Growth of Two Dimensional Materials – Applications in Energy and Sensing

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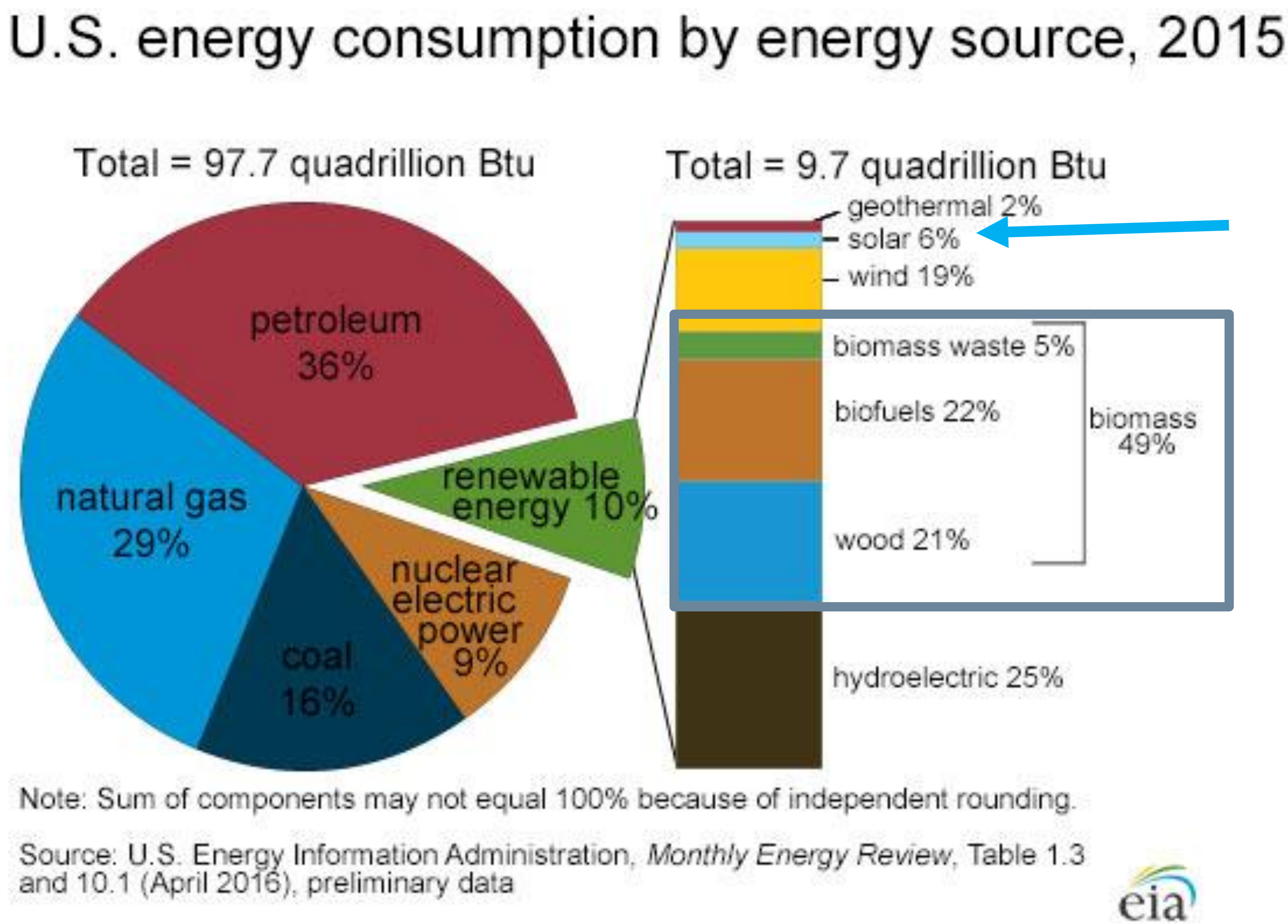
Overview

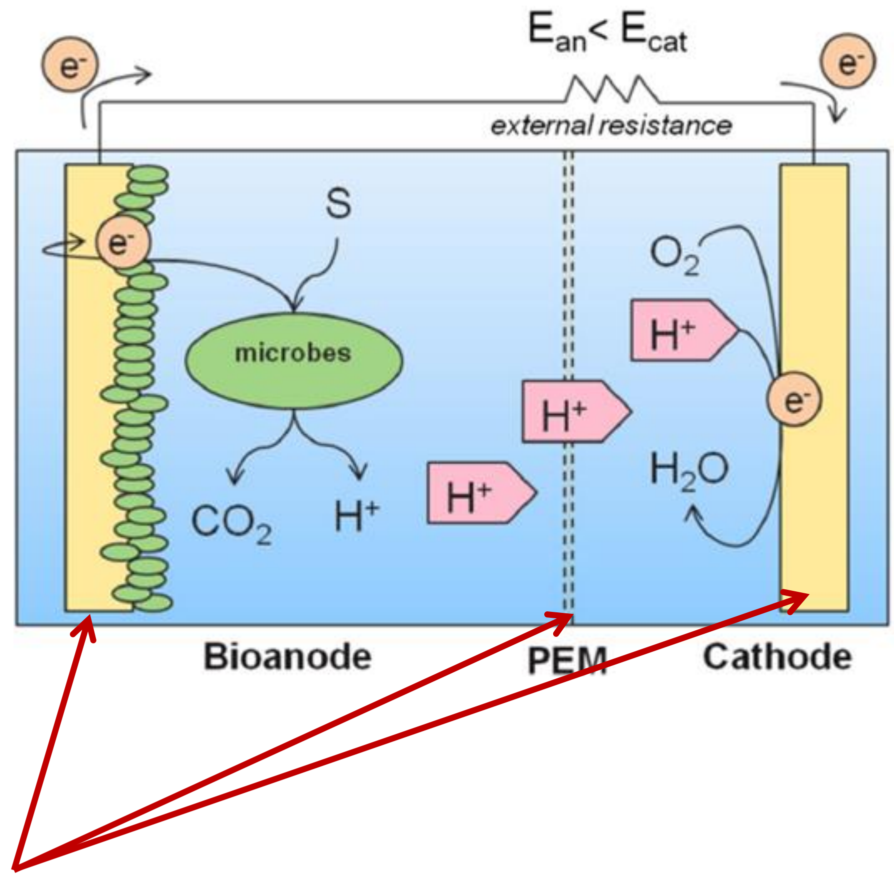
- **Section 1: Motivation**
- **Section 2: Quasi-freestanding Epitaxial Graphene via Hydrogen**
  - Section 2a: Narrow THz Plasmon Resonance
- **Section 3: Biocompatibility of Epitaxial Graphene**
  - Section 3a: Label Free Potentiometric Sensor
- **Section 4: Future Work**
  - Section 4a: Cellular Redux Potentials
  - Section 4b: Exploration of other 2D Materials
  - Section 4b: Growth of TMDs and TMOs
  - Section 4c: Intercalation of van der Waals Materials
  - Section 4d: van der Waals Heterostructures

Motivation


U.S. energy consumption by energy source, 2015
Total = 97.7 quadrillion Btu
Total = 9.7 quadrillion Btu
petroleum 36%
natural gas 29%
coal 16%
nuclear electric power 9%
renewable energy 10%
geothermal 2%
solar 6%
wind 19%
biomass waste 5%
biofuels 22%
wood 21%
biomass 49%
hydroelectric 25%
Note: Sum of components may not equal 100% because of independent rounding.
Source: U.S. Energy Information Administration, *Monthly Energy Review*, Table 1.3 and 10.1 (April 2016), preliminary data
eia

Microbial Fuel Cells

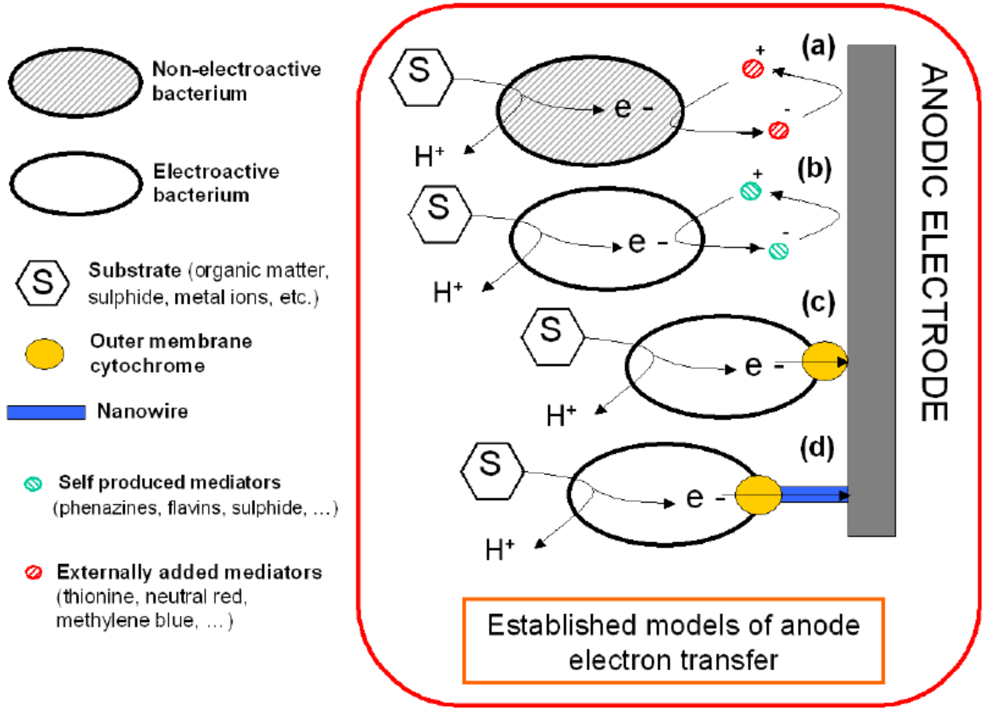
- Energy efficient
  - >90 conversion from biomass (30% for combustion)
- Zero net carbon emission
- Waste remediation
- Electricity generated by bacteria metabolic process

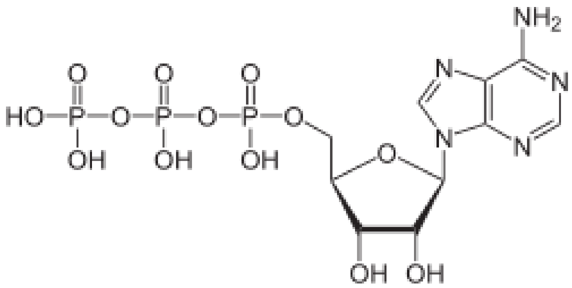


Low power density due to electrodes

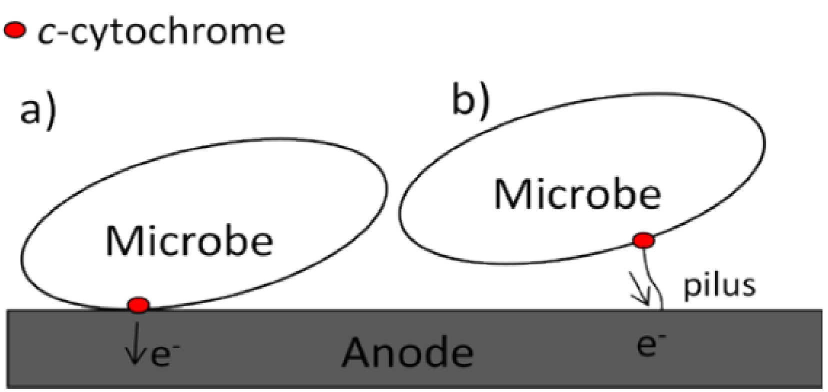
A. ElMekawy et. al; Bioresource Technology 142, 672-682 (2013)

Electron Transfer of Bacteria

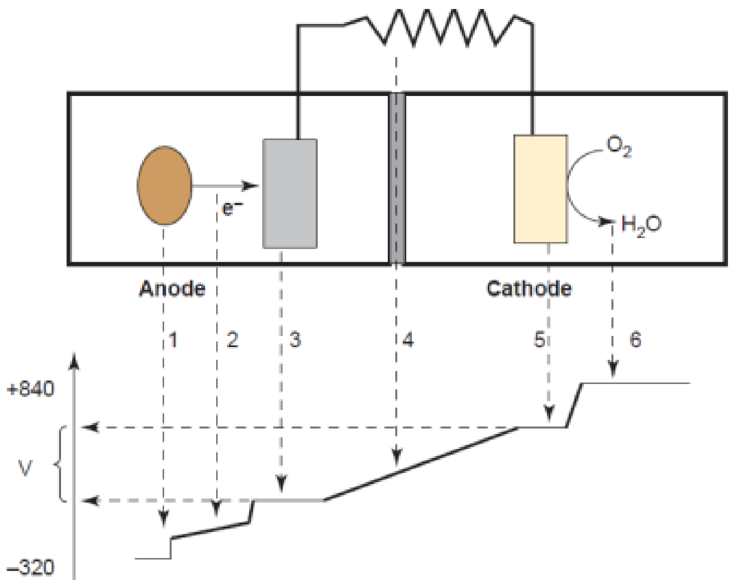




Adenosine triphosphate (ATP)



Electrodes



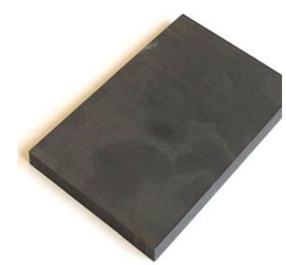
1. Losses in bacteria electron transfer.
2. Losses in solution resistance.
3. Losses at anode.
4. Losses at proton exchange membrane.
5. Losses at cathode.
6. Losses at electron reduction.

Losses ∝ ↑ Resistance

$$P = \frac{V_{OC}^2}{R} \qquad R \propto \frac{1}{A_{ELECTRODE}}$$

Low surface area of the electrodes

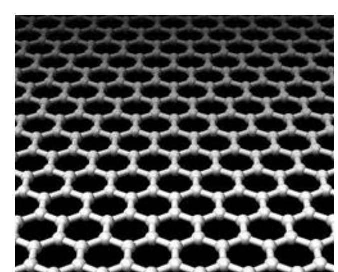
= Poor bacterial adhesion and low power density



High Surface Area ► Two-Dimensional Materials

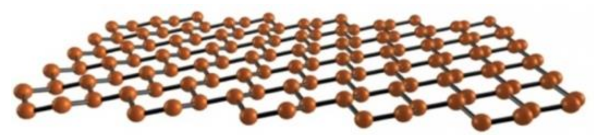
↓ electrode distance and internal resistance

↑ bacterial adhesion and charge transfer.

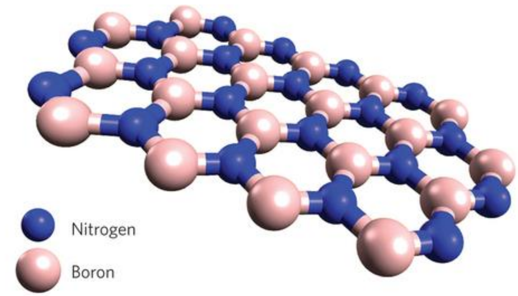


2D Materials

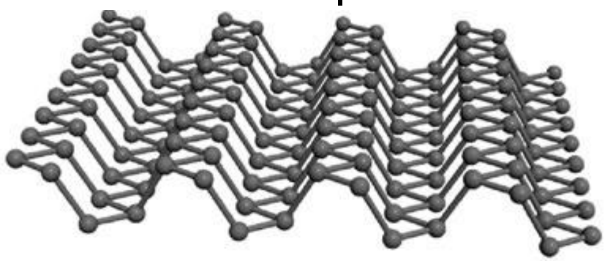
Silicene



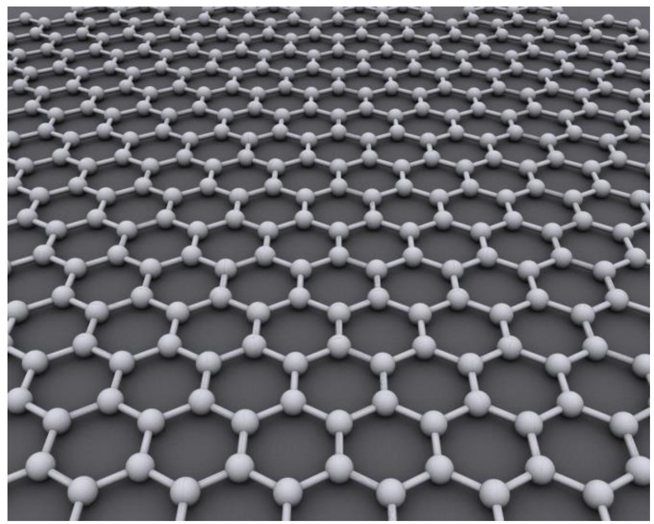
h-BN



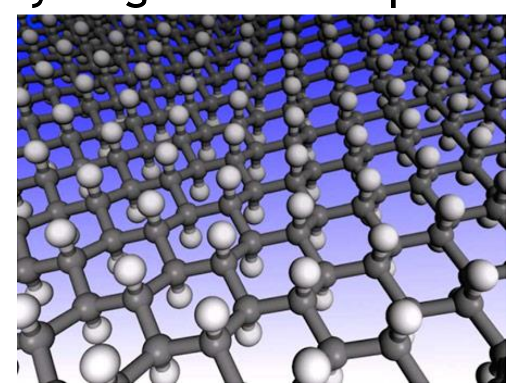
Black Phosphorous



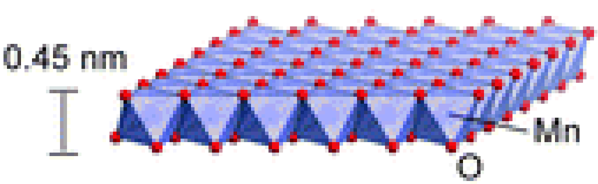
Graphene



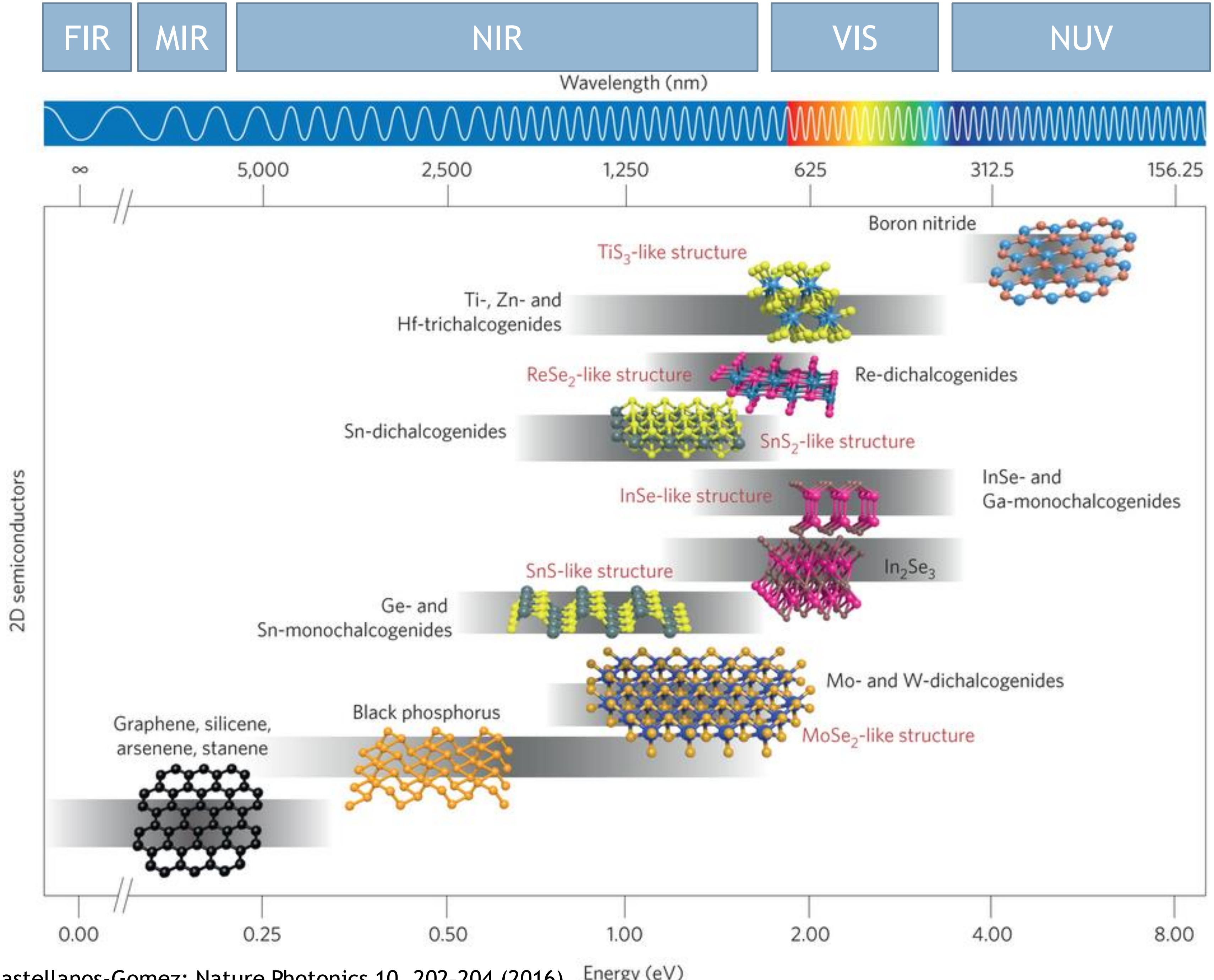
Hydrogenated Graphene



MnO_2

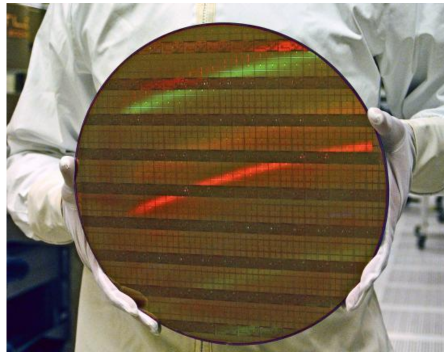


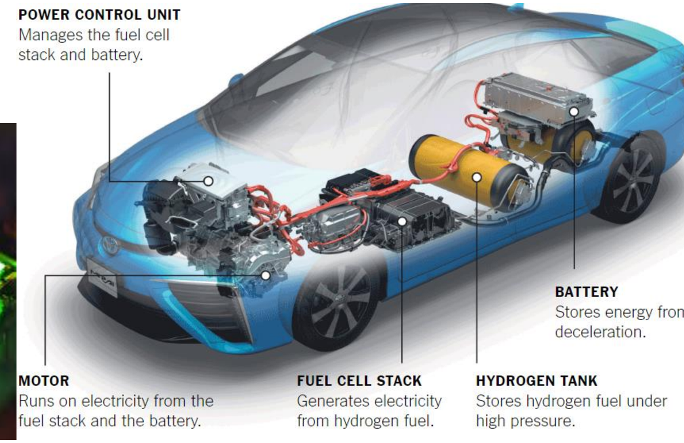
MoS_2

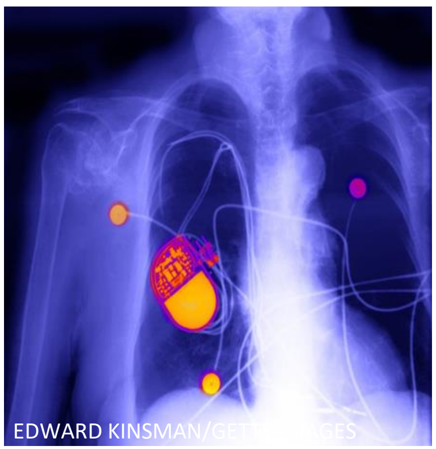


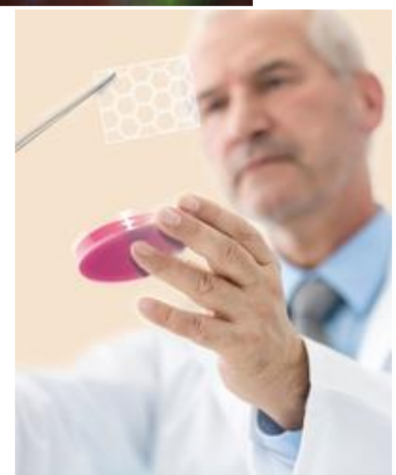
A. Castellanos-Gomez; Nature Photonics 10, 202–204 (2016)

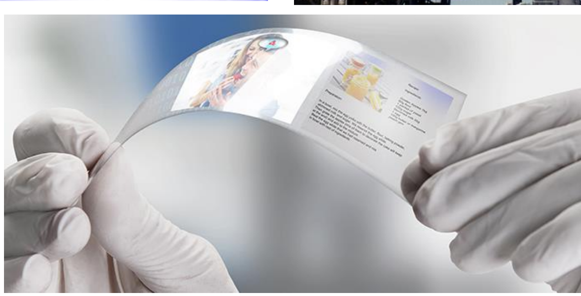
Why 2D Materials

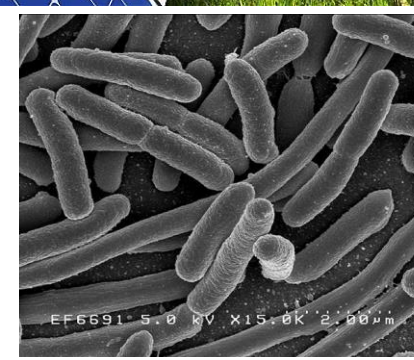








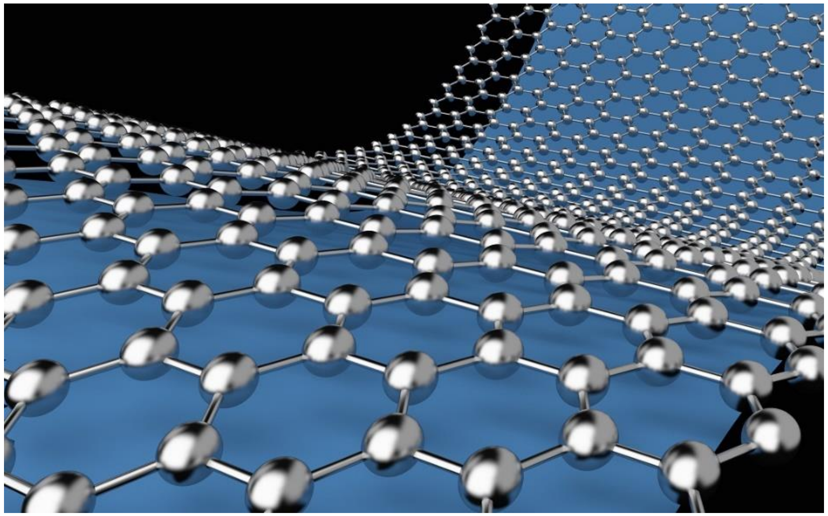




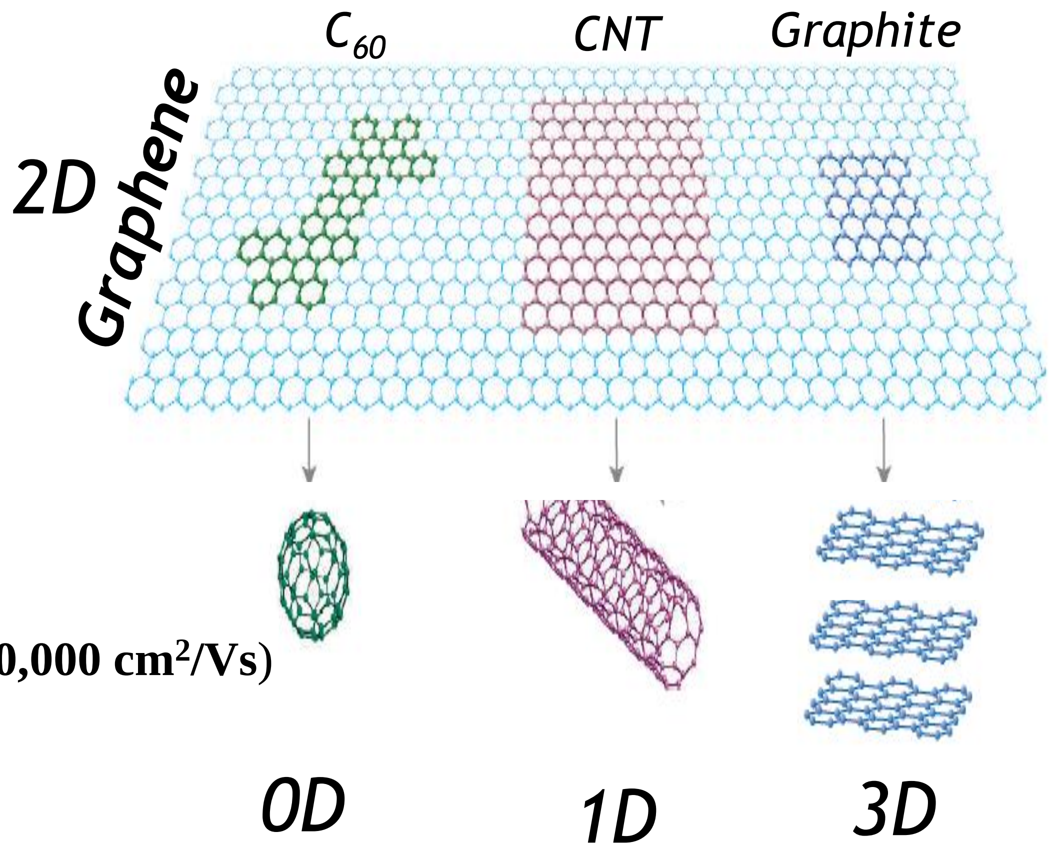
Make up for deficiencies in existing technology

10 Growth of Epitaxial Graphene

The First 2D Material-Graphene



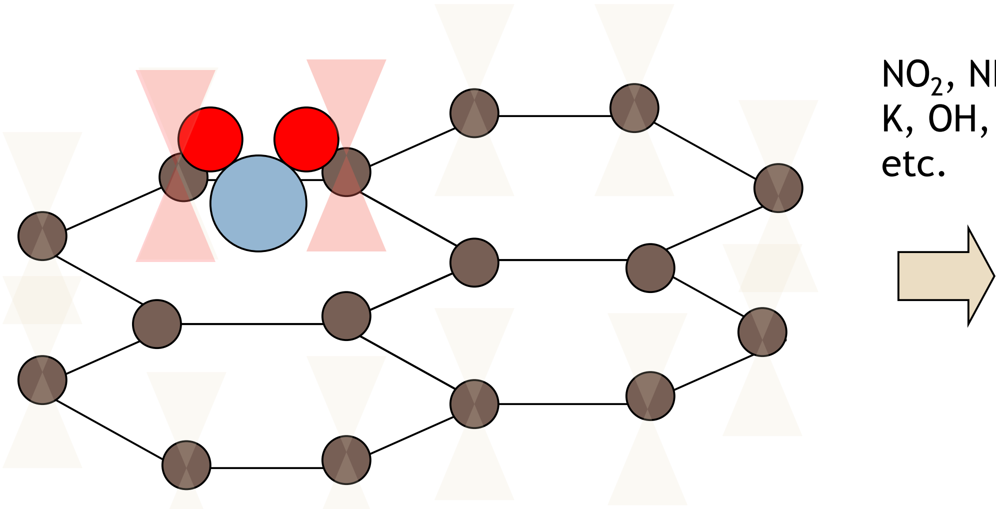
An atom thick (1.7A)

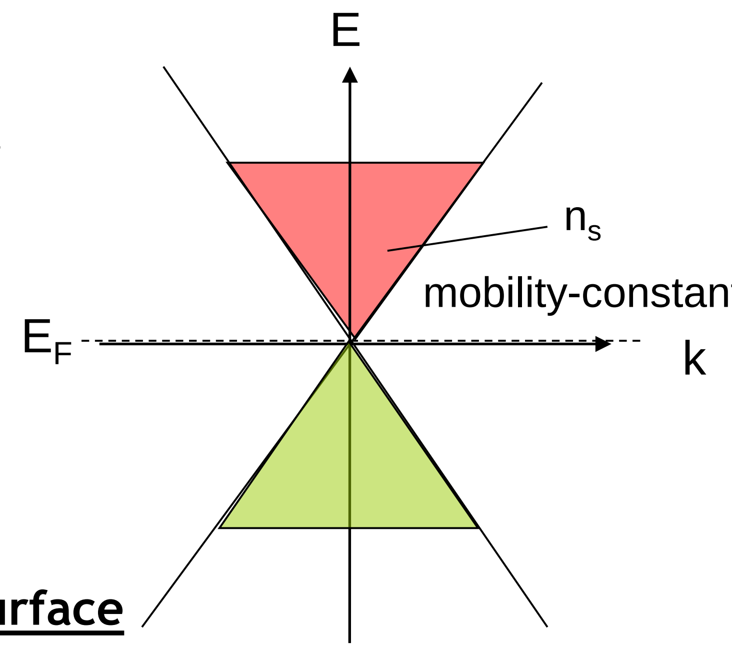


- Exceptional Properties
  - High Electrical Conductivity
  - High Room Temperature Mobility (**100,000 cm²/Vs**)
  - High Surface Area (**2630 m²**/g)
  - High Current Capacity
  - Quasi-ballistic Transport
  - Low Noise

- Graphite
  - Poor Surface Area
- Carbon Nanotubes
  - Toxic to Bacteria

Physisorption on Graphene



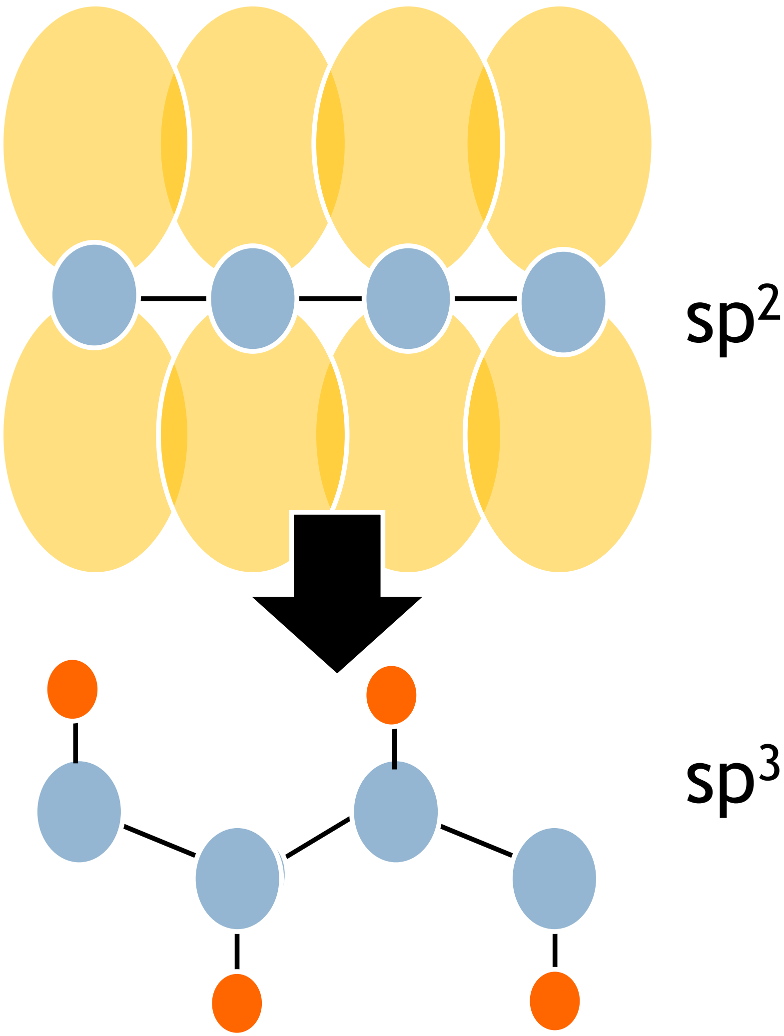


<u>**Entire volume exposed to surface**</u>

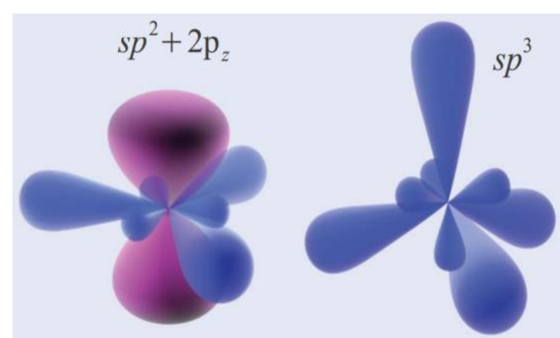
- Weakly attached molecules act as donors/acceptors
  - van der Waals force ($E_{ads} \leq 100\ \text{meV}$)
- Changes in carrier concentrations
- Remains highly conductive

F. Schedin et. al., Nature Mat. 6, 652-655 (2007)
B. K. Daas, W. K. Nomani, K. M. Daniels, T. S. Sudarshan, G. Koley and MVS Chandrashekhar., Mater. Sci. Vol. 717-720 665-668 (2012)

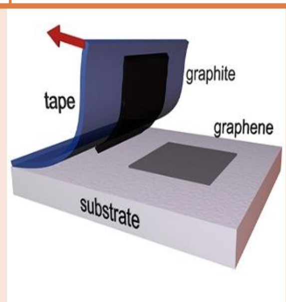
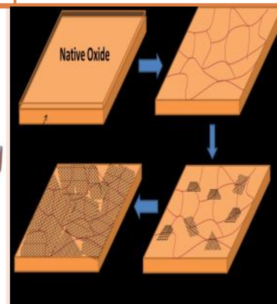
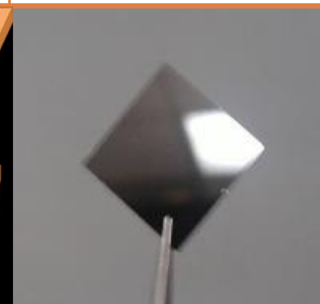
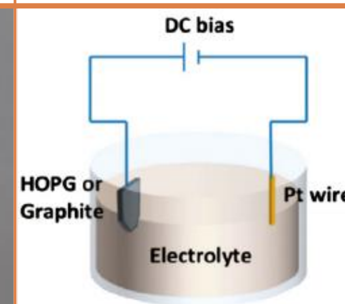
Chemisorption of Graphene



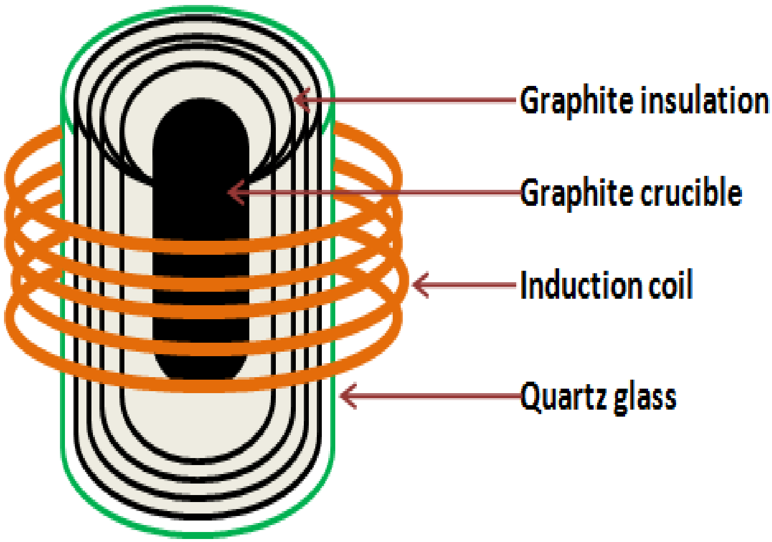
- Forms covalent bonds with ions/cations ($E_{ads} \geq 500$ meV)
  - Charged atoms/molecules
  - F^-, OH^- and H^+
- Arranged periodically
- Bond to π orbitals
  - Form σ bond
  - Changes in lattice
    - sp^2 to sp^3
  - Semi-metal to insulator

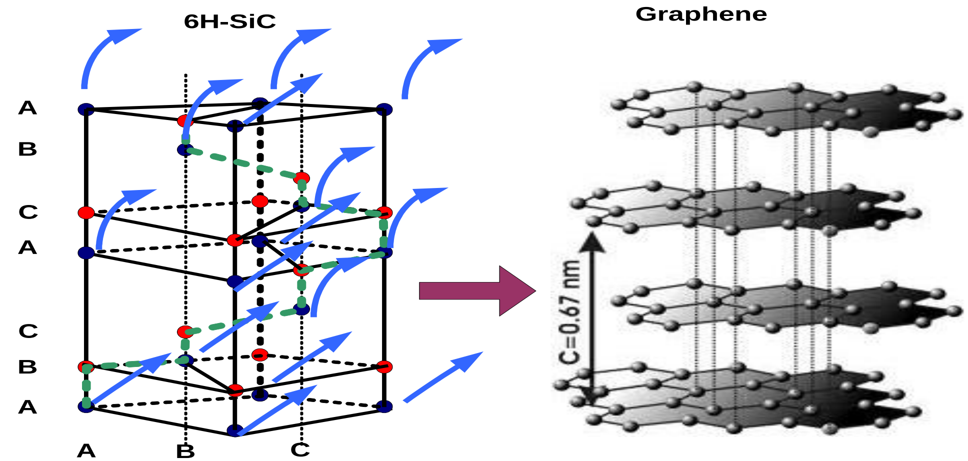


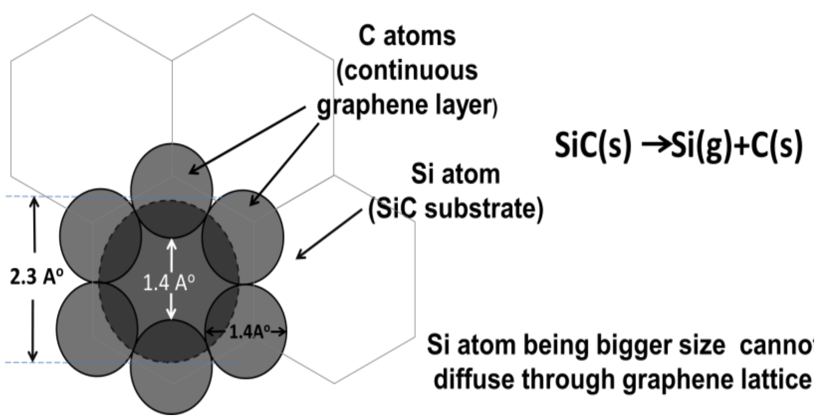
Graphene Synthesis

	Exfoliated	CVD	Epitaxial	Electrochemical	Reduction
Synthesis					
Pros	Cheap	Large Area	Single crystal Large grain size ~mm Easy to process	High yield	High yield
Cons	Small area Poor yield	Need to be transferred Grain sizes ~10-20μm	Cost of SiC Carrier scattering from SiC	Poor control Electrolyte contamination	Poor control Defects

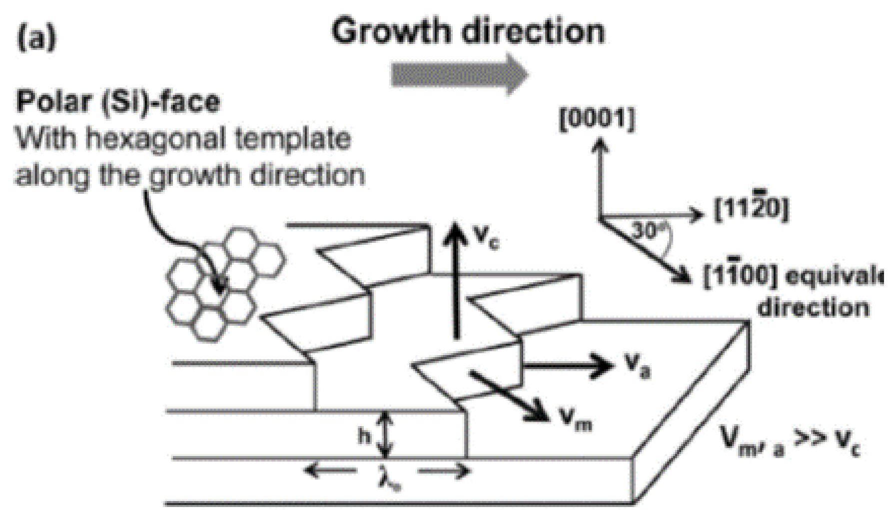
Growth of Epitaxial Graphene





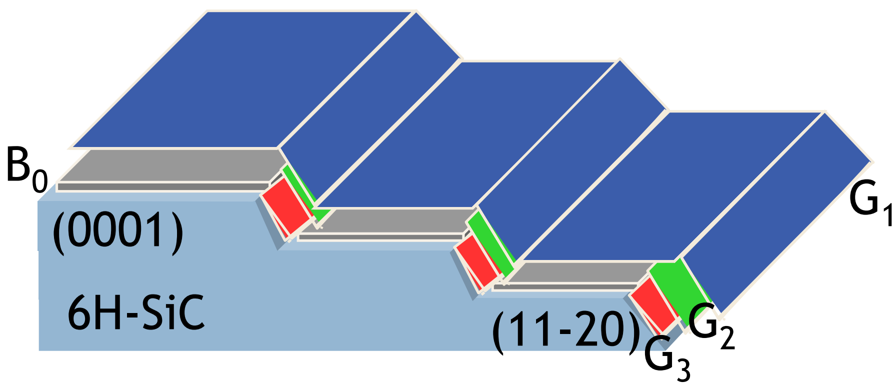


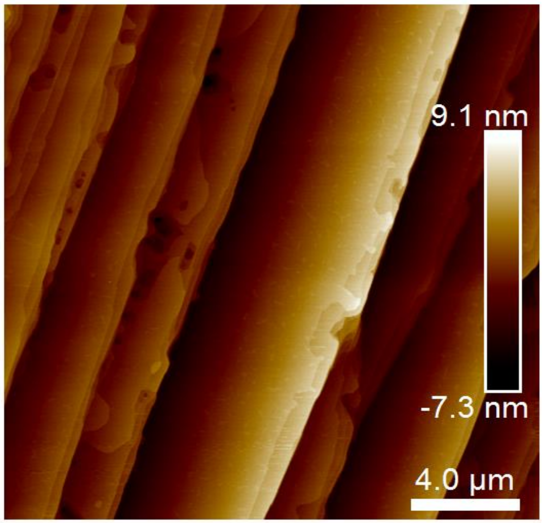
$SiC(s) \rightarrow Si(g) + C(s)$

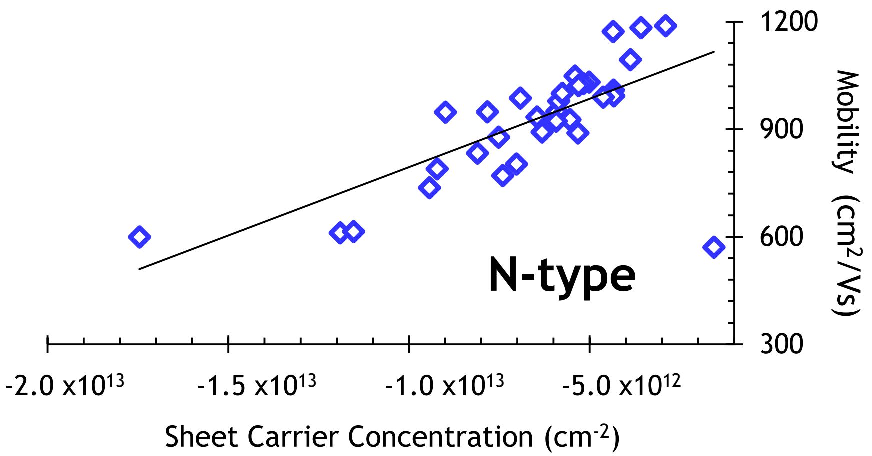


The 6√3 Buffer Layer - SiC Phonon Scattering

SiC was ramped to 1570°C under 10slm, 100mbar of H_2.
Graphene was grown by Si sublimation of SiC at 1580°C under 10slm, 200mbar of **Ar** for 20 min.



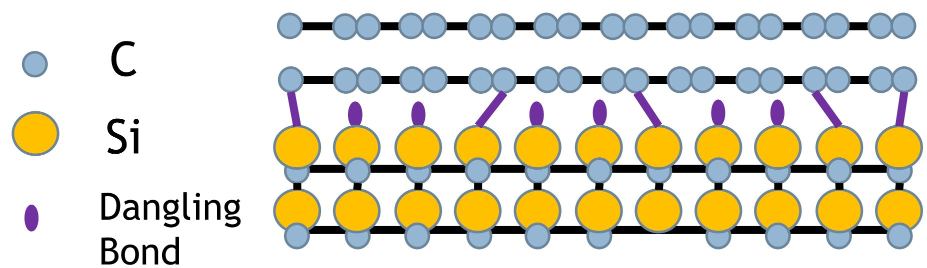




n_s decreases with increasing μ

R_{sheet}~3000 Ωcm^{-2}

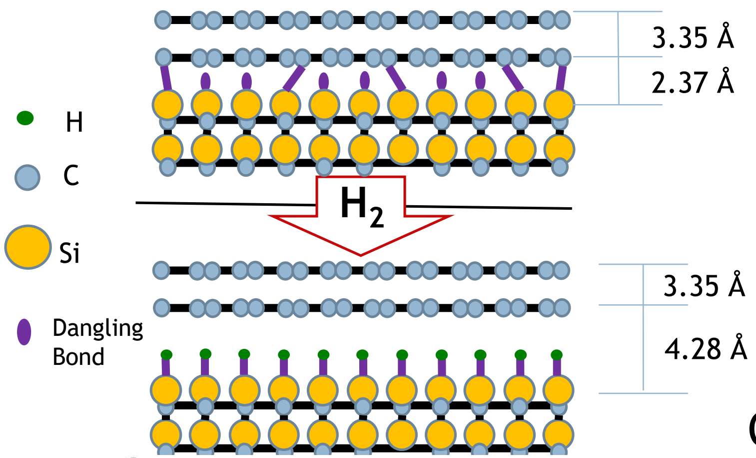
Due to interactions of 6√3 buffer layer

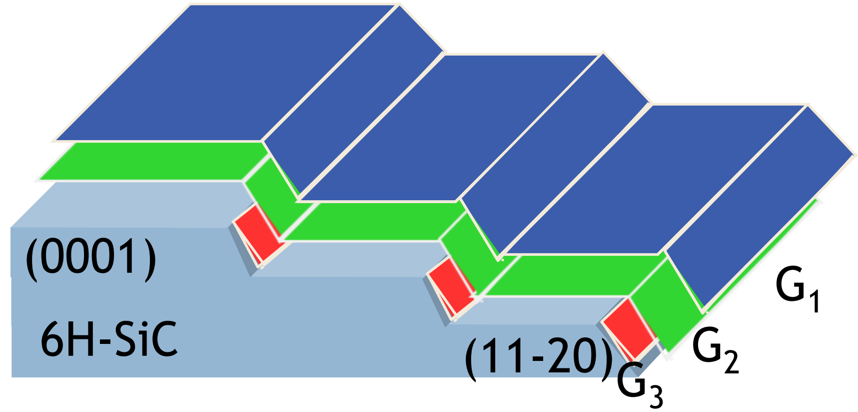


Graphene buffer layer can be released from SiC substrate via hydrogen intercalation

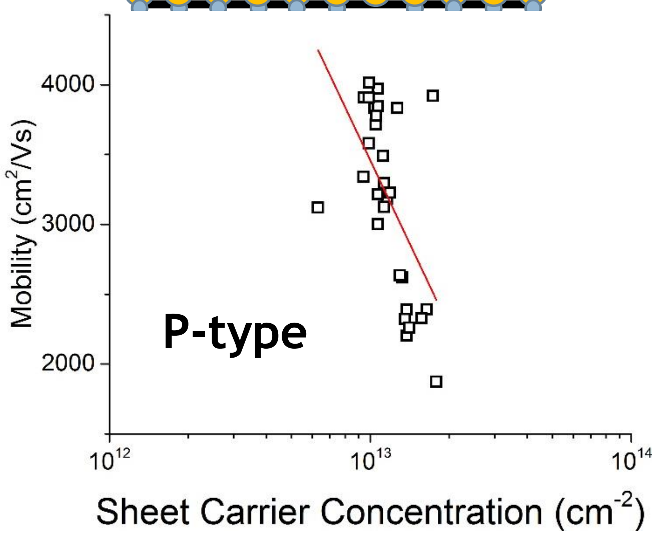
Quasi-freestanding EG via H-intercalation

Samples H-intercalated in 50slm, 900mbar H_2 at 1050°C for 15-75 min. (60 min. optimal)
H-intercalation was performed during EG growth and on previously grown EG





Quasi-freestanding Bilayer Epitaxial Graphene



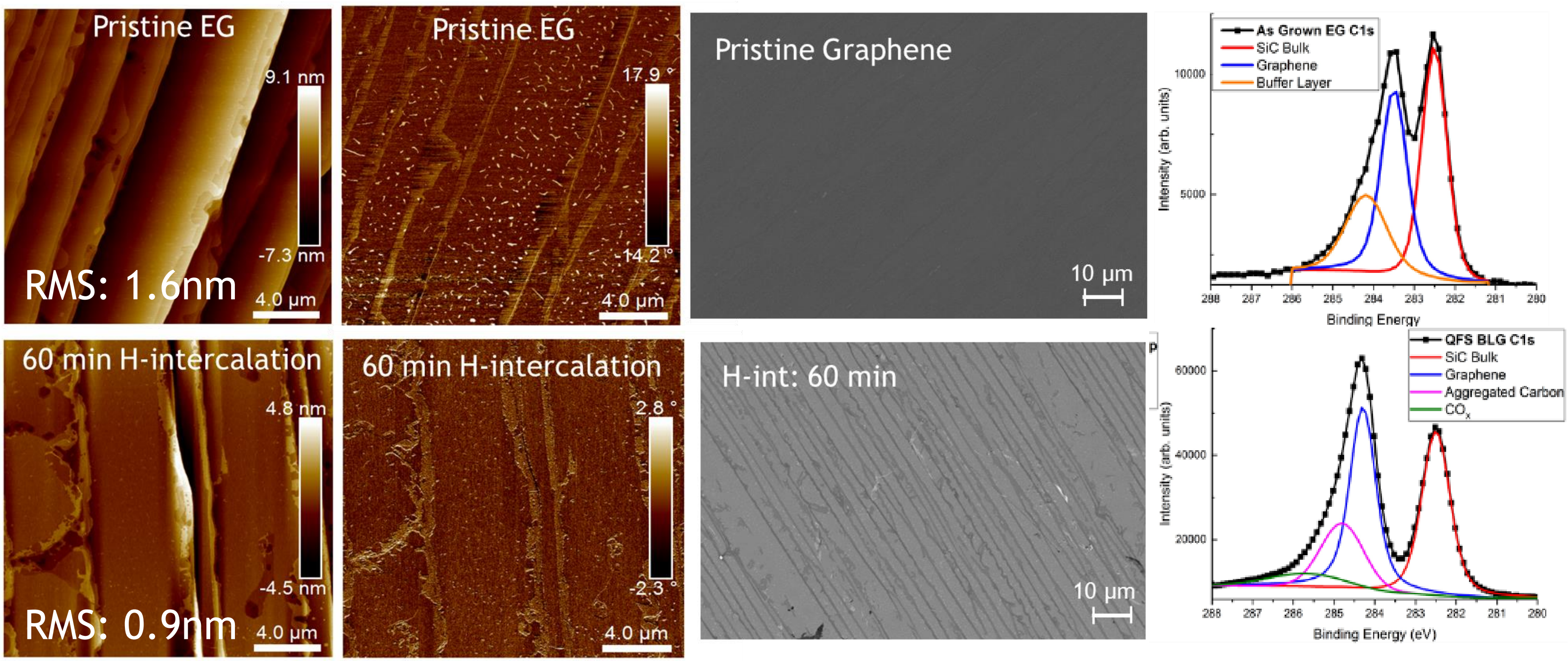
R_{sheet}~300 Ωcm^{-2}

Major Takeaways:

(1) H_2 gas does not react with graphene
(2) 4x increase in carrier mobility
(3) High sheet carrier concentration (10^{13})
(4) Order of magnitude drop in sheet resistance

C. Riedl *et al*. Phys. Rev. Lett. (2009)
F. Speck *et al*. Appl. Phys. Lett. (2011)
J.A. Robinson *et al*. *Nano Lett*. (2011)

Fully Intercalated H-intercalated EG



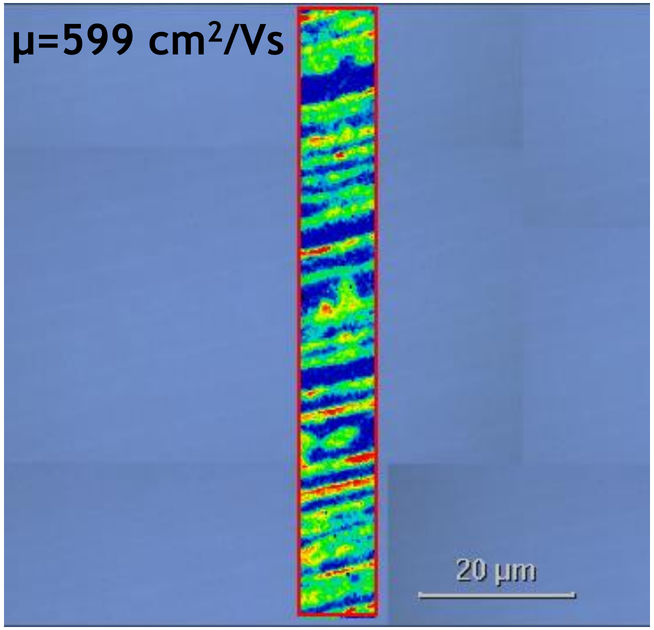
AFM-Height | AFM-Phase | SEM | XPS-C1s Peak

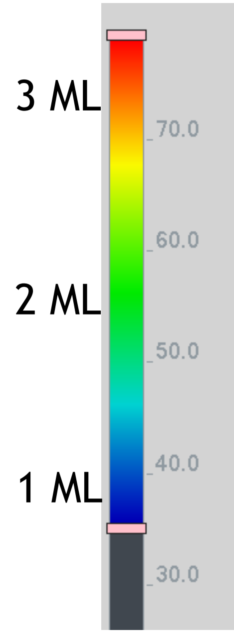
Improvement of surface uniformity and release of the BL from SiC as observed by AFM, SEM and XPS

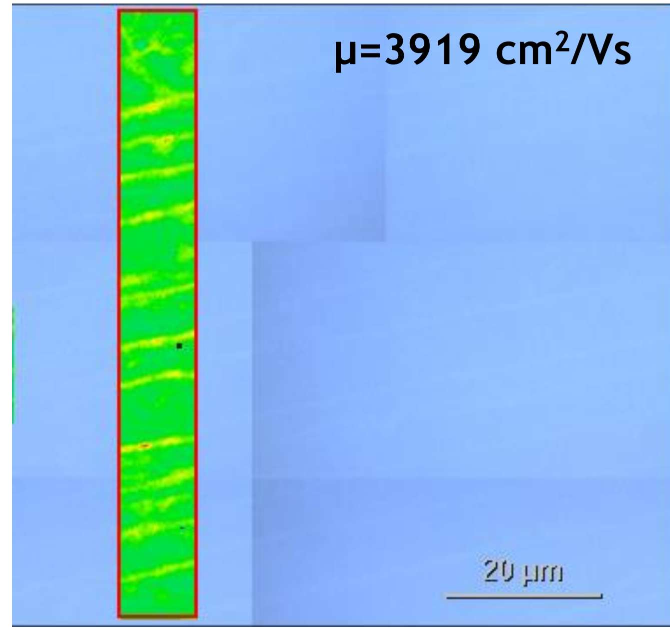
Mapping Graphene Layer Thickness

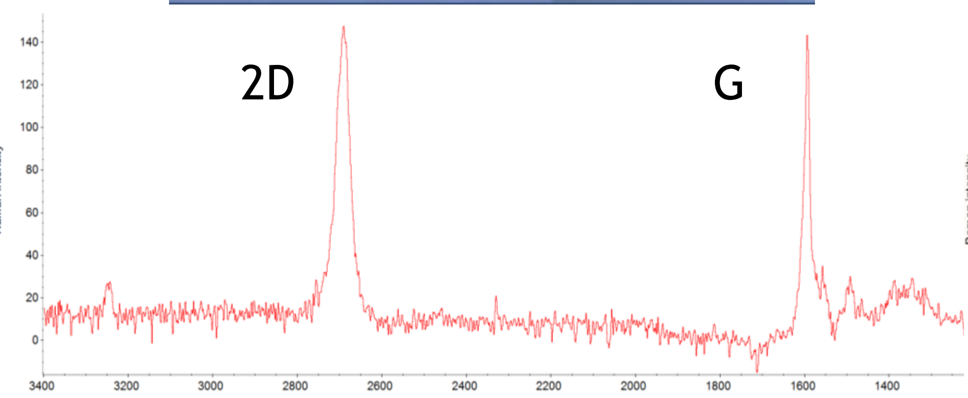
Before H-intercalation

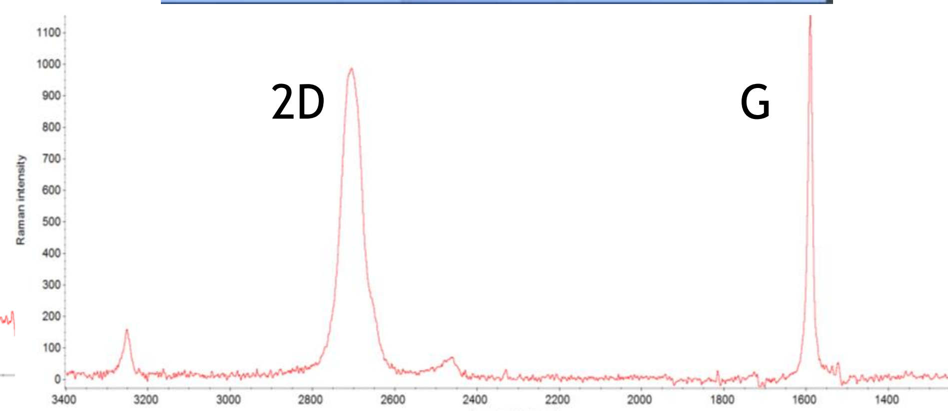
After 60 min H-intercalation





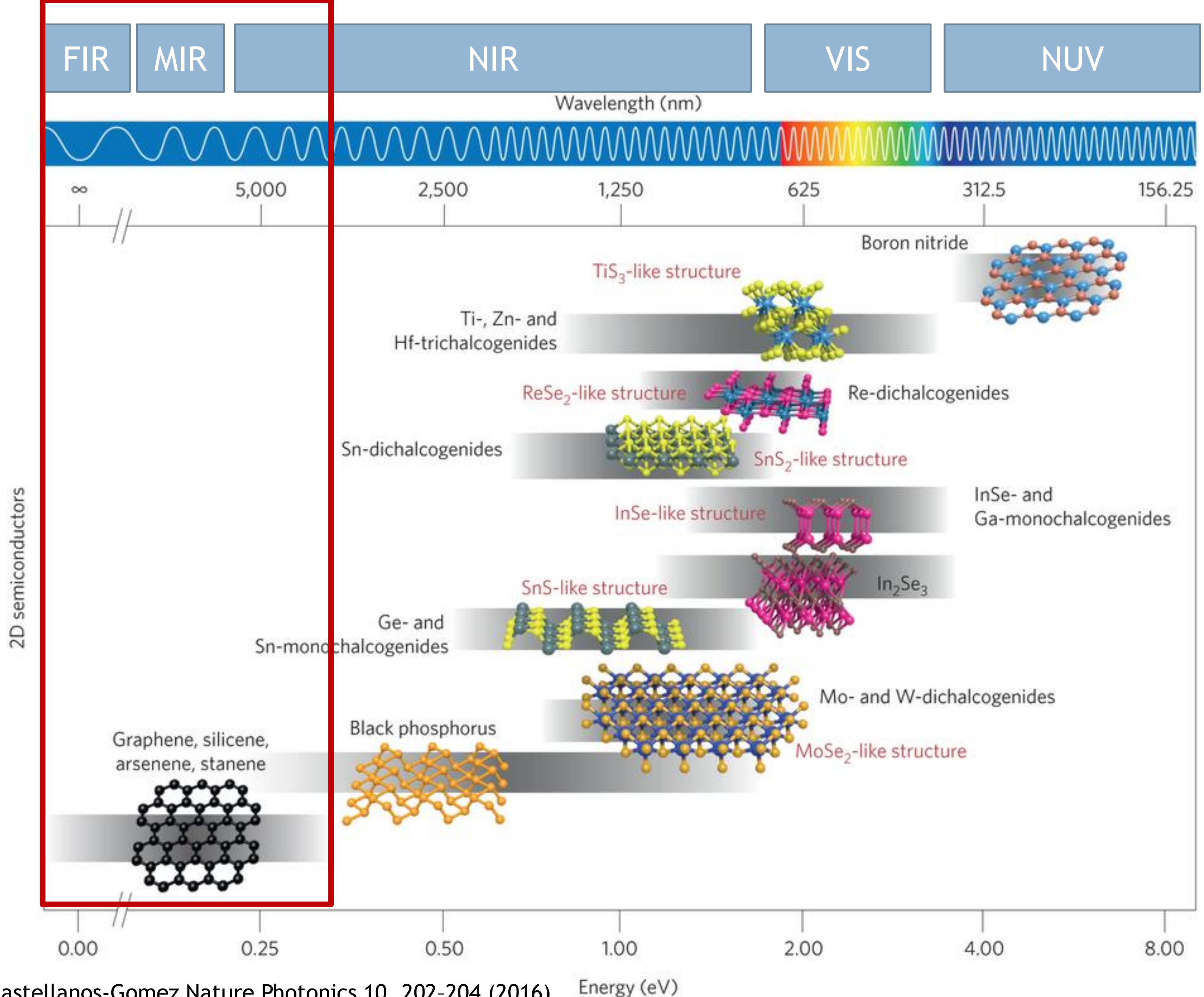






Conforms with M. Ostler stating no buffer layer is formed on the (11-20) surface.

Narrow Terahertz Transmission Resonance of Quasi-freestanding Bilayer Epitaxial Graphene

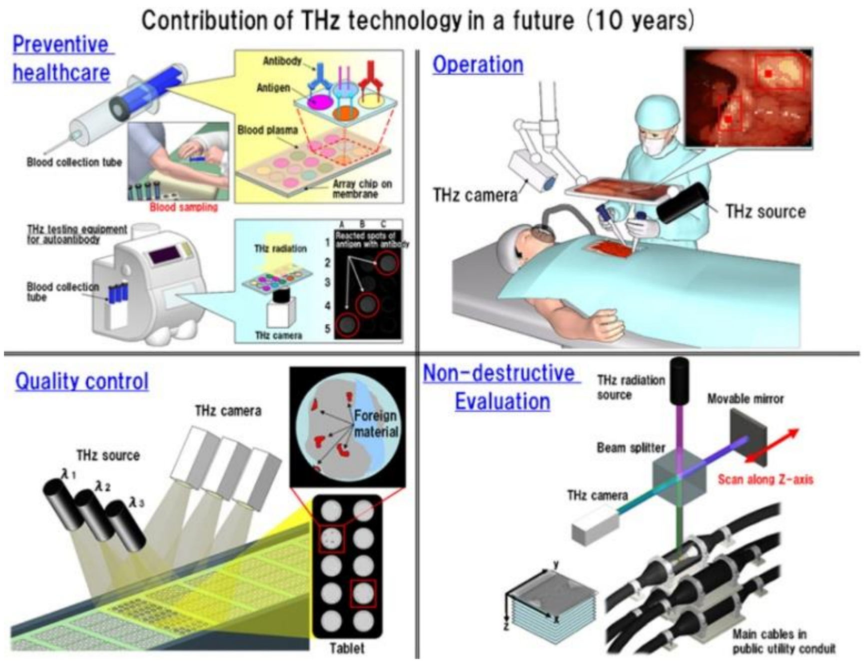


A. Castellanos-Gomez Nature Photonics 10, 202–204 (2016)

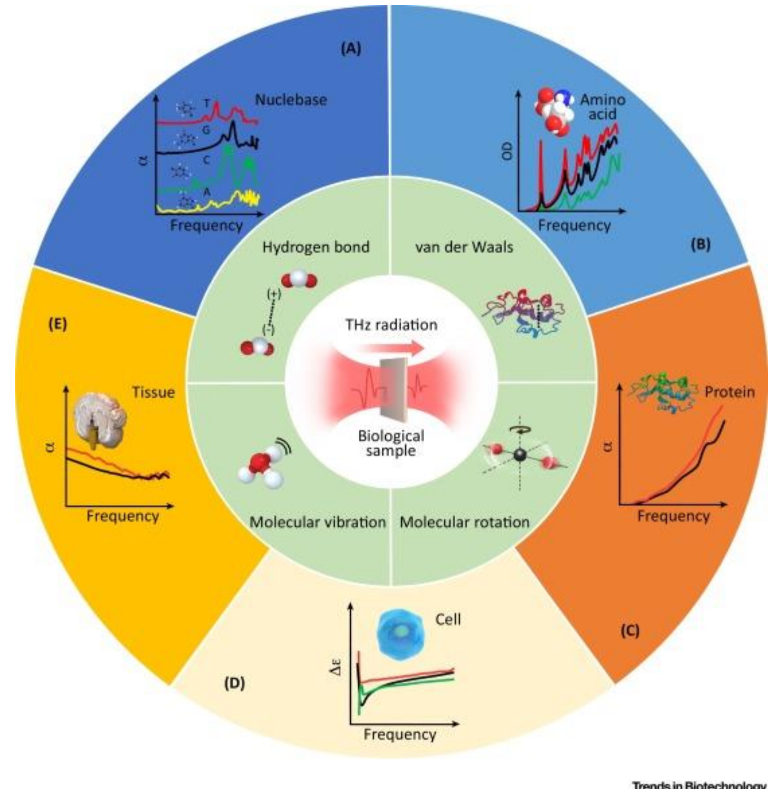
Overview of THz Detection

Applications for THz detection include:

Non-destructive evaluation and medical imaging



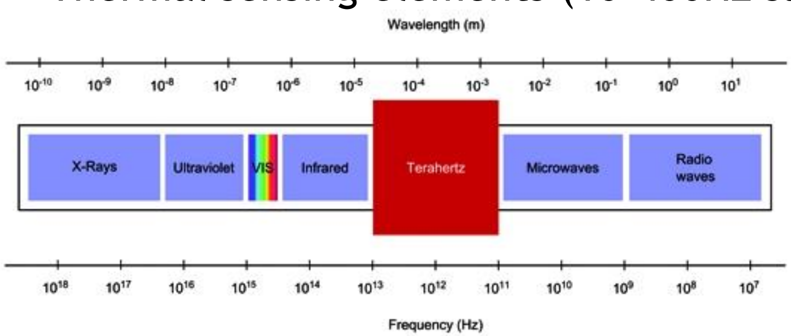
Iwao Hosako and Naoki Oda, SPIE Newsroom. DOI: 10.1117/2.1201105.003651 (2011)



Current methods for THz detection use:

Cryogenic cooled superconductors (bolometers) ***Expensive and cumbersome***

Thermal sensing elements (10-400Hz sampling rate) ***Too slow for rapid detection***



Graphene seen as an ideal material for THz detection:

Operation at room temperature

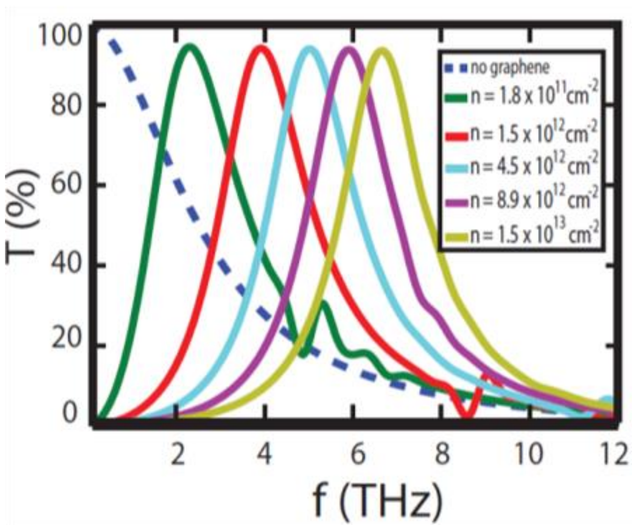
Ideal for applications for rapid detection

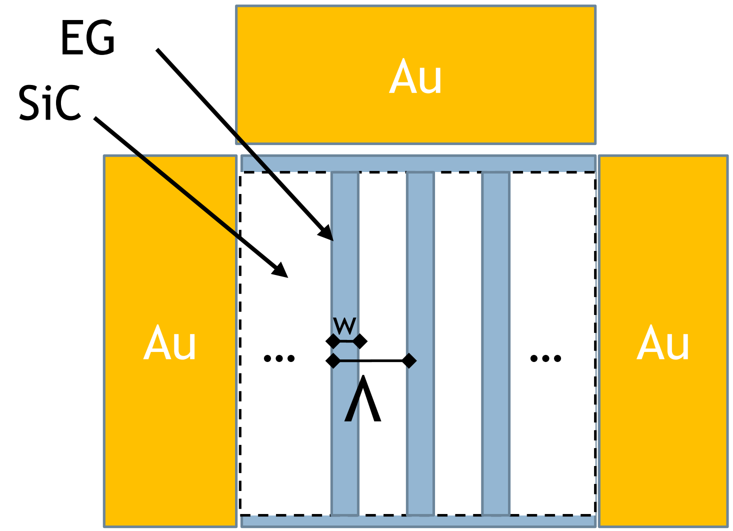
Benefits of epitaxial graphene:

Large area

Surface Plasmon Resonance in EG

- Improve the broad plasmon resonance response observed in graphene based THz optoelectronics by H-intercalation.





M.M. Jadidi *et al.* , Nano letters 15 (10), 7099-7104 (2015)

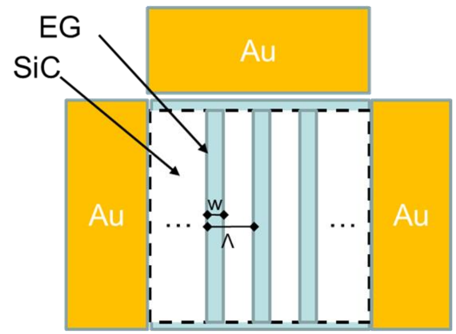
- Patterning confines surface plasmon polaritons (THz regime)
  - Plasmon resonance peak: $\omega_0^2 = \frac{e^2 v_F \sqrt{\pi}}{2\hbar} \frac{\sqrt{n}}{w \epsilon_0 \bar{\epsilon} \ln[2\csc(\pi w/\Lambda)]}$

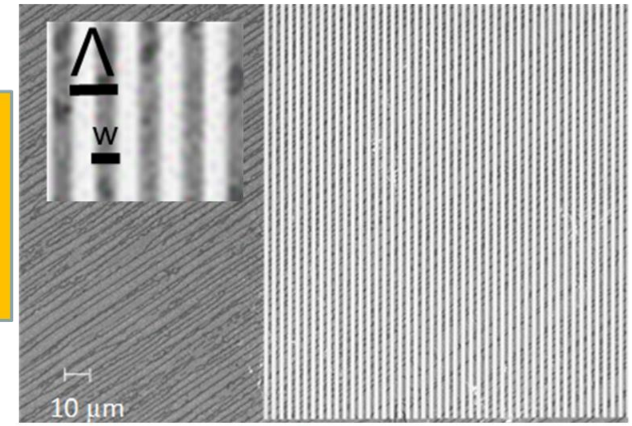
H-Intercalated Patterned THz Transmission

Tuning Plasmon Resonance Frequency

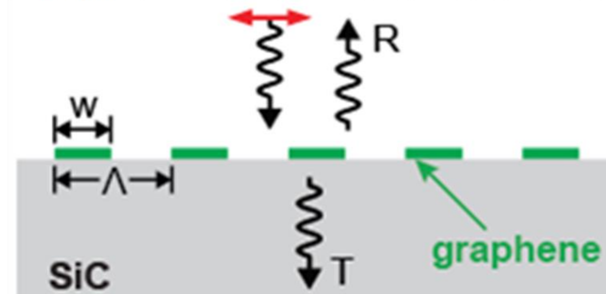
$$\omega_p^2 = \frac{\pi - \Phi}{2\sqrt{\pi}} \frac{e^2 V_F}{\epsilon_0 \hbar} \frac{1}{\epsilon} \frac{\sqrt{n}}{w}$$

1) Changing Carrier Concentration (Gating)
2) Changing Graphene Width (Duty Cycle)

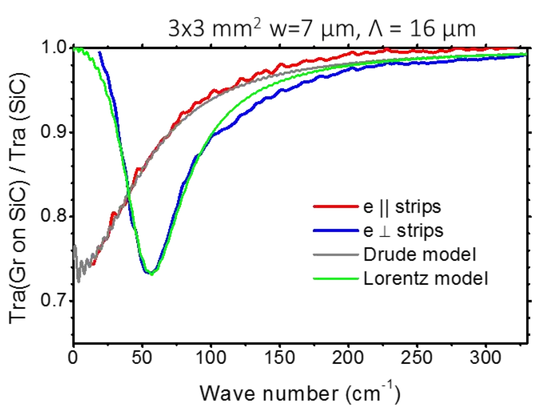


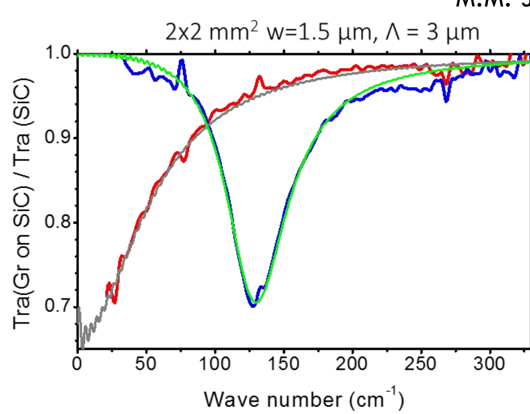


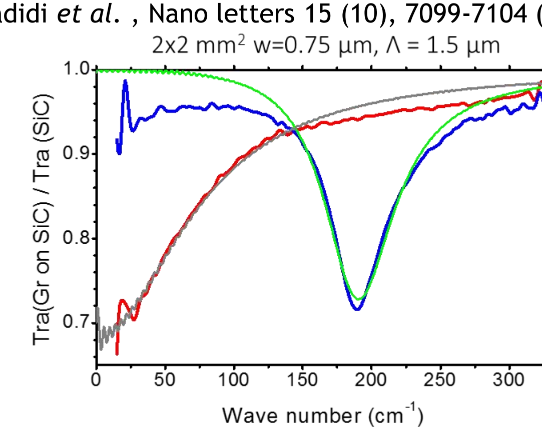
- Far IR simultaneous transmission/reflection measurements
  - Source (Hg Lamp) and two detectors (4K silicon composite bolometers)
  - One on transmitted other on reflected side
- Polarizer used in beam path to pass polarization perpendicular to EG strips
- THz beam illuminates the backside of the device
  - Through a 1.5mm diameter aperture in Cu



M.M. Jadidi *et al.* , Nano letters 15 (10), 7099-7104 (2015)







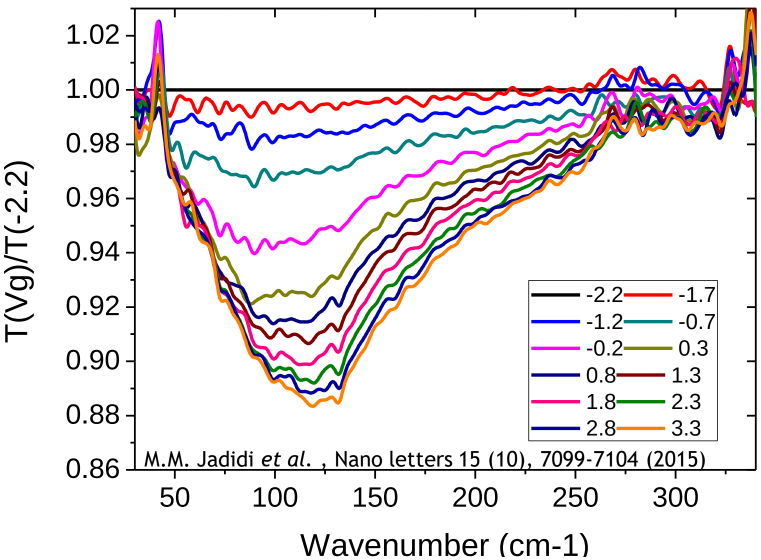
Kevin M. Daniels, M. Jadidi, A. Sushkov, A. Nath, A. Boyd, K. Sridhara, H. Dennis Drew, T. E. Murphy, R. Myers-Ward, D. K. Gaskill., "Narrow Terahertz Transmission Resonance of Quasi-freestanding Bilayer Epitaxial Graphene", 2D Materials 4 (2), 025034, (2017)

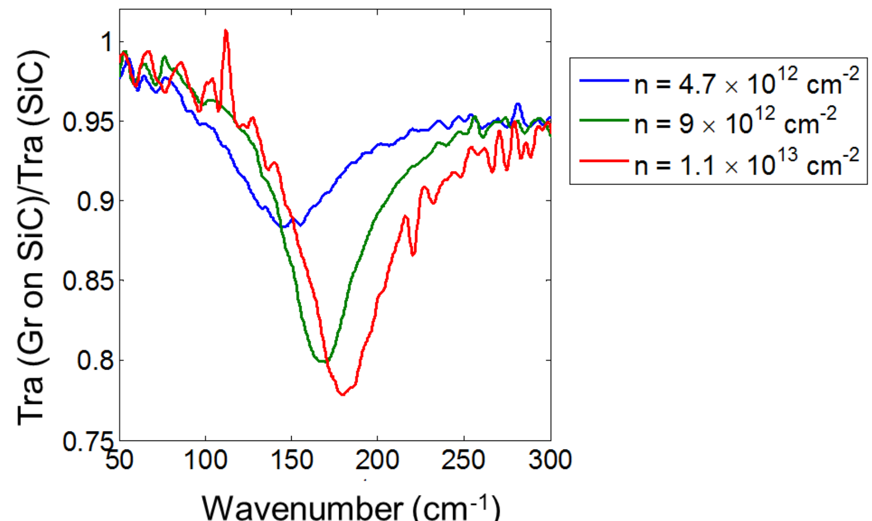
Gated (electrolyte) Comparison of Plasmon Resonance

Sample gated with $LiClO_4$ electrolyte

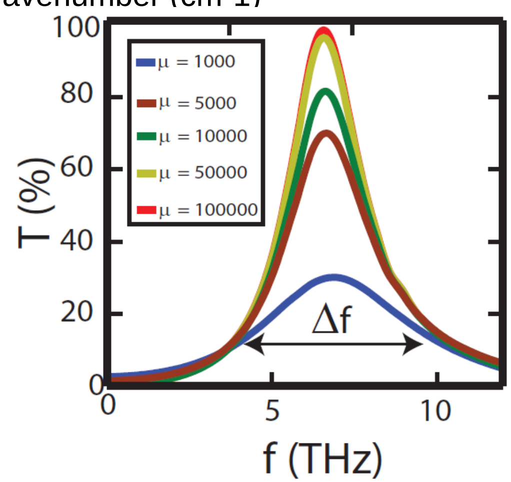
Non-intercalated, w=2.3 μm, Λ =4.46μm, 1.5 mm^2

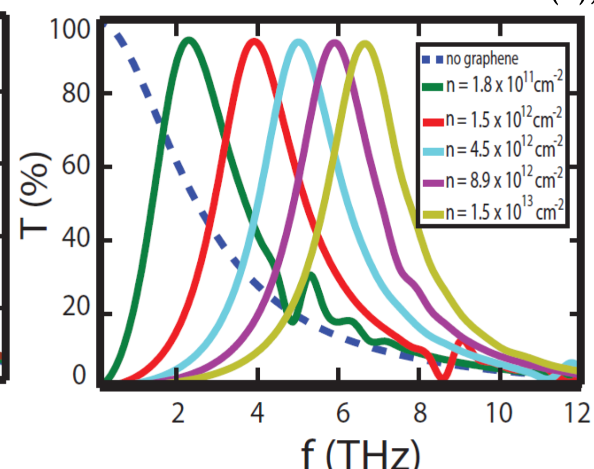
Intercalated, w=0.75 μm, Λ = 1.5 μm, 2 mm^2





K. M. Daniels et al. 2D Materials 4 (2), 025034, (2017)





1/τ a μ [scattering rate] *ω_0 a $n^{1/4}$ [f of THz response]*

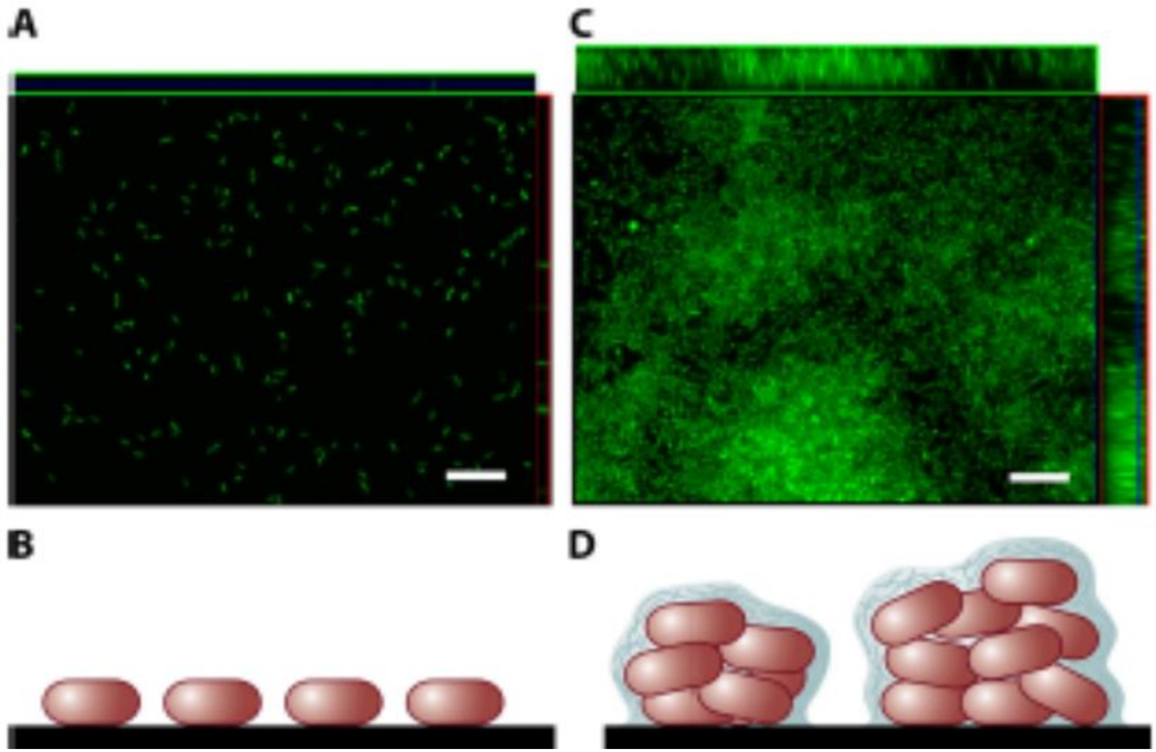
M.M. Jadidi *et al.* , Nano letters 15 (10), 7099-7104 (2015)

26 Biocompatibility of Epitaxial Graphene

Background: Biofilm

Biofilm formed as a protection mode of growth for bacteria

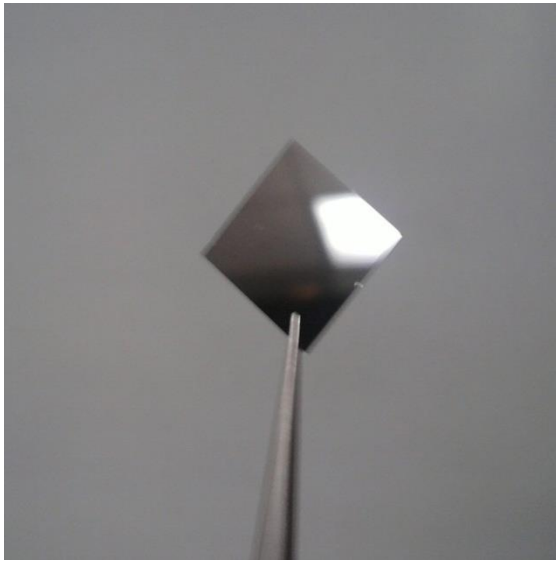
- Can form on abiotic (i.e. minerals) and biotic (i.e. humans)
- Allows cells to survive in hostile environment
- Promotes cell to cell communication



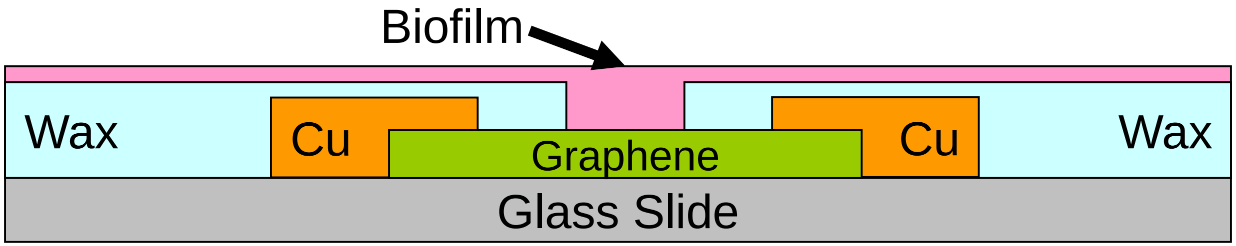
Karatan et. al.Microbiol. Mol. Biol. Rev. **June 2009** vol. 73 no. 2 **310-347**

Experimental Details: Graphene

- **Biocompatibility confirmed by**
  - Optical Microscopy
  - Confocal Microscopy
    - Stained with flourochromes



- **Graphene mounted on glass slide**
  - Copper contacts to measure resistance
  - Sealed with wax
  - Placed in Bioreactor
    - Resistance measured throughout growth



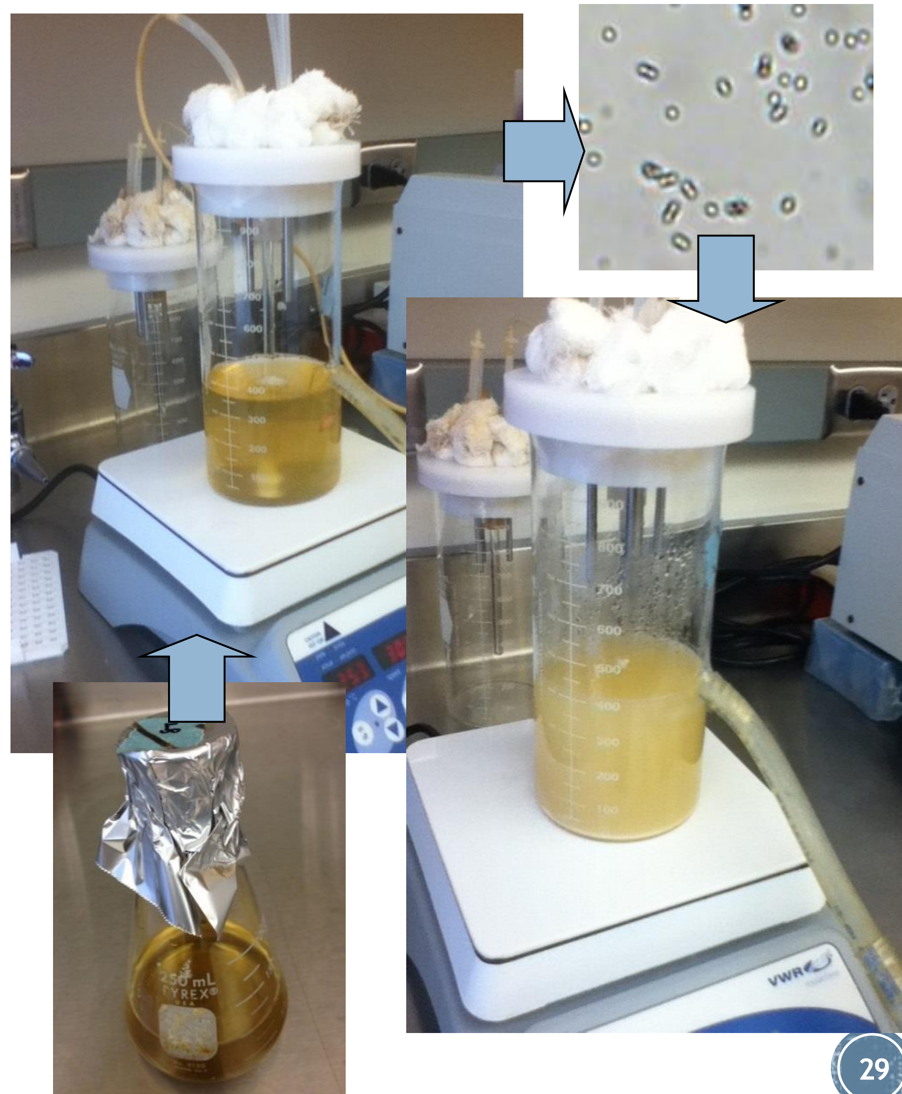
Kevin M. Daniels, N. Aich, K. P. Miller, B. K. Daas, N. Saleh, A. W. Decho, T. S. Sudarshan, MVS Chandrashekhar "Biological Sensing Applications of Epitaxial Graphene"

BioReactor

- CDC Biofilm Reactor
  - Biosurface Technologies (Bozeman, MT)

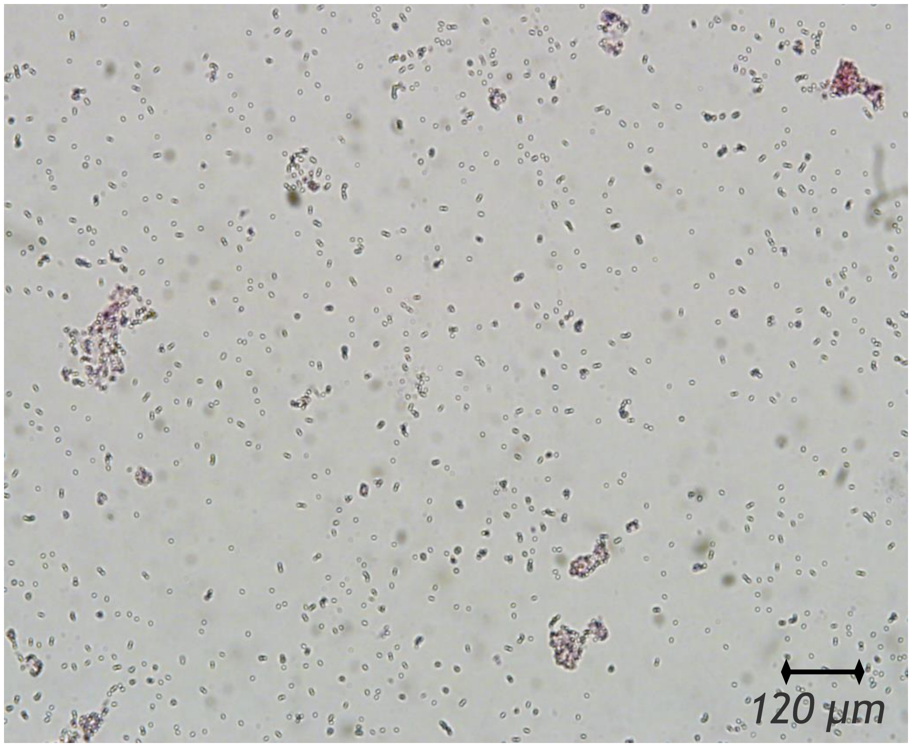
- K12 Growth Medium
  - Food for the bacteria
  - Consists of 37 g/L EC Media
  - Flow rate 0.1 mL/min
  - Stirred at 400 rpm

- *E. coli* strain 25922
  - 3mL introduced at inoculation
  - Gram negative bacterium
  - Surface charge measured

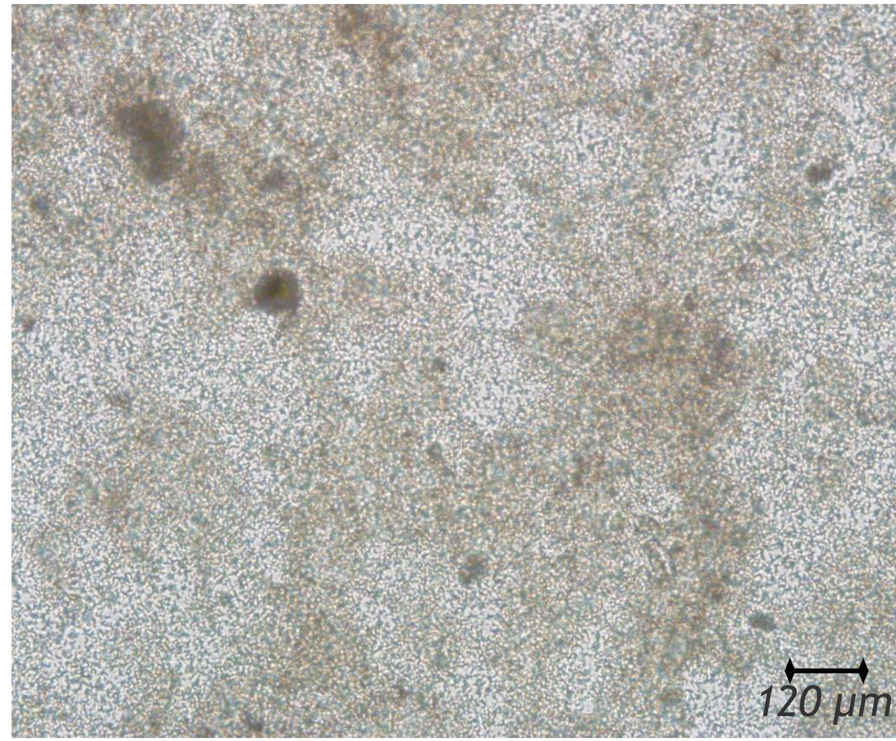


Results: Optical Microscopy

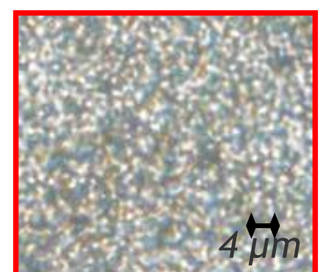
40x E. coli gram stain on glass slide



40x E. coli biofilm on epitaxial graphene

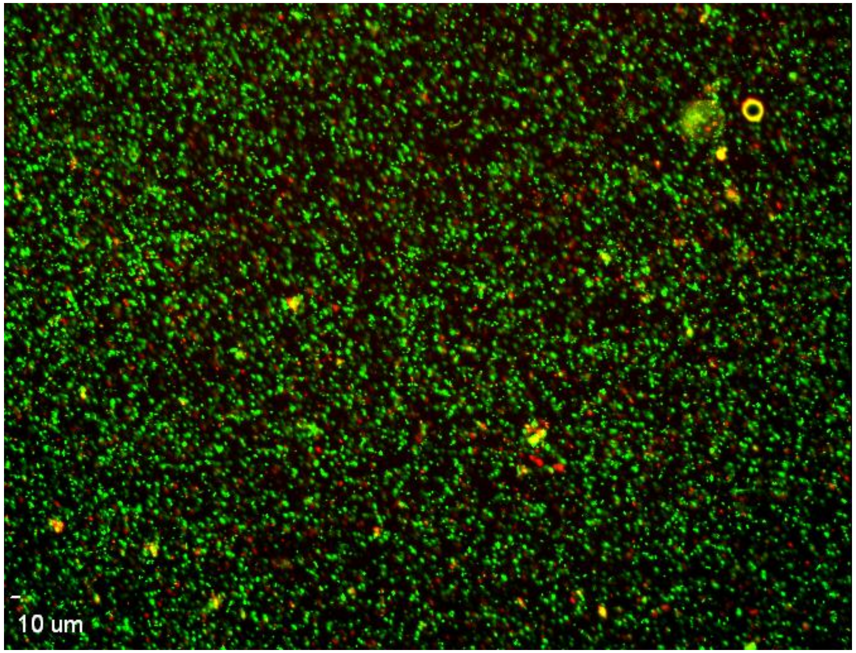


Formation of Biofilm on graphene confirmed

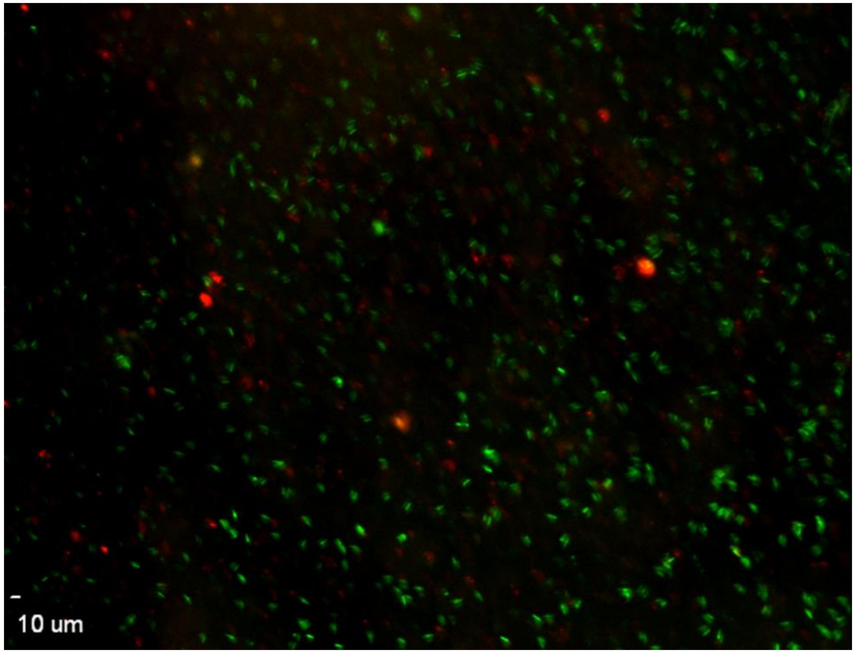


Scaffold for Bacteria Growth

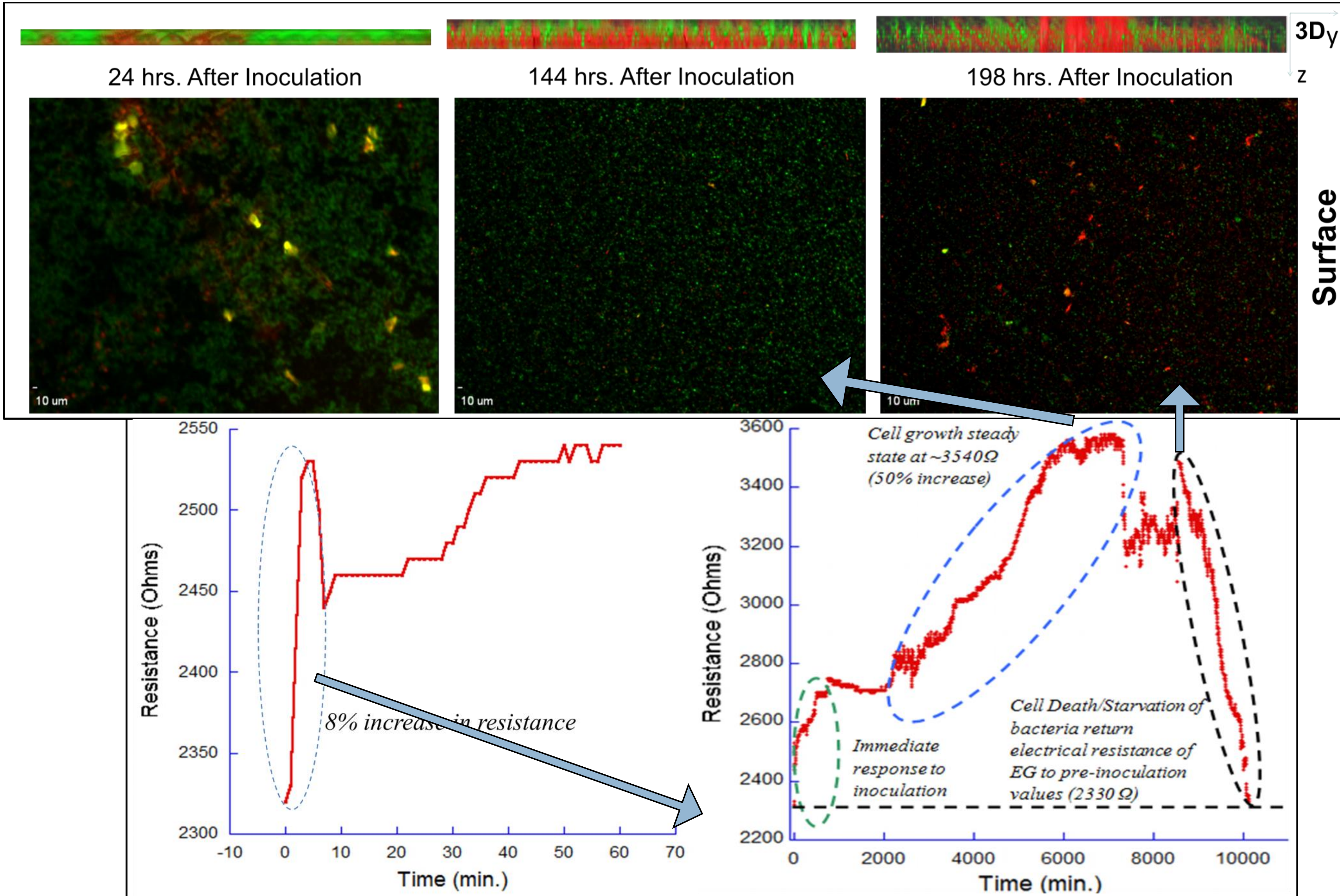
- Bacteria on Graphene
  - Formation of Biofilm



- Bacteria on SiC
  - Planktonic Cells

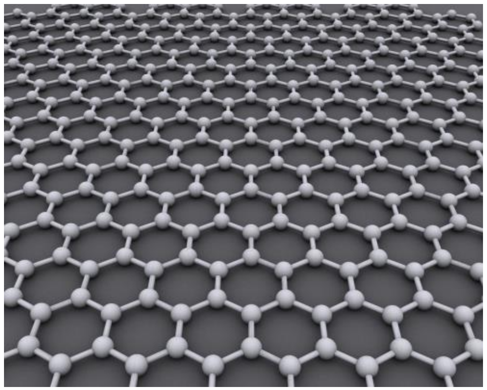


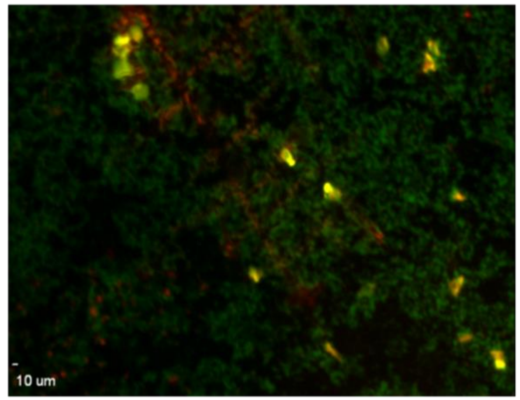
Electrical Sensing of Bacteria on Epitaxial Graphene

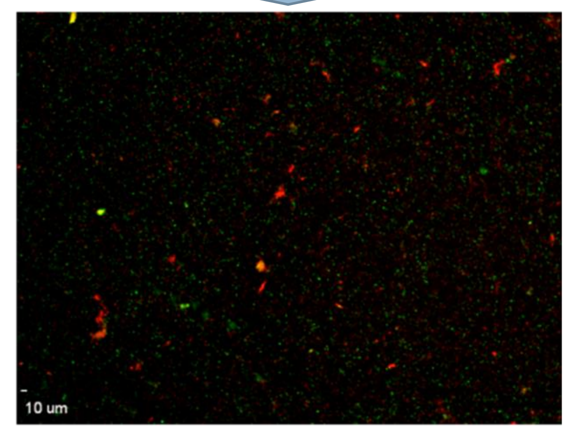


Kevin M. Daniels, N. Aich, K. P. Miller, B. K. Daas, N. Saleh, A. W. Decho, T. S. Sudarshan, MVS Chandrashekhar "Biological Sensing Applications of Epitaxial Graphene"

Graphene as a Label-free Testbed







http://kabirdental.com/sterilization/

https://www.cascademicrotech.com/images/SourceImage/eps150rf_angled.jpg

Outline for Future Work

- Van der Waals Electronics
  - Large, Single Crystal Epitaxial Graphene Framework
  - 2D Material Stacks (Metal Oxides and Dichalcogenides)
  - Intercalated Growth of Semiconductors into EG (GaN)

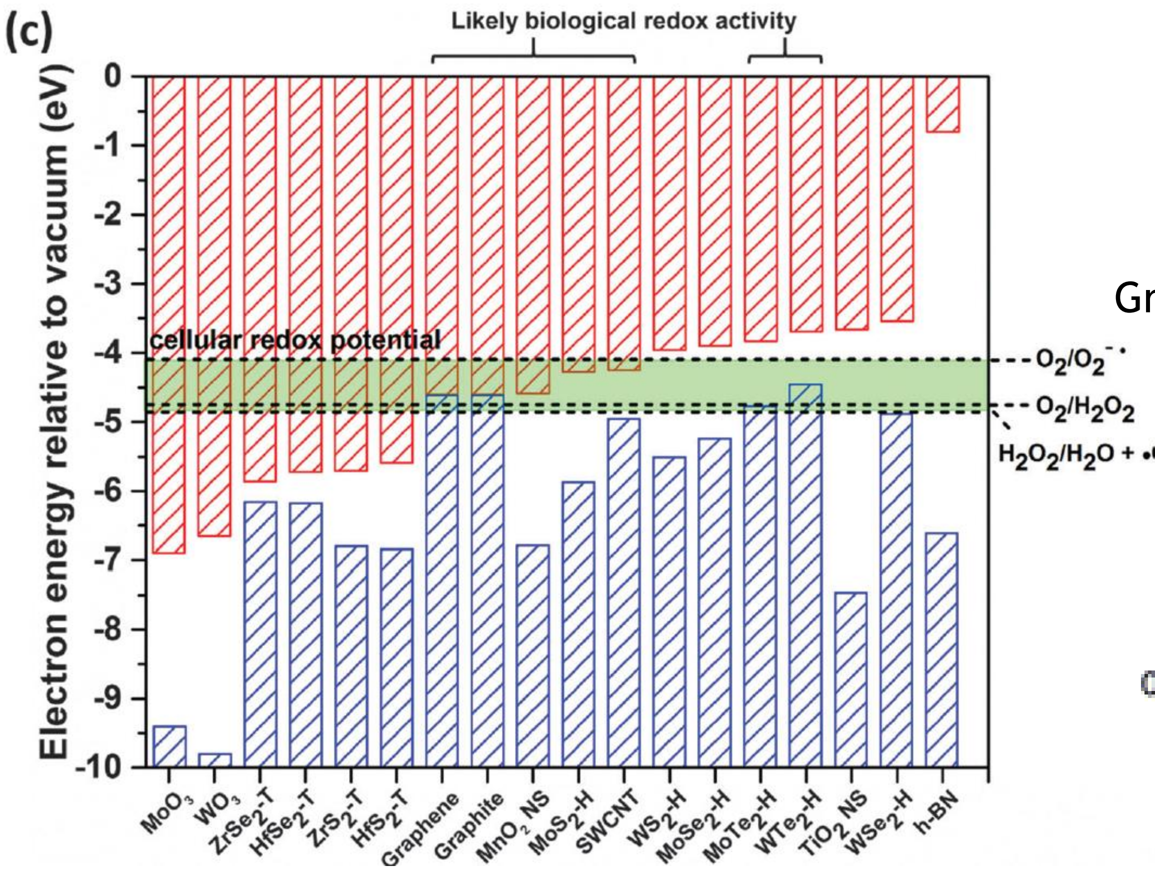
- Simulations by COMSOL
  - Stack Physics
  - Theoretical Fuel Cell Configurations

- Sensors
  - Pathogens
  - Biomedical
  - Environmental

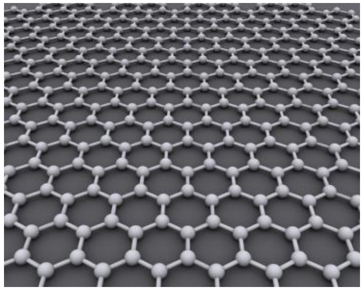
- Growth of 2D Materials
  - Stack by Transfer
  - Flexible Electronics

Electrodes for Energy
- Fuel Cells
  - Microbial, Biofuel
- Batteries
- Capacitors

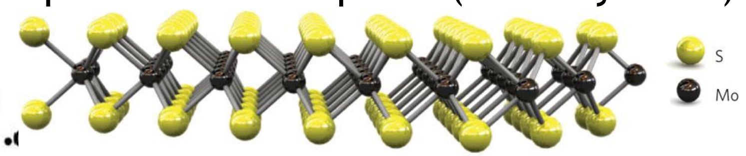
Cellular Reduction-Oxidation Potential



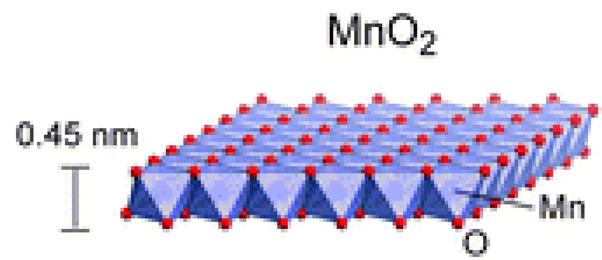
Chem. Soc. Rev., 2016, 45, 1750-1780



Graphene and Graphite (Multilayer EG)



MX2 (MOS_2,$MoTe_2$,WTe_2)

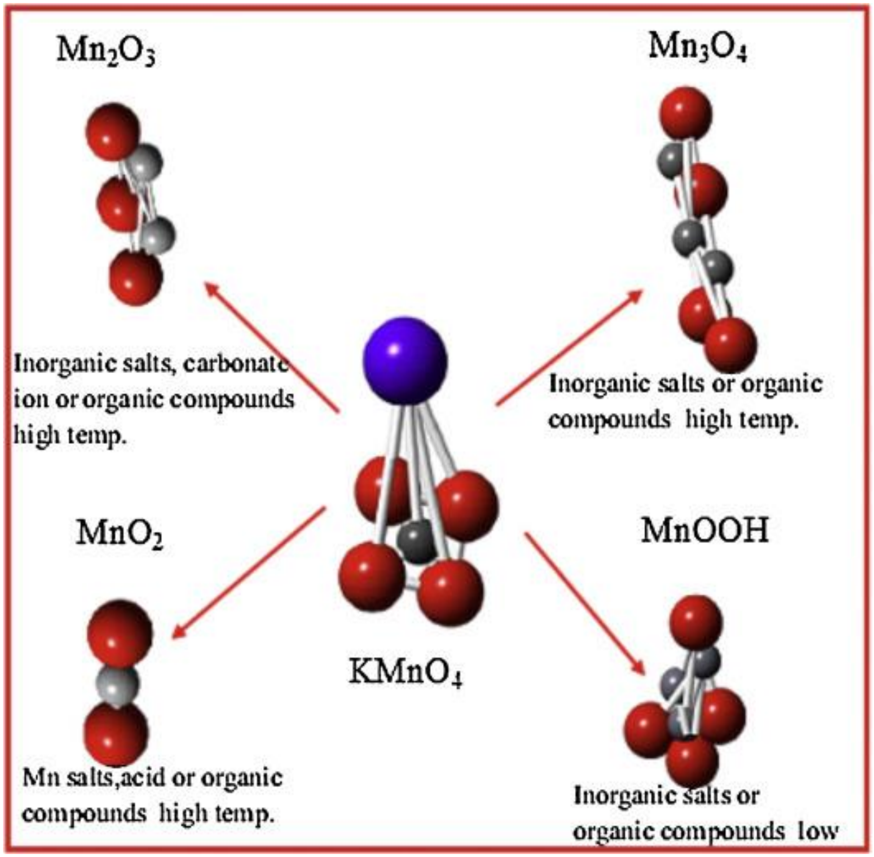


Growth of single layer EG and TMDs are established

Growth of single layer MnO_2 is the challenge

$KMnO_4$ Reduction towards Mn_xO_x Nanostructures

Journal of Taibah University for Science, Volume 10, Issue 3, 2016, 412–429

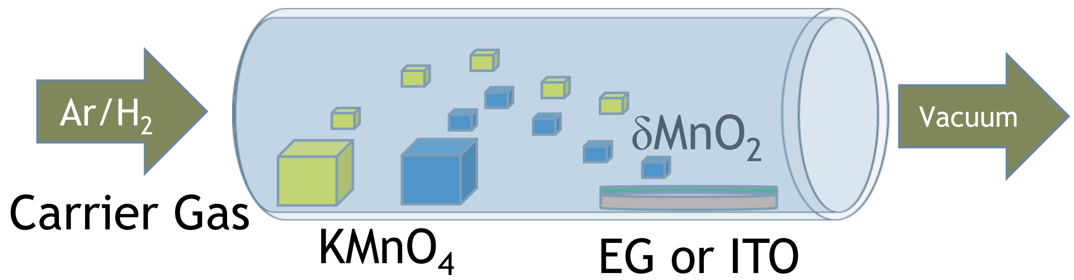


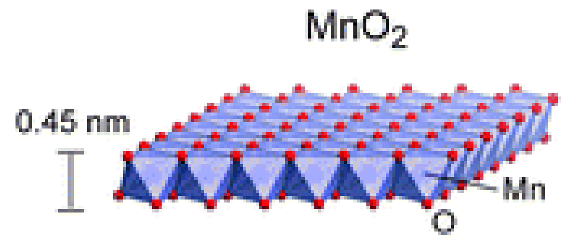
MnO_2 has a 2.6% lattice mismatch to EG

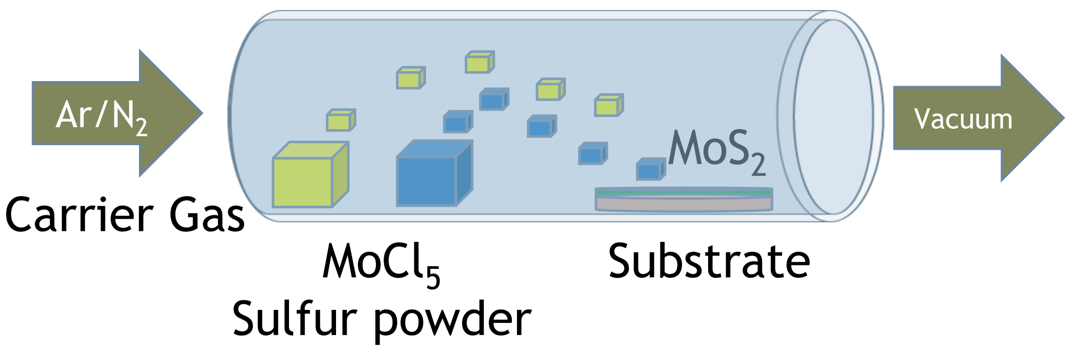
Attempt thermal decomposition of $KMnO_4$ and vapor transport of MnO_2 to EG

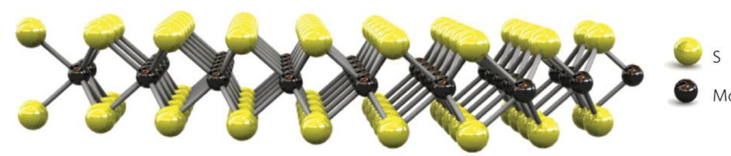
Chem. Mater., 1999, *11* (3), pp 557–563

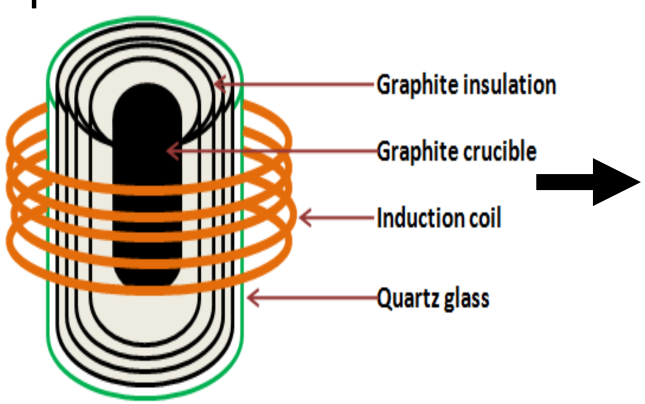
Growth of 2D Materials

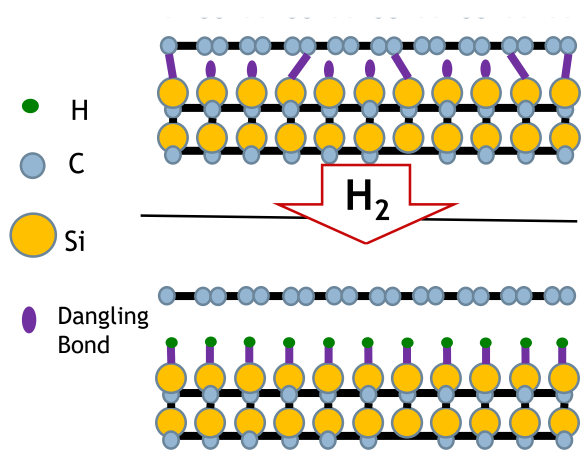




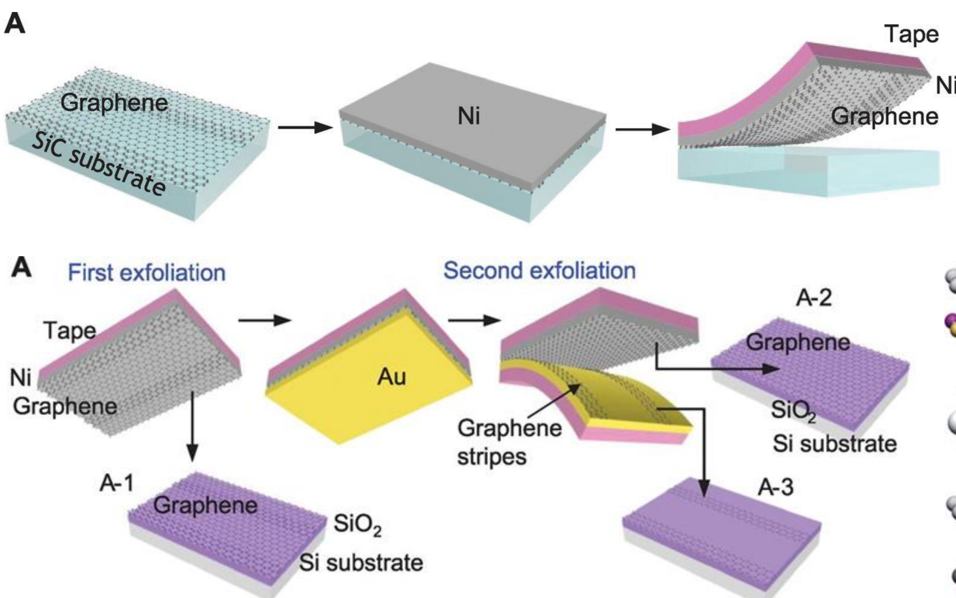




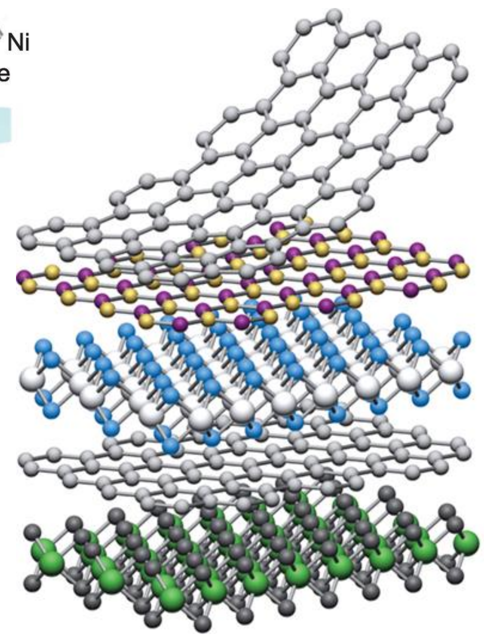


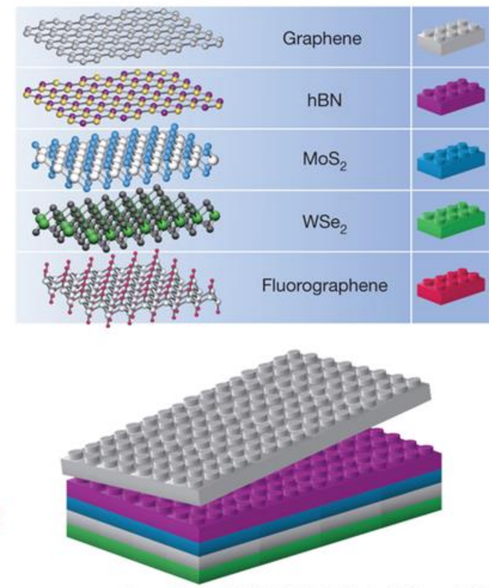


2D Heterostructure Stacks



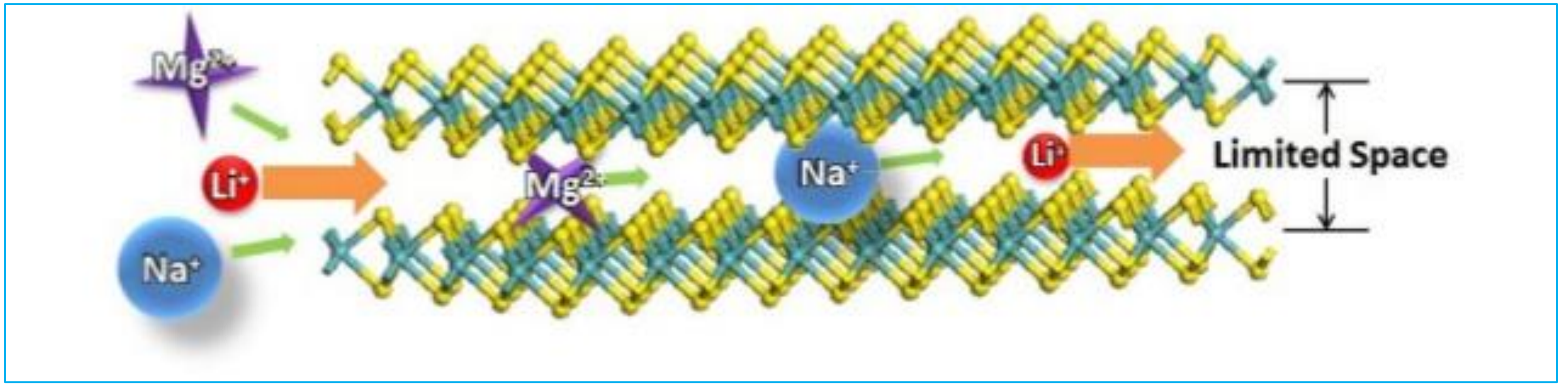
Jeehwan Kim et al. Science 2013;342:833-836





Nature 499, 419–425 (25 July 2013) DOI: 10.1038/nature12385

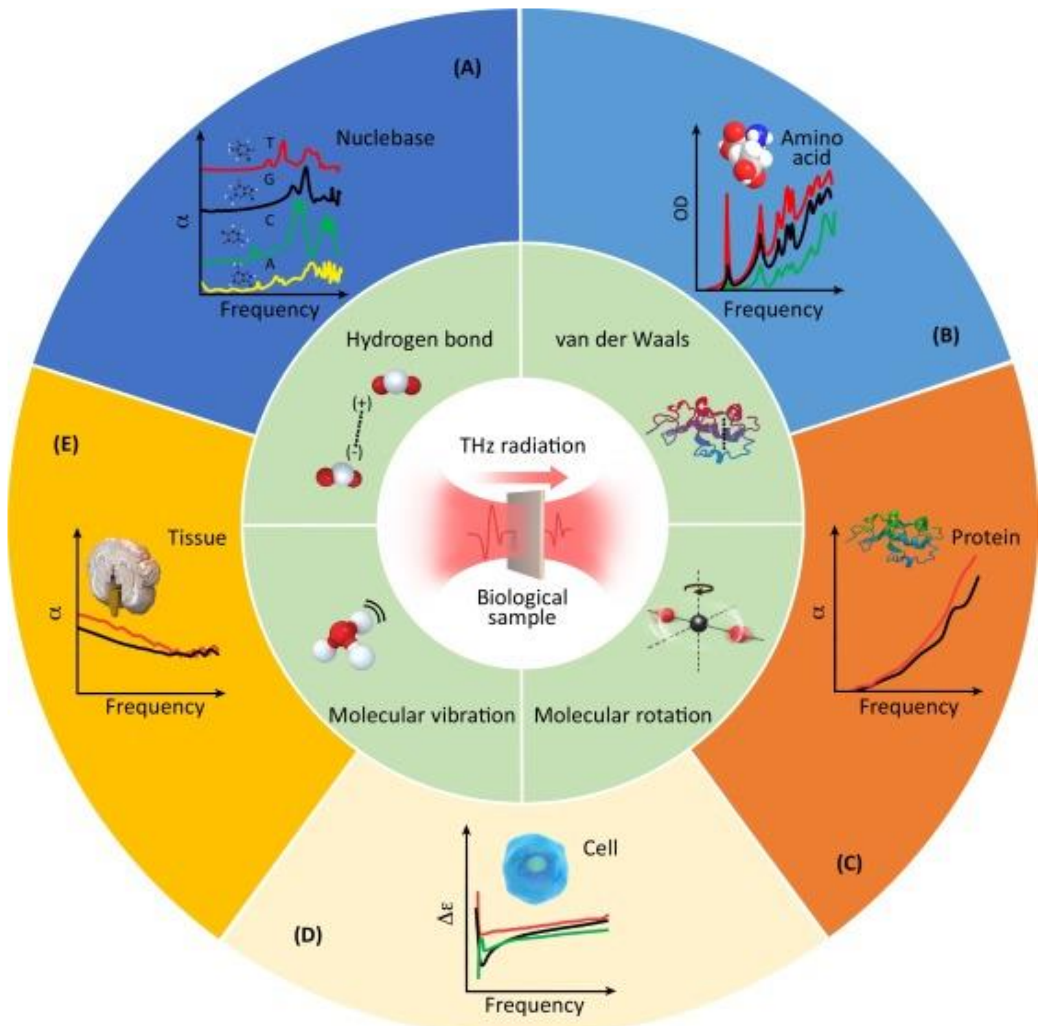
Towards Capacitor and Battery Electrodes



- Interlayer Distance in van der Waals Materials
- Less expensive batteries utilizing Na^{+} and Mg_2^{+} ions
- δ-MnO_2~7Å

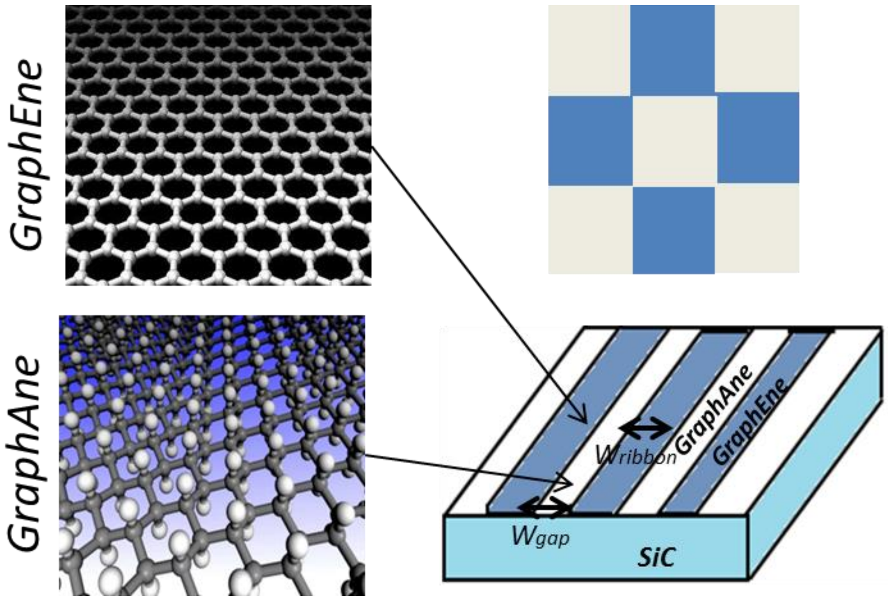
Bacteria Detection via THz

Exploiting the THz Regime

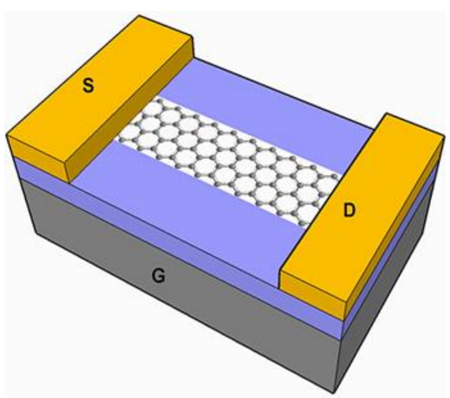


Trends in Biotechnology

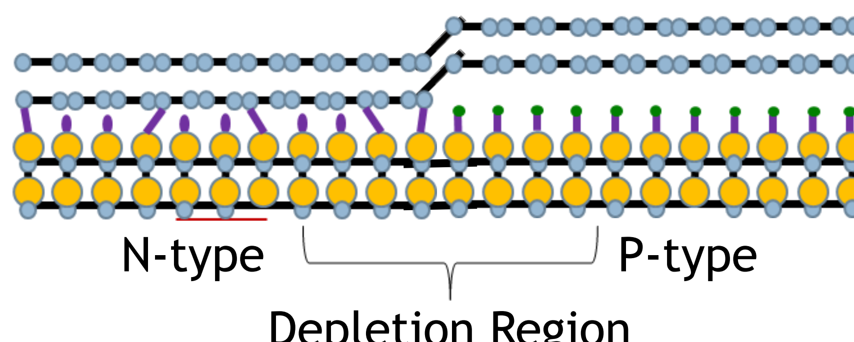
Adatom and Intercalation Graphene Structures



- Atomic Device Structures
  - Metamaterial Structures
    - Conductor (Graphene)
    - Insulating (Graphane or Fluorinated Graphene)
- Graphene/Graphane Logic Switches



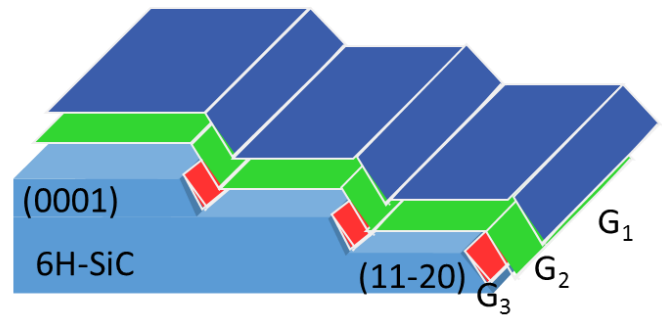
Atomic PN Junction
N-type (EG) and P-type (QFS EG)



Conclusion

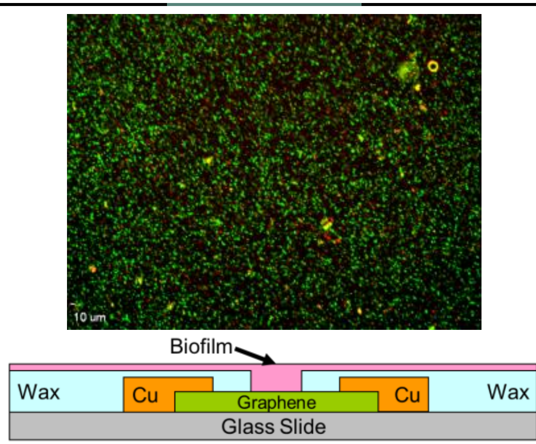
Hydrogen Intercalation weakens SiC electron-phonon interactions

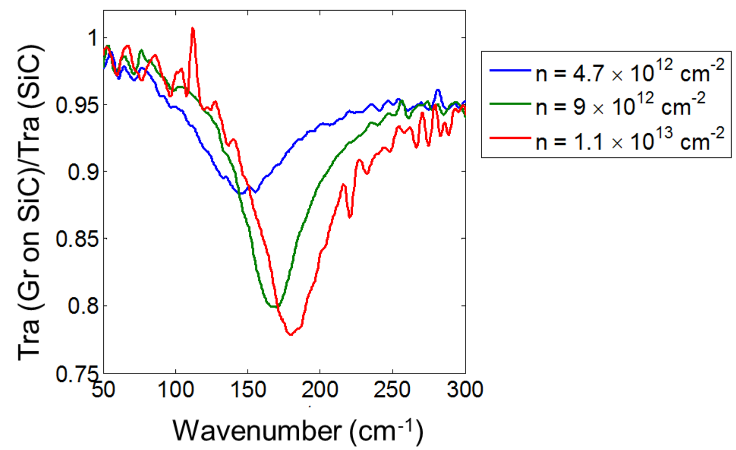
Narrow THz Plasmon Resonance of QFS BLG



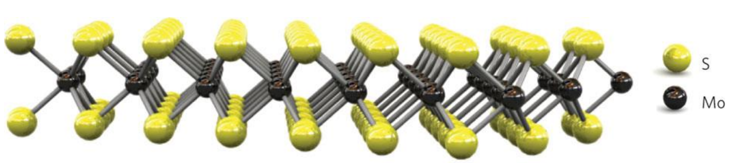
Formation of bacteria biofilm on graphene

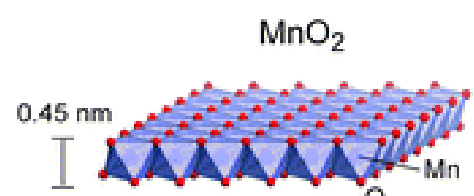
Graphene based biosensor demonstrated





Exploration of sensing and electrode capabilities of different novel 2D materials





Collaborators and Acknowledgement

- **NRL:** Dr. Rachael Myers-Ward, Dr. Kurt Gaskill, Dr. Chip Eddy, Dr. Fritz Kub, Dr. Glenn Jernigan, Dr. Michael Maestro, Dr. Jennifer Hite, Dr. Ginger Wheeler, Dr. David Tulchinsky, Dr. Anindya Nath, Dr. Anthony Boyd, Dr. Alex Kozen
- **UMD:** Dr. Thomas Murphy, Dr. Andrei Sushkov, Dr. Dennis Drew
- **USC:** Dr. MVS Chandrashekhar, Dr. Tangali Sudarshan, Dr. Alan Decho, Dr. Chris Williams, Dr. John Weidner, Dr. Andrew Greytak
- **Georgetown:** Dr. Paola Barbara
- **Monash:** Dr. Michael Fuhrer
- **MIT:** Dr. Jeehwan Kim
- **Carnegie Mellon:** Dr. Randall Feenstra
- **Clemson:** Dr. Goutam Koley
- **Max Planck:** Dr. Ulrich Starke
- **Stuttgart:** Dr. Petr Neugebauer
- **Vanderbilt:** Dr. Joshua Caldwell
- **Center for Nanotechnology Innovation (Italy):** Dr. Camilla Coletti
- **UC Berkeley:** Dr. Lili Jiang