Accelerating the Development of Transparent Graphene Electrodes through Basic Science-Driven Chemical Functionalization

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LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Early Career R&D Program

Sandia National Laboratories

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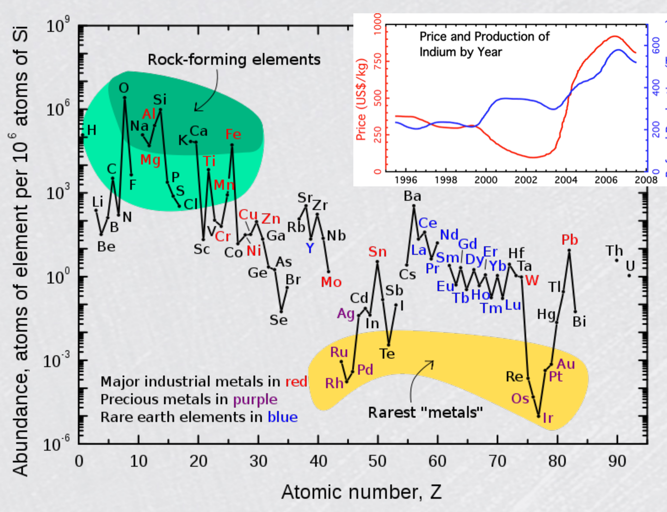
Problem

- Transparent conductors are critical for optoelectronics and ECIS applications.
  - photovoltaics
  - light-emitting diodes / displays
  - IR coatings / electrochromic windows
- Conducting oxides, i.e., ITO
  - ✓ High conductivity and transparency
  - ✓ Resists moisture and scratching
  - × Brittle and non-conformable
  - × Difficult to tune chemical/physical properties
  - × Rare/expensive materials (indium)

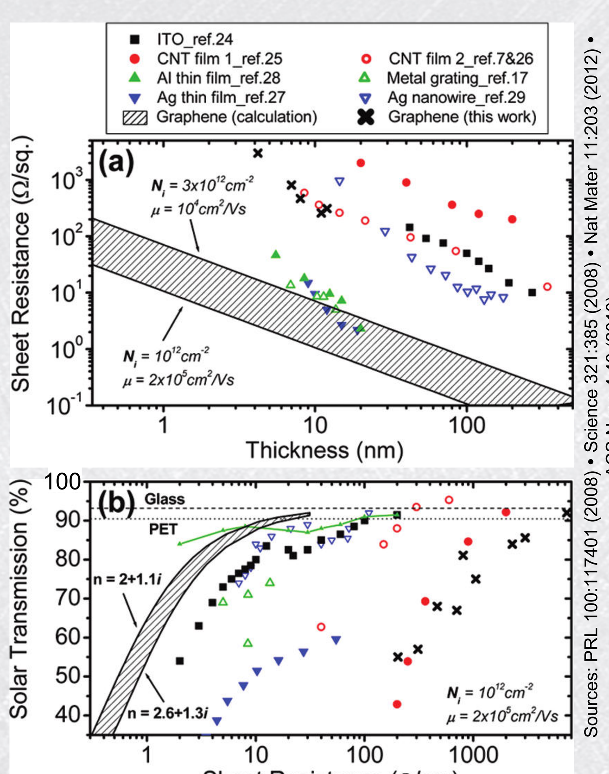


Approach

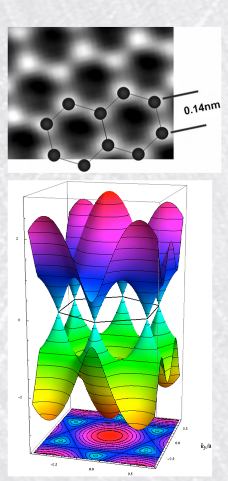
Graphene as a Transparent Electrode

- "Ideal" for transparent electrodes:

Resistivity	1 mΩ/□ (0.65x Cu)
Transparency	0.98
Thermal Conductivity	5000 Wm^{-1}K^{-1} (~diamond)
Mechanical Strength	1 TPa (200x steel)

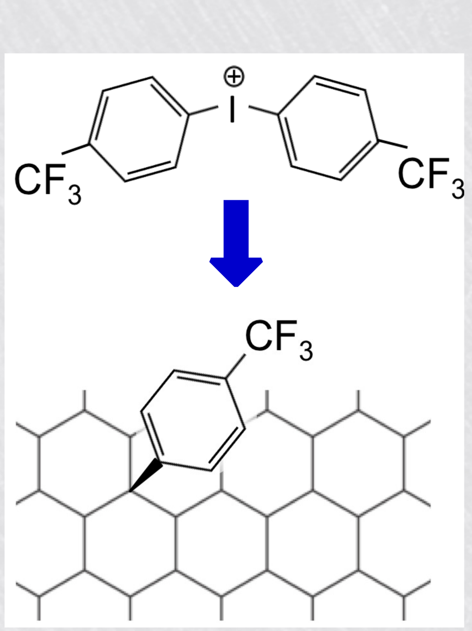


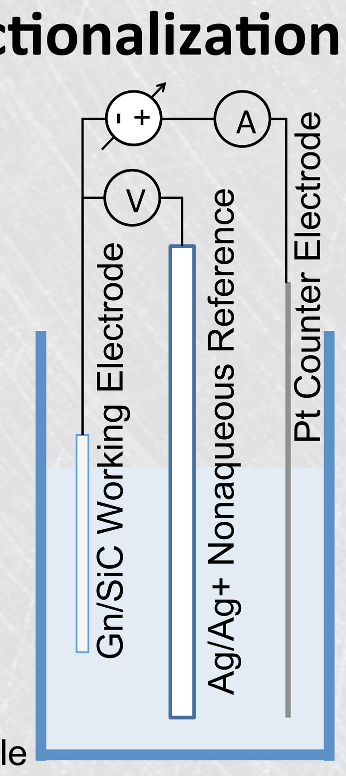
- Issues
  - These are "perfect" values
  - How to get charge in/out?
    - Van der Waals "out-of-plane"
    - Momentum/energy matching
  - Device fabrication
    - Surface energy/wettability
    - Work function/charge injection



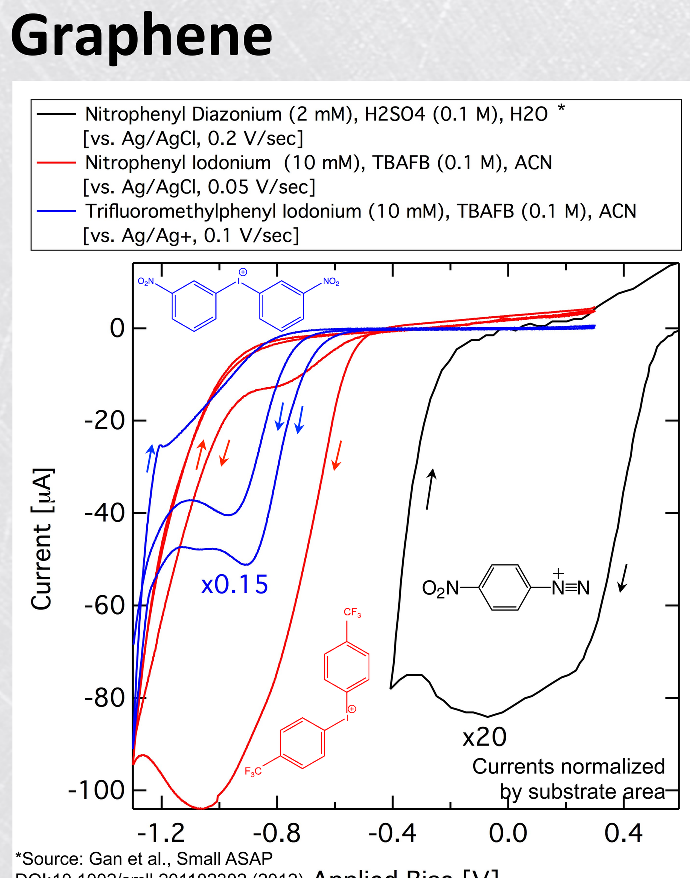
Electrochemical Functionalization

Iodonium Functionalization of Graphene





20 mL Acetonitrile
0.1 M TBAFB
0.01 M CF_3-aryl iodonium$^+$/TfO$^-$



- Iodonium functionalization of graphene is a novel approach.
  - More controlled than diazoniums used in most literature approaches.
- **Substrate: Epitaxial graphene on n-6H-SiC(0001).**
  - H-etched at 1400 °C, 20 min, Ar-annealed at 1600 °C, 30 min
- **CF_3Ph functionalization from iodonium precursor.**
  - Cyclic voltammetry (1-2 scans)
  - Chronoamperometry, diffusion- and kinetically-limited regimes (1-30 sec)
  - Simple dip coating

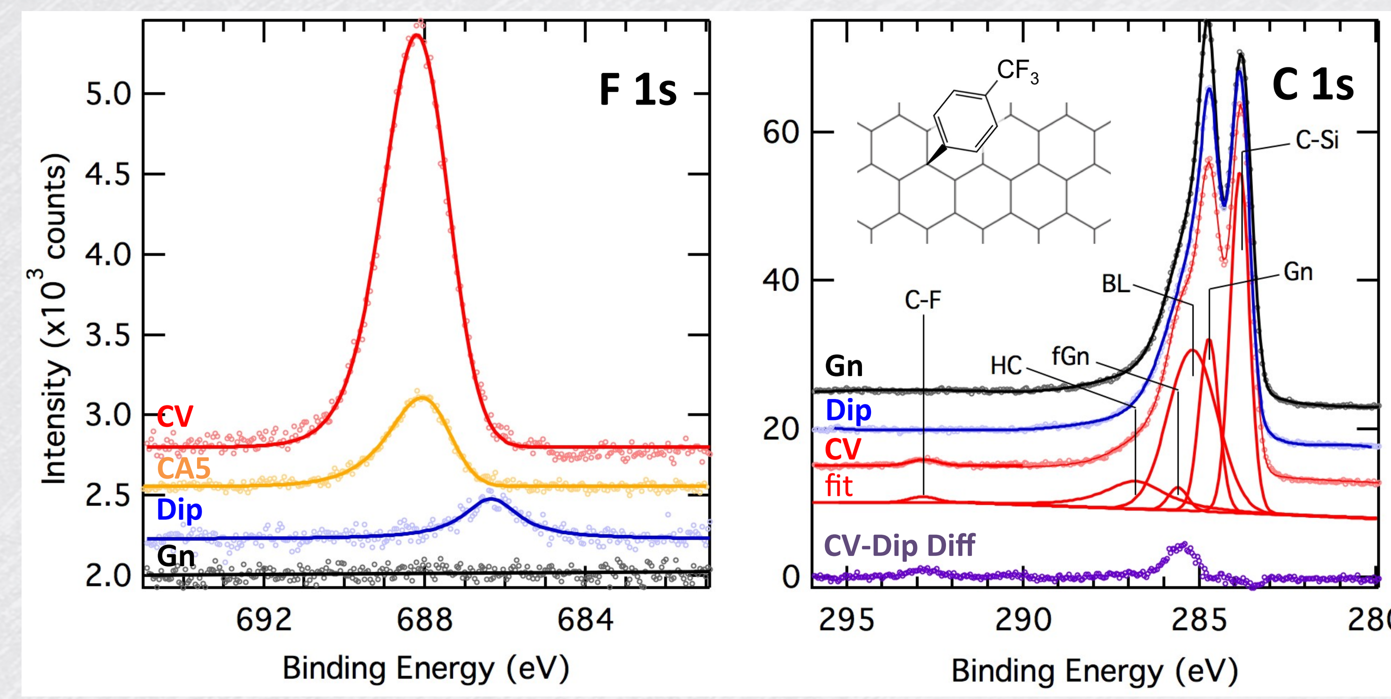
Significance

- Demonstrated controlled basal plane chemical functionalization of near-perfect epitaxial graphene grown on SiC(0001).
- Phenylene functionalization can serve as linkages for attaching other molecules; first step to more directed functionalization.
- Changes in electronic structure promising for tailored properties in integrated circuits, quantum wells, and transparent electrodes.

Results

Chemical States: X-Ray Photoemission

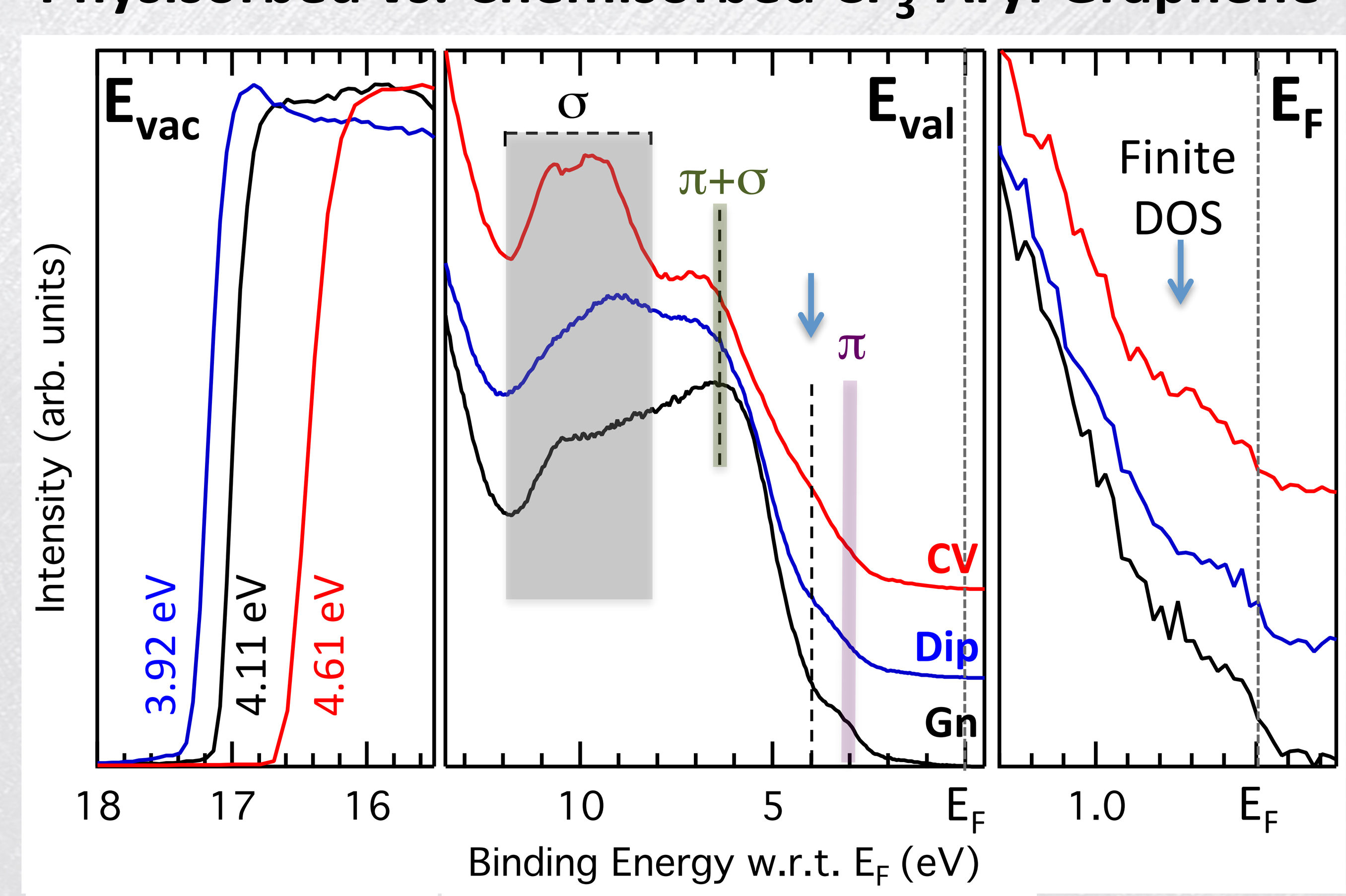
Physisorbed vs. Chemisorbed CF_3Ph on Graphene



- CF_3Ph interact with graphene through phys- and chemisorption.
- Chemisorbed CF_3-aryl graphene shoulder can only be fit with an additional peak +1 eV from graphene peak: graphene e^- ➔ CF_3.
- 3.2 x 10^{14} CF_3Ph molecules-cm^{-2} ➔ Closed-pack monolayer

Electronic States: UV Photoemission

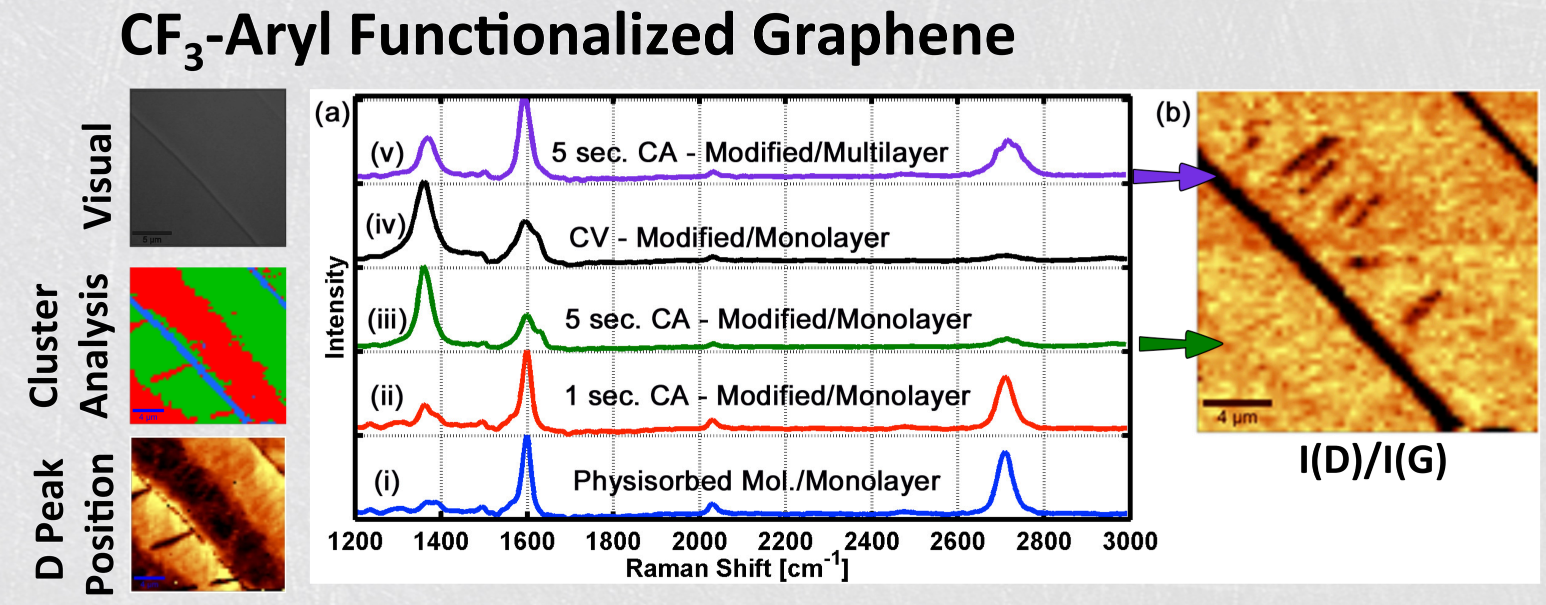
Physisorbed vs. Chemisorbed CF_3-Aryl Graphene



- **Dip**: Increased σ intensity from CF_3Ph; broad indicates disorder
- **CV**: Sharper σ peak ➔ better orientation by covalent anchoring
  π states to HBE ➔ sp^2 to sp^3 conversion by covalent bonding
- Work function differences also due to molecular orientation.

Uniform Coverage: Scanning Raman

CF_3-Aryl Functionalized Graphene



- Functionalization introduces a graphene "defect" peak in Raman.
  ➔ Breaking of sp^2 configuration, conversion to sp^3 bonds.
- Functionalization is very uniform over the basal plane.
- Two different monolayer regions present with differing strain.

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