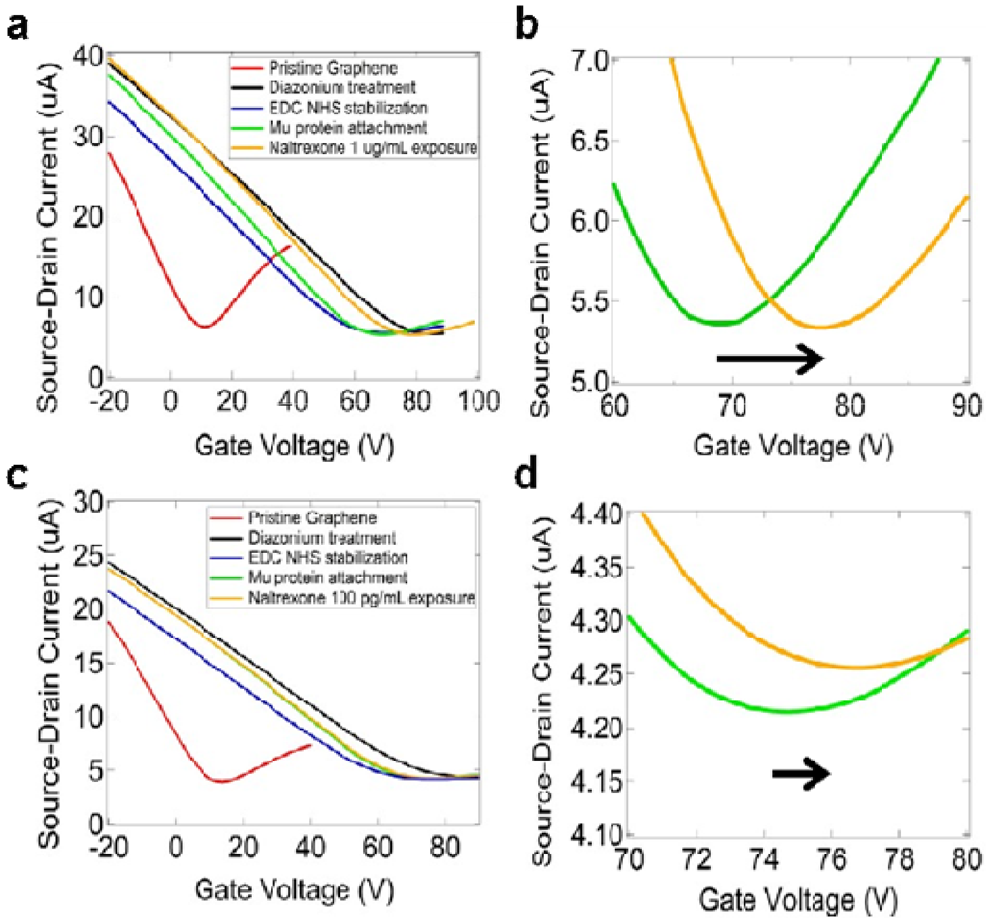
- Raman spectra show strongly enhanced D-band (near 1360 cm^{-1}) after diazonium treatment
- Indicates the **formation of sp^3 hybridized carbon-carbon bonds** on the graphene surface.

AFM image of mu receptors decorating the graphene surface

Histogram of the heights of proteins indicates that the 46 kDa mu receptor **monomer is ~4 nm tall on the surface**, with dimers and trimers of 8 nm and 12 nm respectively.

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Opioid Functionalization

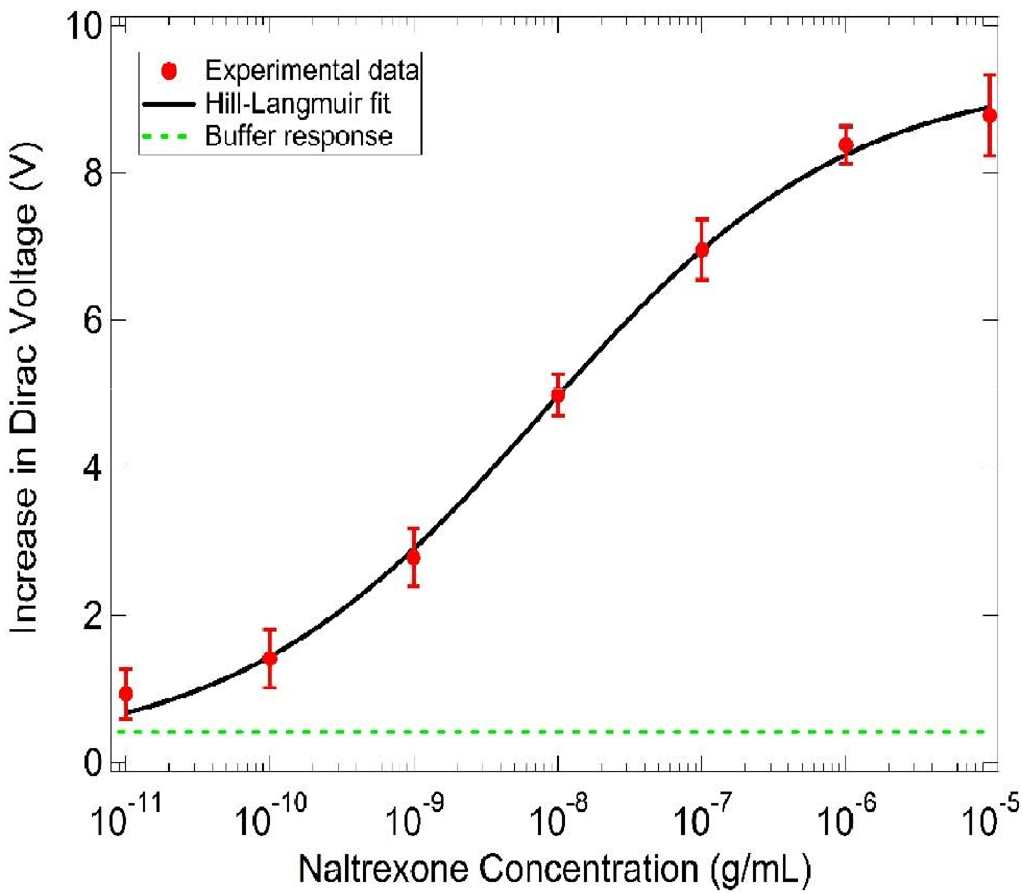


Current-gate voltage (I-V_G) characteristic measurements:

a) I-V_G plots after successive functionalization steps at 1µg/mL naltrexone
b) Naltrexone in buffer leads to an **increase in the Dirac voltage** of 8.5 V (green curve to orange curve).
c) I-V_G plots after successive functionalization steps at 100 pg/mL naltrexone
d) Naltrexone in buffer leads to an increase in the Dirac voltage of 1.8 V (green curve to orange curve).

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Opioid Functionalization



$$f(C) = A\frac{C^n}{{K_d}^n + C^n} + Z$$

Sensor response (increase in Dirac voltage) shows **discernable signal from the bare buffer response at 10 pg/mL naltrexone**.

The data are well explained by a modified Hill-Langmuir equation (black curve).

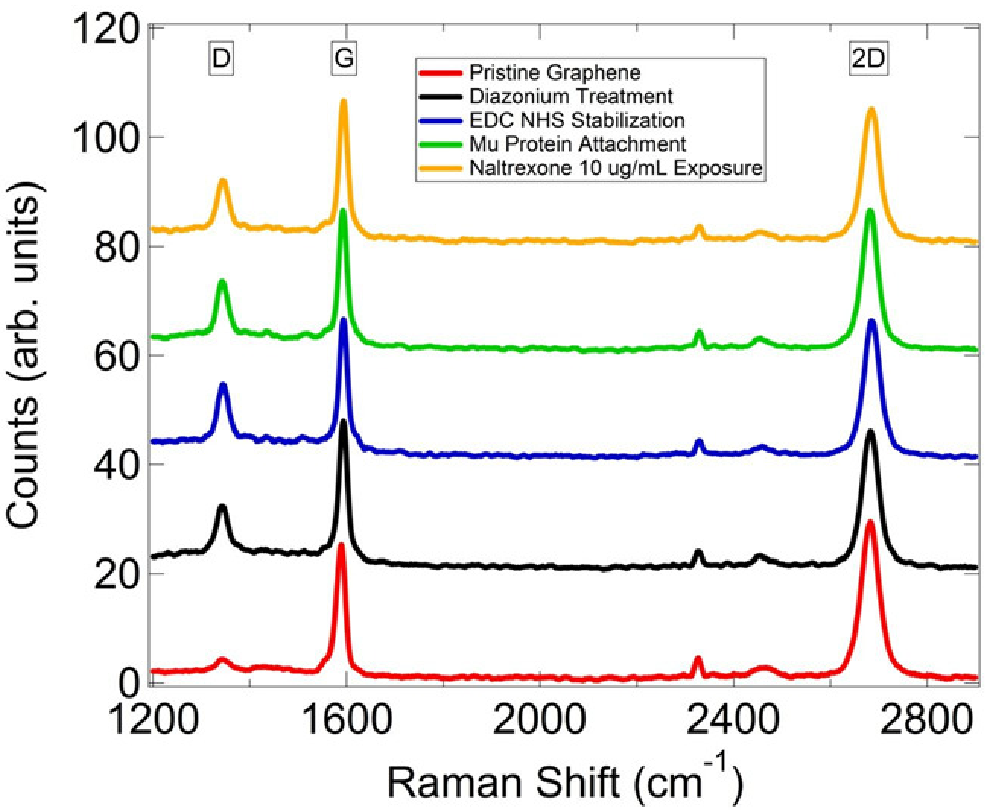
[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Opioid Functionalization

Sample	Analyte	Average Dirac Voltage Shift (V)
MUR-GFET	Buffer with no Naltrexone	0.04 ± 0.38
MUR-GFET	Flumazenil at 10 µg/mL	-0.23 ± 0.43
MUR omitted	Naltrexone at 10 µg/mL	-0.25 ± 0.35
anti-HER2 scfv-GFET	Naltrexone at 10 µg/mL	-0.31 ± 0.48
MUR-GFET	Naltrexone at 10 µg/mL	8.78 ± 0.55

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Raman Readout



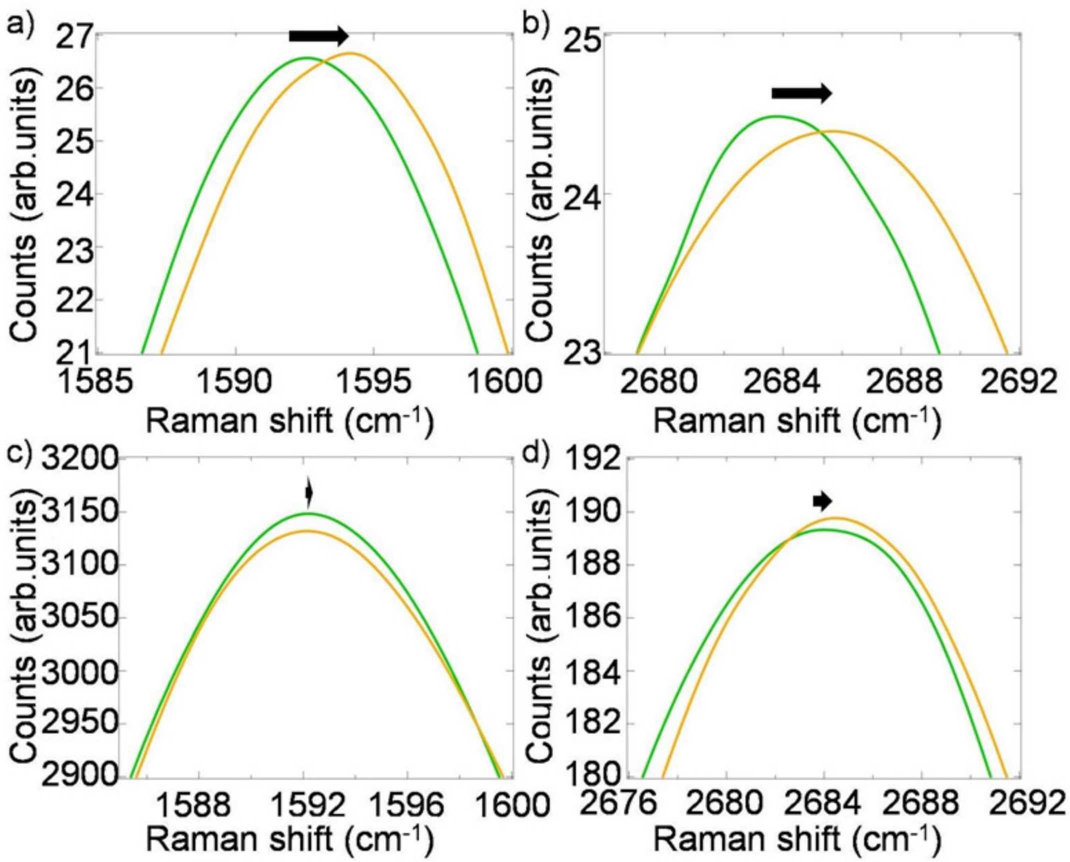
Raman spectra during functionalization steps:

1) D/G ratio increased after diazonium treatment and 2D/G ratio decreased from 1.5 to 0.95
2) Little change between diazonium treatment and mu protein attachment

Upon exposure to Naltrexone, there were **significant shifts in the G-peak and 2D peak positions** which were concentration dependent

[1]Lerner et al., Nano Letters (2014)

Chemical Detection Platform: Raman Readout



a) **Mu-functionalized device showing Raman G peak shift** of ~1.5 cm^{-1} before (green) and after (orange) Naltrexone exposure at 10 µg/mL.

b) **2D peak position shift of ~2 cm^{-1}** for same device

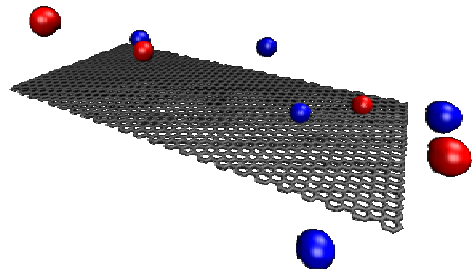
c) For device exposed to pure buffer, G peak does not appreciably shift

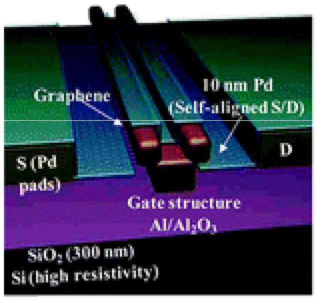
d) 2D peak position is only slightly affected by buffer exposure, shifting only 0.5 cm^{-1} for this device.

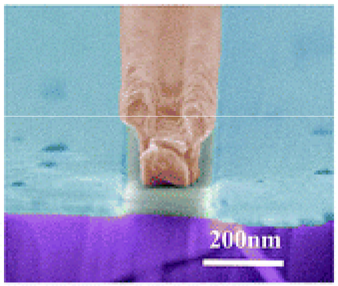
[1]Lerner et al., Nano Letters (2014)

Conclusions

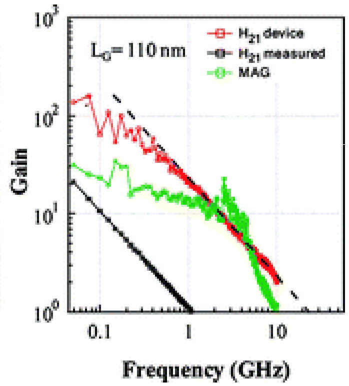
- Many publications cite contamination as an issue in production of lithographically defined graphene devices
- Performance of complex device architectures suffer
- Better understanding of the contamination mechanism and alternative fabrication procedures are needed to have graphene devices realize their ultimate potential.

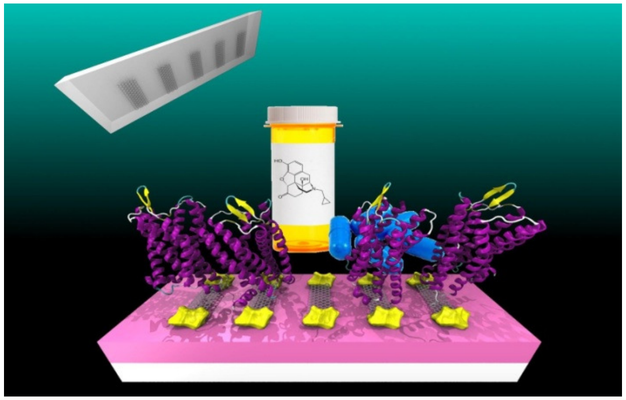






Badmaev et al., ACS Nano (2012)





SPAWAR Systems Center PACIFIC

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SMART Science, Mathematics & Research for Transformation
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Department of the Navy ONR Science & Technology

NBIC Nano / Bio Interface Center

CDMRP Department of Defense

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