SAND2011-6550P

Functionalizing Graphene as a Template for Understanding Charge Separation & Transfer

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Project Visit
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Collaborators & Contributors

- **David Wheeler**, SNL – Synthetic Organic Chemistry
- **Taisuke Ohta**, SNL – Synthesis of Epitaxial Graphene on SiC
- **Thomas Beechem**, SNL – Scanning Raman Spectroscopy
- **T.J. Ross & Stephen Howell**, SNL – CMOS Fabrication

- **Keith Stevenson**, UT Austin
- **Xiaoyang Zhu**, UT Austin

- **John Grey**, U. New Mexico – Molecular orientation

- **Jose Luis Cruz-Campa**, SNL – Inorganic thin-film PV

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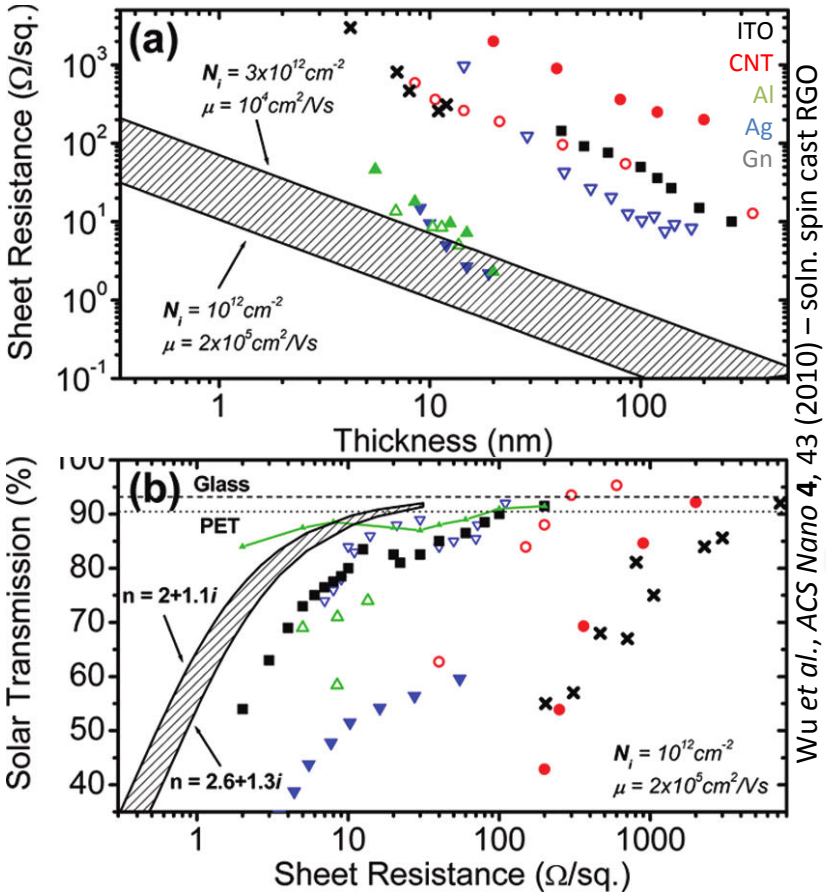
Motivation

EC-LDRD

Develop transparent electrodes with well-controlled electrical & chemical properties for PV applications



Wu *et al.*, *ACS Nano* **4**, 43 (2010) – soln. spin cast RGO

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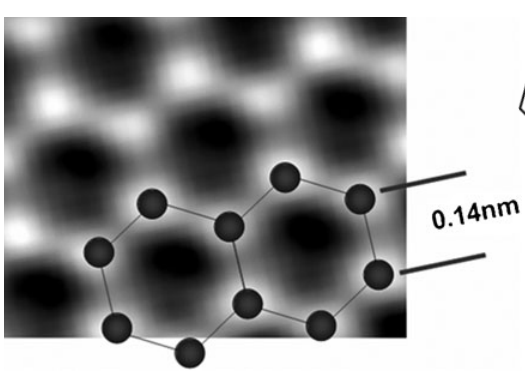
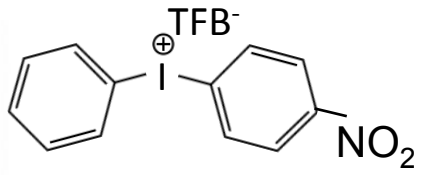
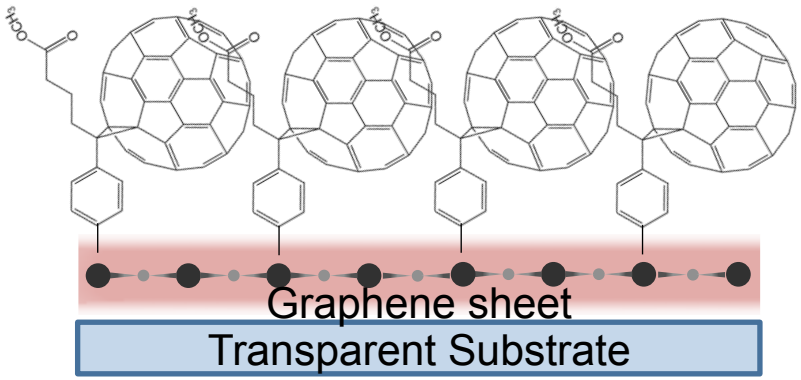
Synthesize model substrates and interfaces to understand charge separation & transfer in PV & energy storage devices







LDRD

Enable graphene-based microelectronics by tailoring electronic properties via chemistry

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Graphene

- Gaps in the literature
  - Functionalization on basal plane of perfect sheets
  - Charge transfer to/from basal plane
  - Functionalization vs. device perf.
- Use "perfect" 1-2 ML graphene
  - Epitaxially grown on SiC
  - Grain sizes ~ millimeters to wafer
  - 1 ML: T = 0.97, $R_{\square}$ = 1.5 kΩ/□
- Systematically tune electronic, chemical, structural properties
  - Controlled functionalization
  - Understand chemical kinetics and dynamics
- Understand the effects on charge transfer to/from graphene
- Correlate to device properties

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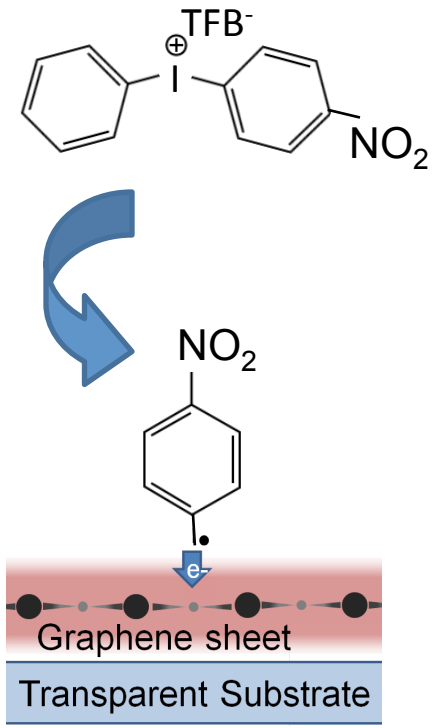
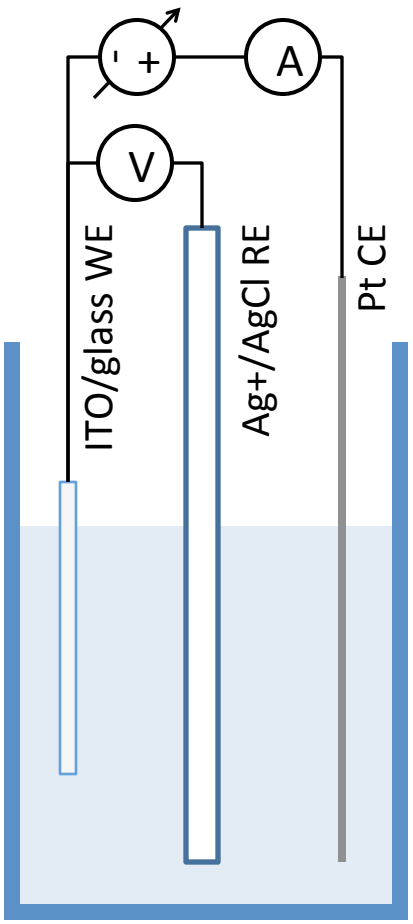
ITO Functionalization with NO_2-phenyl iodonium

- 4-nitrophenyl iodonium tetrafluoroborate
  - Iodonium reactions are electrochemically controlled
  - NO_2 can be electrochemically counted & detected with XPS
  - NOT symmetric
- Goal: Achieve single and sub-monolayer coverage of graphene
- Tried experiments on ITO first (epitaxial graphene is manpower intensive)



Cyclic voltammetry
0.3 V -> -1.3 V -> 0.3 V
Scan rate = 0.05 V/sec
2-10 scans



20 mL Acetonitrile
0.1 M TBAFB
0.01 M NO_2-aryl iodonium$^+$/TfO^-

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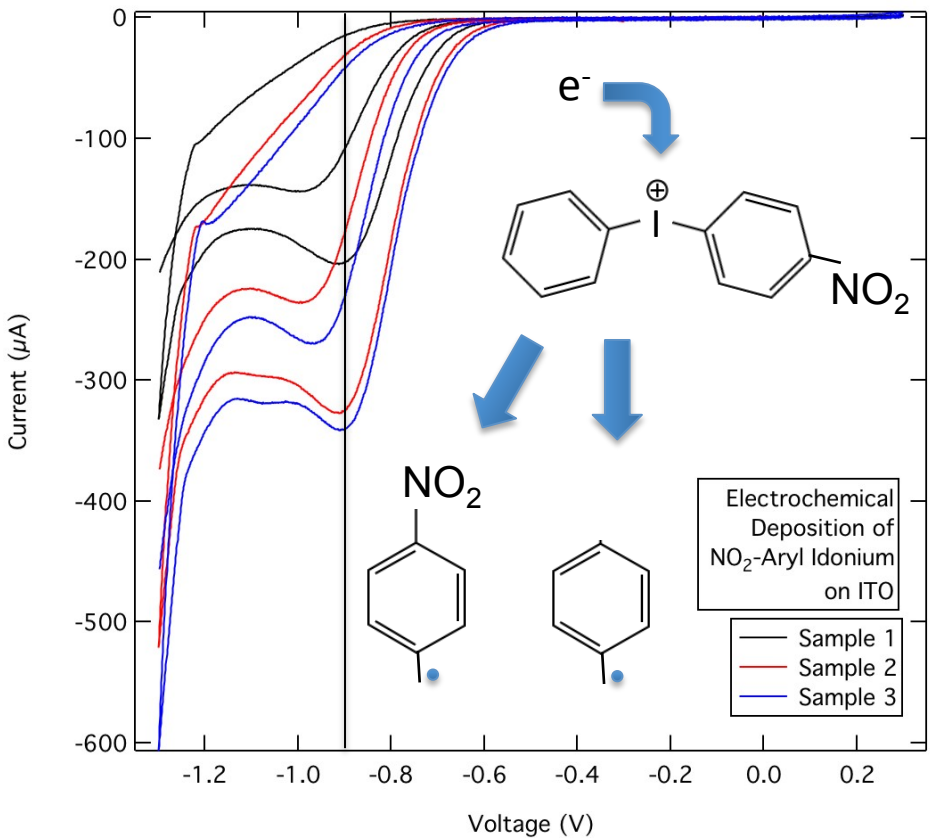
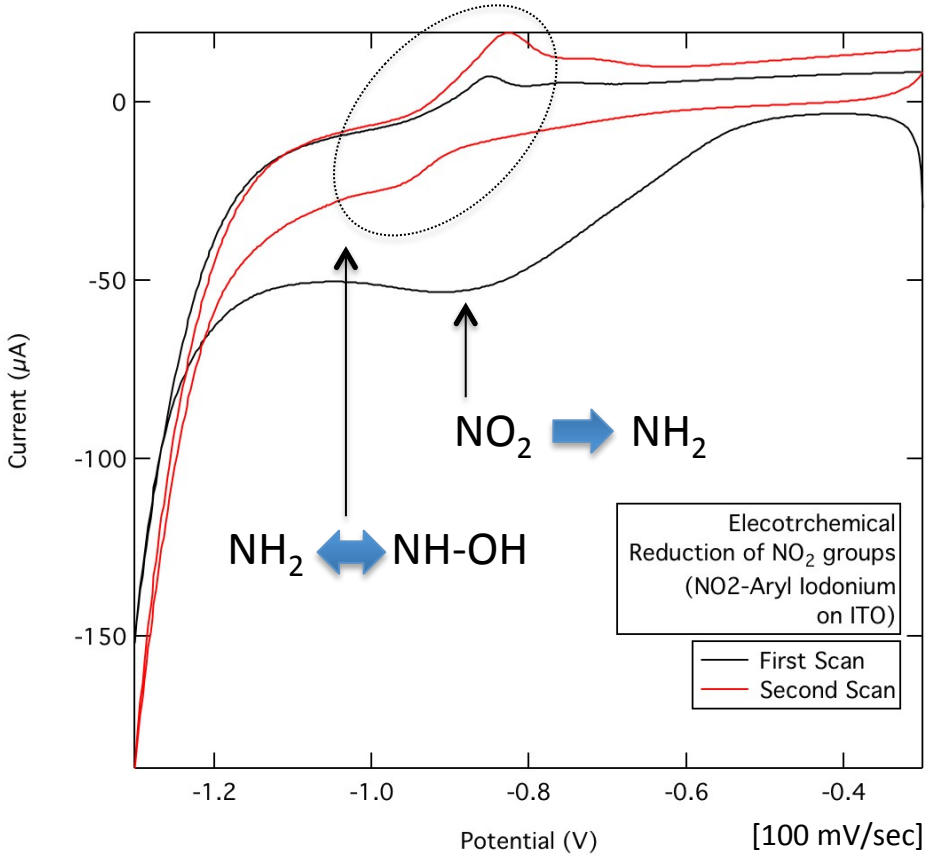
NO_2-phenyl ITO – CV Deposition & Detection





$Q = nFA\Gamma$

Q = charge passed through cell = 5.767 x 10^{-5} Coul

N = number electrons in reaction = 6

F = Faraday's constant = 96485.3415 Coul mol^{-1}

A = area of working electrode = 0.80 ± 0.02 cm

Γ = molecular density

Γ = 1.26 x 10^{-10} mol cm^{-2}
= 7.59 x 10^{13} molecules cm^{-2}

(Graphene = 4 x 10^{15} C cm^{-2})

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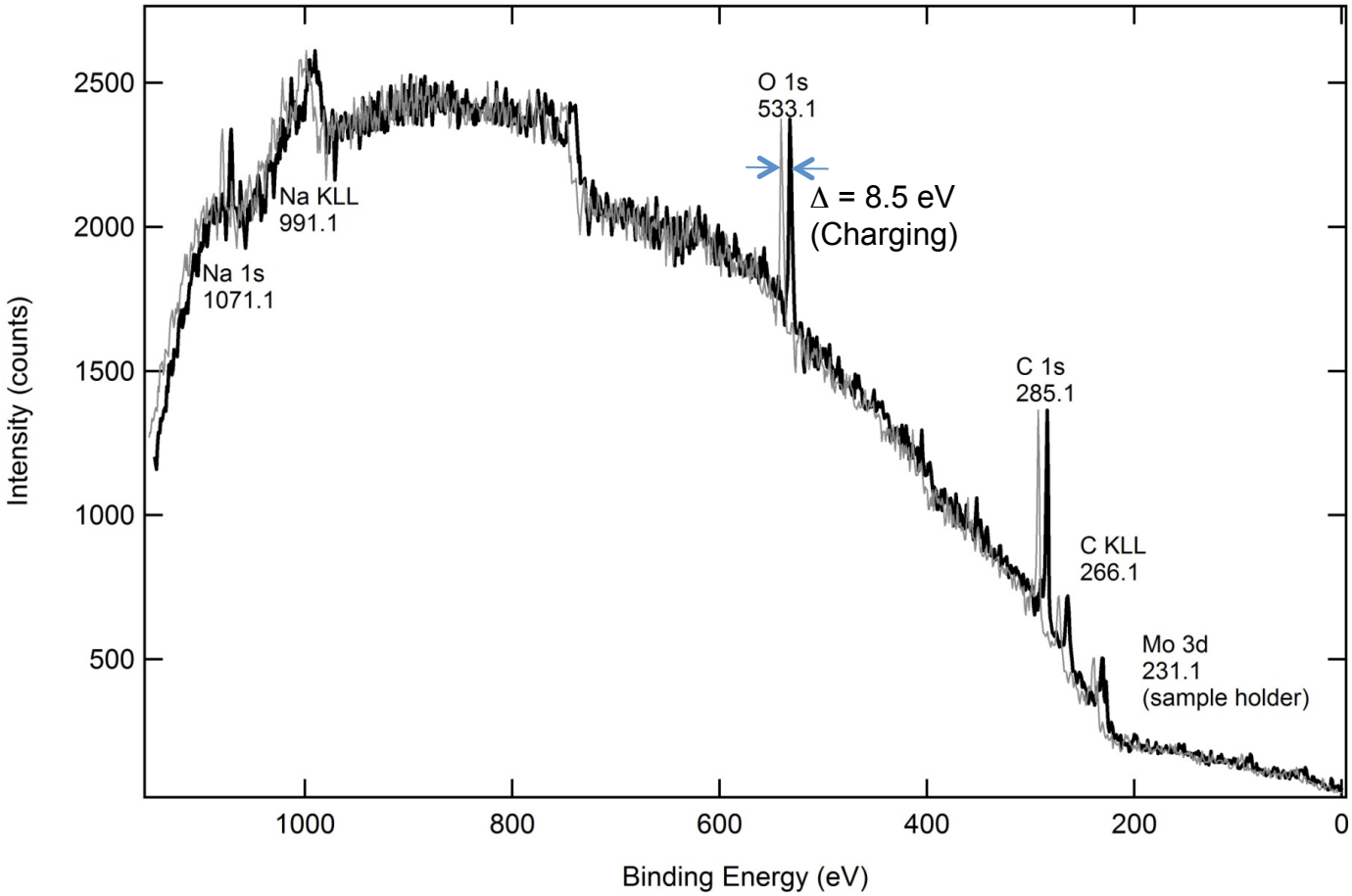
NO_2-phenyl ITO – XPS

- XPS indicates charging => thick film



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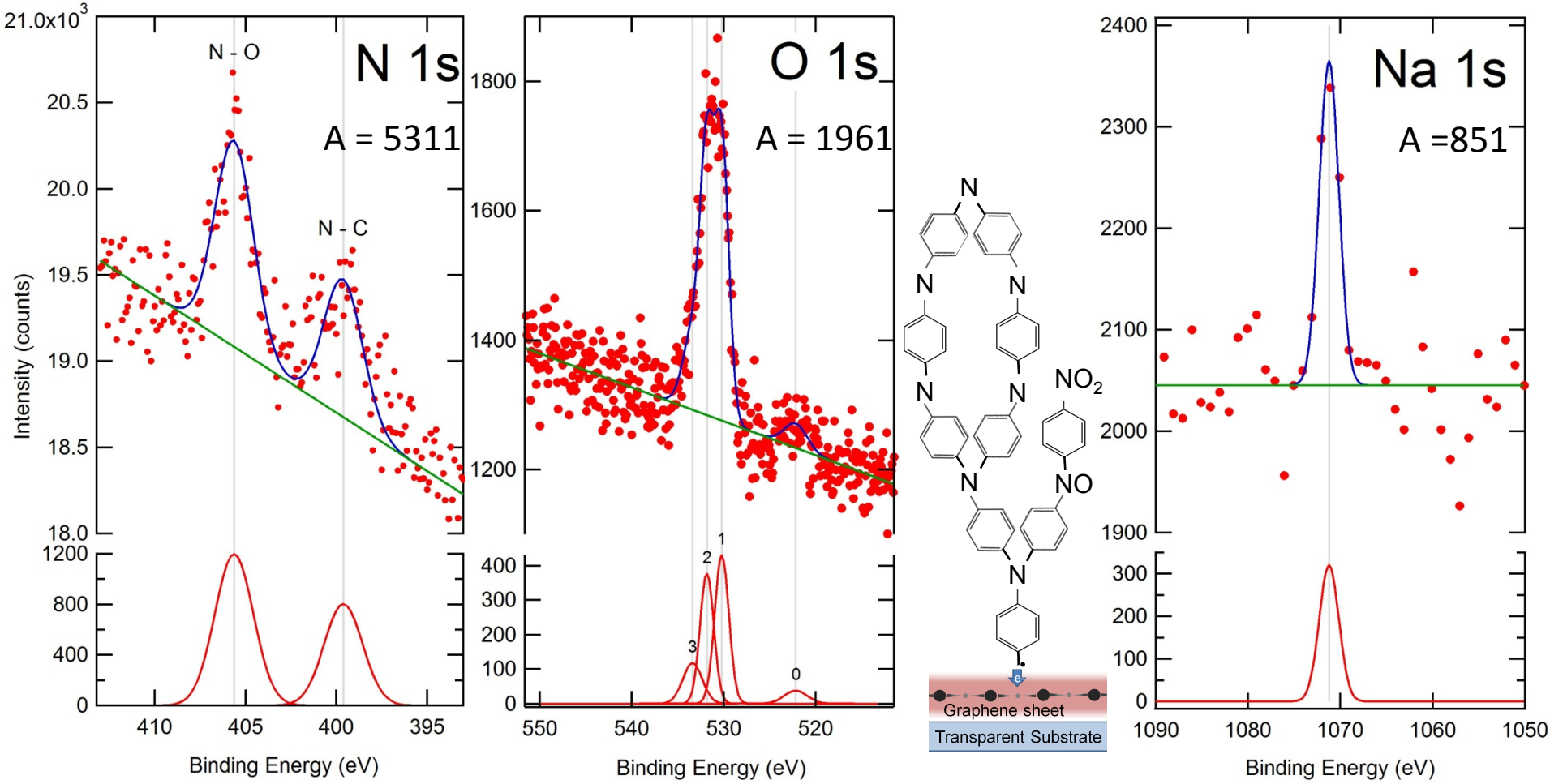
NO_2-phenyl ITO – XPS



N:O ratio = 2.7, NOT 0.5 as expected!
Polymerization of NO_2-aryl groups? => thick insulating film

Contamination from NaCl used in Ag/AgCl RE

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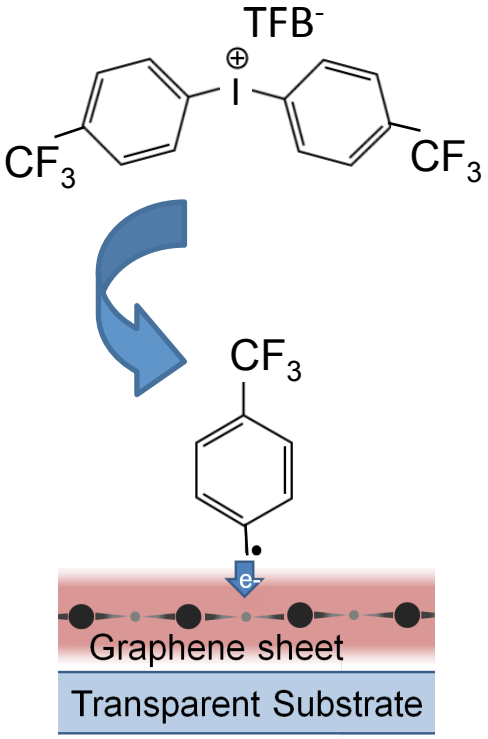
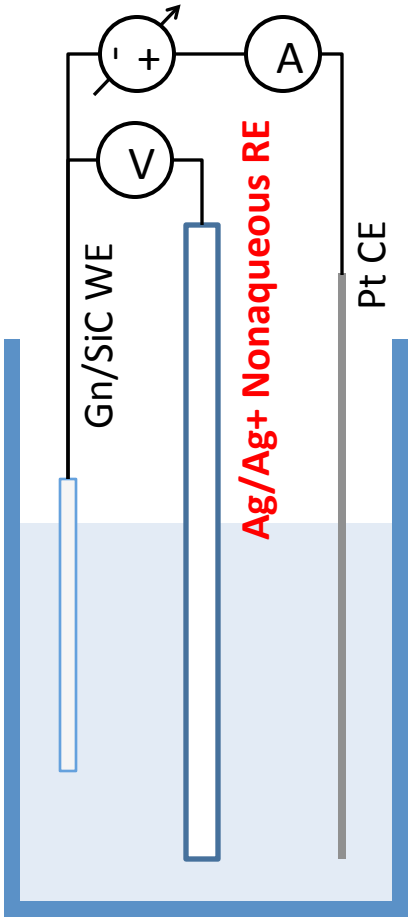
Graphene with CF_3-phenyl iodonium

- Epitaxial graphene
  - N-doped 6H-SiC(0001)
  - Hydrogen-etched 1400 °C, 20 min
  - Argon annealed 1600 °C, 30 min
- Bis(4-trifluomethylphenyl) iodonium tetrafluorborate
- Cyclicvoltammetry
  - 0.3 V -> -1.3 V -> 0.3 V
  - 0.05 V/sec
  - 2 scans
- Chronoamperometry
  - Vapp = -1.2 V
  - 5, 10, 25 sec
  - NO difference based on time





20 mL Acetonitrile
0.1 M TBAFB
0.01 M NO_2-aryl iodonium$^+$/TfO^-

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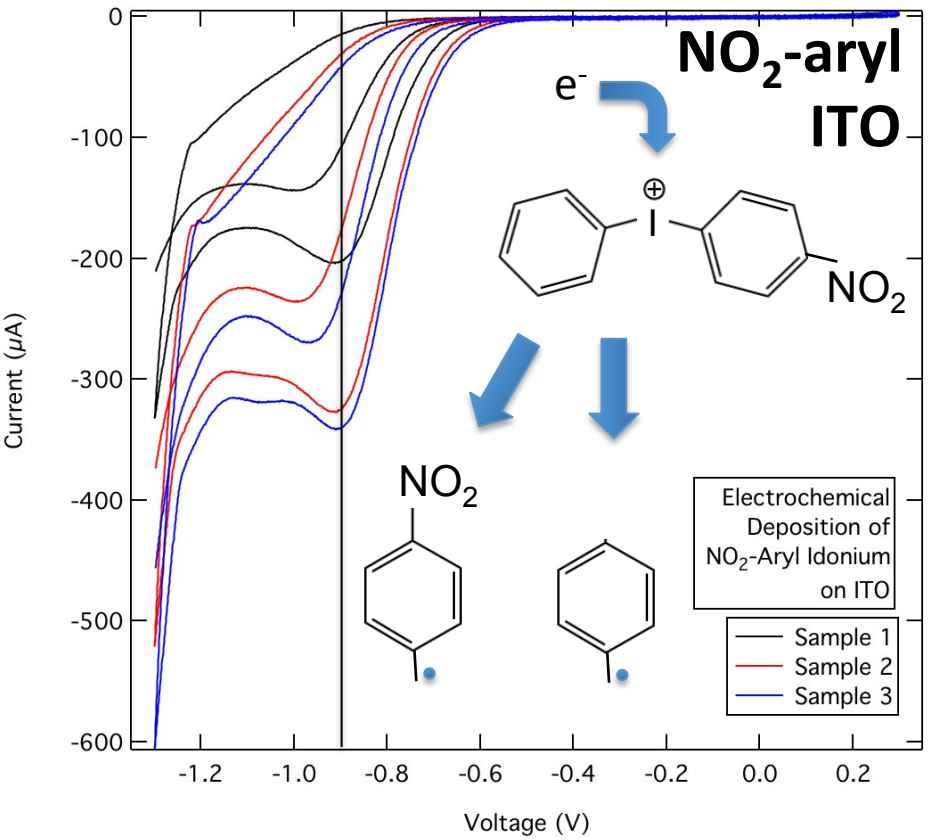
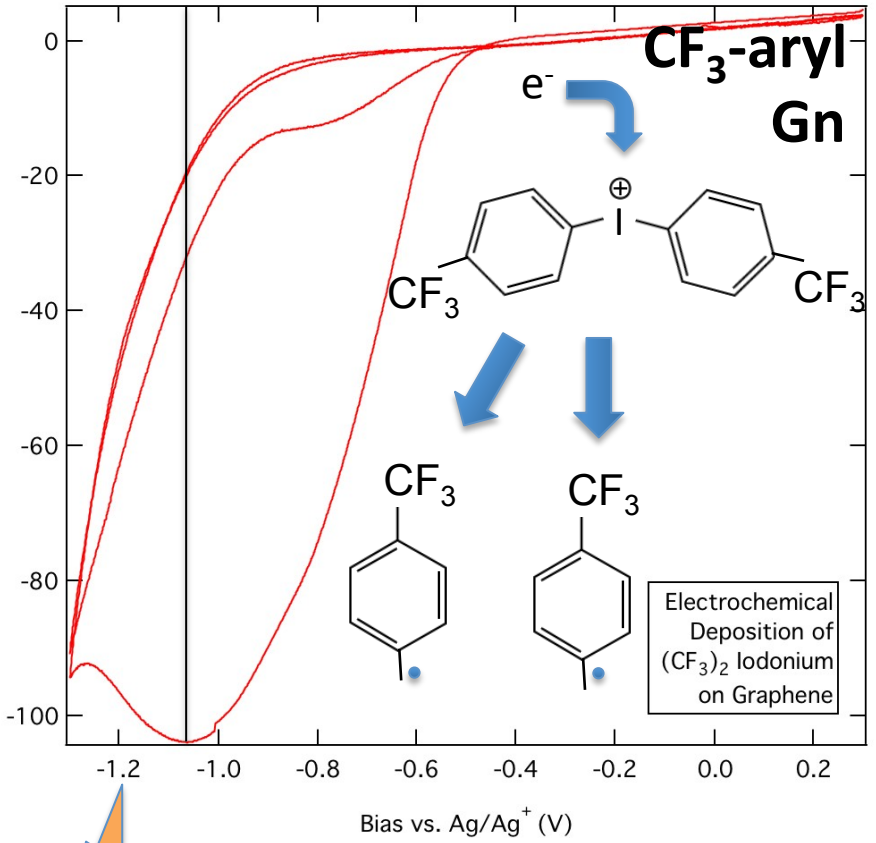
CF_3-phenyl Graphene – Electrochemistry





Chronoamp performed at
V = -1.2 V for t = 5, 10, 25 sec.
Exponential decay is observe.

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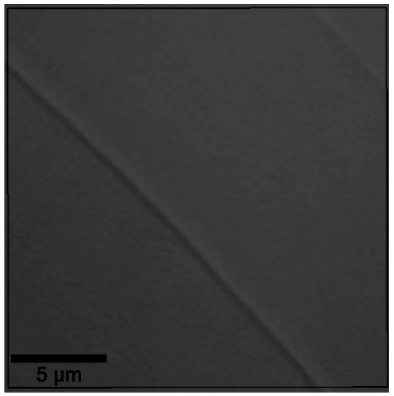
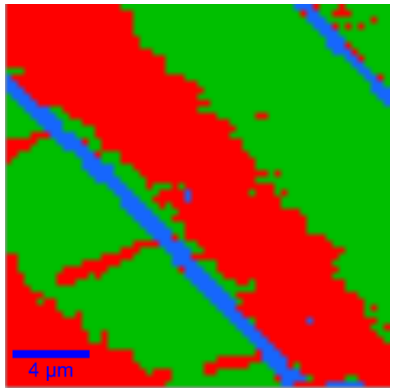
Data calibrated to Si and SiC.
SiC background subtracted out.

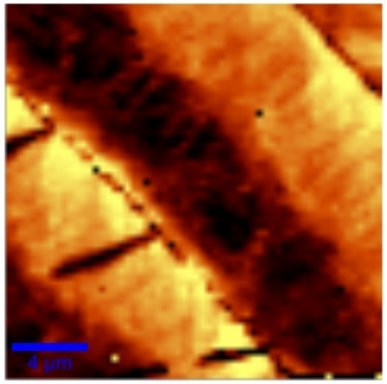
CF_3-phenyl Graphene – Raman



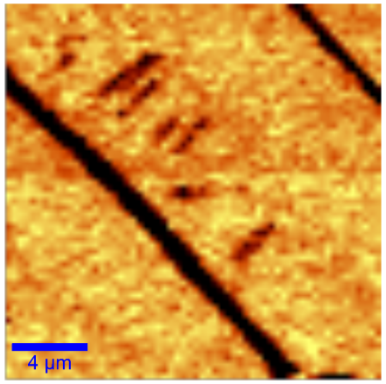
Visual



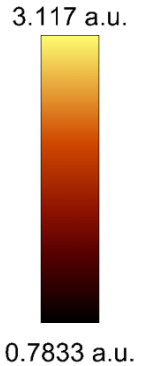
Cluster Analysis

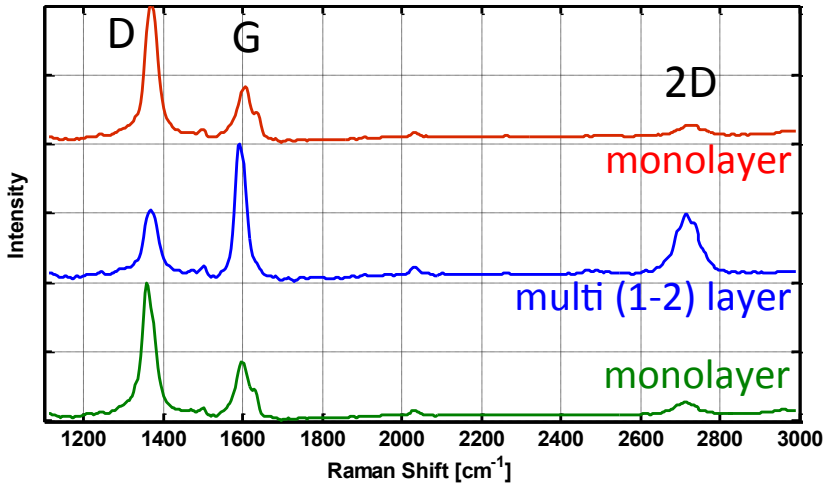


Peak Position (D)



I(D)/I(G)





2 different monolayer regions.
One strained relative to the other.
Very uniform otherwise, e.g., defect density.

Name	D-Peak	G-Peak	2D-Peak	2D-FWHM
Bilayer	1368.6	1593.9	2718.3	67
Monolayer 1	1361.6	1598.2	2714.1	86
Monolayer 2	1369.7	1603.6	2728.9	100

Additional Notes:

- Level of defectiveness is not greatly different than that of S090120 (25 sec CA method) that had "higher" degree of functionalization.
- Avg Monolayer I(D)/I(G)=2.42

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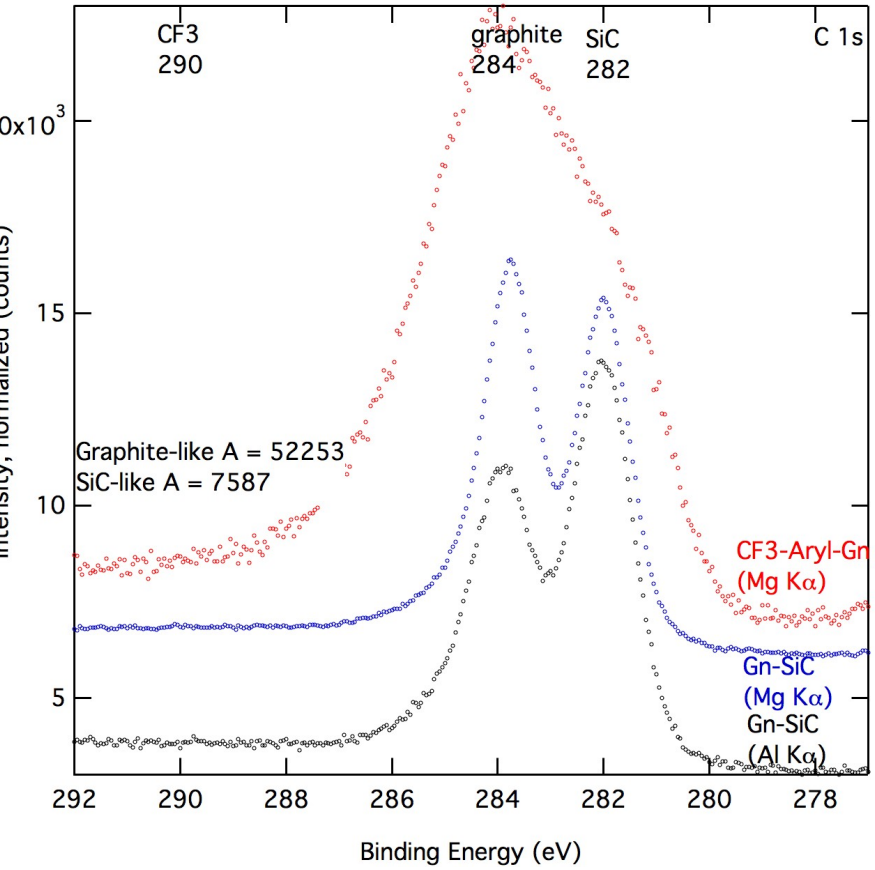
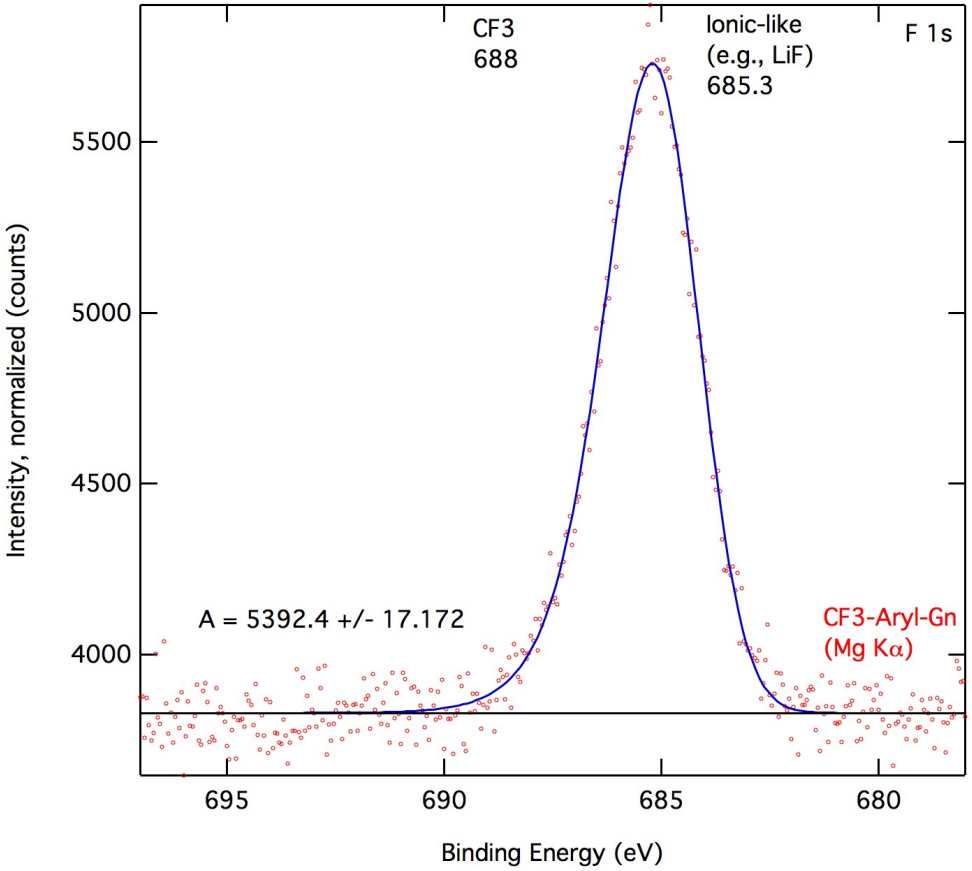
CF_3-phenyl Graphene – XPS





- Graphitic C 1s peak is very broad – disorder?
- Higher electron density around C 1s orbitals than expected – delocalization, screening, etc.?

- Higher electron density around F 1s orbital than expected – again a sign of delocalization or screening (or something else)?ß

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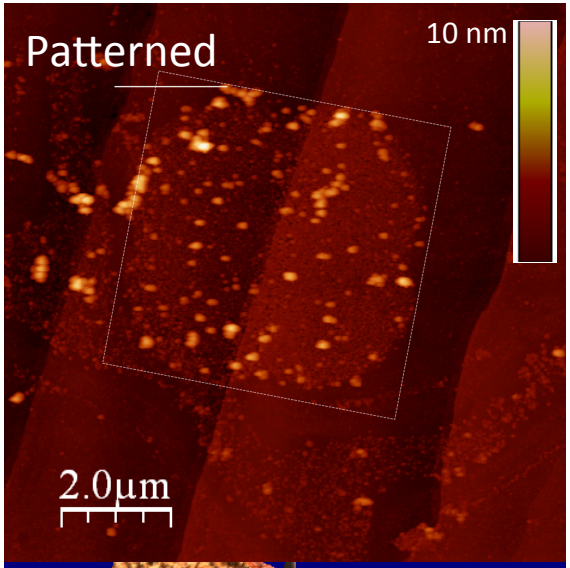
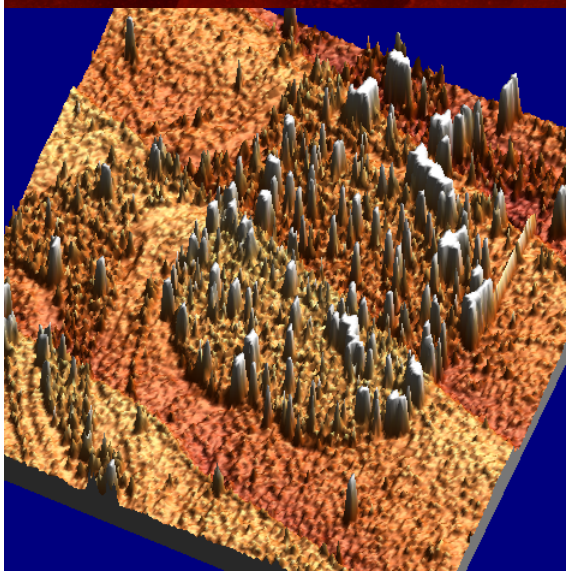
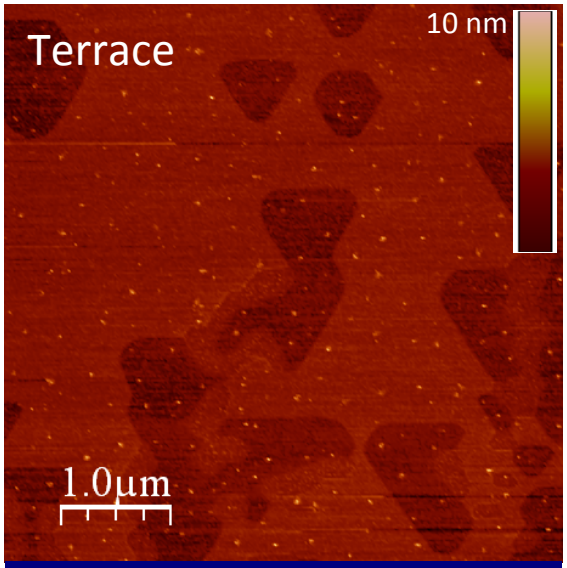
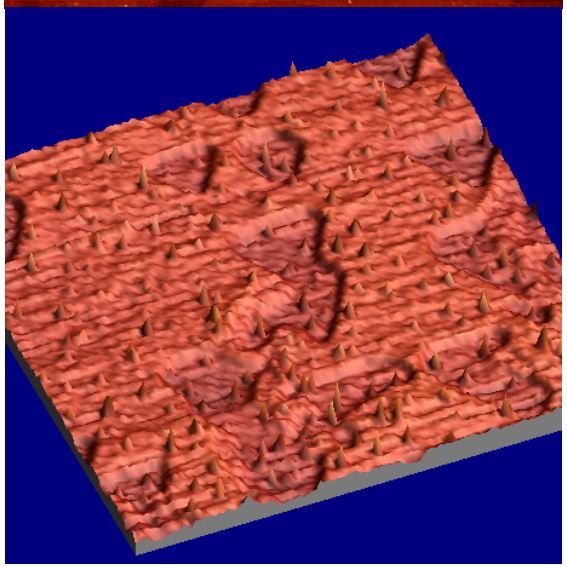
Details on step edge growth of Gn
Ohta et al., PRB 81, 121411R (2010)

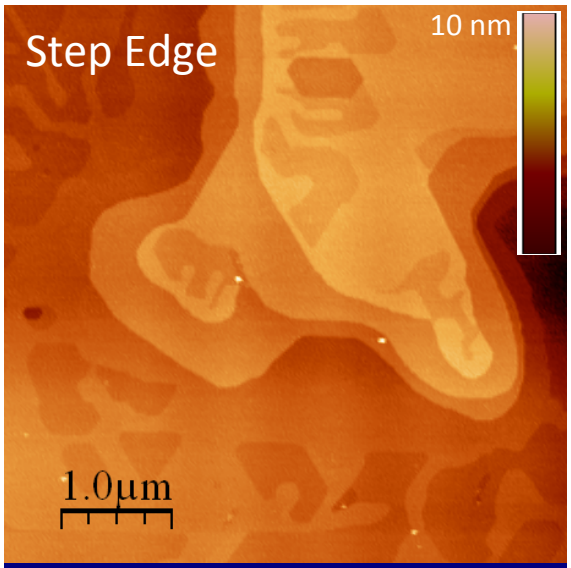
CF_3-phenyl Graphene – AFM

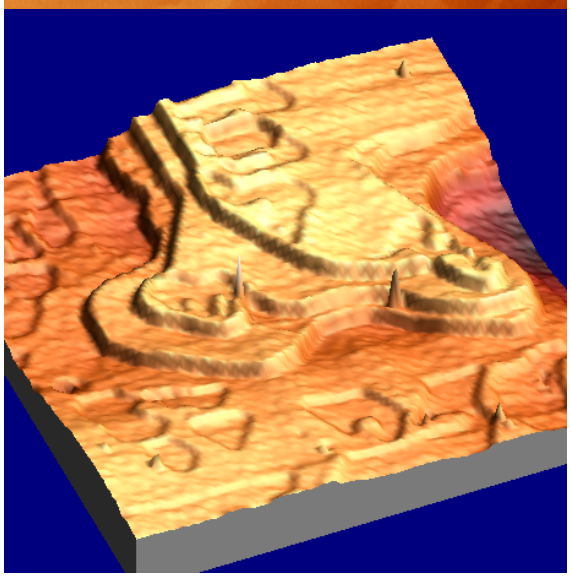












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Next Steps

- Complete installation of UV lamp to perform UPS.
- Obtain single and sub-monolayer films
  - Pulse chronoamperometry at $V < V_{p\text{-}red}$
- Repeat & perform additional electrochemical deposition on graphene
  - Understand electronic, chemical, and structural changes as a result of various covalent, noncovalent, and function group modifications
  - Monitor their effects on charge transfer to/from graphene, and ultimately on device behavior
- Modify functional groups to make ideal interfaces for studying charge transfer and separation processes

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