Understanding structure and Properties of electronic and biomaterials by Near Edge X-ray absorption Fine structure Spectroscopy

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Acknowledgements

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- Students of Banerjee Group

  Robert Dennis, Theodore Alivio
- BNL Chemsitry Jose Rodriguez, Sanjaya Senanayake, Duong Nguyen Phan

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Outline

- Materials explored in my 15 year of Synchrotron radiation Career
  - Photoresists
  - Polymers-Ultrahigh Molecular Weight Polyethylene, P3HT
  - Hard Disk Lubricants/SAM
  - Zeolites in-situ Catalytic reactions
  - C- allotropes-Carbon Nanotubes, Graphene
  - Metal Oxides/composites with Graphene structure and reactions

- Techniques used
  - Synchrotron Based X-ray absorption Methods
  - Electronic and magnetic structure via XMCD
  - IR Microscopy
  - Raman
  - GC

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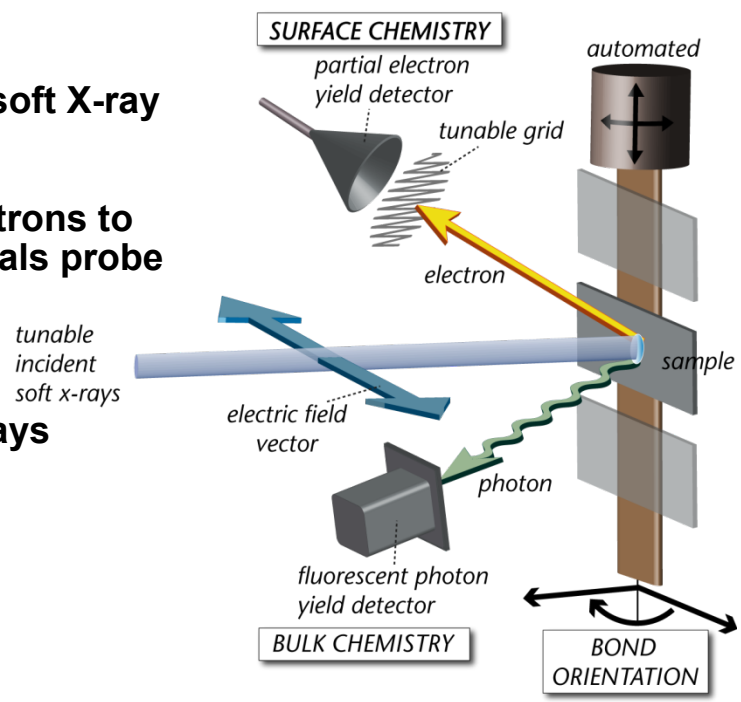
NEXAFS Surface Structure and Orientation at a Molecular Level- Synchrotron Facility

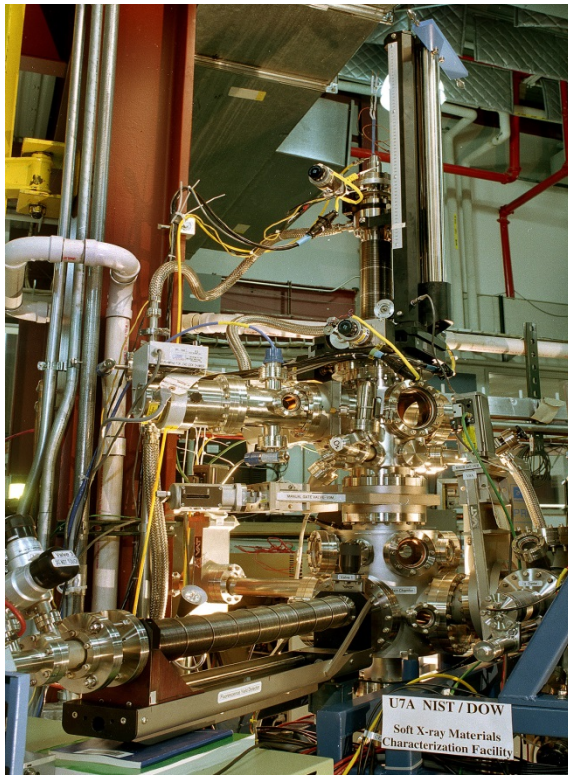
Unique Perspectives of NEXAFS

Near-edge x-ray absorption fine structure (Surface 3-5 nm)

- **Elemental absorption of soft X-ray radiation**
- **Excitation of K-shell electrons to unoccupied molecular orbitals probe Bonding environment**
- **Highly Polarized Soft X-rays**
- **Polarization dependence**
- **Fully Automated**
- **Non-destructive**
- **Molecular orientation information from partially or highly ordered systems**

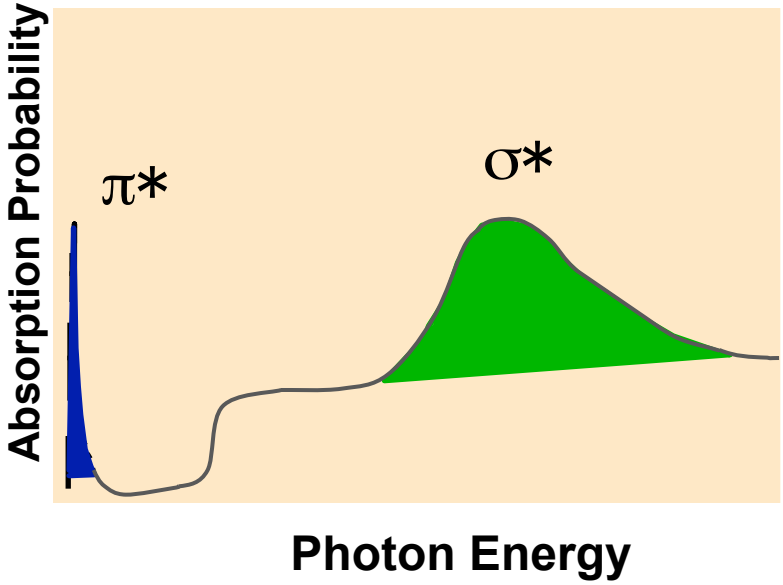


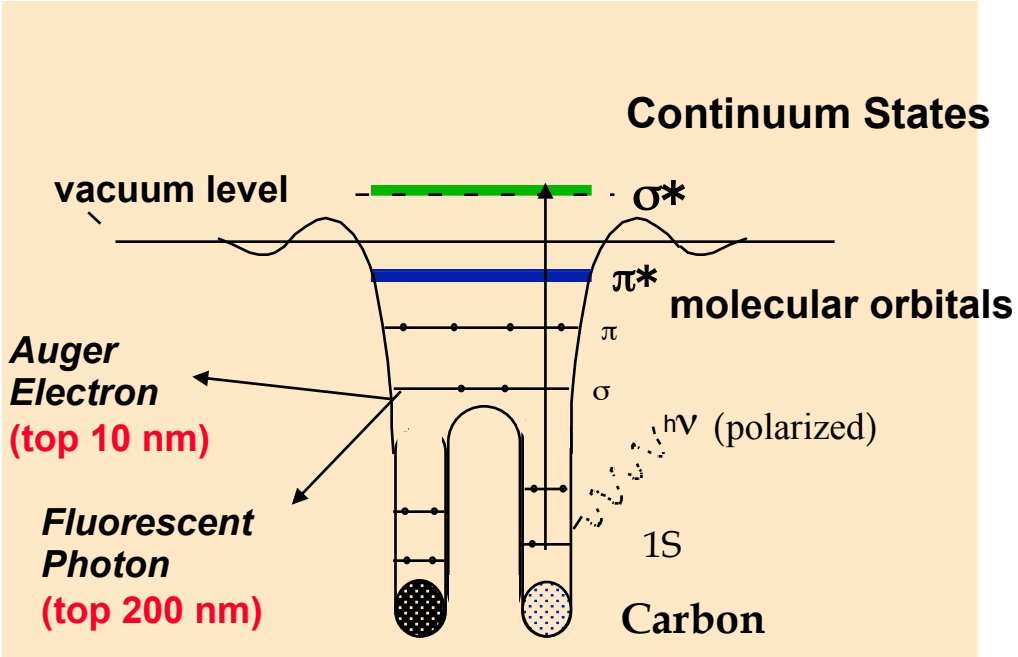
NEXAFS
U7A, Brookhaven National Laboratory



NEXAFS
(Near Edge X-ray Absorption Fine Structure)

- Elemental selectivity
- Chemical bond sensitivity
- Orientation Information
- Depth selectivity



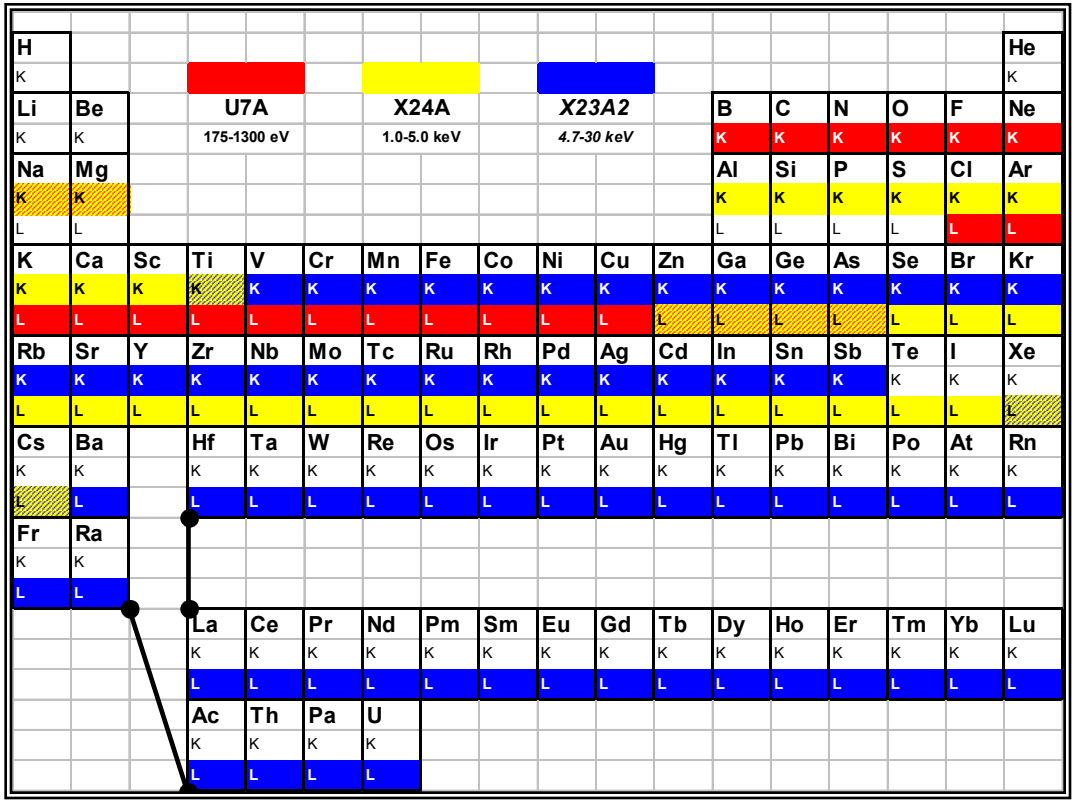


NIST Synchrotron Measurement Science Vision at NSLS

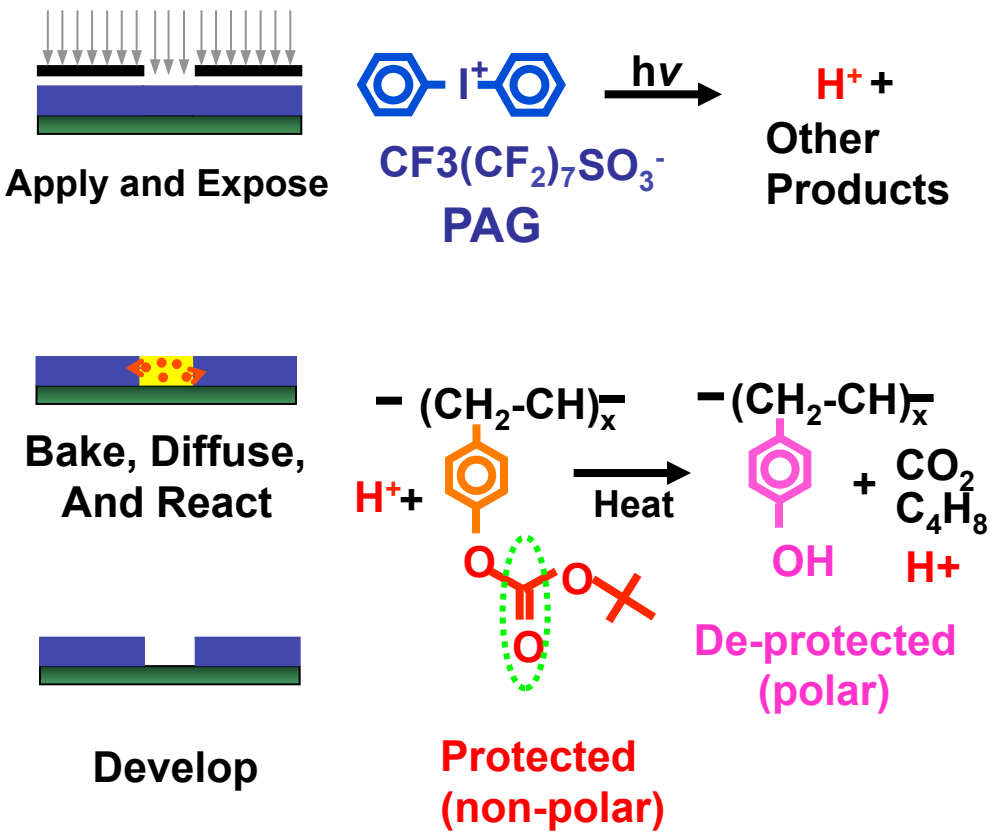
- ✓ *Establish structure function relationships for rational materials design to promote innovation and industrial competitiveness*
- ✓ *Developing and exploiting new experimental methods, detectors and physics approaches in synchrotron measurement science*

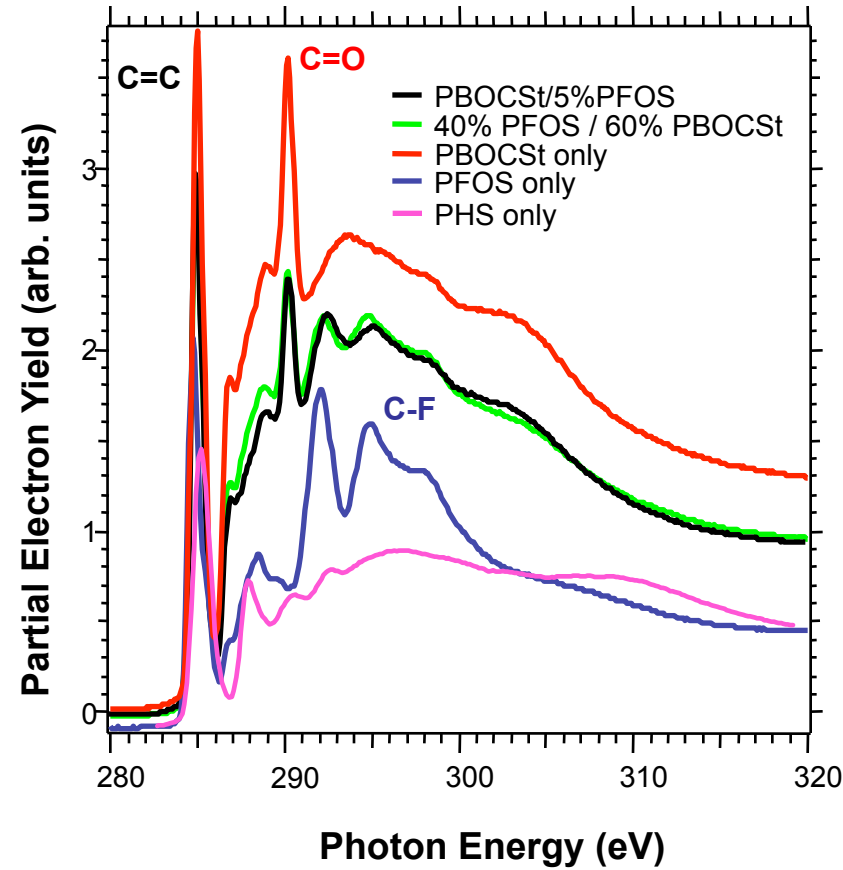
A suite of three NIST beamlines spanning the entire periodic table!

U7A: ***NEXAFS, XPS***
X24A: ***XPS, NEXAFS***
X23A2: ***XAS***



Photolithography

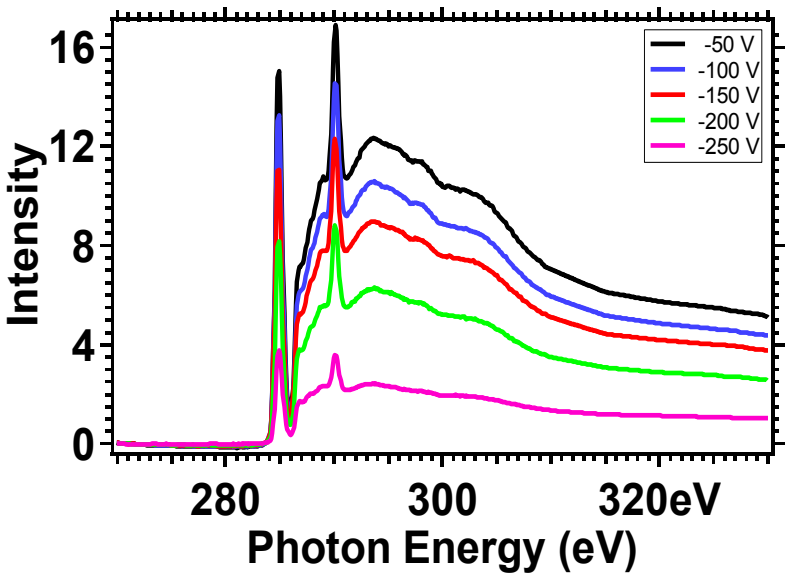




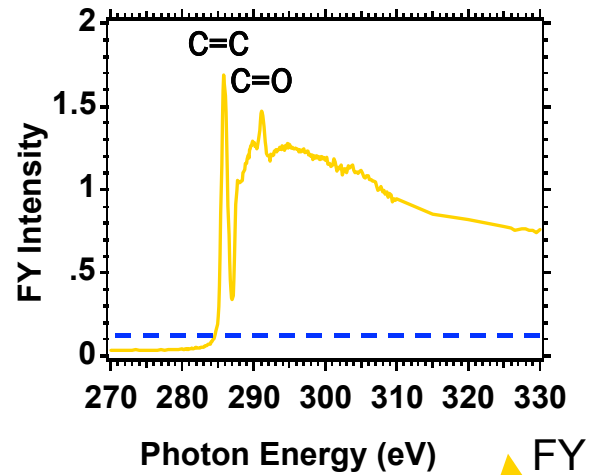
V Prabhu, S Sambasivan, et. al, Quantitative Depth Profiling of Photoacid Generators in Photoresist Materials by Near-edge X-ray Absorption Fine Structure Spectroscopy, *Appl. Surf. Sci.*, **253**, 1010-1014 (2006).

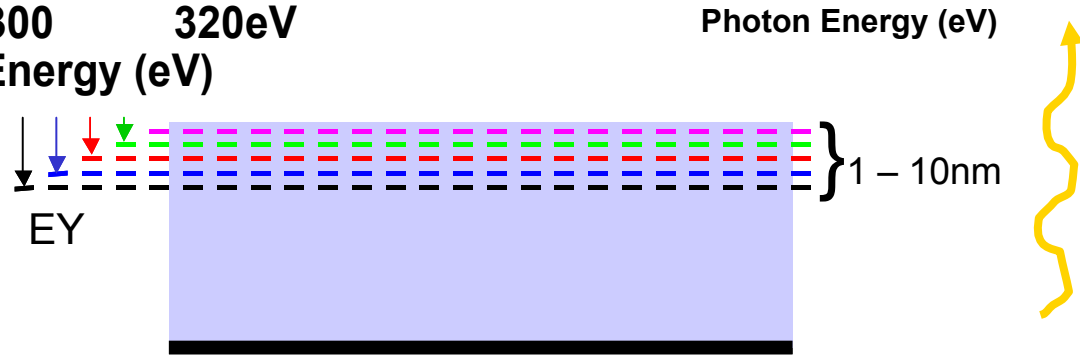
Depth profiling with NEXAFS

Electron Yield -Surface



Fluorescence Yield -BULK





Chemical composition v. depth

Surface Compositional Profile of Photoacid generator: Effects of Water Immersion
S Sambasivan, V M. Prabhu, D A. Fischer, L K. Sundberg, R D. Allen, PMSE preprints vol (101) p112, 2009

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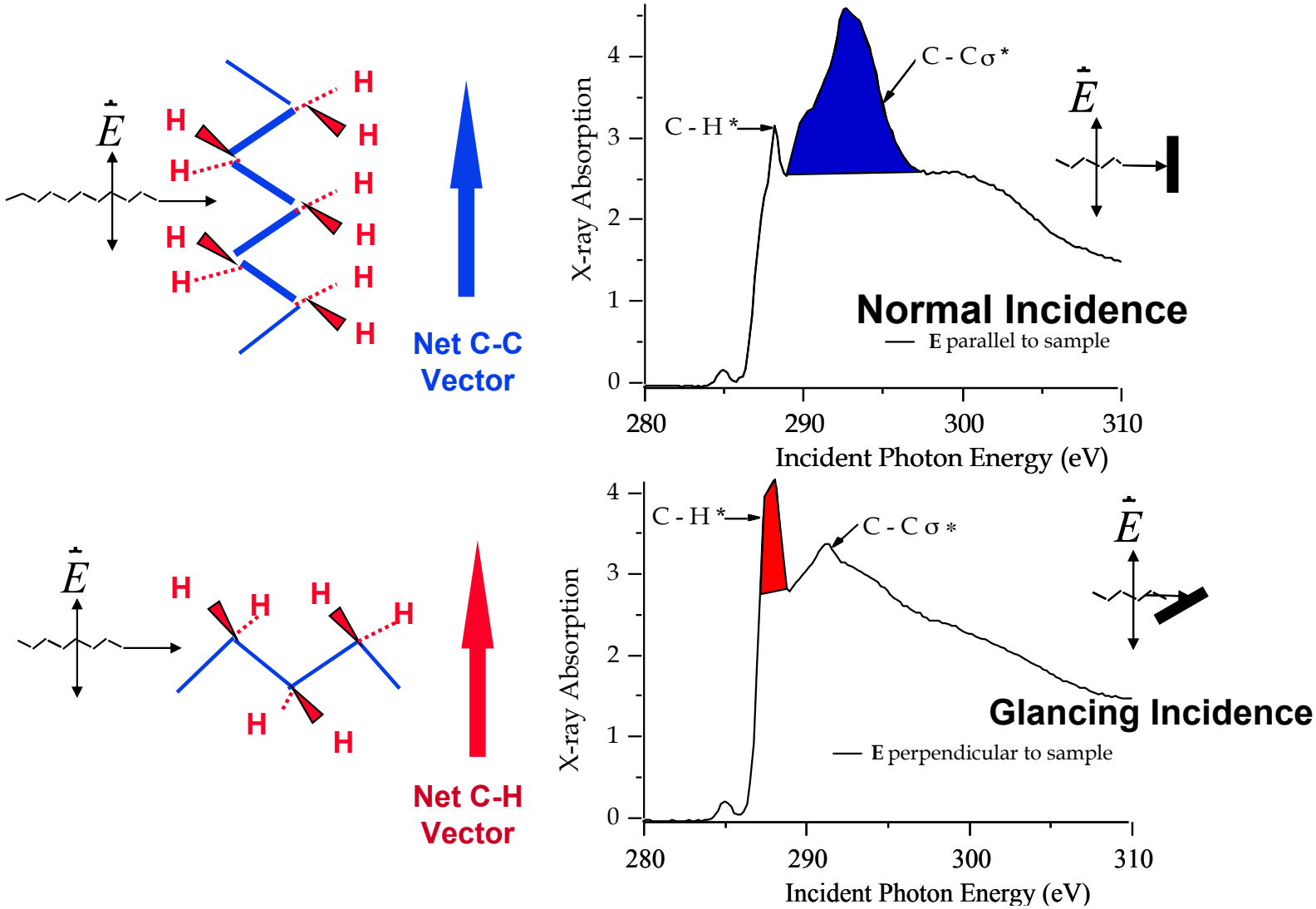
Molecular Orientation: NEXAFS Polarization Anisotropy



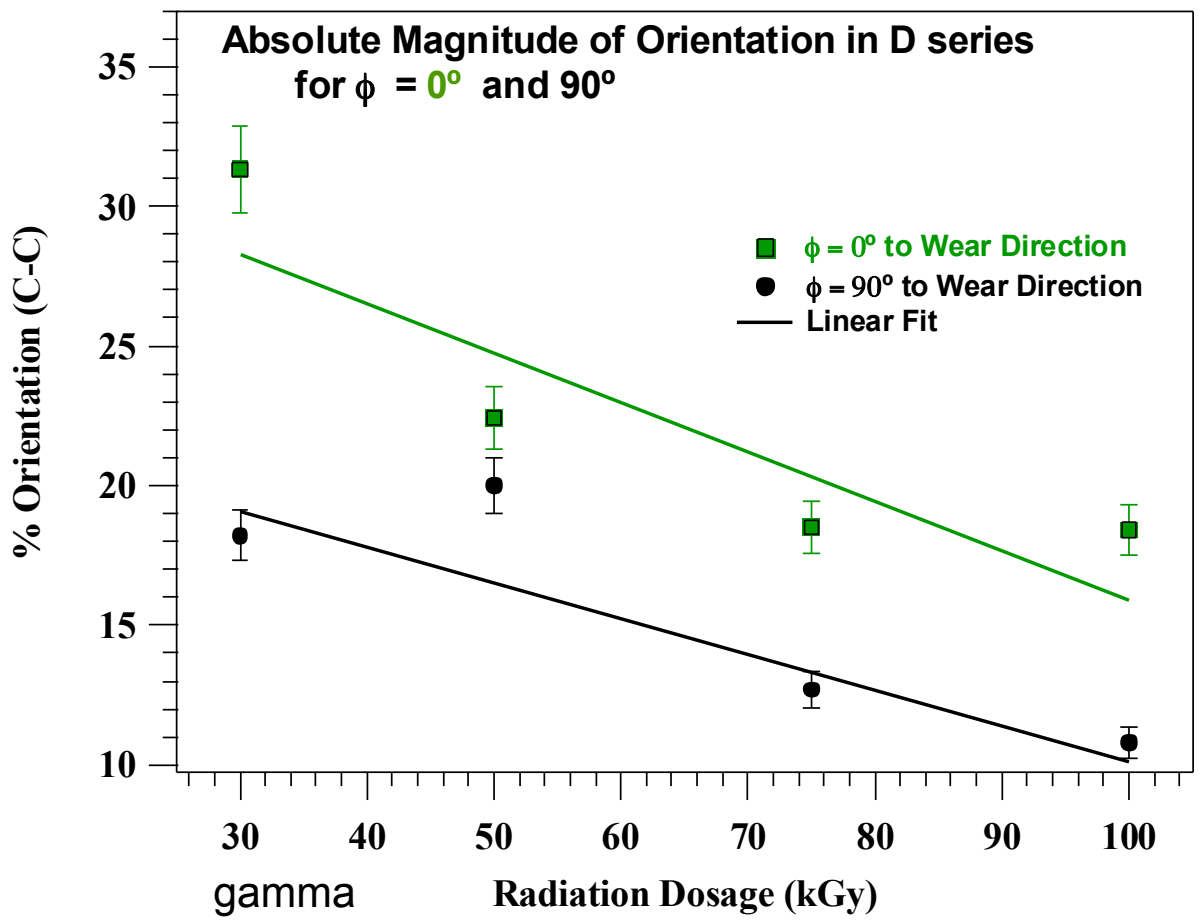
S Sambasivan, D Fischer, S Hsu, Effect of Cross-Linking Ultrahigh Molecular Weight Polyethylene: Surface Molecular Orientation and Wear Characteristics, *J. Vac. Sci. Technol., A*, 25(4), 932 (2007).

Effect of Radiation Dose

Effect of Radiation Dose on Orientation UHMWPE – GUR1050

GUR 1050 various doses of Gamma irradiated

- Samples (0 kGy to 100 kGy)
- Samples subjected to MTS knee simulator for 5 million cycles of duration
- NEXAFS at normal and glancing incidence
- NEXAFS at (ϕ =) 0º and 90° to wear direction
- ϕ = 90° has low %C-H orientation than ϕ = 0°
- **Increased gamma dose decreases molecular orientation of UHMWPE**



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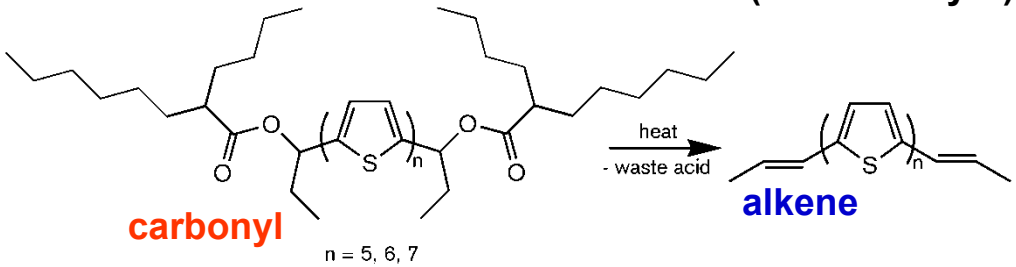
High Throughput NEXAFS: Soft Matter Structure and Chemistry

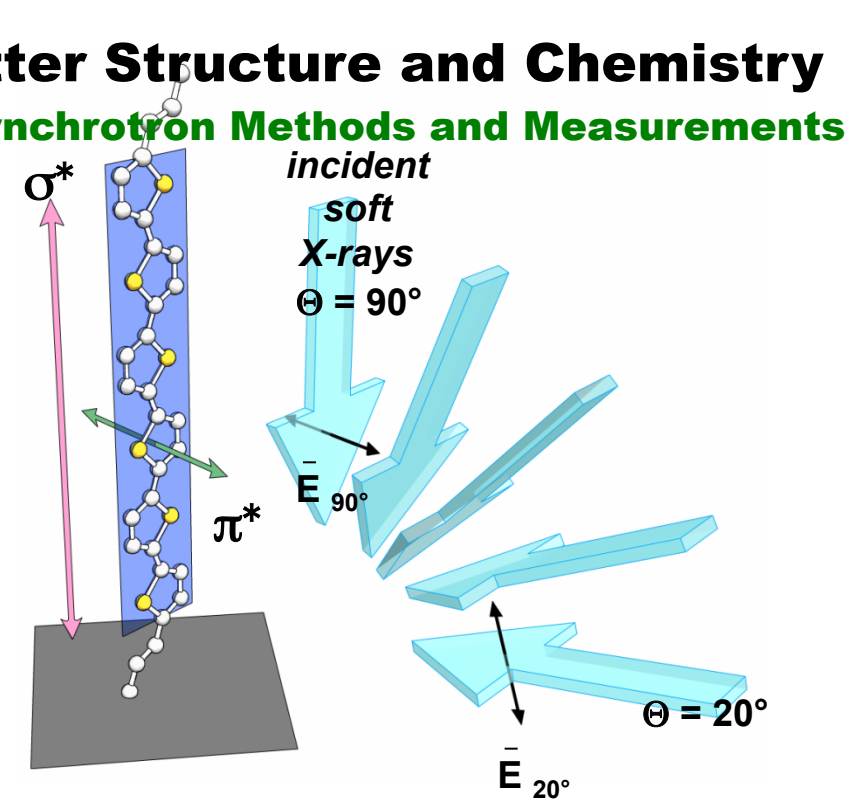
Synchrotron Methods and Measurements

Organic Semiconductors

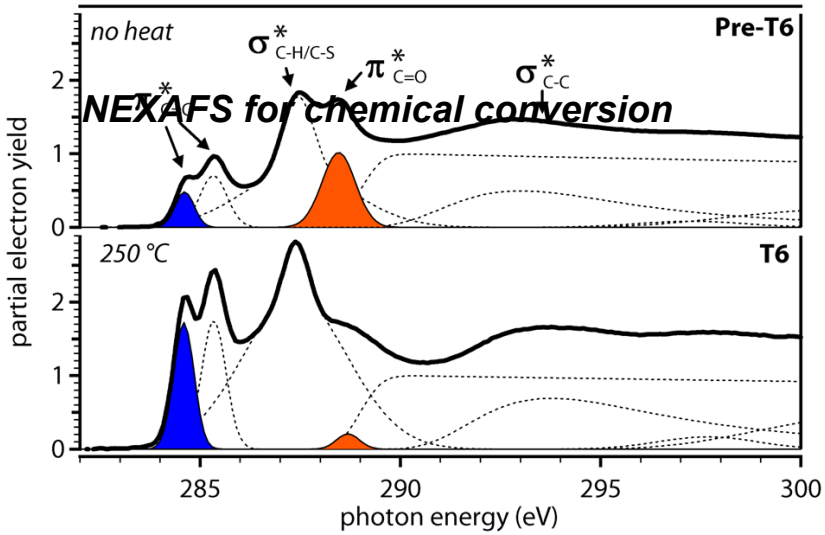
Collaboration with D. Delongchamp and J. Fréchet

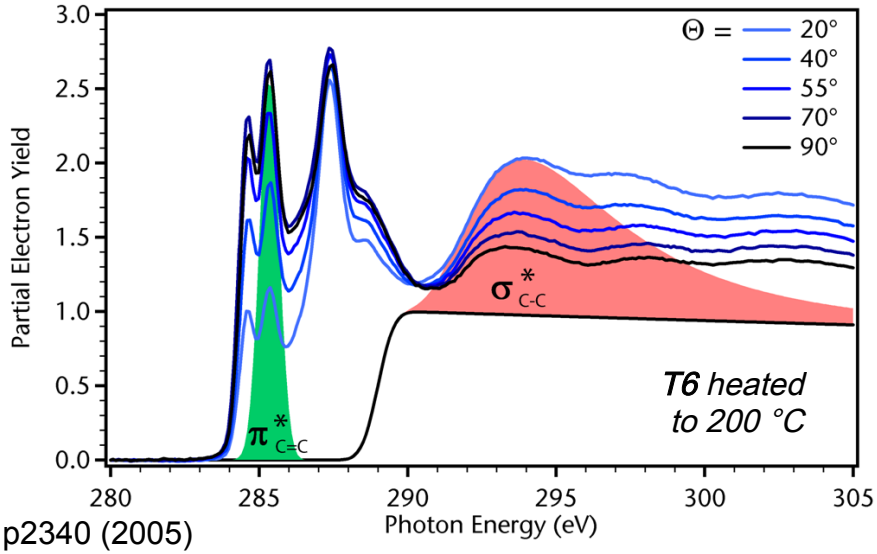
- **Soluble and printable**
- **Convert at 150-250°C**
- **Carrier mobility up to ~0.05 cm²/V·s**
- **Film thickness from 20 nm to 3 nm (~1 monolayer)**





NEXAFS for molecular orientation

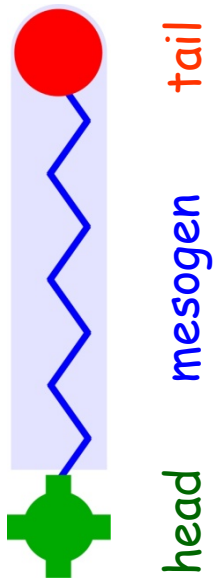


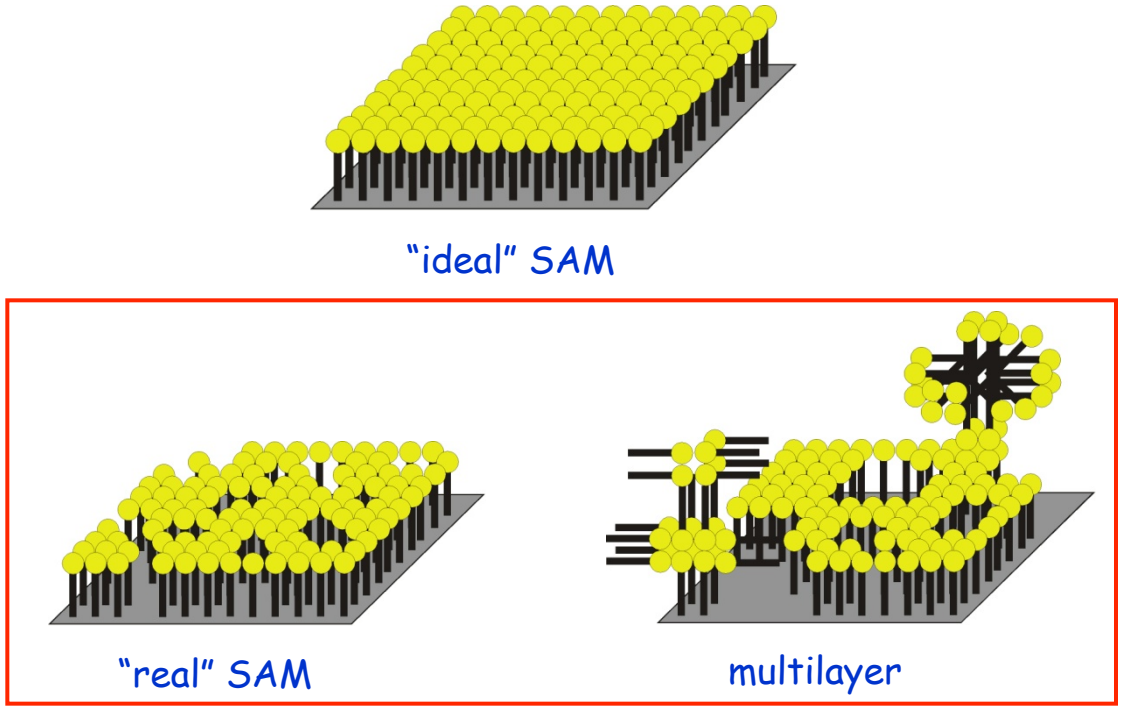


Delongchamp, D, Sambasivan, S, Fischer, D, Lin, E, Adv. Mater. **17,** p2340 (2005)

Self-assembled monolayers

Ordered, chemically and thermally stable two-dimensional aggregates that are formed spontaneously by the adsorption of surface active molecules onto a solid.





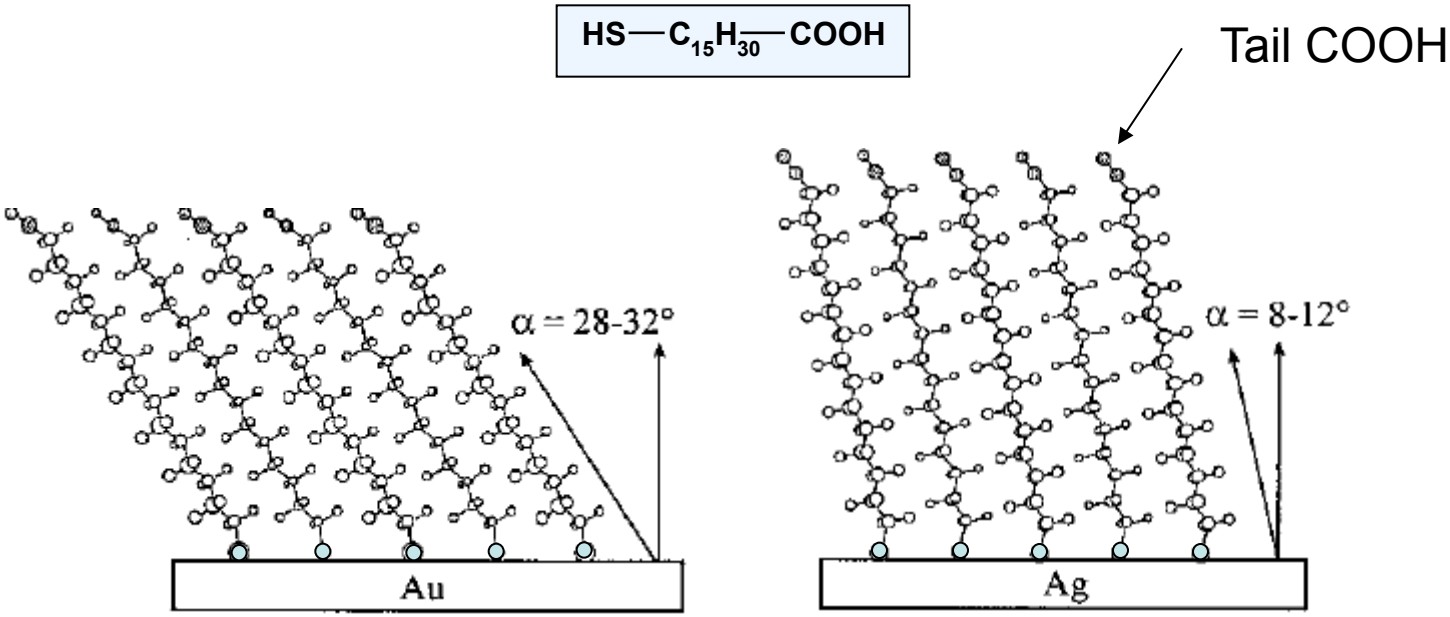
The surface active molecule features:

head group	offers strong interactions (or even chemical bonding) with substrates;
mesogenic moiety	controls 2D packing and favorable lateral interactions with the NNs
tail/end group	determines the surface wettability of the newly formed solid surface.

Abraham Ulman: An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembled Monolayers, Academic Press, Boston, 1991; Younan Xia & George M. Whitesides, *Angew. Chem. (Int. Ed.)* **37**, 550 (1998).

Courtesy: Prof. Jan Genzer NCSU

Self-assembled monolayers

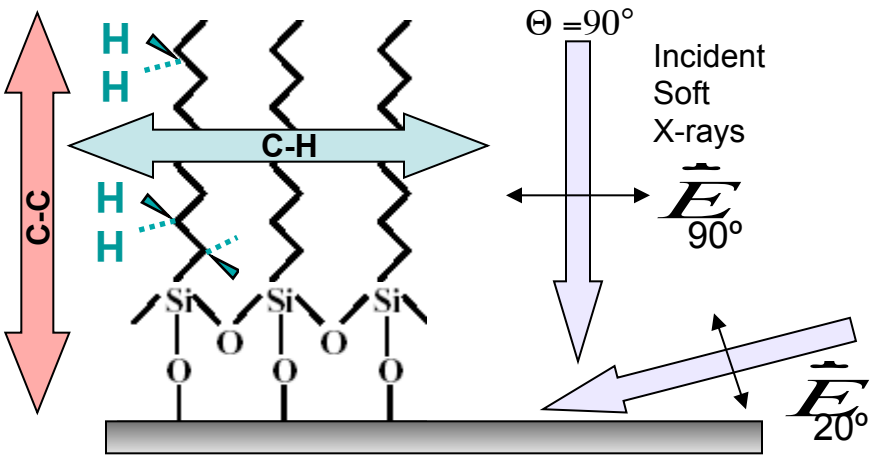


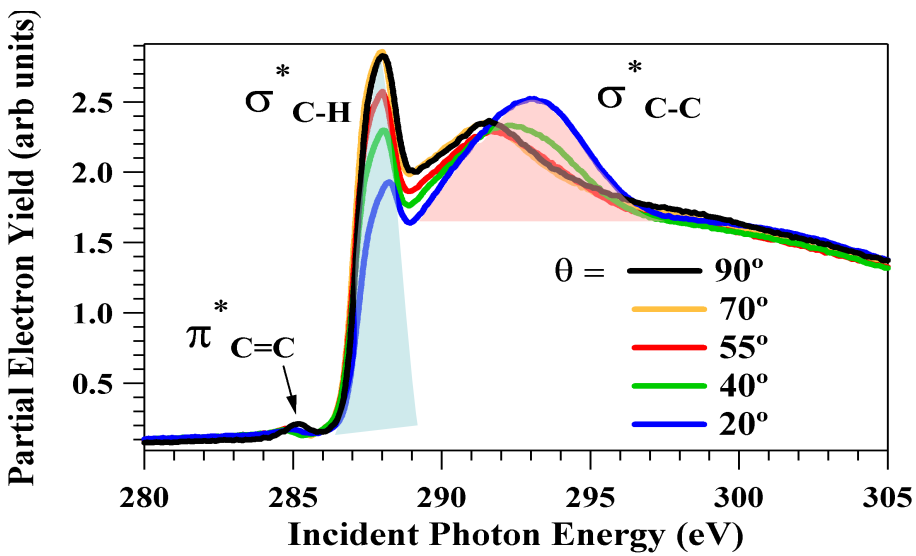
- Substrate affects chain tilt angles
- End group or tail determines wettability and serves as controlled nucleation sites
- Soft Lithography, flexible substrates
- Biosensors, MEMS, NEMS devices
- Lubrication

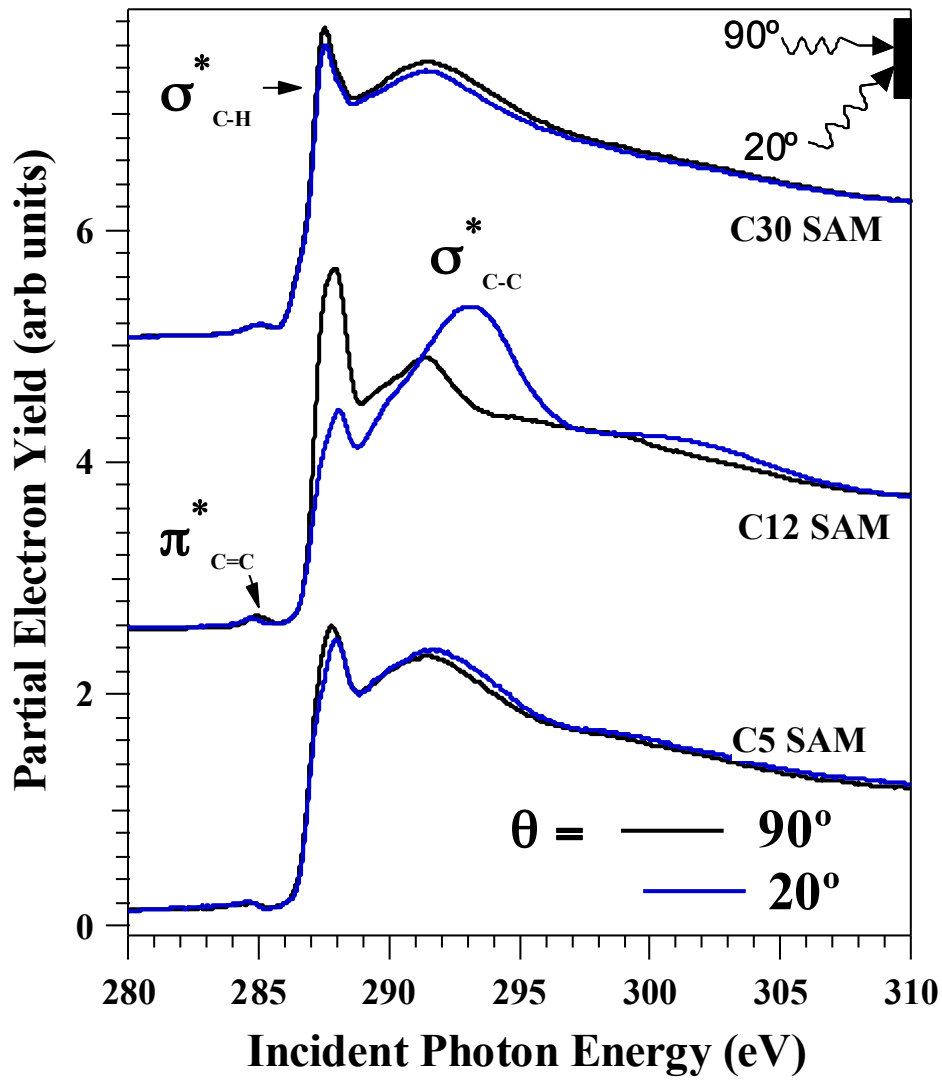
Aizenberg et al. *JACS* **121** 4500 (1999)

Molecular orientation with NEXAFS

- Highly Polarized Soft X-rays
- Angular Dependence of Resonances
- Highly ordered "Anisotropic "system







$\sigma^*_{C\text{-}H}$ resonance is largest at 90° incidence

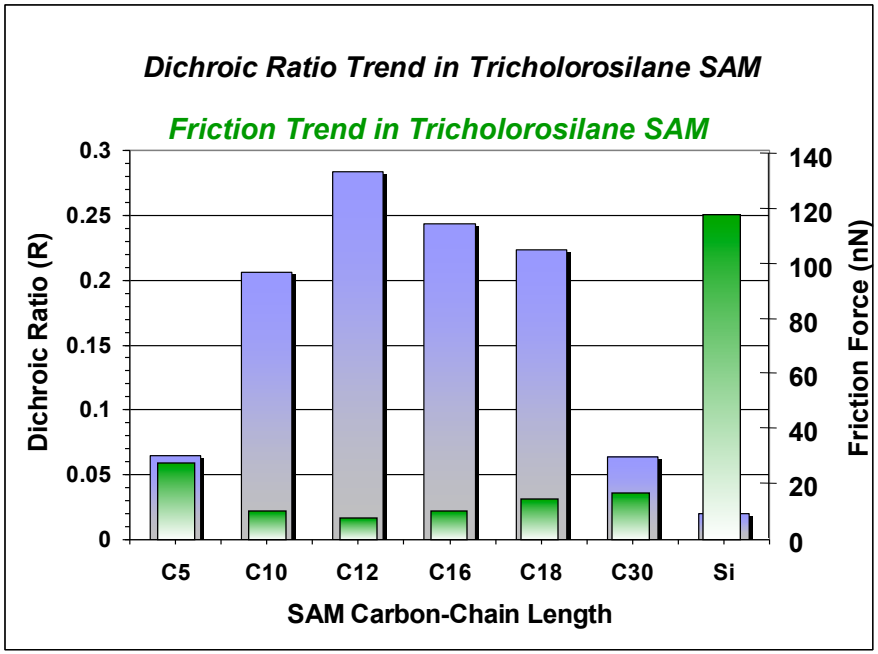
$\sigma^*_{C\text{-}C}$ resonance is largest at 20° incidence

Alkyl chains are "standing up."

Courtesy: Dr. Delongchamp

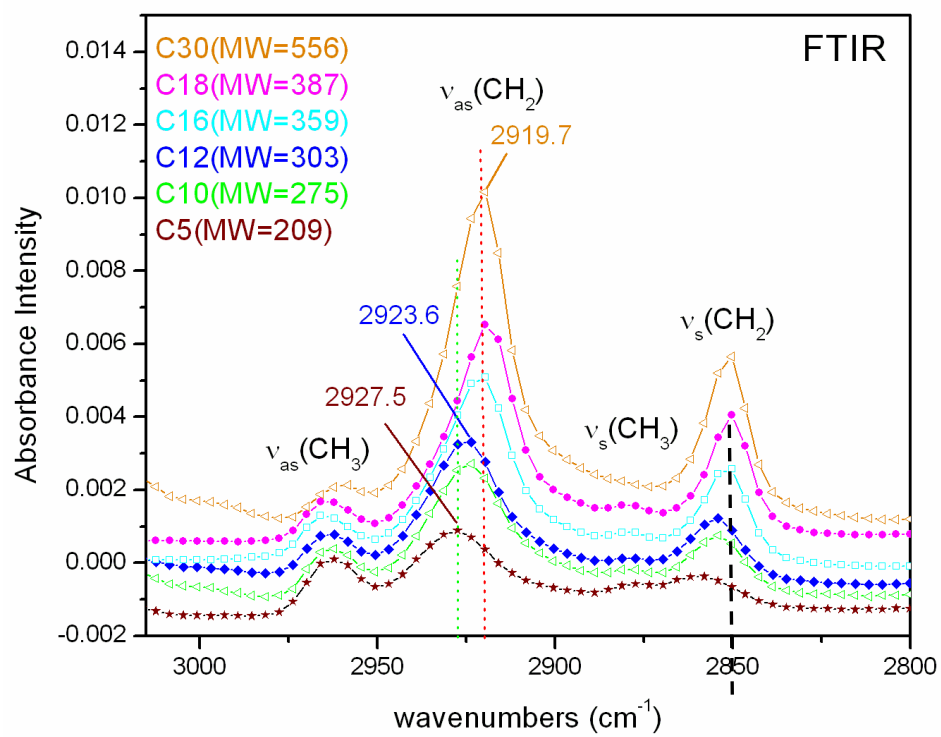
NEXAFS vs. FTIR

NEXAFS



C5 not ordered
C10, partially ordered
C12, C16, C18 Highly Ordered
C30 not ordered

FTIR



C5 not ordered
C10, C12 partially ordered
C16, C18 Highly Ordered
C30 Highly Ordered

S Sambasivan, S Hsieh, D Fischer, S Hsu, Molecular Understanding of Nanofriction of Self-Assembled Monolayers on Silicon Using AFM, *Surfactants in Tribology*, p. 173-188, CRC Press, Taylor & Francis Group, Boca Raton (2008).

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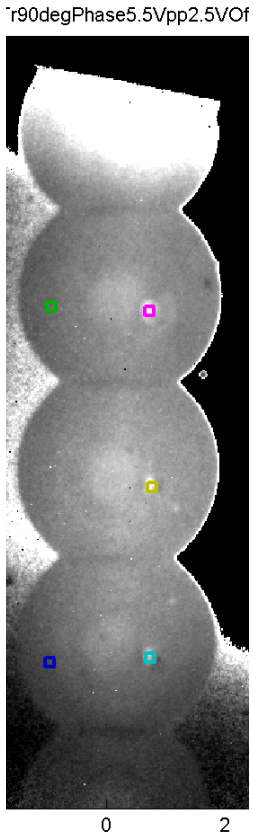
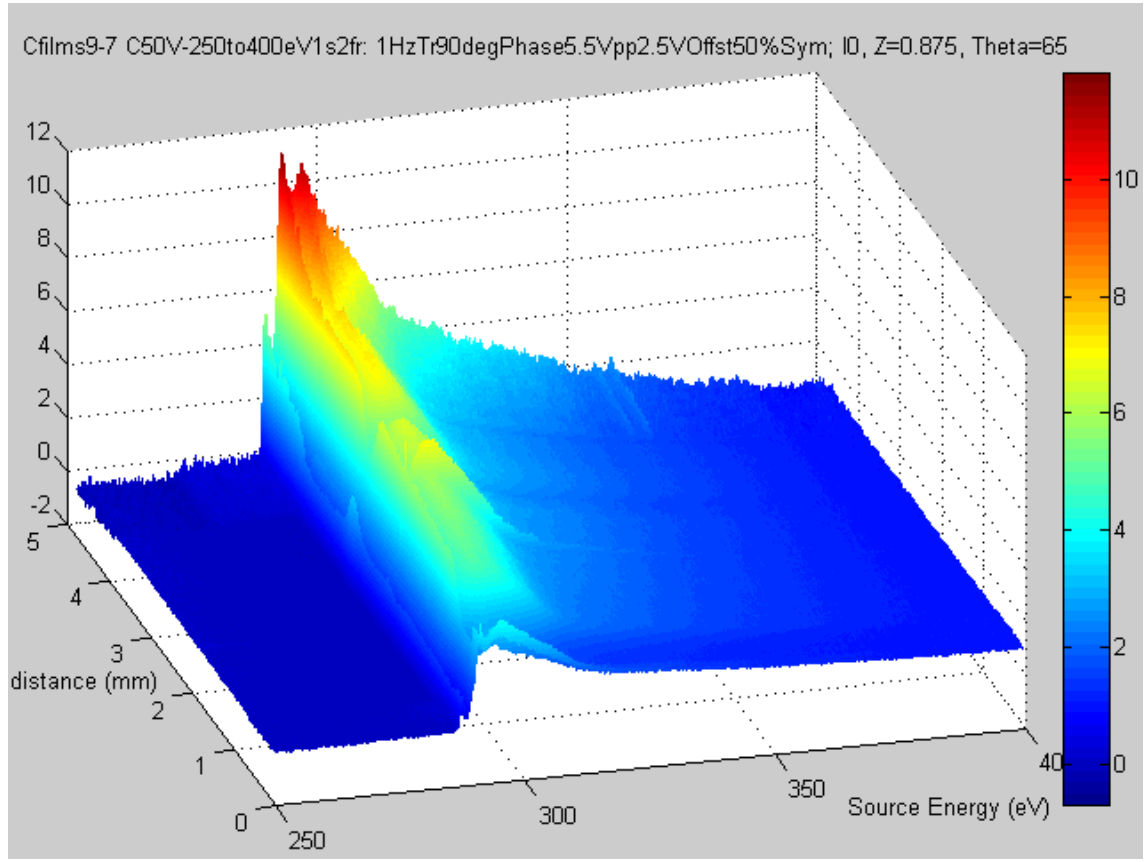
Imaging NEXAFS Application



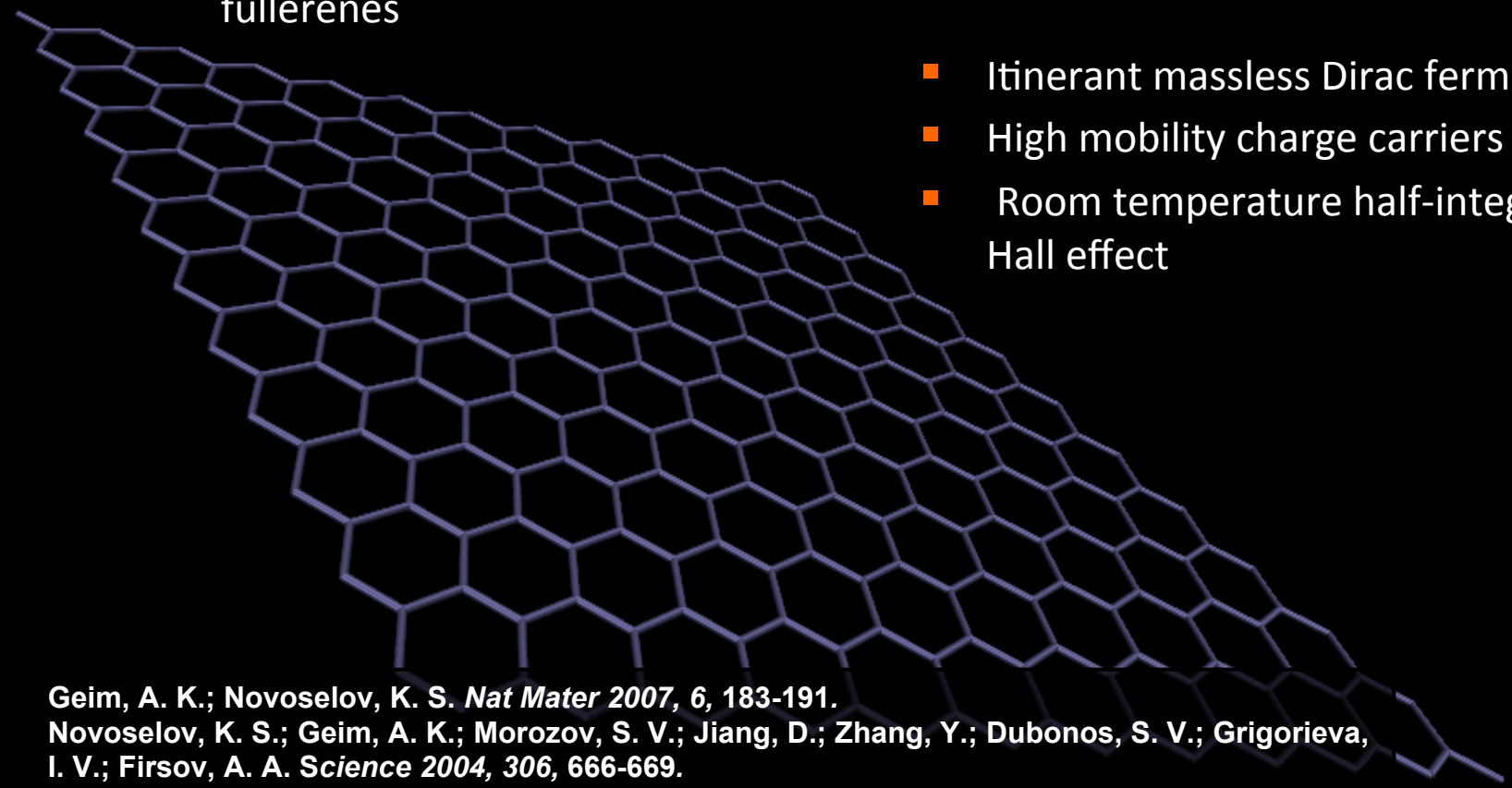


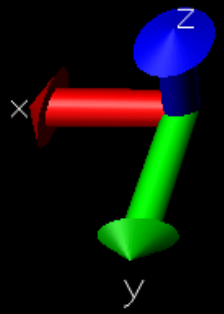
- NEXAFS images of the carbon pi* peak..
- C K-edge NEXAFS spectra taken from the ROI (0.15mm x 0.15mm) from laser-treated (bright) and background (dark) regions.

- Areas with laser treatment show higher amounts of aromatic carbon with laser-treated ROIs

Graphene

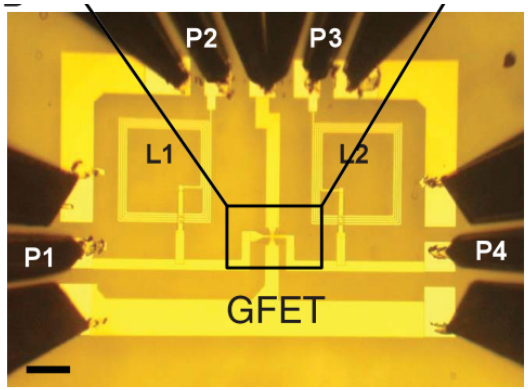
- Synthesized in 2004 through mechanical exfoliation a.k.a. "scotch tape" method (Nobel Prize in Physics, 2010)
  - Single and bi-layer graphene are semimetals
  - Conceptualized as the building block of graphite, carbon nanotubes and fullerenes
  - Itinerant massless Dirac fermions
  - High mobility charge carriers
  - Room temperature half-integral quantum Hall effect

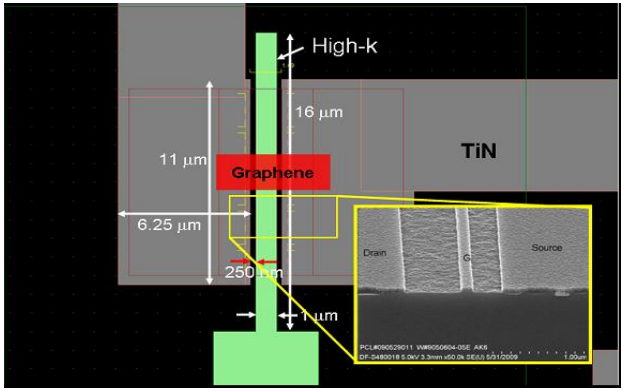


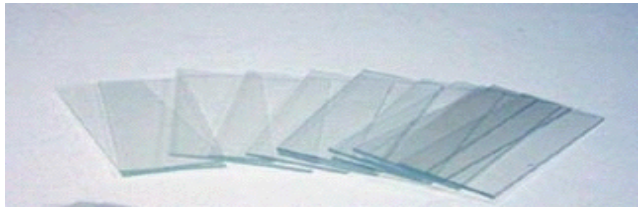


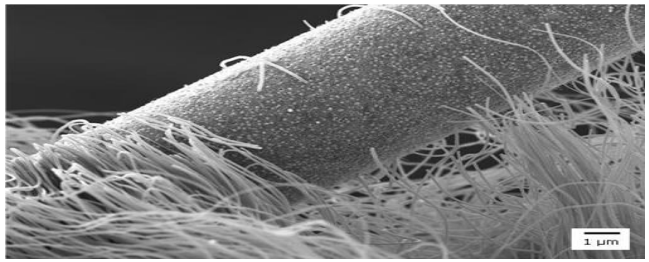
Geim, A. K.; Novoselov, K. S. *Nat Mater 2007, 6,* 183-191.
Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. S*cience 2004, 306,* 666-669.

Applications of Graphene









Properties

- Ultrahigh mobilities
- Ballistic conduction
- Defect less Band Gap tuning
- High Mechanical Strength
- Flexibility Graphene based composites
- Corrosion Resistance

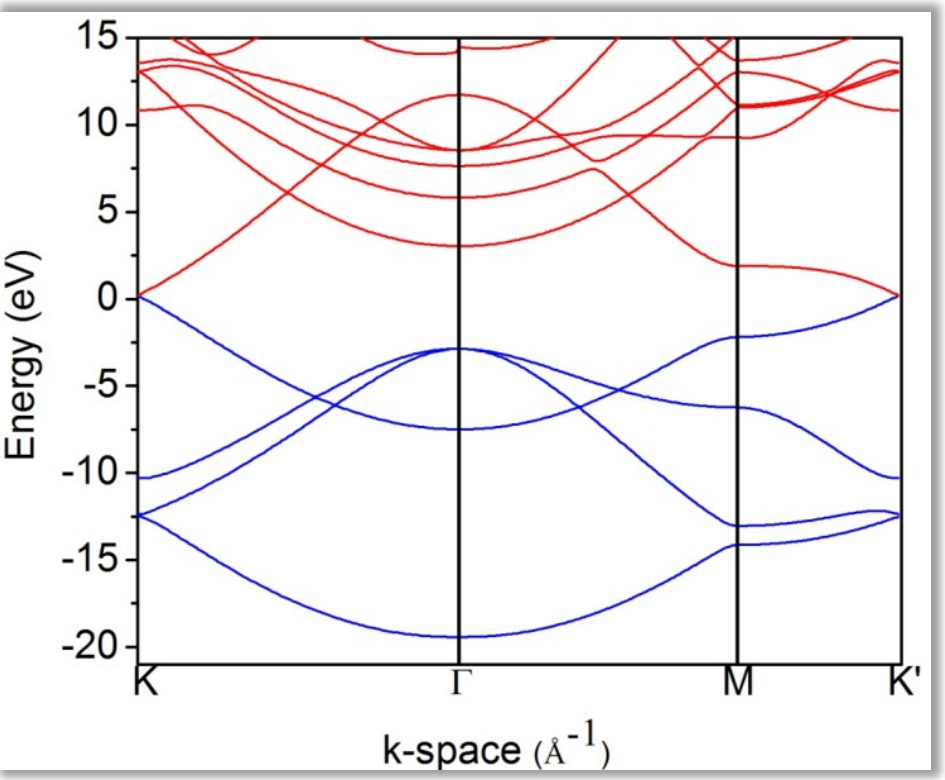
Applications

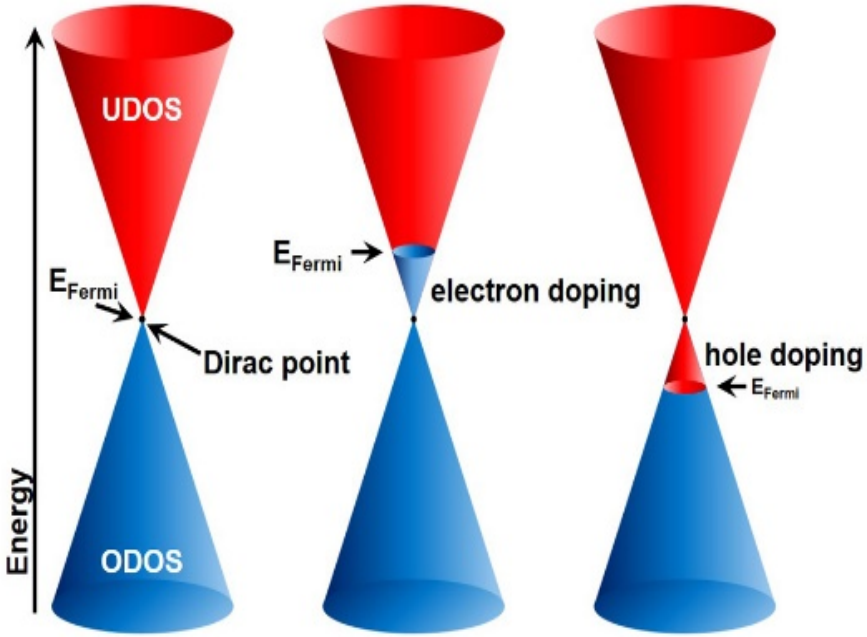
- Flip chip transistors
- Ultrafast electronics
- Electrical interconnects
- **Composites and Coatings**
- ITO Replacement
- High-Strength Polymer and Metal Composites

Lin, Y.-M. et al. Wafer-scale graphene integrated circuit. *Science* **332**, 1294-7 (2011).
Bae, S. et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology* **5**, 1-5 (2010).

Electronic Structure of Graphene: The Ideal Case

- Linear dispersion of bands ±1 eV from conical Dirac point
- Dirac point located at *K* and *K*'





NEXAFS for Graphene

- Element specific probe of local and global electronic structure

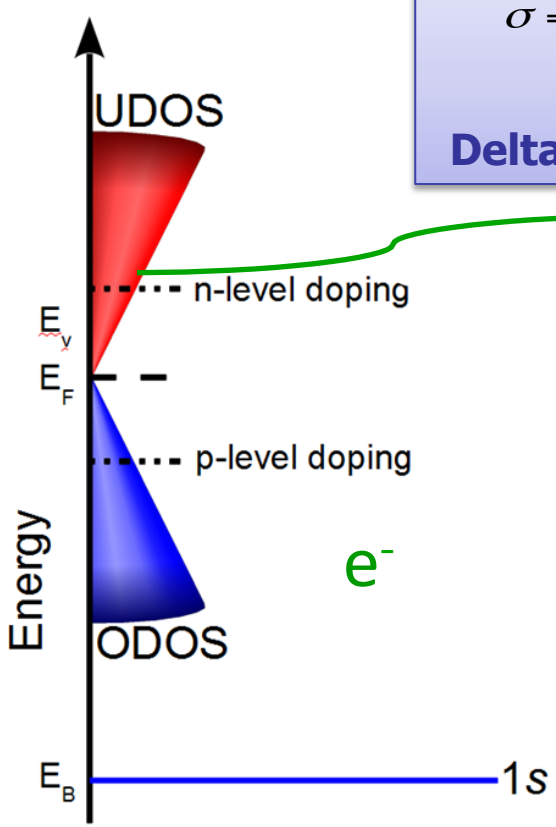
-peak positions and lineshapes directly related to density of states

Energy density of the final state

$$\sigma = \frac{4\pi h^2 e^2}{m^2 hc h\omega} \zeta(E) \left| \langle \phi_f | \mathbf{e} \bullet \mathbf{p} | \phi_i \rangle \right|^2 \delta(h\omega + E_i - E_f)$$

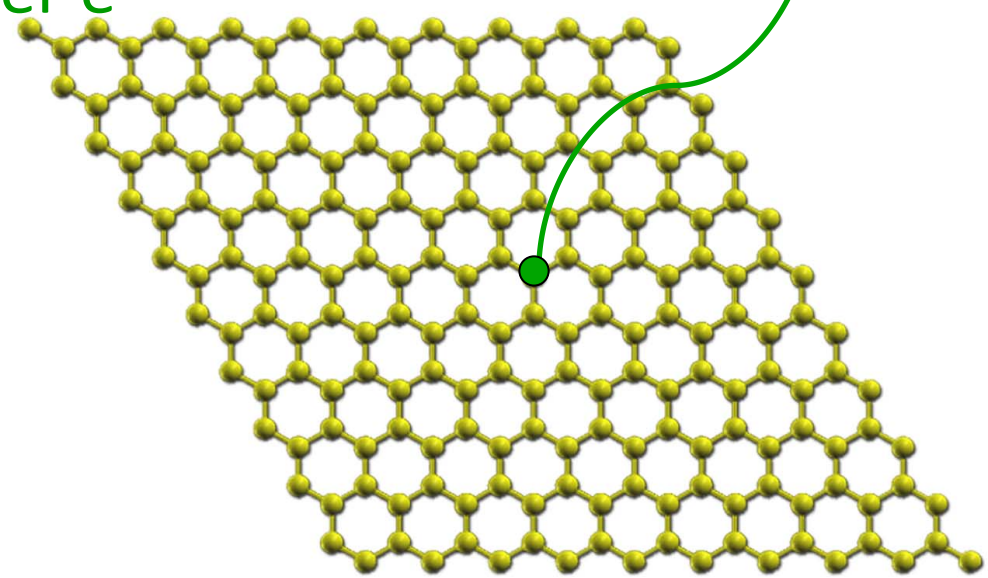
Dipole matrix term

Delta function for the conservation of energy

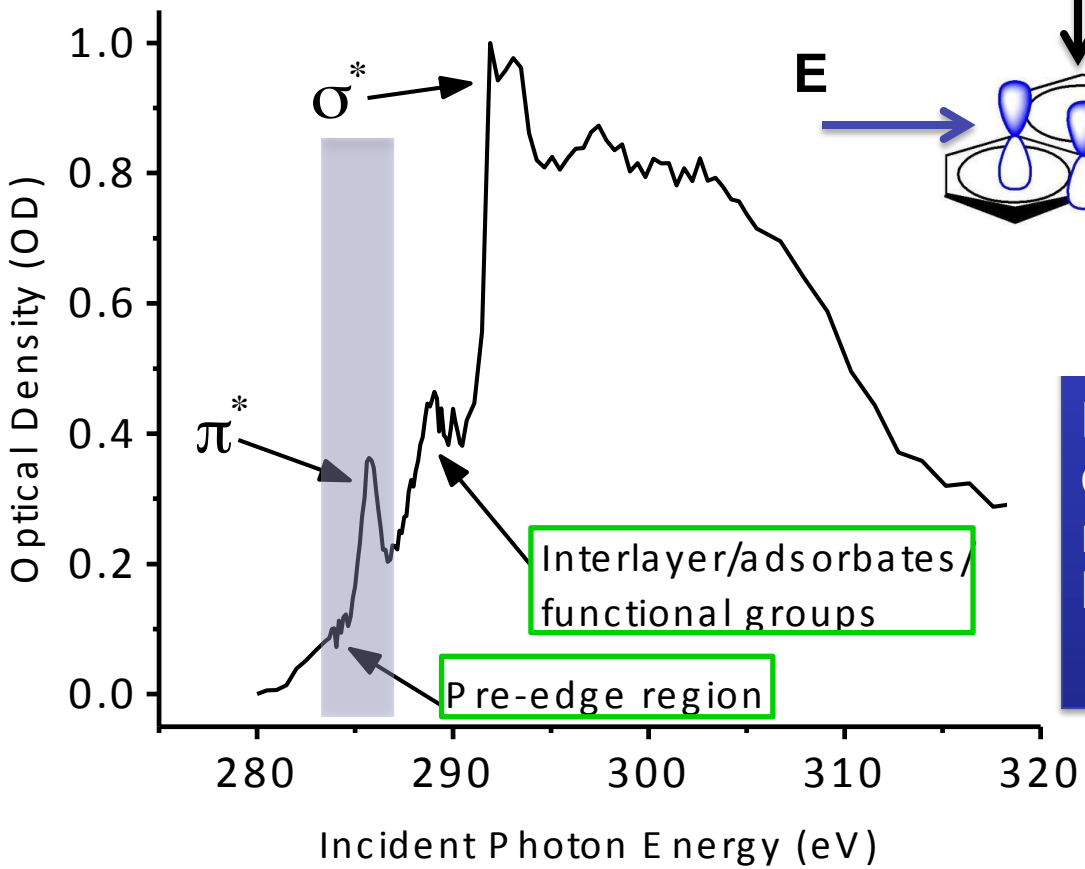


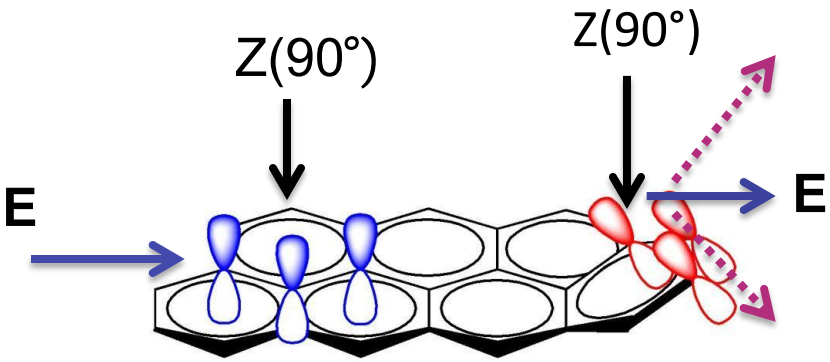
Auger e^-

remove core e^-



XAS Spectrum of Single-Layered Graphene





Manifestation of Dirac physics depends sensitively on defects: rippling, adsorbates, interfacial hybridization

B. J. Schultz, C. J. Patridge, V. Lee, C. Jaye, P. D. Lysaght, C. Smith, J. Barnett, D. A. Fischer, D. Prendergast, S. Banerjee,* *Nature Commun.*, **2011**, *2*, 372/1-372/8.

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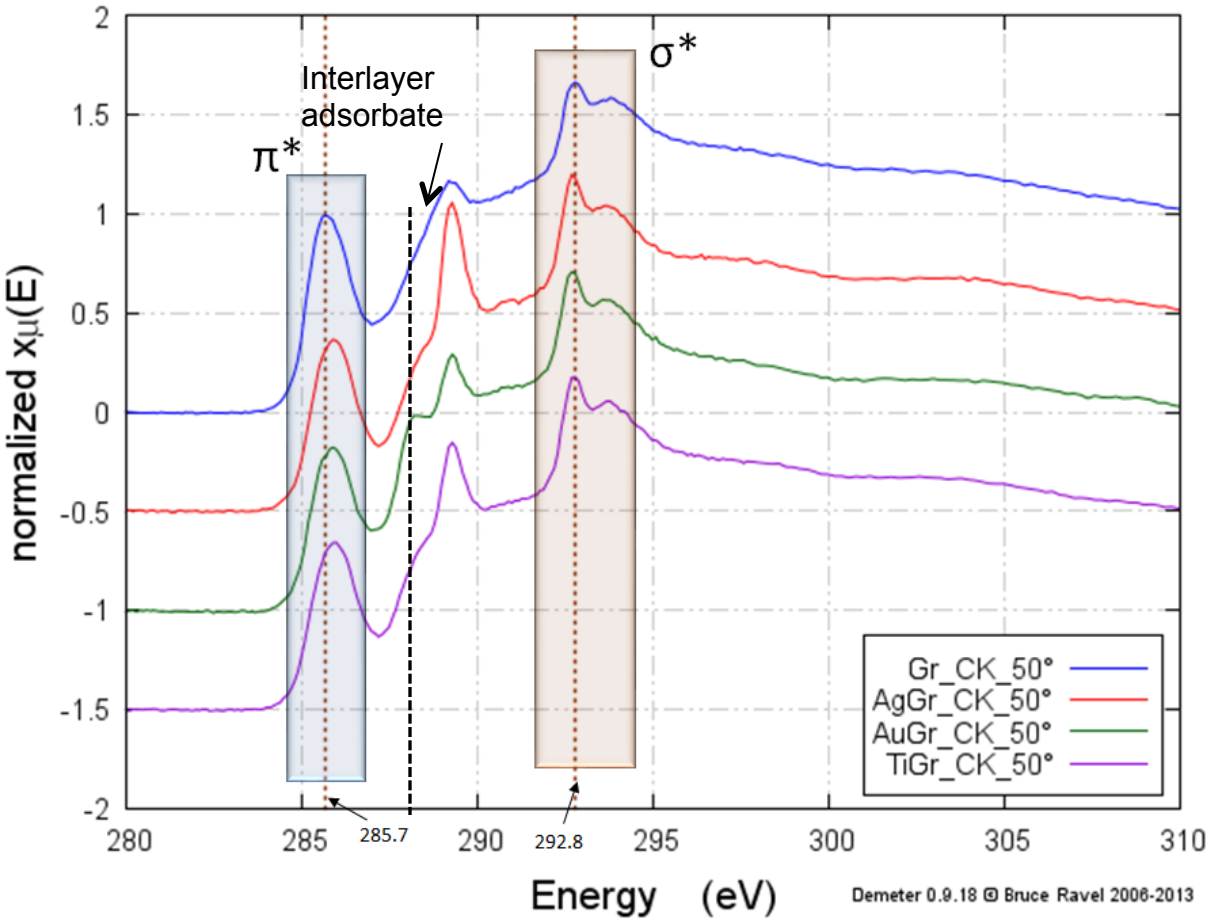
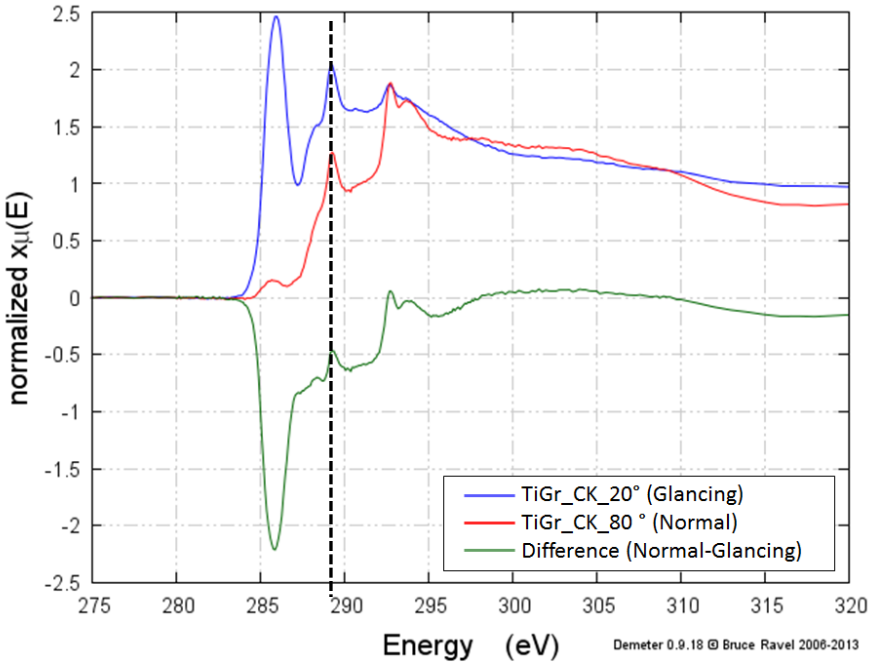
Au, Ag or Ti Doped Graphene NEXAFS

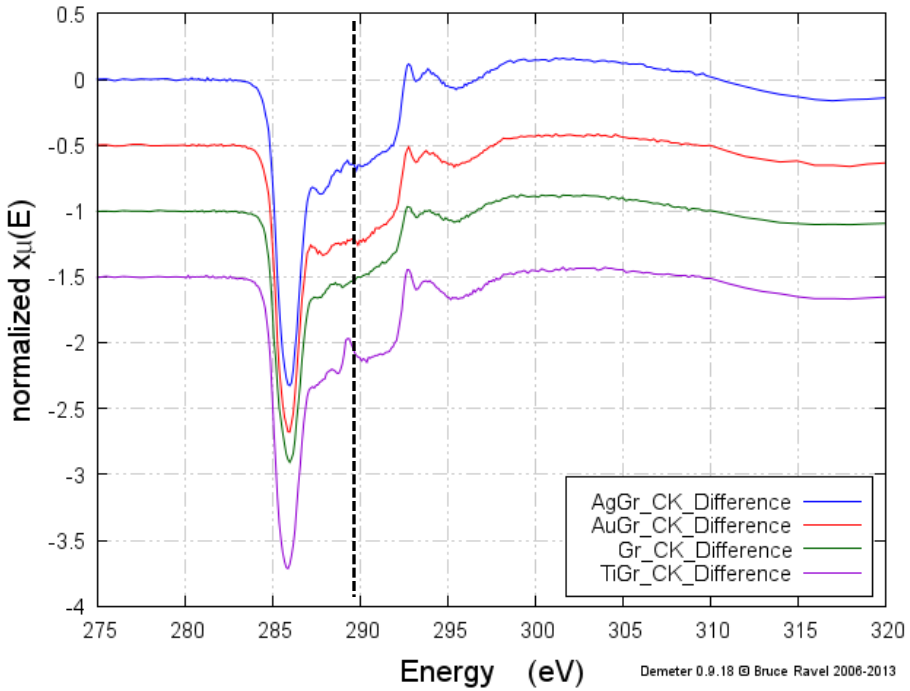


- More pronounced interlayer adsorbate peak in doped graphene
- Au-Doped shows a strong split in interlayer adsorbate peak

Archibald et. al

NEXAFS Difference spectra (85-20º)



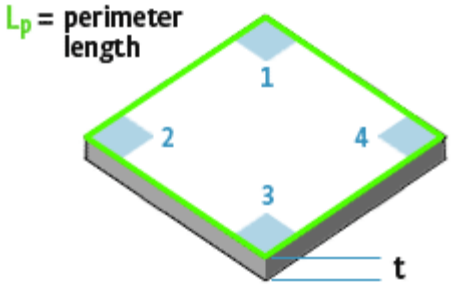


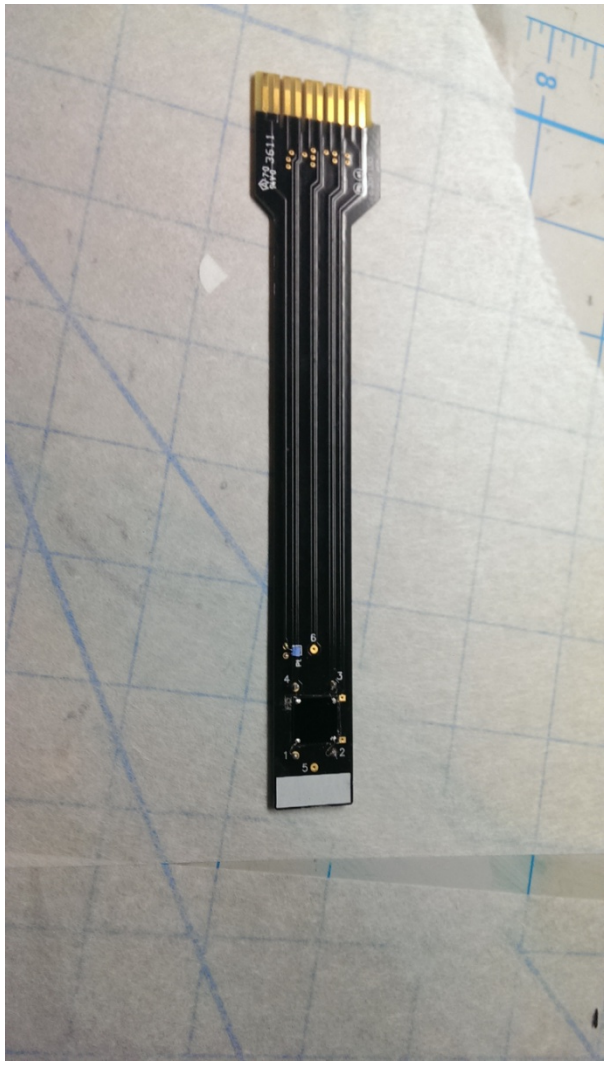
Preliminary Results

- Exemplifies orbital anisotropy of π^*, σ^*
- Interlayer adsorbate peak exhibits higher degree of anisotropy in the case of Ti doped Graphene
- Au-Doped interlayer peak is isotropic

Archibald et. al

Hall Effect Electron Mobility Measurement

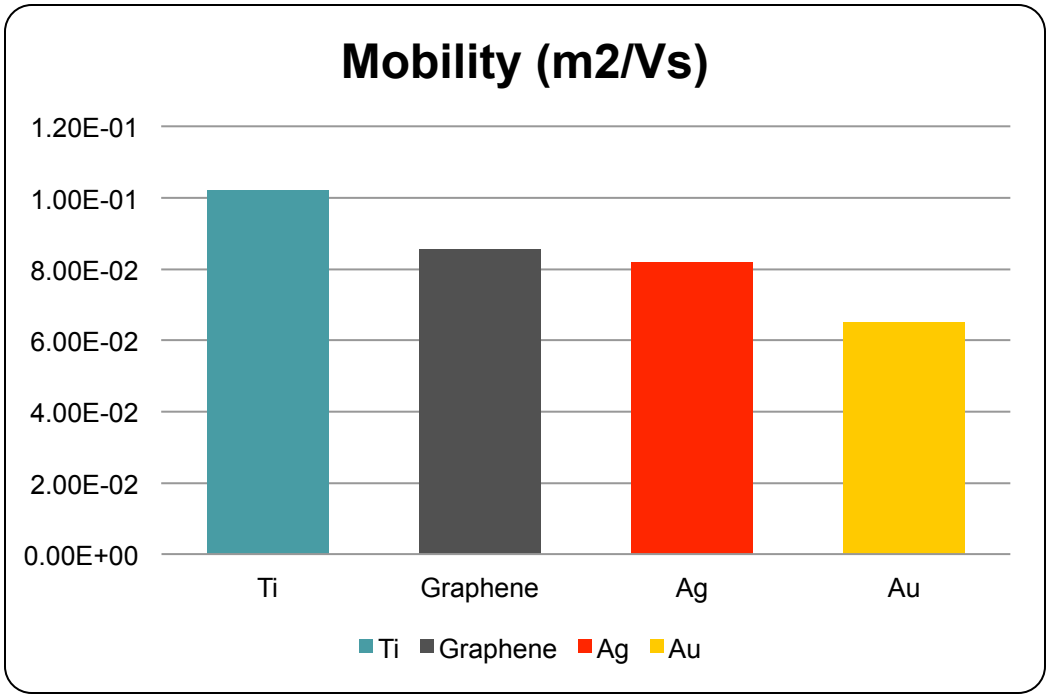




Archibald et. al measurement at CFN

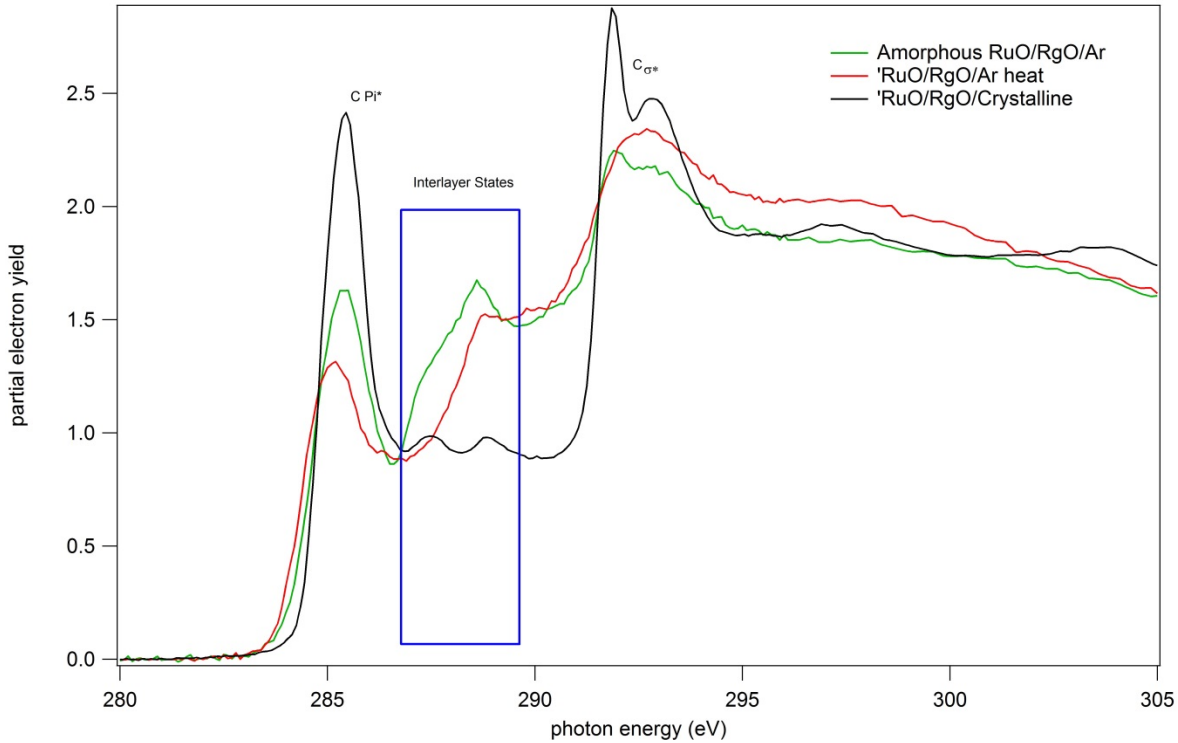
Results from Mobility

System	Mobility (m2/Vs)
Ti	1.02E-01
Graphene	8.56E-02
Ag	8.18E-02
Au	6.50E-02



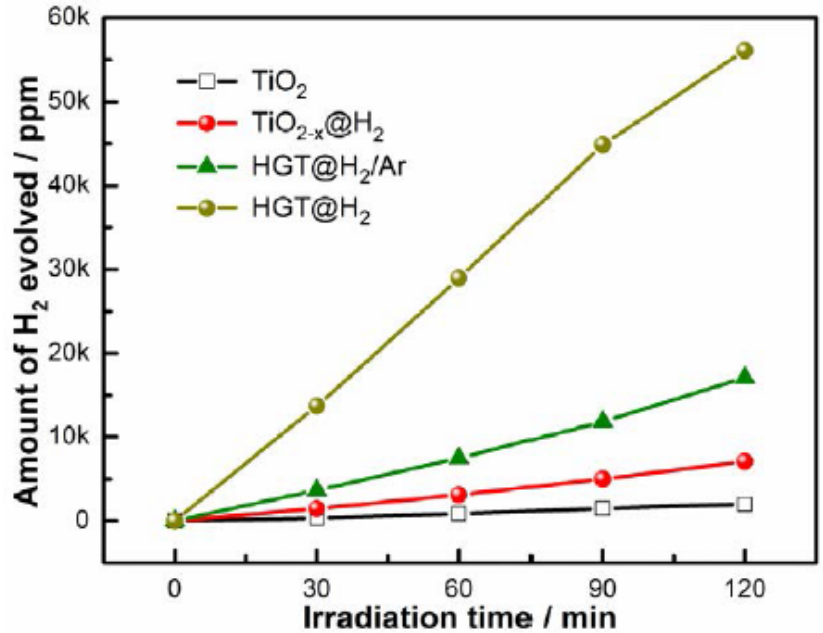
Does Interlayer Adsorbate Anisotropy affect the electron Mobility?

Results from Metal oxide/Graphene System in Super capacitor application



- Crystalline graphene-RuO2 sample has no inter layer adsorbate state which could be responsible to explain the results low conductive properties. In Dr. Amir's experimental studies on efficient of electrode she found that amorphous and porous RuO_2/graphene samples were more efficient in conductive properties than the crystalline

Photocatalytic water splitting – H_2 evolution

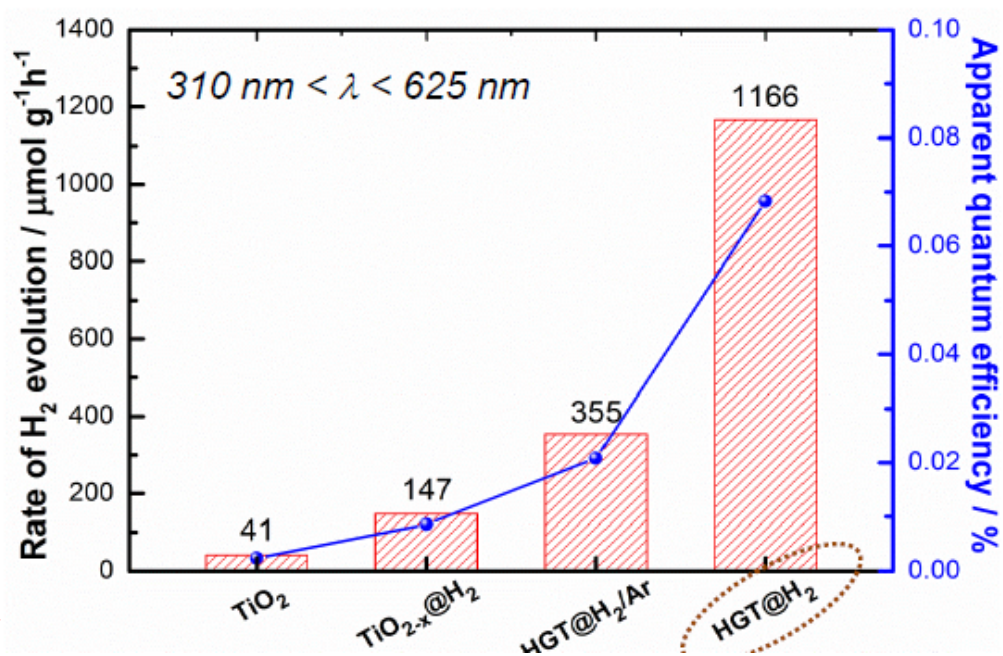


- Sacrificial agent: 20% CH_3OH-H_2O (v/v)
- Noble-metal-free
- Catalyst loading 1 g L^{-1}

$$QE\% = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} * 100$$

$$= \frac{\text{number of evolved } H_2 \text{ molecules} * 2}{\text{number of incident photons}} * 100$$

- Both hydrogenation and modification of HG accelerated H_2 generation
- HG – accepts and conducts electron, maximizes intimate interfacial contact
- Oxygen vacancies – electron donor



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Summary

- NEXAFS: Direct information of molecular orientation and orbital anisotropy Non-destructive for wide variety of systems

- Graphene/metal interfaces show rich chemistry: covalent hybridization of π cloud to metal *d* orbitals, opening of bandgap, charge transfer as seen from mobility measurements

- Pinning of graphene π cloud reduces electronic accessibility for further functionalization.

- RuO_2/RGO preliminary analysis in Super capacitor application concluded that the crystalline graphene-RuO_2 sample has no inter layer adsorbate state which could be responsible to explain the results low conductive properties. In Dr. Amir's experimental studies on efficient of electrode she found that amorphous and porous RuO_2/graphene samples were more efficient in conductive properties than the crystalline

- Future/Ongoing Studies: Extract H_2 from H_2O using inexpensive graphene-based metal oxide catalysts study *in-situ* catalytic reaction

Thank You!!

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Thank You !!

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- **Students of Banerjee Group**

Robert Dennis, Theodore Alivio

- **BNL Chemsitry** **Jose Rodriguez, Sanjaya Senanayake, Duong Nguyen Phan**

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Scalable Synthetic Routes to Graphene

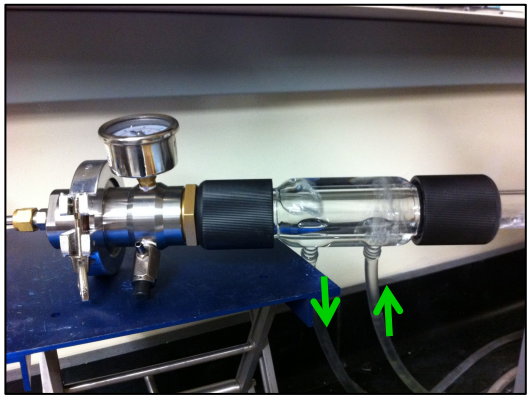
Chemical Vapor Deposition

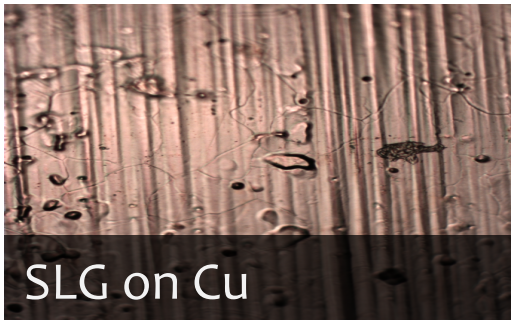
Oxidation of Graphite Followed by Exfoliation and Reduction

Solution-Phase Exfoliation of Graphite

CVD Growth of Graphene

- Precursors
  - Methane
  - Ethanol bubbler
  - Acetylene
- Parameters
  - Cooling rate (quenched)
  - Gas flow/ partial pressure (Ar = 300 sccm, H_2 = 10 sccm, CH_4=98 ppm)
  - Temperature (980°C)
  - Time (10-30 min.)





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