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Graphene-Based Materials: Model Systems for Understanding Interfacial Charge Separation & Transfer

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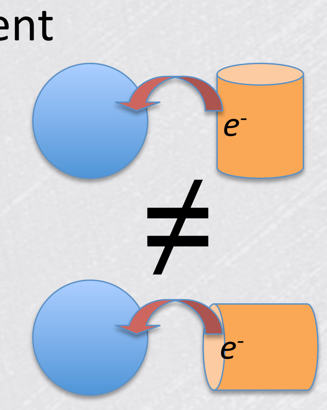
EFRC CST

Problem

Interfacial Charge Separation and Transfer

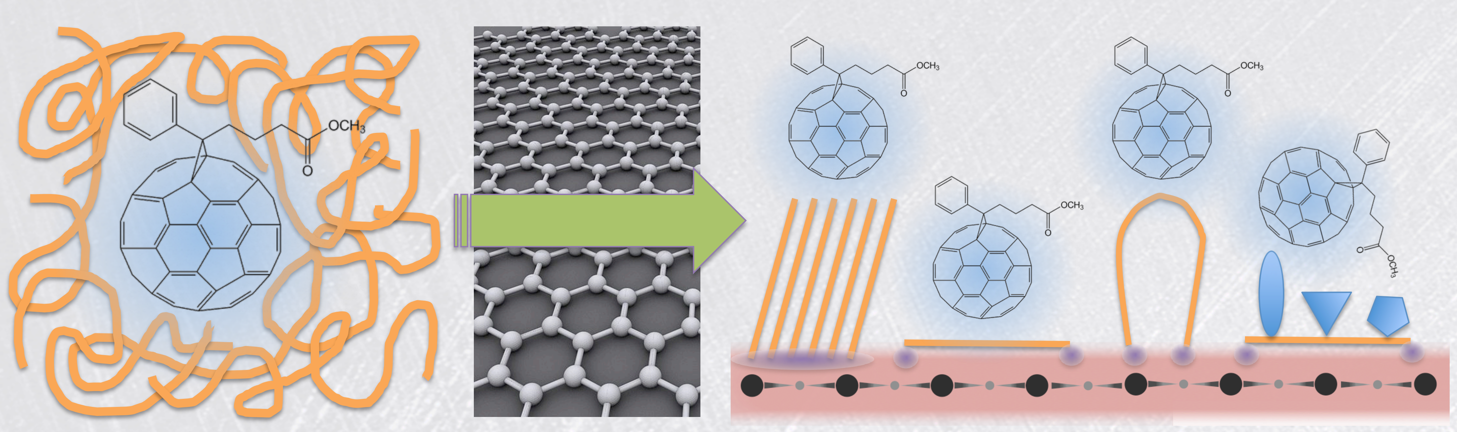
- Photovoltaic and energy storage devices rely on efficient interfacial charge separation and transfer.
  - Why are some materials systems better than others for CST?
  - What factors lead to efficient CST?
    - molecular and intermolecular electronic structure
    - molecular conformations and molecule-molecule morphology
    - intramolecular and intermolecular screening
    - excited state dynamics, energy cascades, assymmetries, *etc.*



- **No platform to independently control these properties.**

Approach

Graphene as a Molecular Template

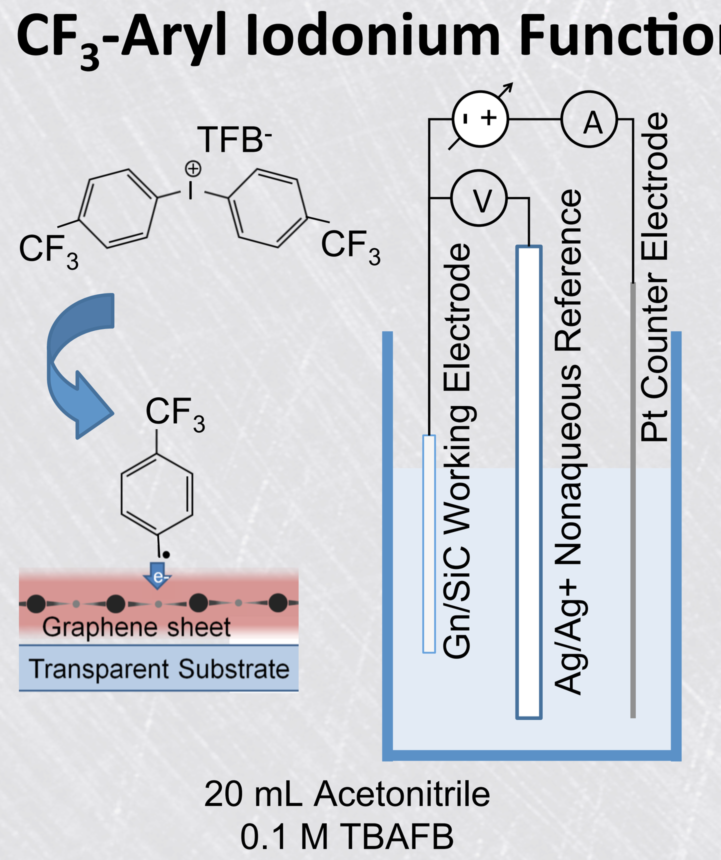


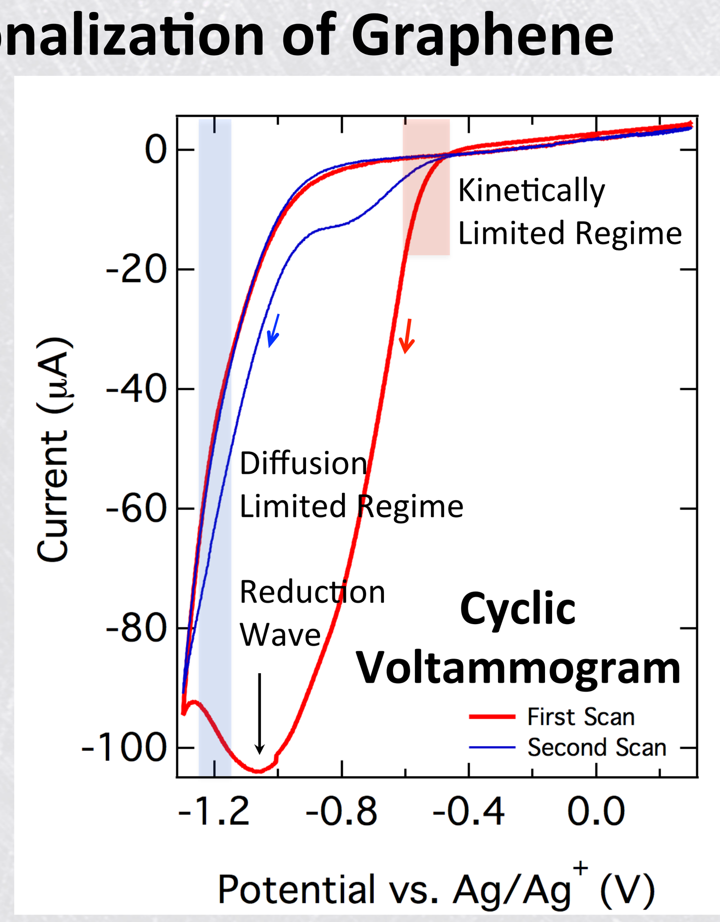
Hard to characterize: PCBM surrounded by a random polymer network has certain ill-defined properties.

An ideal template: Highly ordered graphene is well-suited for tailoring chemical and physical properties through molecular design. Graphene can also be used for its similarity to π-conjugated molecular systems.

Electrochemical Functionalization

CF_3-Aryl Iodonium Functionalization of Graphene





- **Substrate is near-perfect epitaxial graphene on n-6H-SiC(0001).**
  - H-etched at 1400 °C, 20 min
  - Ar-annealed at 1600 °C, 30 min
- **Bis(4-trifluoromethylphenyl) iodonium tetrafluoroborate** (CF_3-aryl) functionalization using electrochemical methods.
  - Cyclic voltammetry (1-2 scans)
  - Chronoamperometry, diffusion- and kinetically-limited regimes (1-30 sec)
  - Simple dip coating

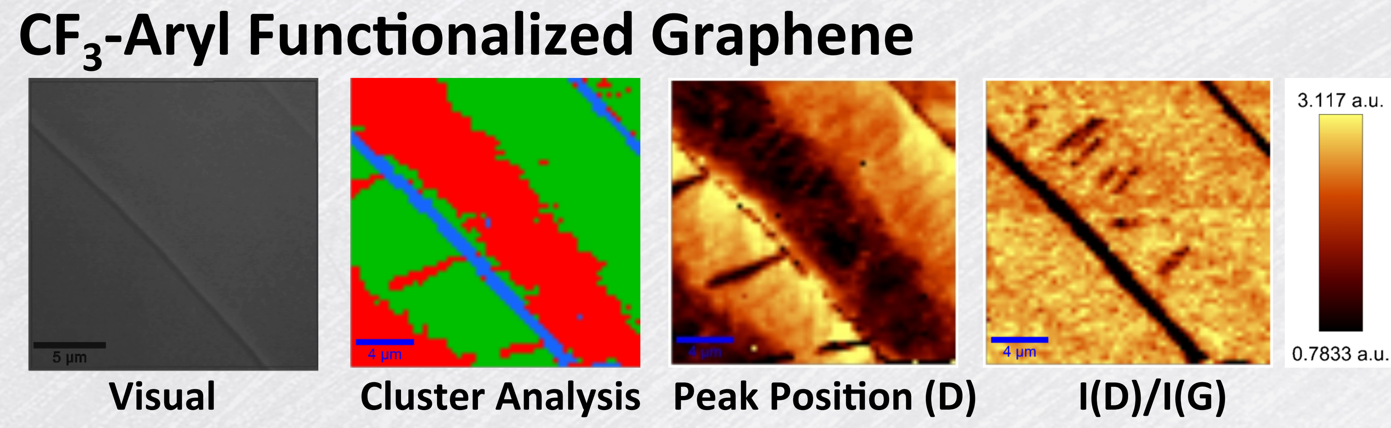
Significance

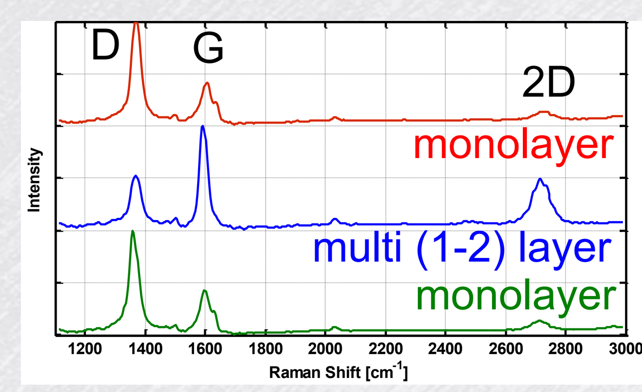
- Demonstrated controlled basal plane chemical functionalization of near-perfect epitaxial graphene grown on SiC(0001).
- Arylene functionalization can serve as a linkages for attaching other molecules; first step to more directed functionalization schemes.
- Changes in electronic structure promising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

Results

Uniform Coverage: Scanning Raman

CF_3-Aryl Functionalized Graphene



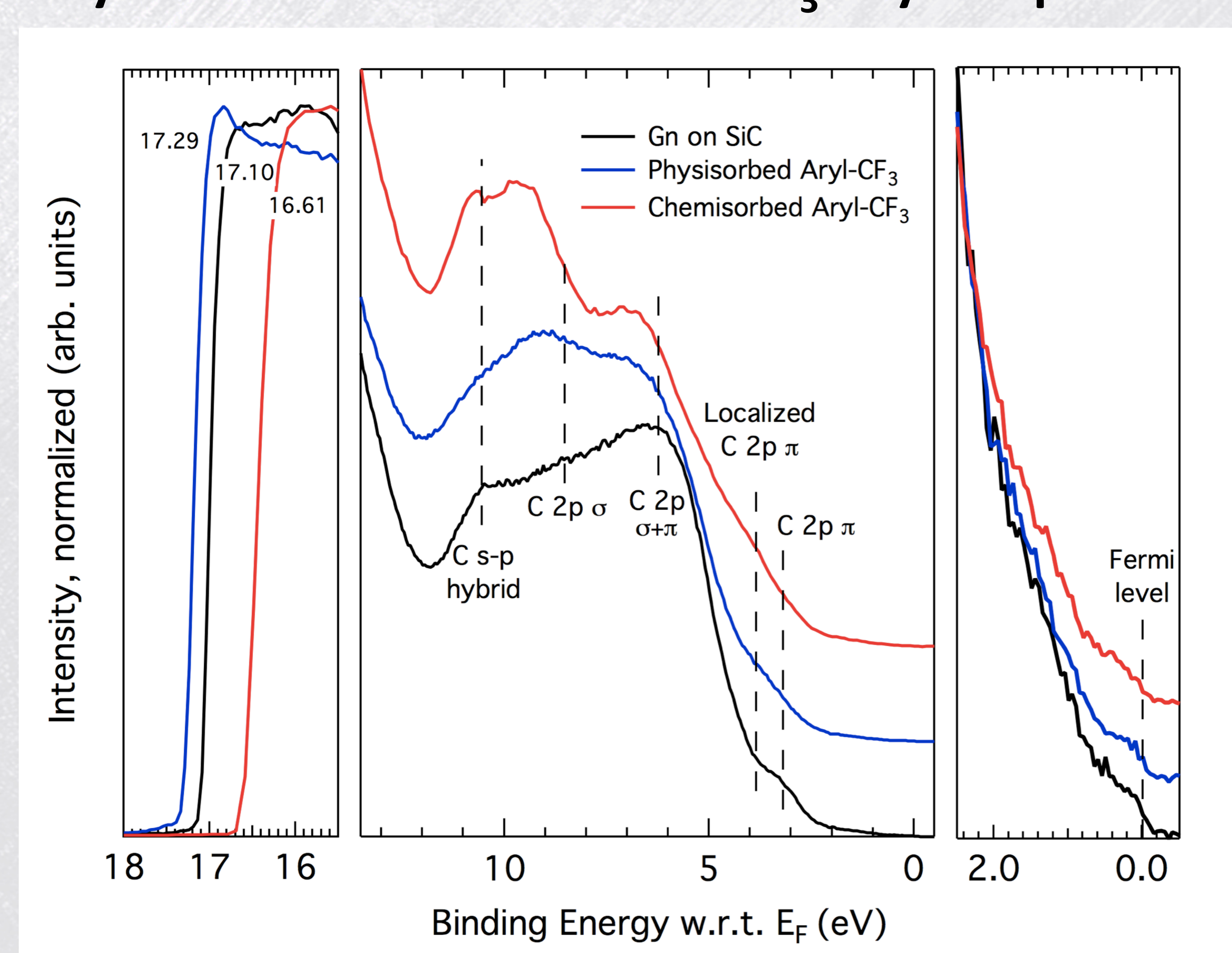


Name	D-Peak	G-Peak	2D-Peak	2D-FWHM
Bilayer	1368.6	1593.9	2718.3	67
Monolayer 1	1361.6	1598.2	2714.1	86
Monolayer 2	1369.7	1603.6	2728.9	100

- Functionalization introduces a graphene "defect" peak in Raman.
- Functionalization is very uniform over the basal plane.
- Two different monolayer regions present with differing strain.

Electronic States: UV Photoemission

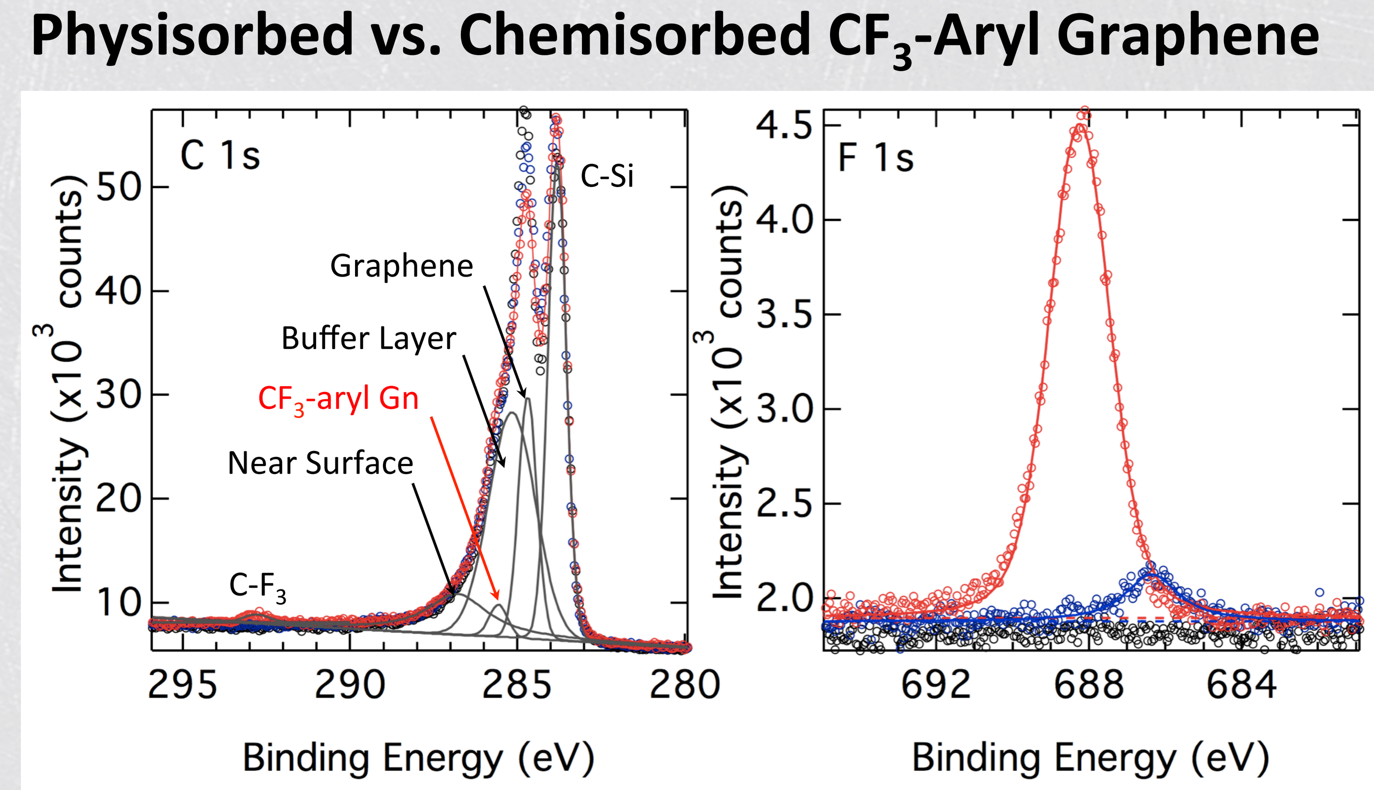
Physisorbed vs. Chemisorbed CF_3-Aryl Graphene



- Physisorbed CF_3-aryl: "pillow effect" decreases work function.
- Chemisorbed CF_3-aryl: charge transfer increases work function.
- Shift from delocalized to localized π states with functionalization.

Chemical States: X-Ray Photoemission

Physisorbed vs. Chemisorbed CF_3-Aryl Graphene



- Clear evidence of CF_3-aryl chemical interaction with graphene.
- Chemisorbed CF_3-aryl graphene shoulder can only be fit with an additional peak +1 eV from graphene peak: graphene e^- ➔ CF_3.

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