Synthesis and Electrochemical Properties of GUITAR: A Breakthrough Material for Energy Storage.

IAS Meeting, Moscow ID March 21, 2014

I. Francis (Frank) Cheng, Isaiah Gyan, Haoyu Zhu

Department of Chemistry
University of Idaho
Moscow, ID 83844-2343
ifcheng@uidaho.edu
208-885-6387

Outline

- **Discovery**
  - Thermolyzed Asphalt Reaction (TAR)
  - Graphene from UI-TAR (GUITAR)
- **Comparison of GUITAR with Literature**
  - What is it?
  - Not Graphene nor Ordinary Graphite
- **Electrochemical Characteristics**
  - Energy storage applications

University of Idaho Thermolyzed Asphalt Reaction

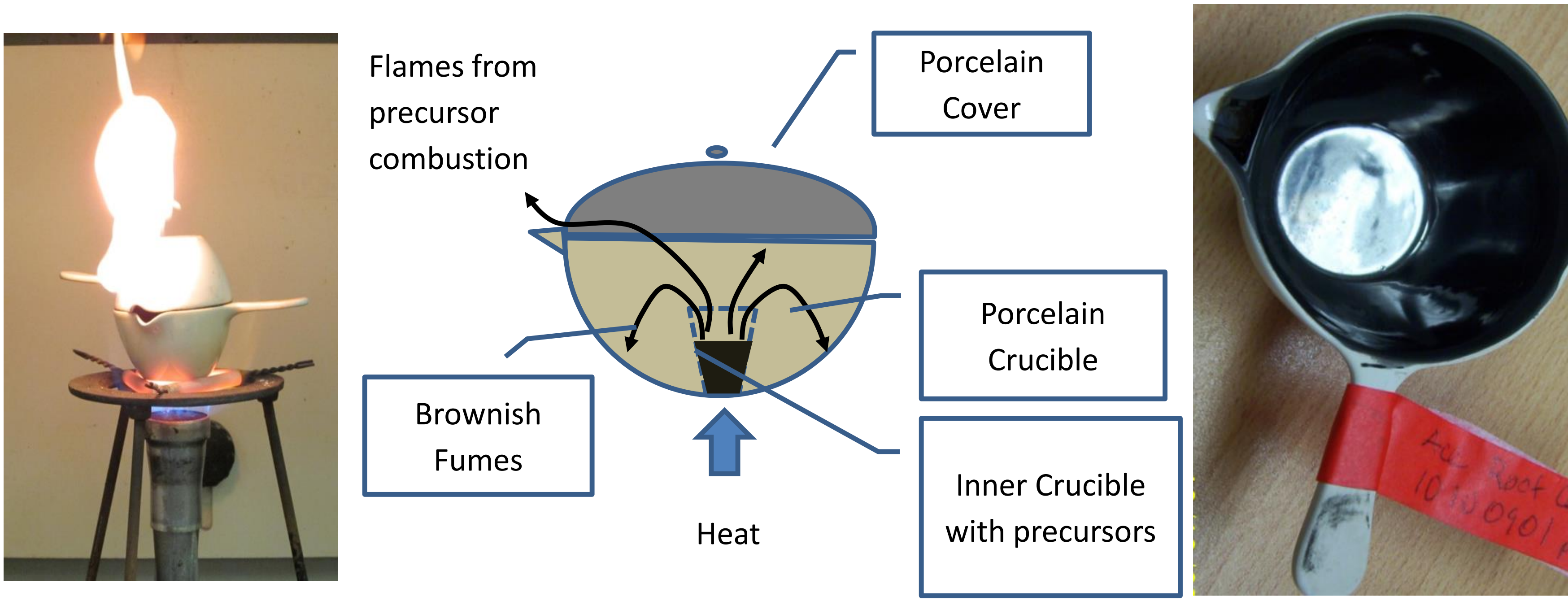


Figure 2.0.1 (Left) Pyrolysis of roofing tar, **(Middle)** schematic of the process, **(Right)** finished product.

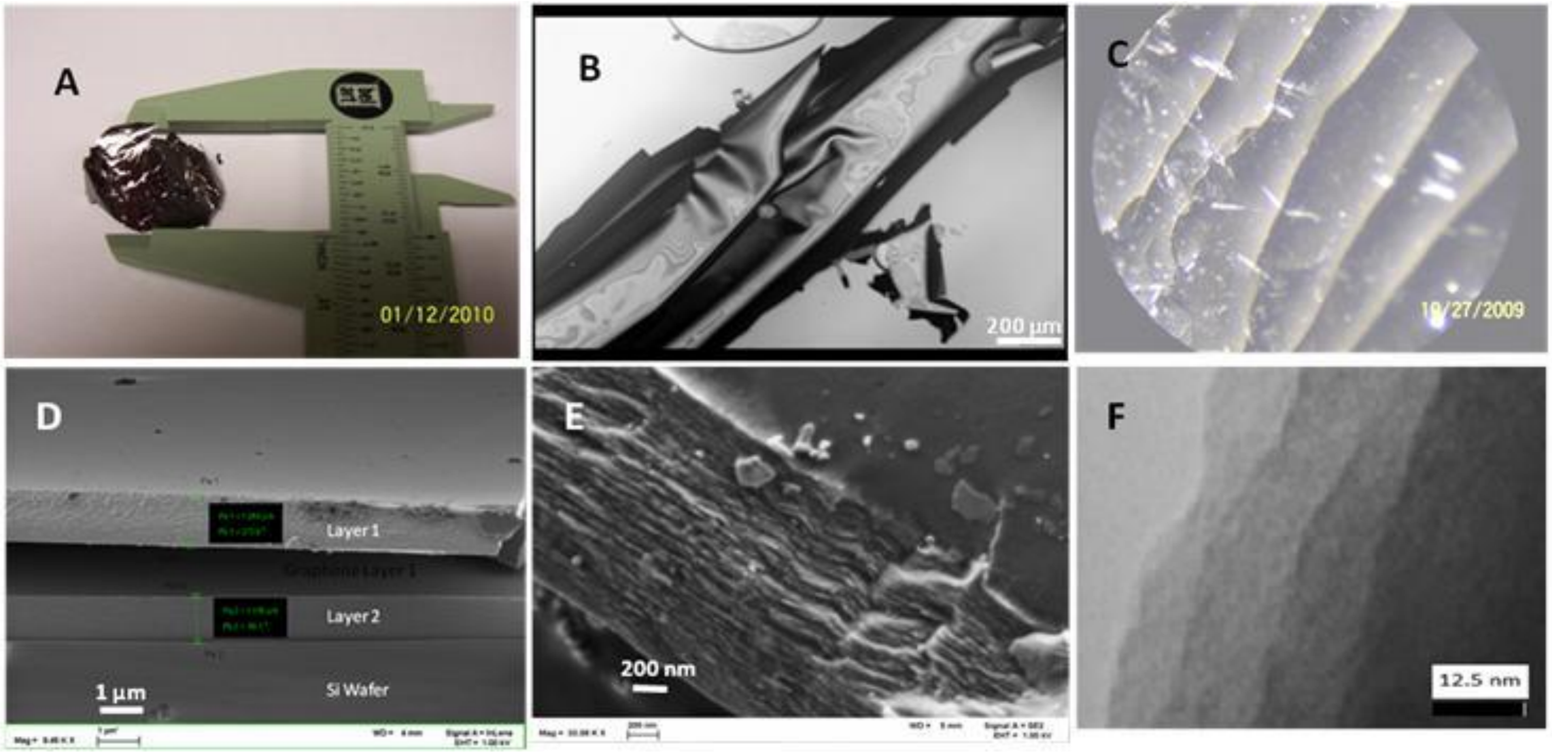


Figure 2.0.2 GUITAR graphene, **A –** a photograph of a flake approximately 25 mm in diameter. **B –** an optical micrograph (400x) in water. **C –** graphene layers (400x). **D –** 9.45K x SEM of microtomed layers on Si. **E –** 23.08K x SEM showing layered characteristics. **F –** A TEM showing layered characteristics on the nanometer scale.

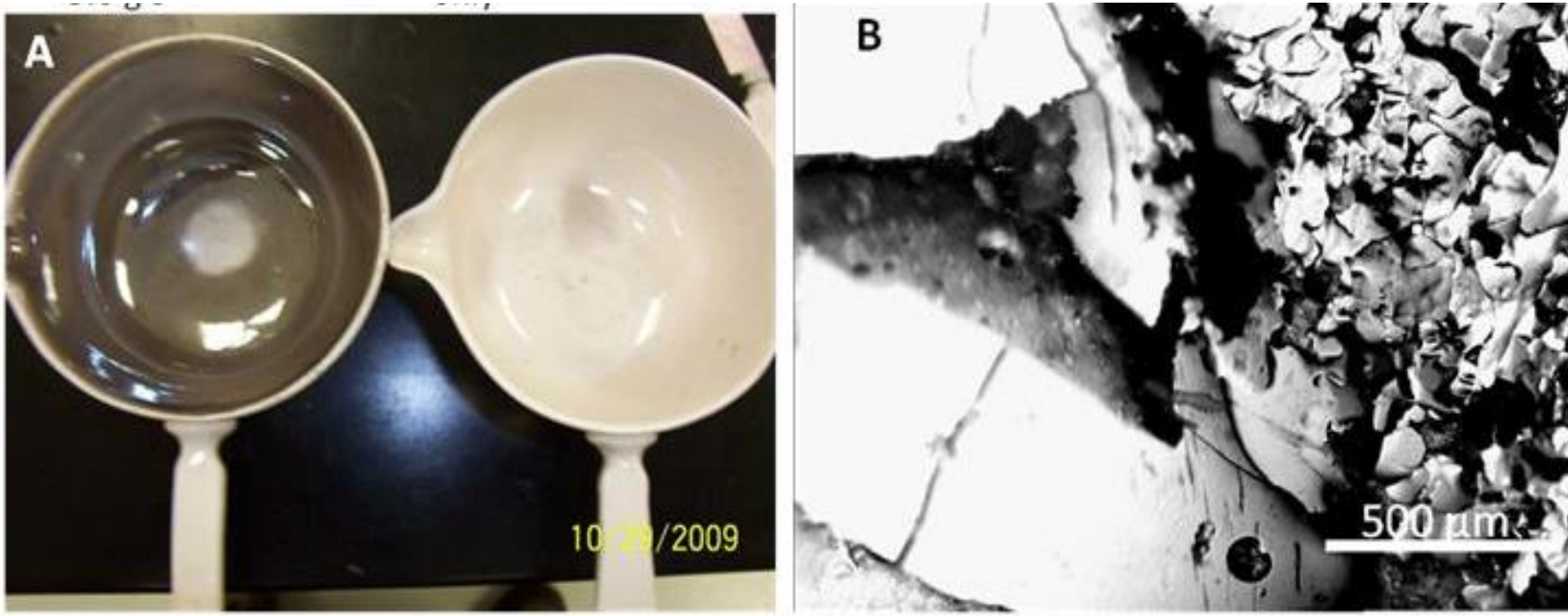
UITAR-University of Idaho Thermolyzed Asphalt Reaction

- **Successful Reagents**
  - Shale Oil
  - Crude Oil
  - Roofing Tar (Ace Hardware)
  - Taco Chips
  - Some Candy Bars
- **Failed**
  - Motor Oil, 5W-20
  - Paraffin
  - Pyrene

Mechanism of Formation

- First Hunch – Sulfur is Involved

cyclohexanol and Sulfur **cyclohexanol only**



Thermogravimetric analysis

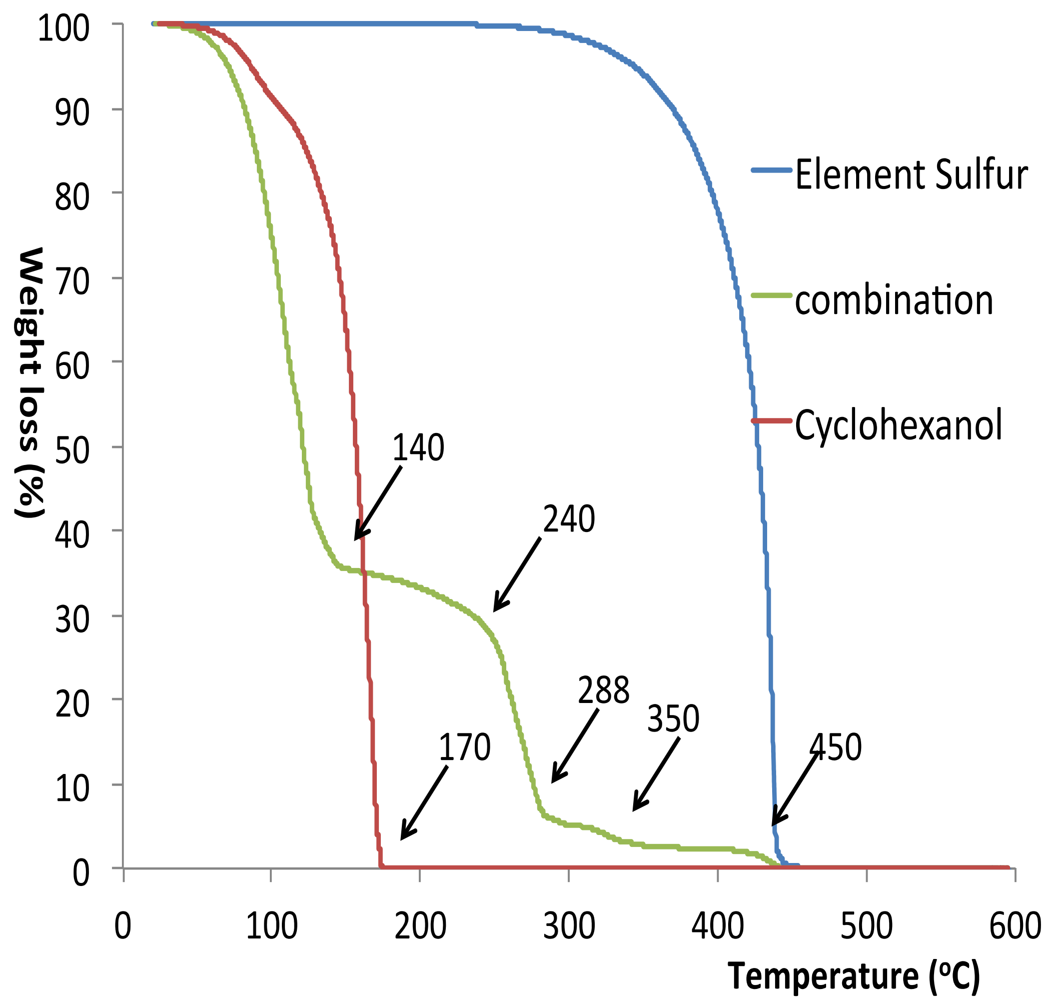
- **Cycohexanol (40 mg)**
- **Element sulfur (1 mg)**
- **Final temperature**

600 ^{0}C

- **Temperature ramp**

10^{0}C/min

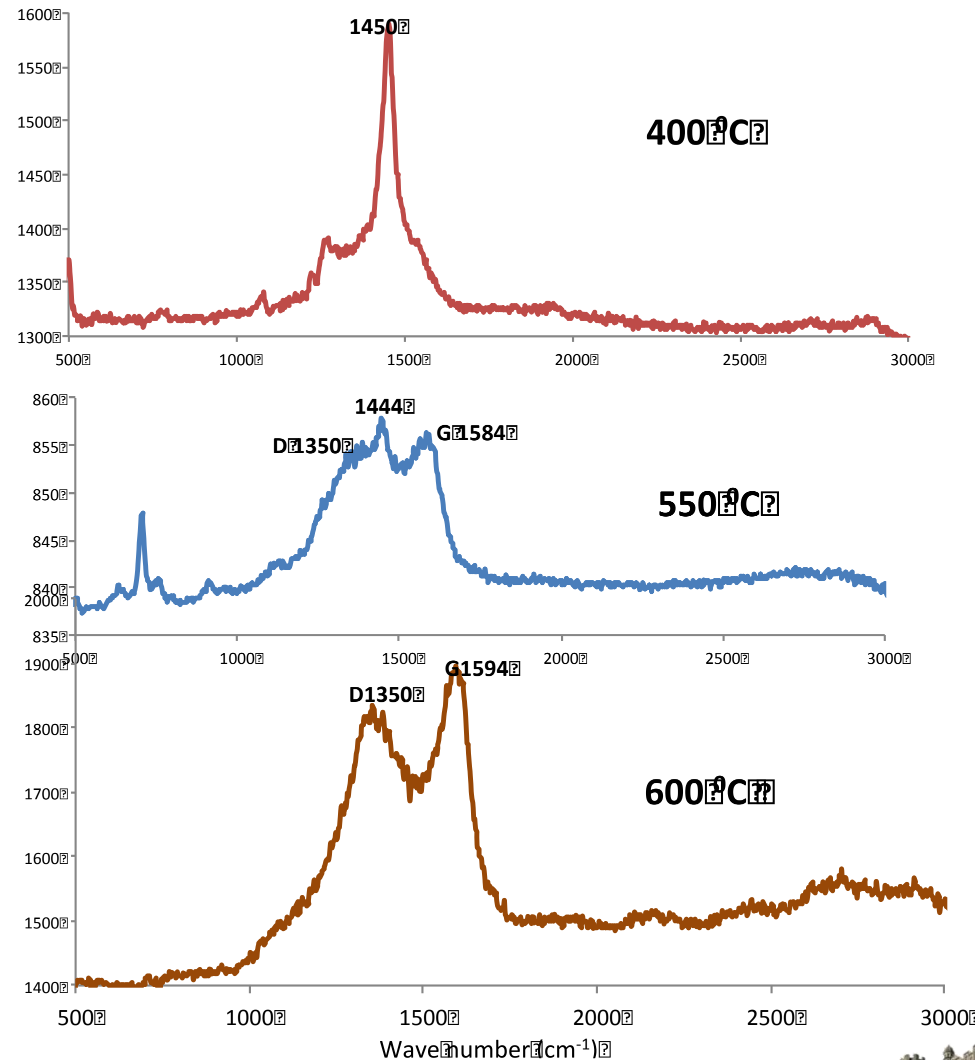
- **Under N_2 purge**

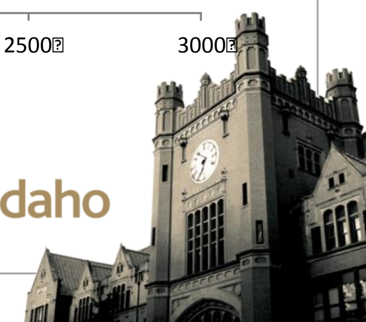


I.F. Cheng, et al. J. Mater. Chem. 2012, 22, 5723-29

Raman indicates an intermediate at 1450 cm^{-1}

- Minimum temperature 600^0C
- O_2 not affect graphene formation
- Graphene forms under N_2
- 1450 cm^{-1} intermediate at 400^0C





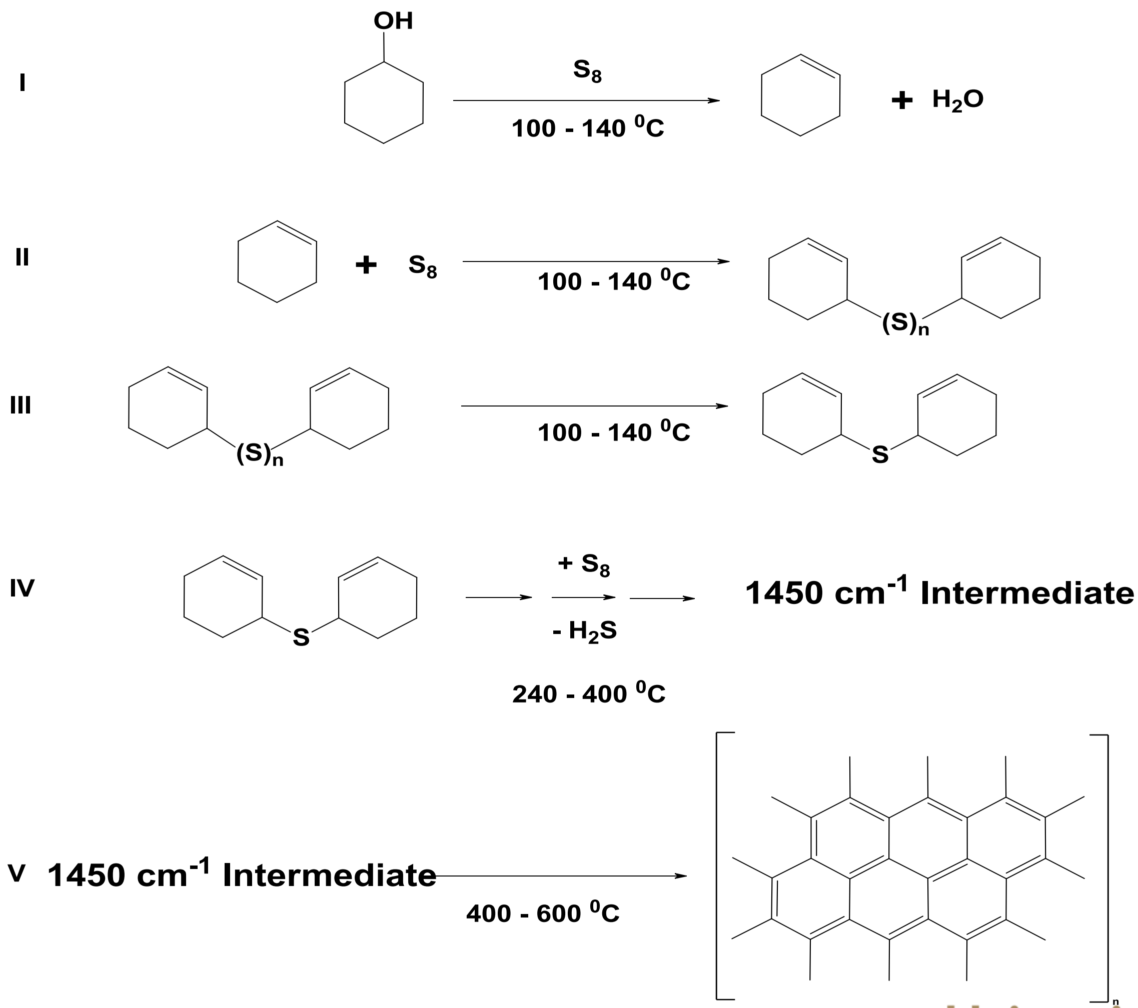
Y. Xie, I.F. Cheng, et al. Submitted

Summary of Formation

- **TGA and Raman Evidence**
  - Intermediates formed with S between 120 – 450 ^{0}C
  - Graphene/Graphite formation at 600 ^{0}C
- **Reagents**
  - Organic BP – MP 100-250 ^{0}C
  - Elemental Sulfur, Organic Sulfur
- **Conformal Coatings**
  - Unique to TAR
  - Deposition onto silica nanostructures

Hypothesized TAR Mechanism

Cheng et al, J. Mater. Chem. 2012, 22, 5723-29



CARBON 49 (2011) 2852–2861

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

ELSEVIER

Synthesis of graphene paper from pyrolyzed asphalt

I. Francis Cheng [a,], Yuqun Xie [a], R. Allen Gonzales [a], Przemysław R. Brejna [a], Jency Pricilla Sundararajan [b], B.A. Fouetio Kengne [b], D. Eric Aston [c], David N. McIlroy [b], Jeremy D. Foutch [a], Peter R. Griffiths [a]*

[a] *Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA*
[b] *Department of Physics, University of Idaho, Moscow, ID 83844-0903, USA*
[c] *Department of Chemical & Materials Engineering, University of Idaho, Moscow, ID 83844-1021, USA*

View Online / Journal Homepage / Table of Contents for this issue

Dynamic Article Links

Journal of Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 5723

www.rsc.org/materials

PAPER

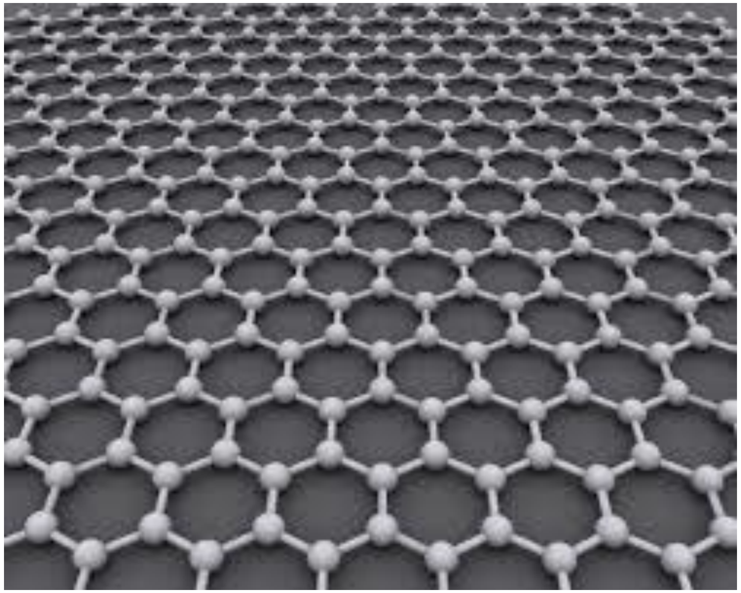
Sulfur as an important co-factor in the formation of multilayer graphene in the thermolyzed asphalt reaction

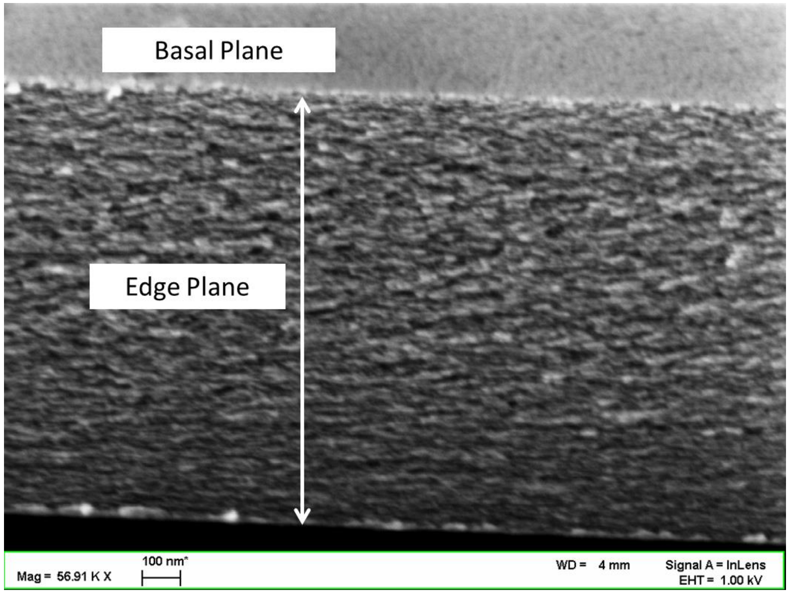
Yuqun Xie,[a] Simon D. McAllister,[a] Seth A. Hyde,[a] Jency Pricilla Sundararajan,[b] B. A. FouetioKengne,[b] David N. McIlroy[b] and I. Francis Cheng*[a]

Received 17th November 2011, Accepted 12th January 2012
DOI: 10.1039/c2jm15934a

What is that Material?

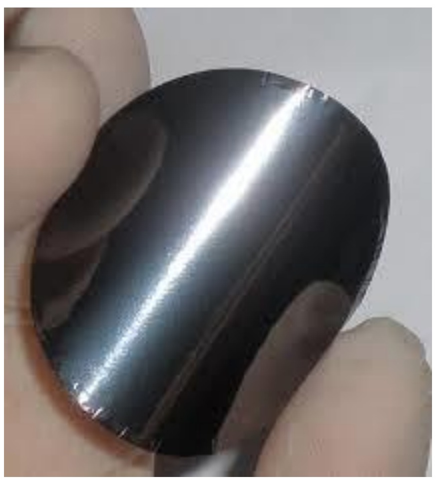
- Graphene (l) vs. GUITAR (r)
  - Graphene is a monolayer
  - GUITAR is multilayer



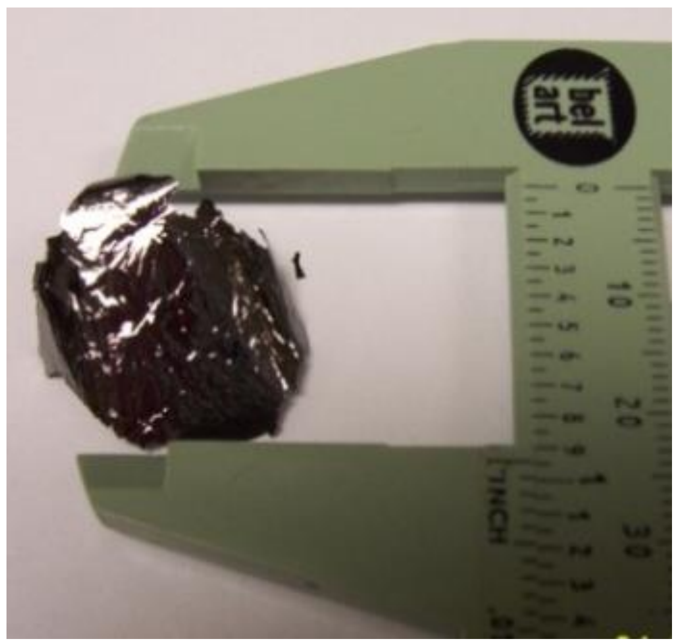


Graphene Paper and Highly Oriented Pyrolytic Graphite

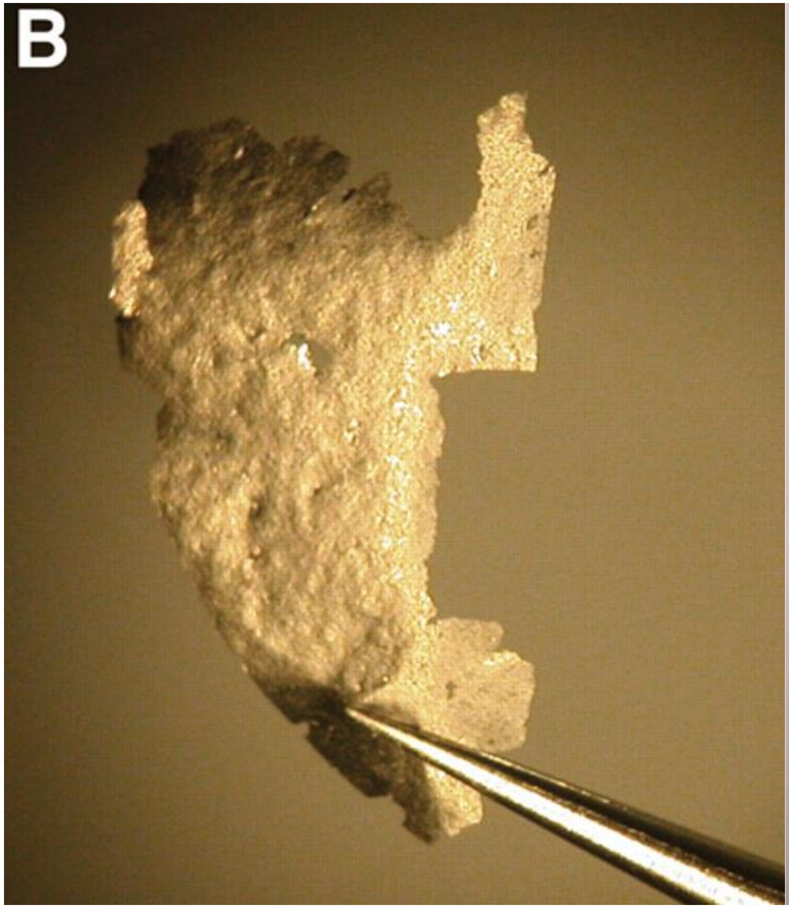
- Is it multilayer-graphene?
    - Graphene Paper (GP) Left
    - Highly Oriented Pyrolytic Graphite (HOPG)? Right

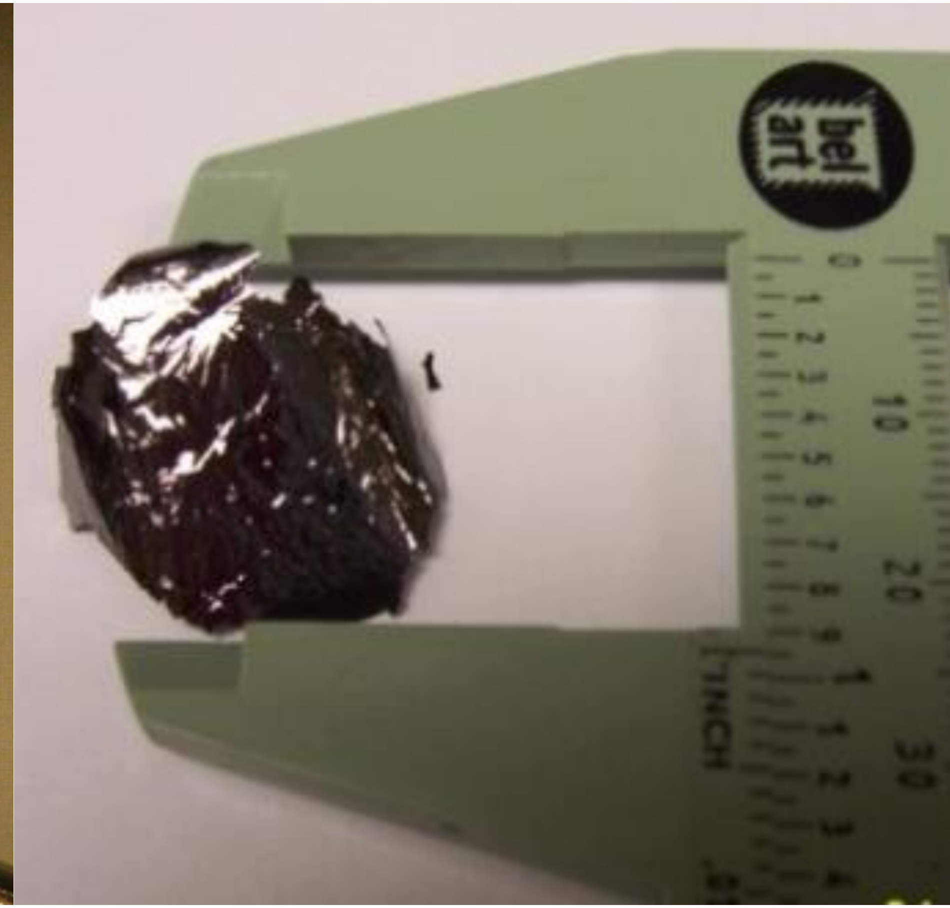


http://users.monash.edu.au/~lidan/



http://www.hqgraphene.com/NaturalGraphiteFlakes.php



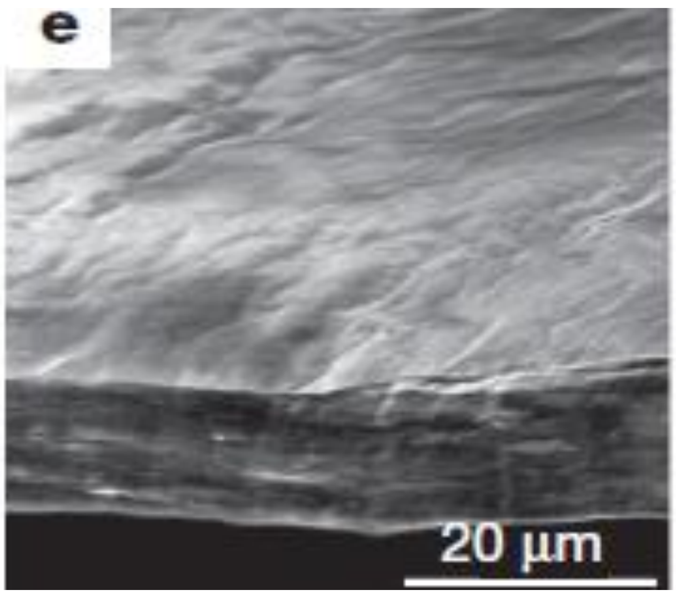


Graphene Paper (GP)

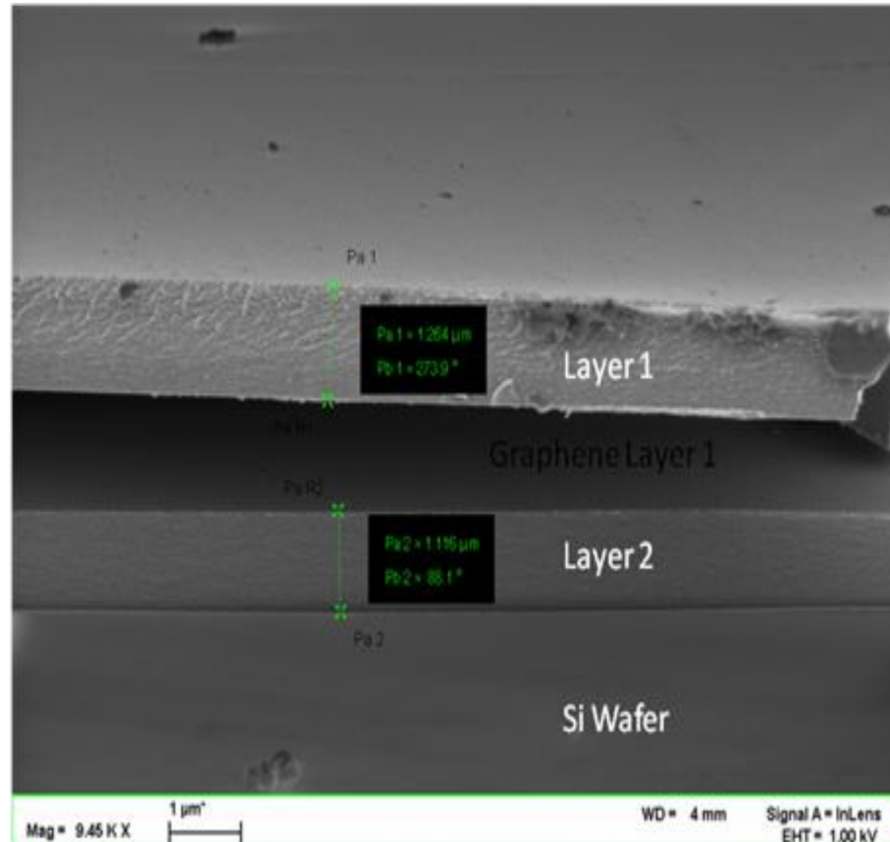
GUITAR

[Geim, Science, 2009, 324, 1530-4]

Morphological Differences GP – GUITAR

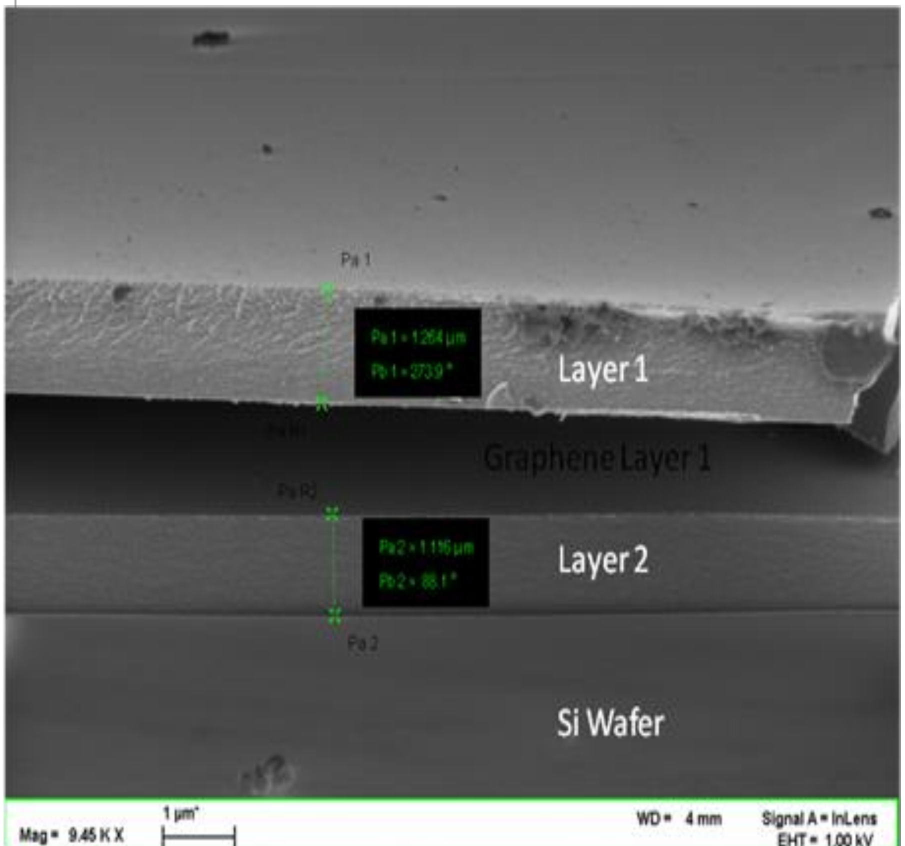


Ruoff, et al. Nature, 2007, (448), 457-460

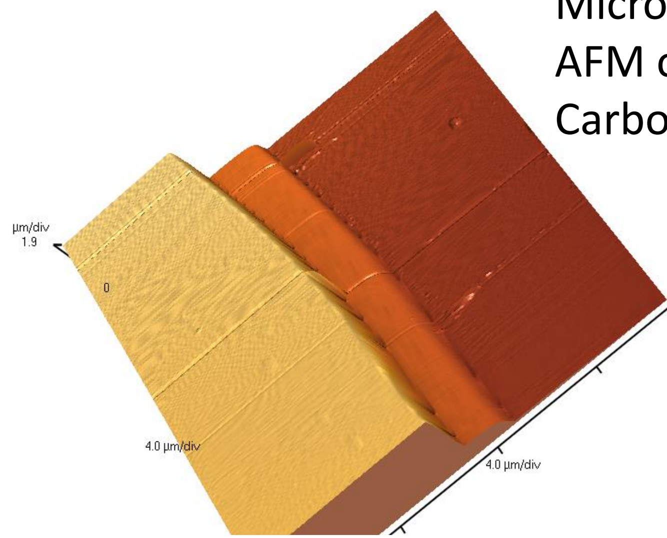


GUITAR

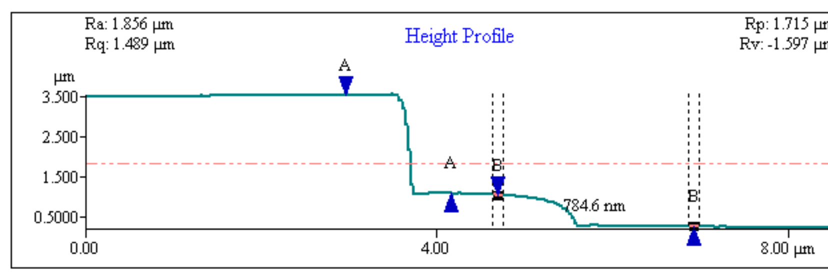
UI Material is Nearly Atomically Flat



Micron Scale AFM of UI Carbon

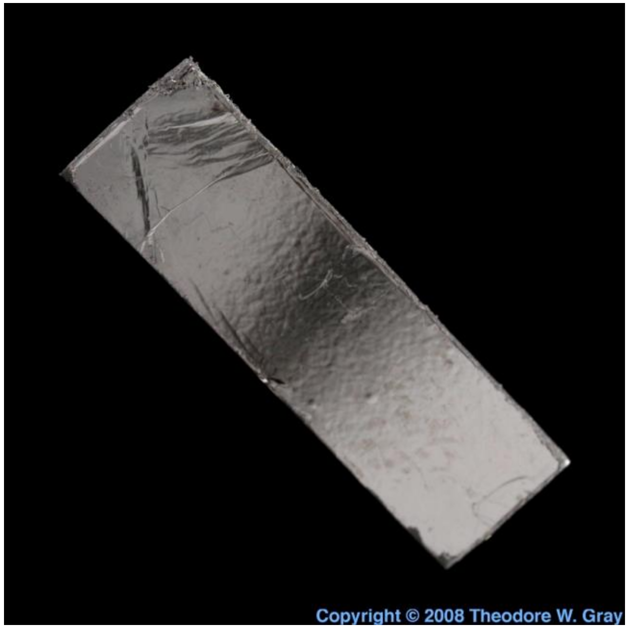


Line analysis on 15 um image



Cursor	Cursor
A h: 2.439 µm	B h: 0.7846 µm

HOPG and UI Carbon



HOPG

GUITAR

http://www.theodoregray.com/periodictable/Elements/006/index.s14.html#sample31

Physical Characterization

Material	XPS	Raman (cm^{-1})	
GUITAR	Nearly Pure sp^2 Carbon	G-band 1593 D-band 1350	Defective graphene structure
HOPG	Same	G-band only	Nearly Defect Free
Graphene Papers	Same	G-band (obs) D-band (obs)	Defective graphene structure

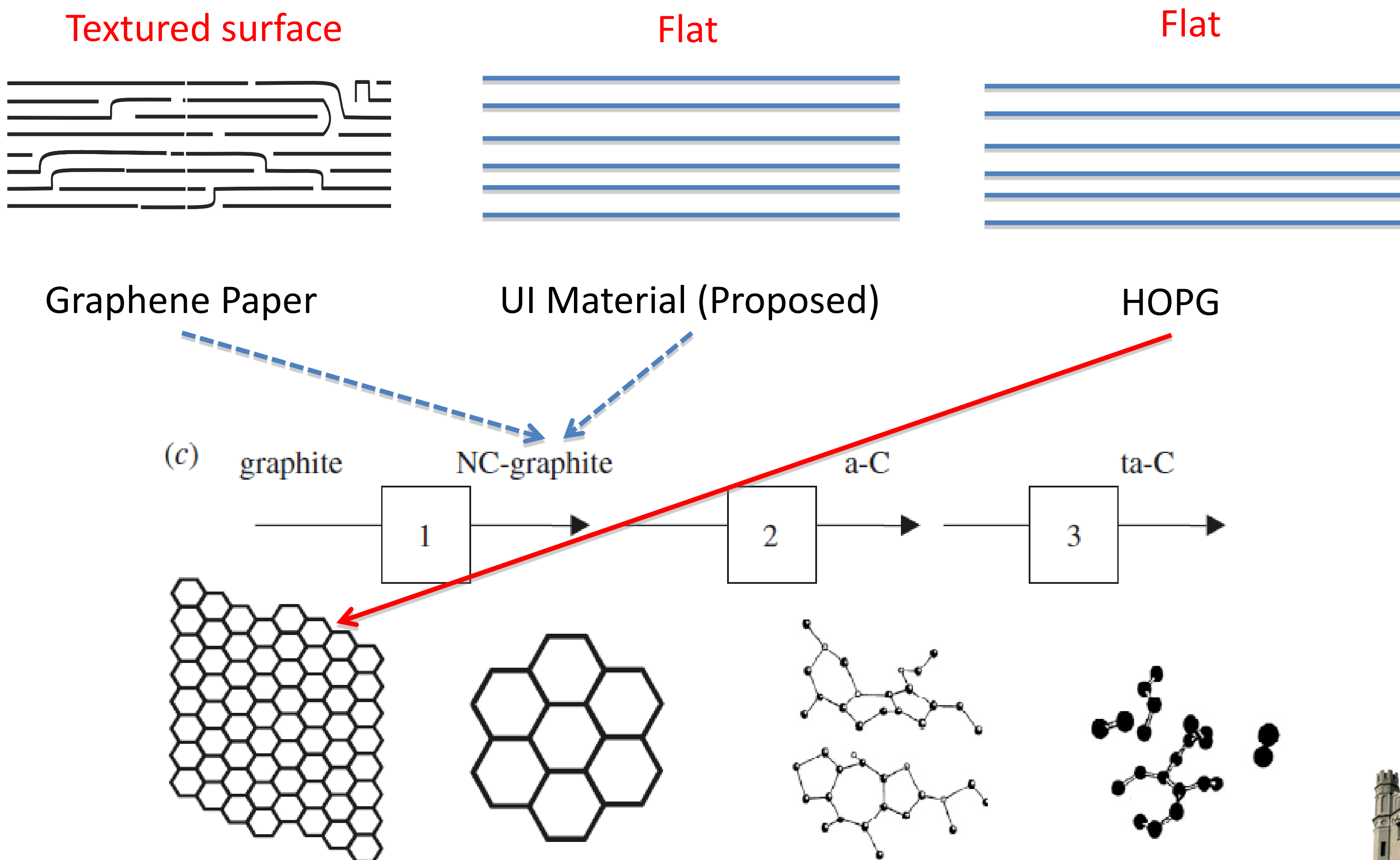
IR - 861 and 1576 cm^{-1} peaks intralayer graphene stretches
No other surface functionalities

UI Carbon

- **SEM and AFM**
  - Flat, layered morphology Resembles Highly Ordered Pyrolytic Graphite (HOPG)
  - Does Not Appear to be literature GP or r-GO paper
- **Raman Studies**
  - Grain Size 5.3 nm (Raman) with GP/r-GO parameters 3-6 nm
  - Closer to GP than HOPG

Neither HOPG or GP -- just graphite?

UI Carbon - Structure



Ferrari, Robertson. Phys Rev. 2000, (B61), 14095-14107

GUITAR Electrochemistry

- Electrochemical Characterization
  - Indicates that GUITAR is a unique graphitic material.
  - Graphene and HOPG are terrible electrodes
  - GUITAR is an excellent electrode
  - Excellent corrosion stability
  - High H_2 overpotential
  - Proposed Applications

RSC Advances

Dynamic Article Links

Cite this: *RSC Advances*, 2011, 1, 978–988

www.rsc.org/advances

PAPER

Electrochemistry of graphene: not such a beneficial electrode material?†

Dale A. C. Brownson, Lindsey J. Munro, Dimitrios K. Kampouris and Craig E. Banks*

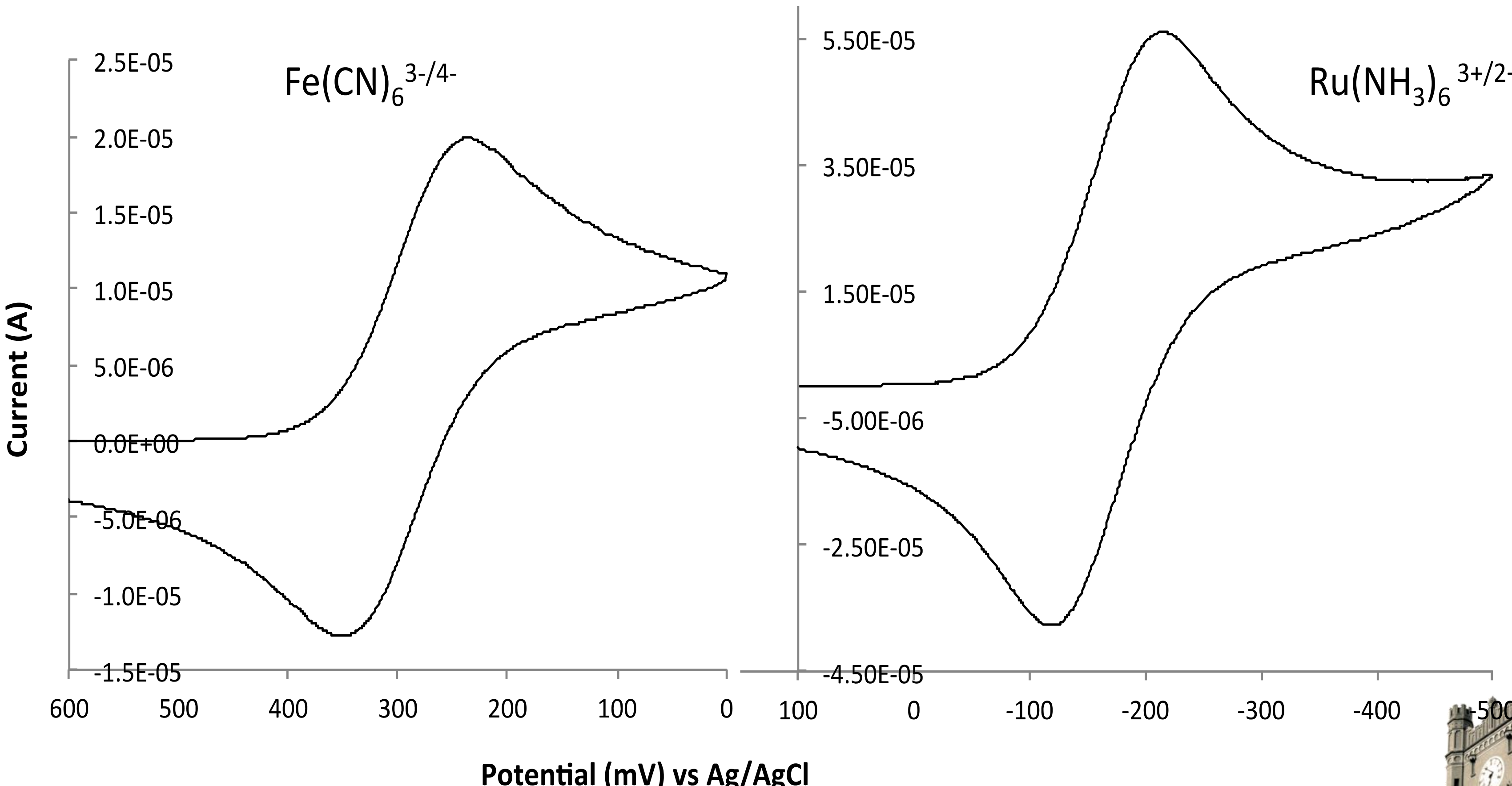
Received 30th June 2011, Accepted 22nd July 2011
DOI: 10.1039/c1ra00393c

GUITAR electrode fabrication

- Deposit GUITAR onto silicon wafer
- Transfer the GUITAR flakes onto mica by vacuum grease or 3M double sided conductive tape

Cyclic Voltammetry Indicates that GUITAR has excellent e- transfer rates with dissolved redox couples.

1 cm^2, 0.1 M KCl(aq) at 0.1 V/s.

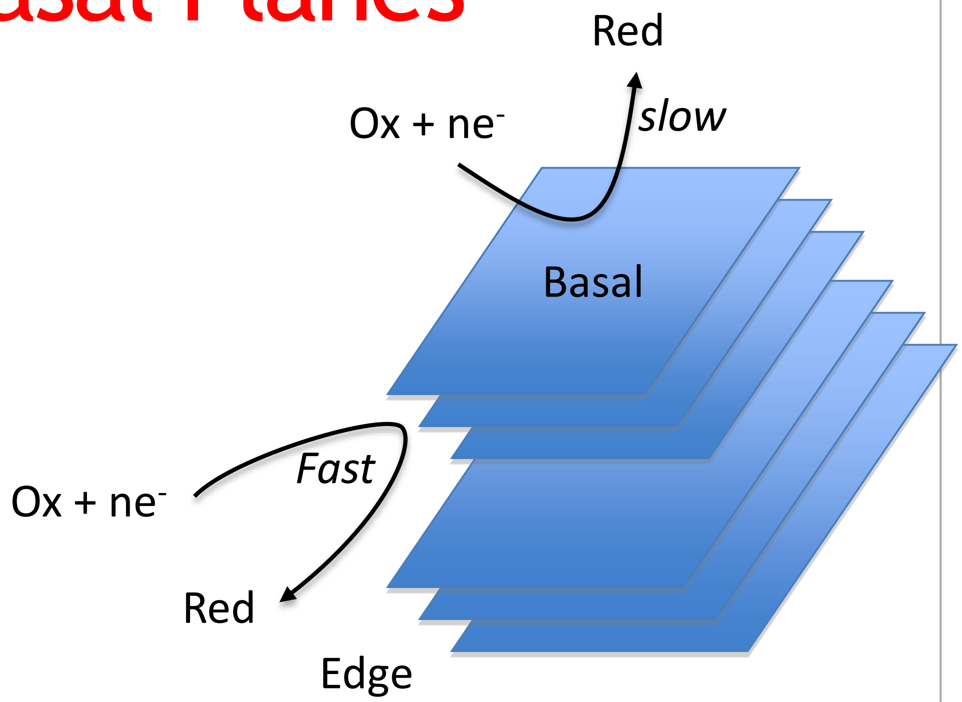


$$Ox + e^{-} \xrightarrow{k^0} Red$$

	$Fe(CN)_6^{3-/4-}$ k^0 (cm/s)	$Ru(NH_3)_6^{3+/2+}$ k^0 (cm/s)
GUITAR	**1×10^{-2}**	**2×10^{-2}**
Graphene (Basal Plane)	3×10^{-10}	5×10^{-3}
HOPG (Basal Plane)	10^{-6}	10^{-3}
HOPG (edge plane)	10^{-1}	--
Glassy Carbon	1×10^{-2}	2×10^{-2}

e- Transfer at Graphitic Electrodes Edge vs. Basal Planes

- Electron transfer rates on HOPG/Graphenes
  - Edge >> Basal Plane
- GUITAR electrodes have only Basal Planes exposed
- GUITAR Basal Planes has fast e-transfer
  - More like disordered systems



Electron Transfer Rate Trends

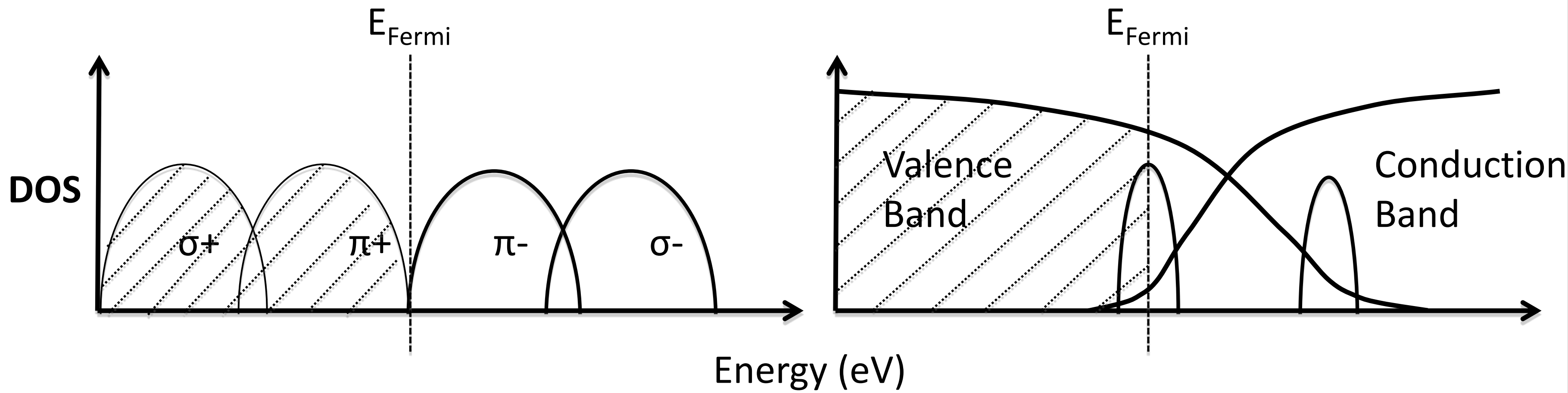
- Fastest Left → Right

GUITAR ≈ Glassy Carbon ≈ Graphite (*edges*)

> Boron Doped Diamond ≈ DLC

> HOPG (*basal Plane*) ≈ Graphene (basal plane)

McCreery et al, J. Phys. Chem. 1994, 98, 5314-5319



Crystalline Graphite

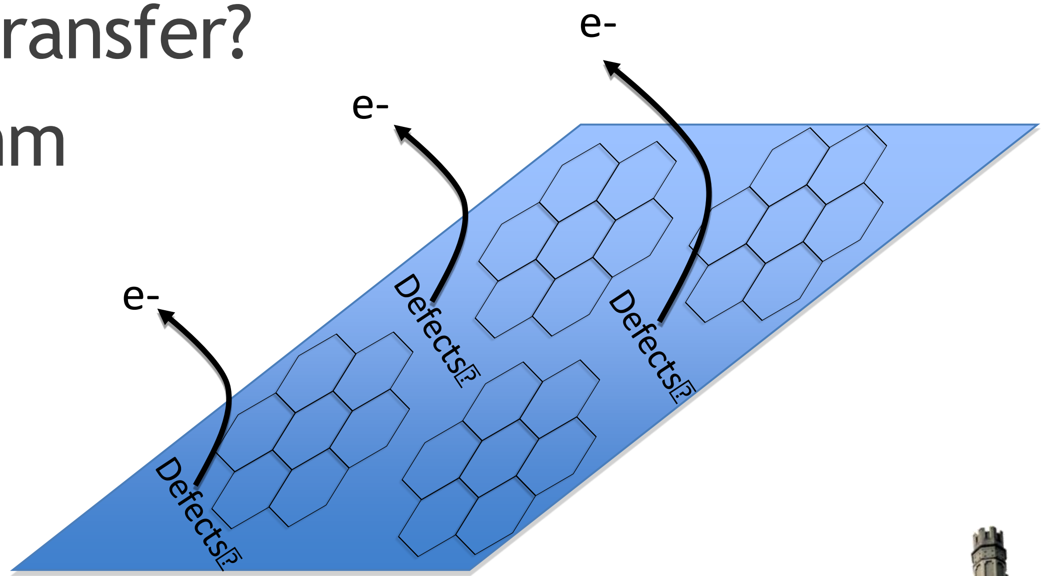
Disordered Graphite

From McCreery Table 5

	Free e- density (cm^{-3})	DOS at Fermi Level states/atom/eV
Au	6×10^{22}	0.28
HOPG	5×10^{18}	2.2×10^{-3}

GUITAR Electrodes

- **Higher DOS along Structural Defects?**
- **Structural Defects**
  - Sites for fast e- transfer?
  - Nano-crystals 5 nm

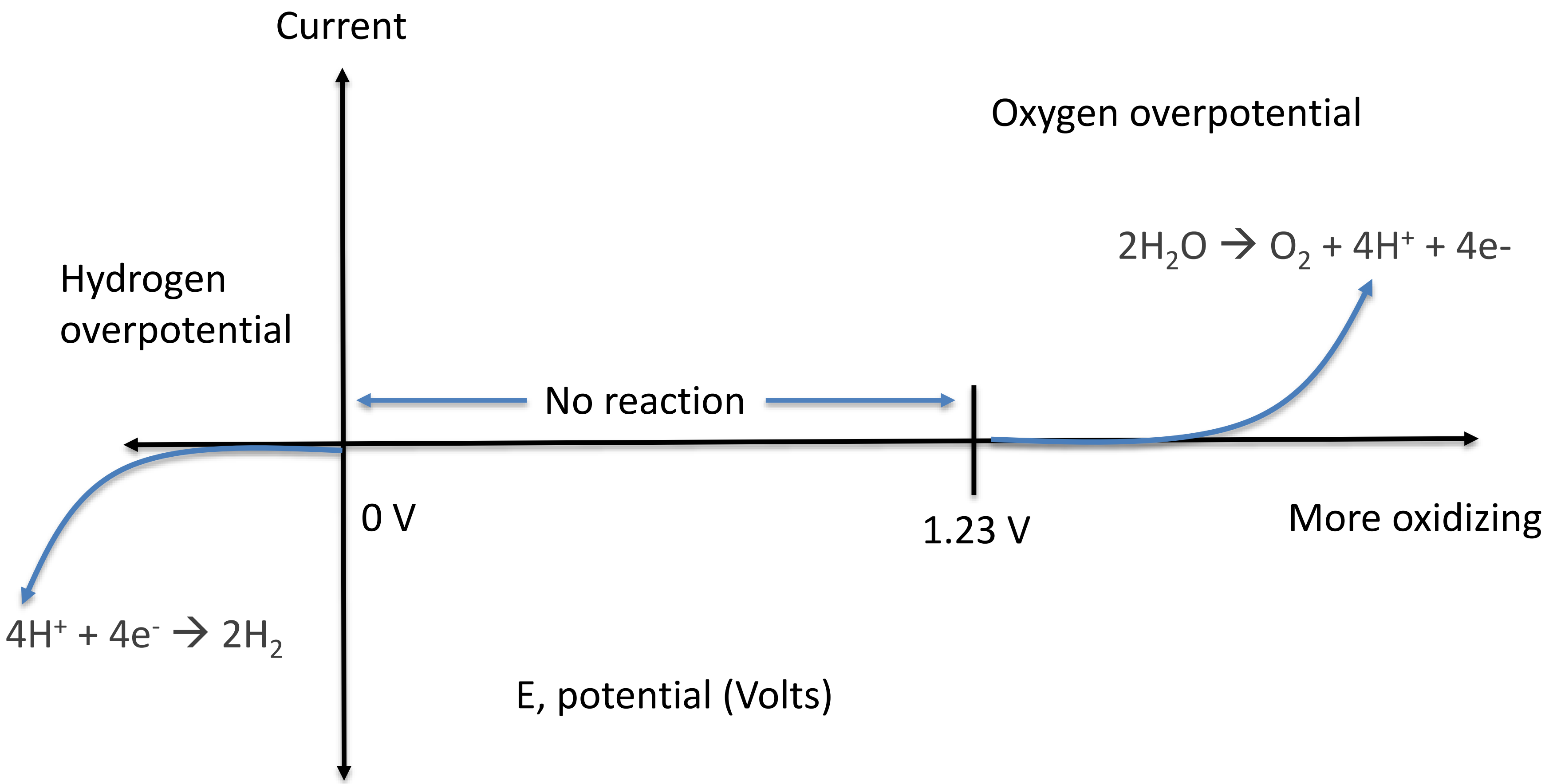


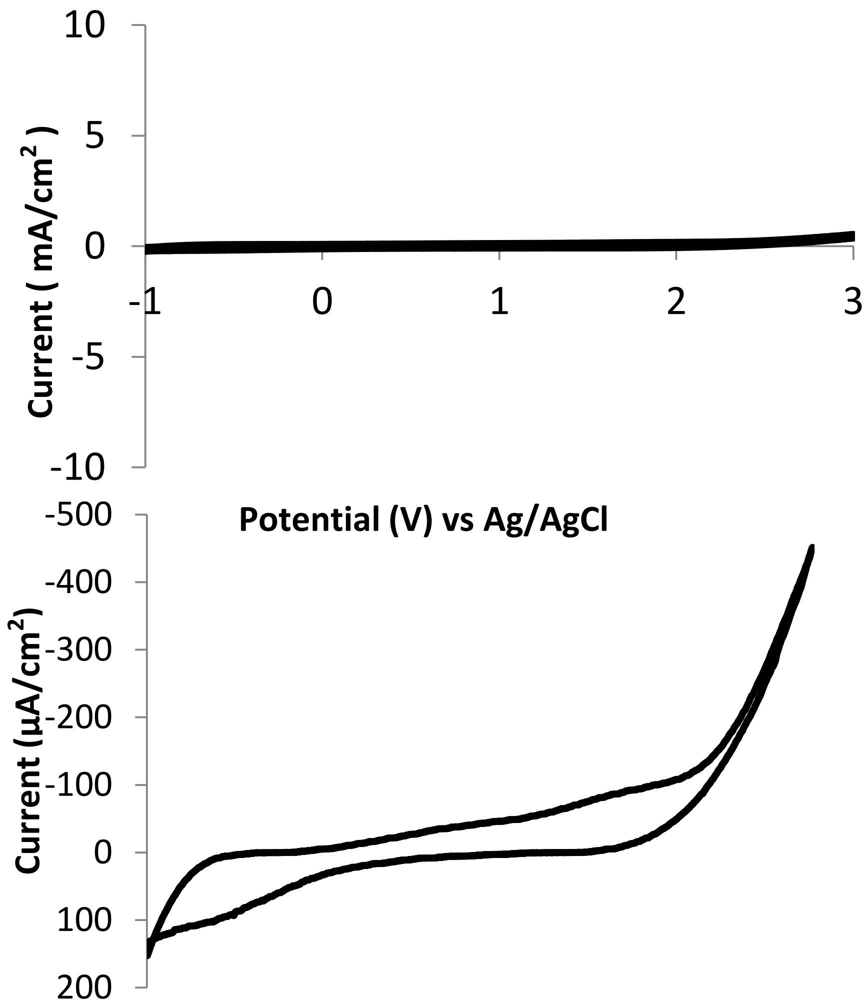
More Evidence that GUITAR is not a just another graphite - Anodic Limits

- **Potential "Window"**

- Anodic Limits
  - Water breakdown
    - $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = 1.23$ volts
  - Corrosion
    - $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ $E^0 = 0.207$ V

- Cathodic Limit
  - Water breakdown
    - $4H^+ + 4e^- \rightarrow 2H_2$ $E^0 = 0.00$ volts


Current
Oxygen overpotential
$2H_2O \rightarrow O_2 + 4H^+ + 4e-$
Hydrogen
overpotential
No reaction
0 V
1.23 V
More oxidizing
$4H^+ + 4e^- \rightarrow 2H_2$
E, potential (Volts)



Cyclic voltammograms of a GUITAR electrode 1M H_2SO_4 υ = 50 mV/s, under Ar.

The anodic limit at 200 µA/cm^2 is 2.1 volts.

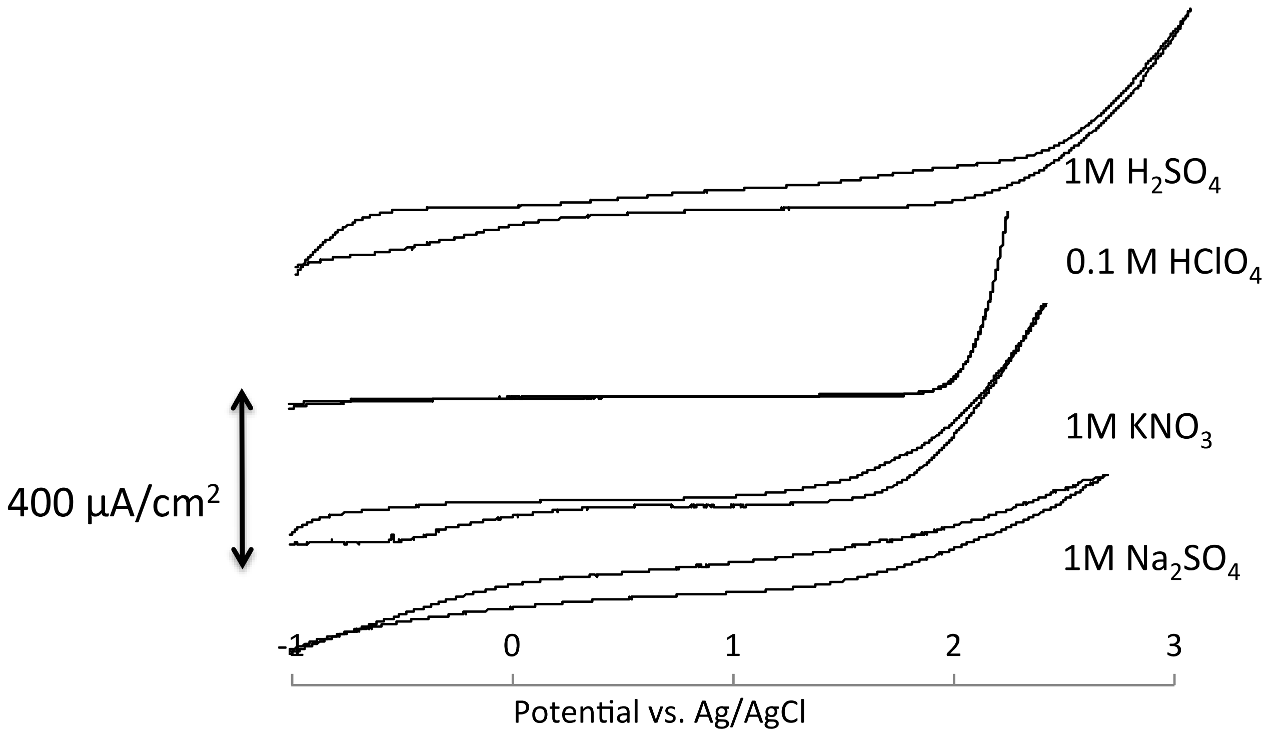
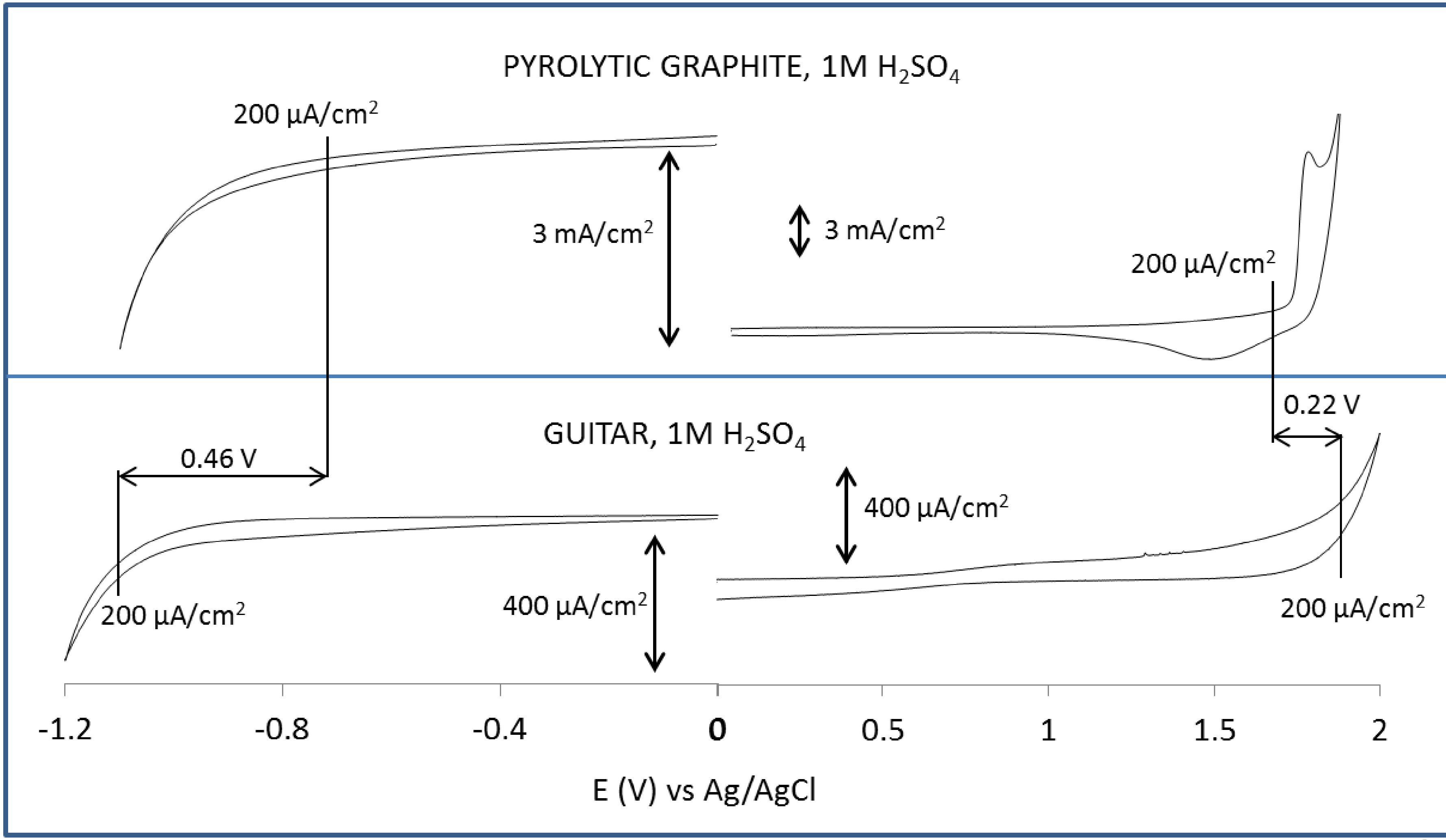


Figure 2.6.2 *Cyclic voltammograms of a 1 cm^2 GUITAR electrode in various electrolytes at 50 mV/s. All the solutions were purged with Ar.*


PYROLYTIC GRAPHITE, 1M H_2SO_4
200 µA/cm²
3 mA/cm²
3 mA/cm²
200 µA/cm²
0.22 V
GUITAR, 1M H_2SO_4
0.46 V
400 µA/cm²
200 µA/cm²
400 µA/cm²
200 µA/cm²
-1.2
-0.8
-0.4
0
0.5
1
1.5
2
E (V) vs Ag/AgCl

GUITAR has a much larger potential window than literature Graphite and HOPG

Material	Anodic Limit (V)	Cathodic Limit (V)	Total window (V)	reference
GUITAR	**2.10 ± 0.03 (15)**	**-0.90 ± 0.08 (n = 15)**	**3.00**	This work
Pyrolytic Graphite	1.88 ± 0.03 (12)	-0.44 ± 0.08 (12)	2.32	
Graphite Foil	1.45 ± 0.01 (10)	-0.51 ± 0.05 (10)	1.96	
HOPG	1.67	-0.41	2.08	Literature
HOPG	1.60	-0.40	2.00	Literature
Exfoliated Graphite	1.71	-0.50	2.21	Literature

Potentials are referenced to the standard hydrogen electrode (SHE).

Anodic limits comparison of the GUITAR anode to boron doped diamond and HOPG in various electrolytes.

Electrode	Electrolyte	Anodic Limits vs. SHE (V)	Current density ($\mu A/cm^2$)	Ref.
GUITAR	1 M H_2SO_4	2.1	200	This work
BDD		1.9 - 2.5	200	1,2,3
HOPG		1.7	200*	4
N-Doped Diamond-Like Carbon	0.5 M H_2SO_4	2.6 V	200	7

**Current density estimated from an average of 0.1 cm^2.*

Reference 4 reports electrodes varied from 0.05 to 0.2 cm^2

Anodic Limits of GUITAR and other Dimensionally Stable Anodes.

Material	Anodic Limit (V) vs. SHE	Conditions	Reference
GUITAR	**2.1**	1 M H_2SO_4	This work
Graphite	1.7	0.5 M H_2SO_4	1,2,3
Ruthenium Oxide	1.47	0.5 M H_2SO_4	4,5,6
Iridium Oxide	1.52	0.5 M H_2SO_4	
Platinum	1.6	0.5 M H_2SO_4	7,8,9
Tin Dioxide	1.9	0.05 M H_2SO_4	10,11,12
Lead Dioxide	1.9	1 M H_2SO_4	13,14,15

Anodic Stability Trends

- **BDD ≈ DLC > GUITAR** > HOPG = Graphite = Glassy Carbon ≈ Metal Oxides > Pt > Metals

GUITAR vs. HOPG Anodic Limits

- **HOPG limit = +1.7 V**
  - Murray et al, Anal. Chem.1995, 67, 2201
  - Can’t do methylene blue degradation @ 2.0 V

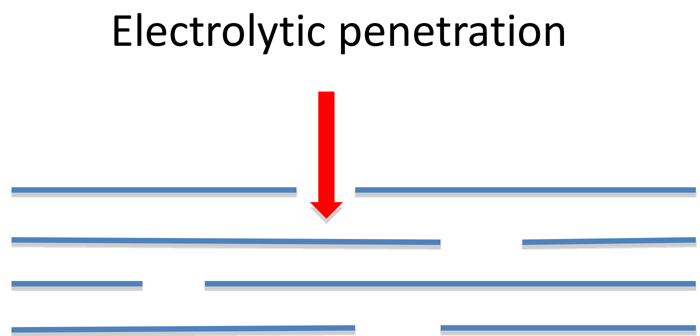
- **GUITAR limit = 2.1 V**

- **Anodic Limit**
  - GUITAR > HOPG
  - Cheng et al, *RSC Advances* 2013, 3, 2379

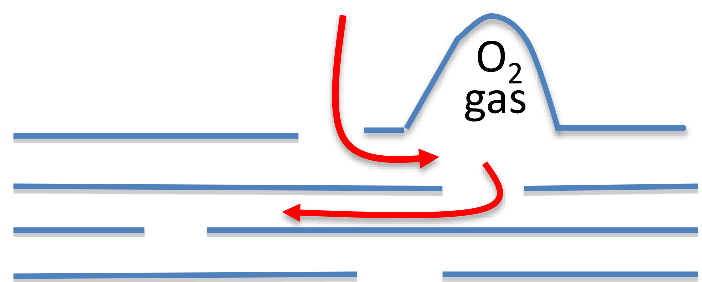
- **Why?**

Corrosion on HOPG is initiated with electrolyte intercalation. Murray et al, Analytical Chemistry, 1995, 67, 2201-2206

HOPG anodic limit 1.7 V
Micron size grains
Gaps between grain boundaries



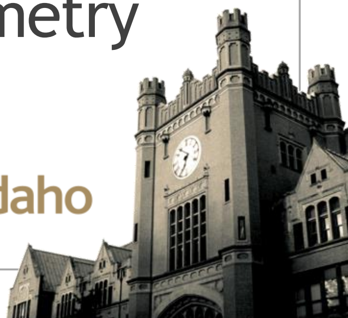
O_2 Gas Evolution
Blister and Pit
Corrosion Formation



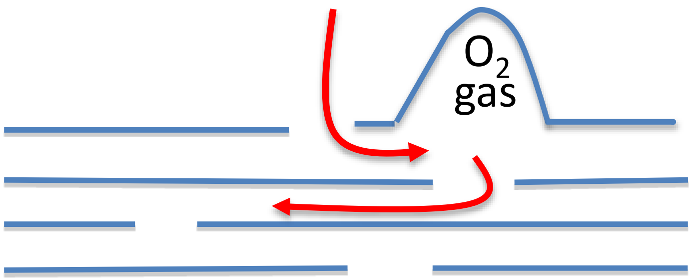
Defects HOPG vs. GUITAR

- **Highly Ordered Pyrolytic Graphite (HOPG)**
  – Grain Defects with Holes, Crevasses
  – Nearly Flawless Structure
    - Raman G-Band only

- **GUITAR**
  – Structural Defects with No Holes
    - Raman D/G band
    - No Electrolyte Intercalation – Cyclic Voltammetry



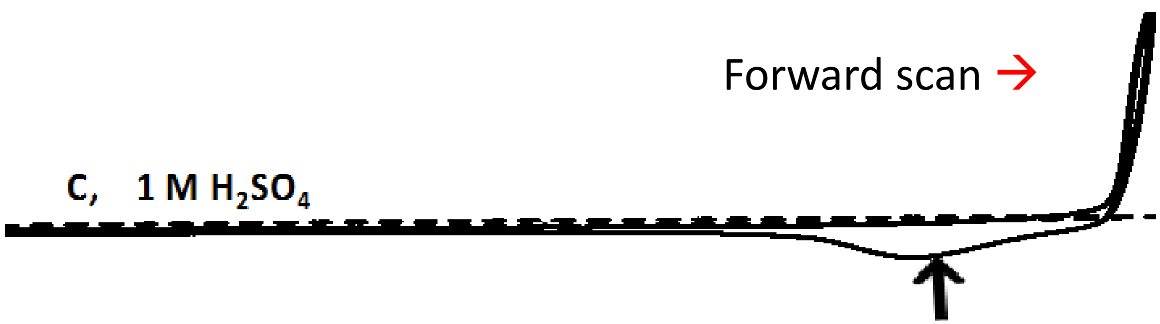
Blister formation on pyrolytic graphite anodes



Gas Evolution, Blister and Pit Formation

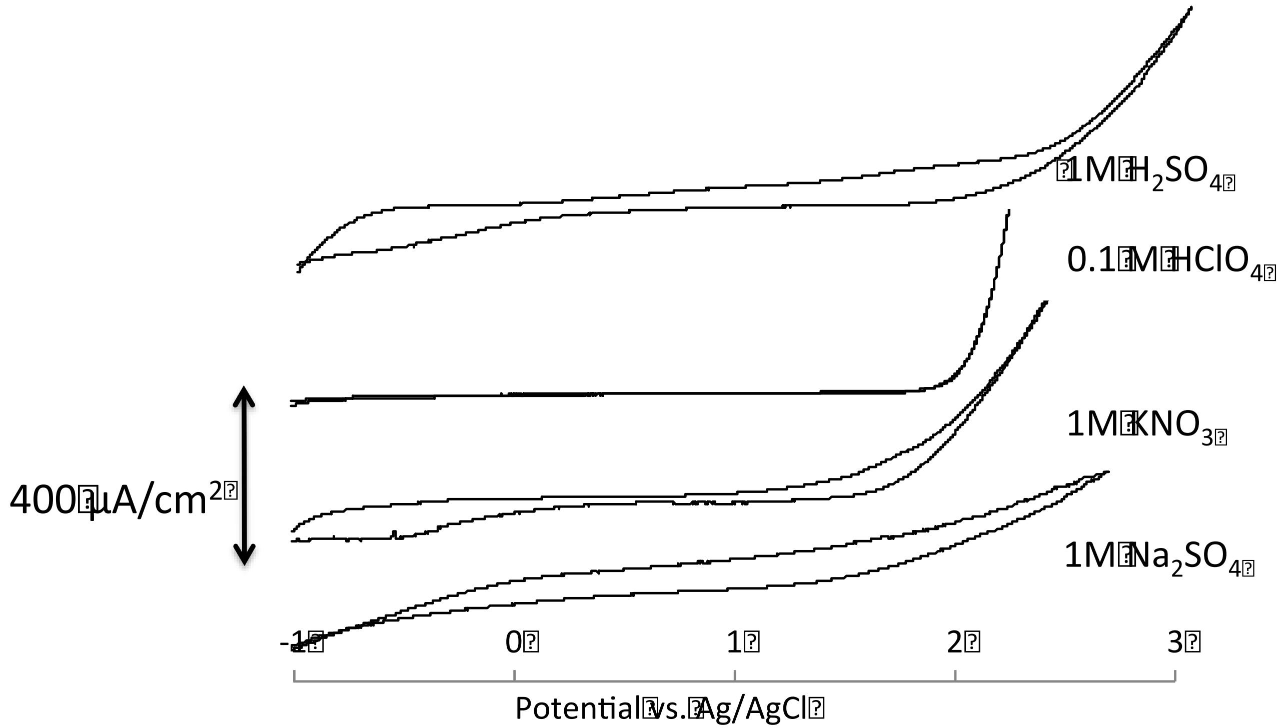
$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ forward scan

$2O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ reverse scan



Murray et al, Analytical Chemistry, 1995, 67, 2201-2206

GUITAR anodes do not exhibit electrolytic intercalation

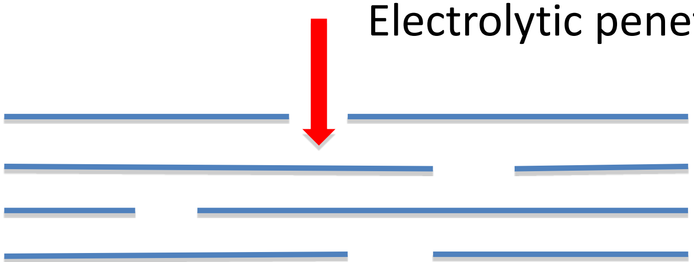


Cyclic voltammograms of a 1 cm^2 GUITAR electrode in various electrolytes at 50 mV/s. All the solutions were purged with Ar.

Current Model

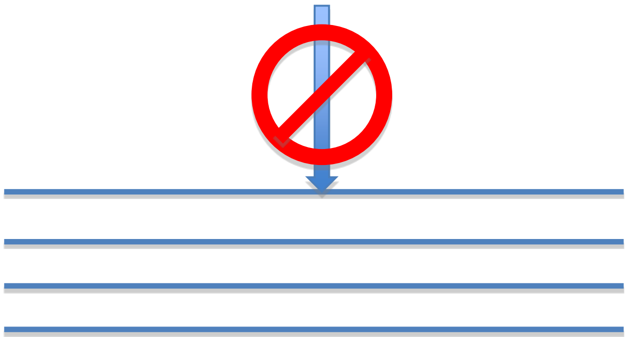
HOPG anodic limit 1.7 V

Electrolytic penetration

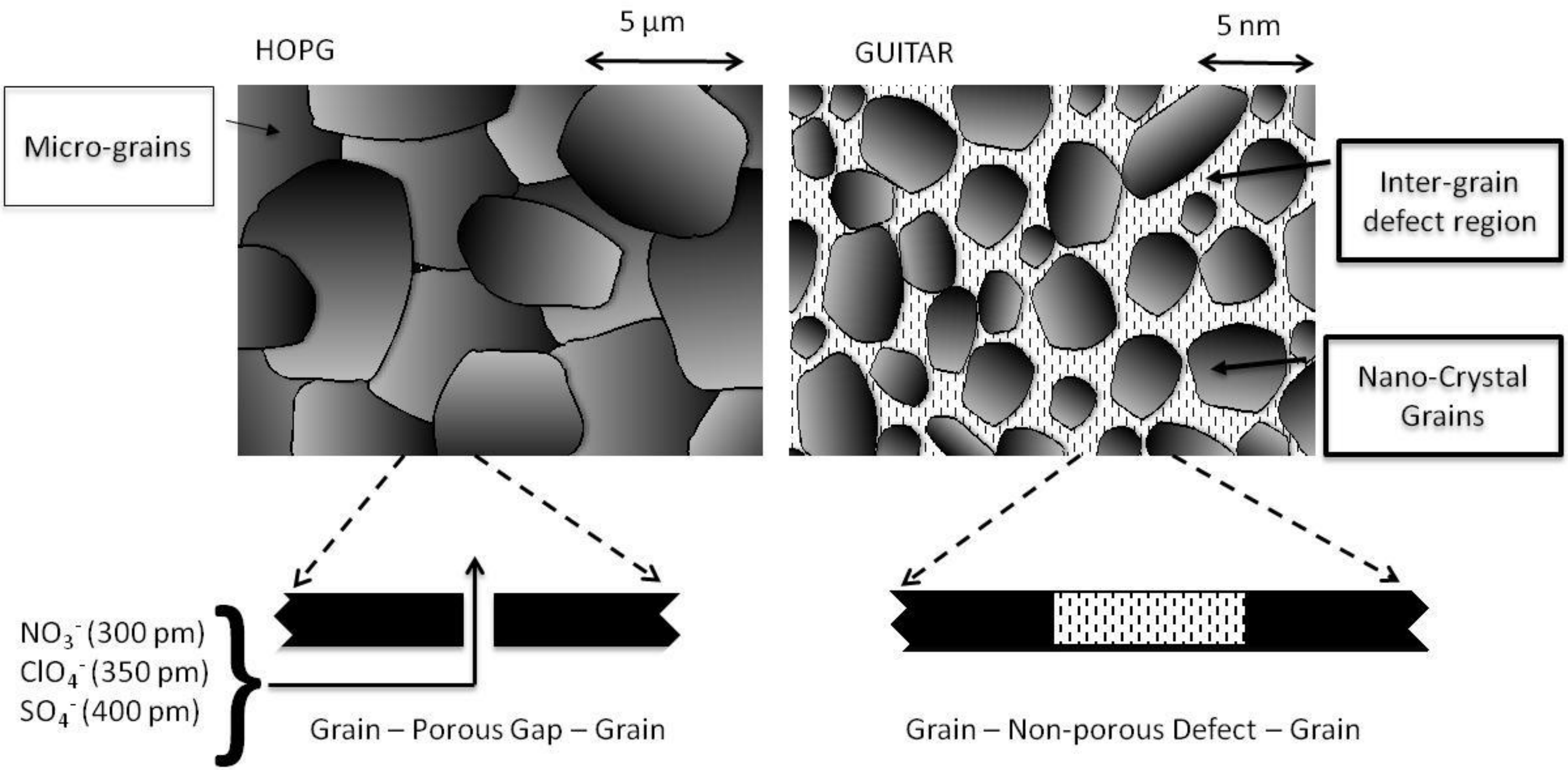


Micron size grains
Pin-Holes
-Fewer DOS

GUITAR anodic limit 2.1 V



Nano-size Grains w/Structural Defects
Pin-Hole Free?
-Higher DOS



5 µm
HOPG
GUITAR
5 nm
Micro-grains
Inter-grain defect region
Nano-Crystal Grains
NO3- (300 pm)
ClO4- (350 pm)
SO4- (400 pm)
Grain – Porous Gap – Grain
Grain – Non-porous Defect – Grain

GUITAR Has the Highest Measured H_2 Overpotential of Graphitic Materials

- Aqueous Media
  - $2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0.00$ V
- Overpotentials
  - Metal electrodes 0.1 to 0.5 V
  - Carbon electrodes 0.2 to 0.6 V
  - GUITAR 1 V

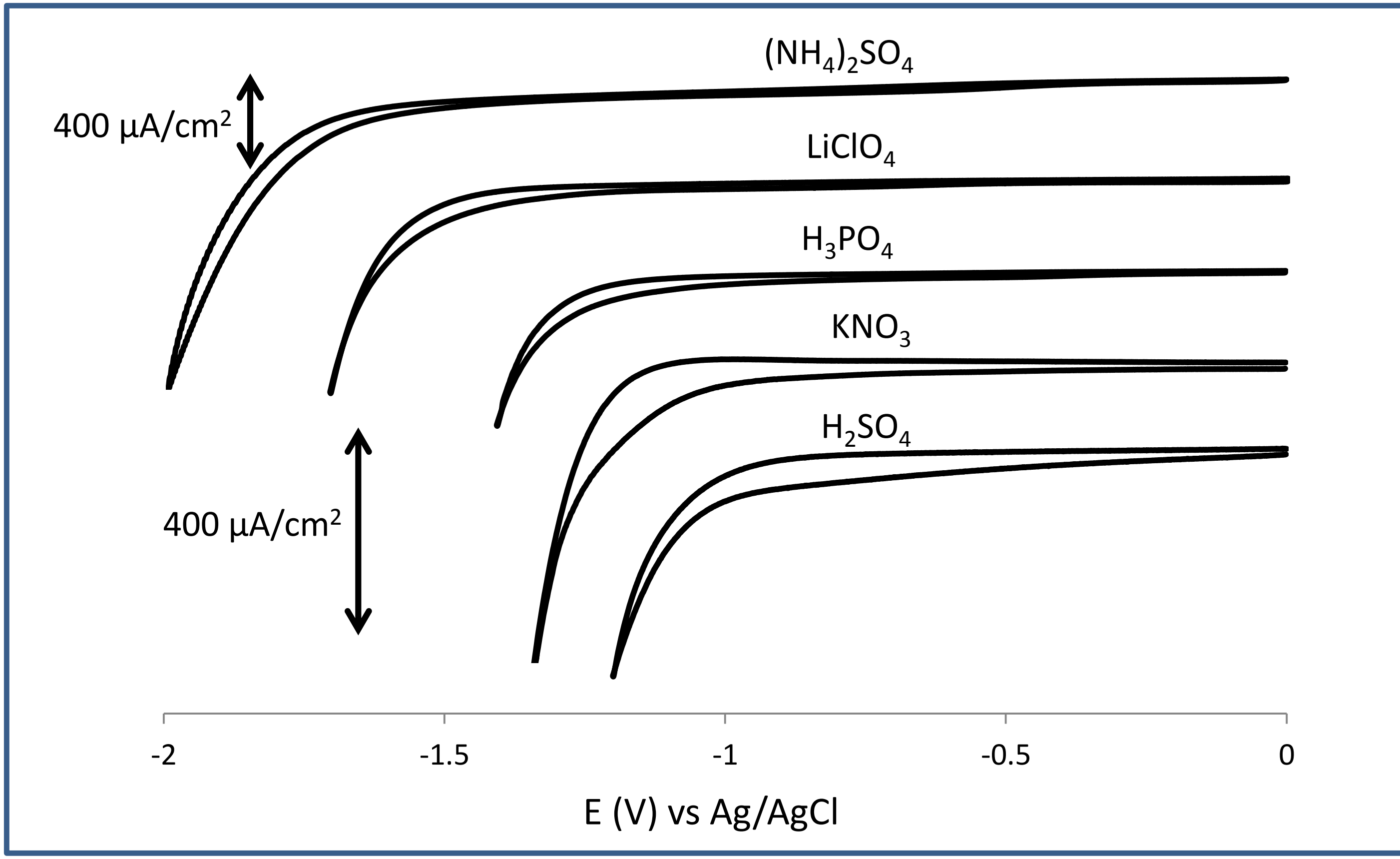


Figure 3. Cyclic voltammograms at GUITAR at 50mV/s in the indicated electrolytes (1M). Starting potential was zero and scan direction was towards more negative potentials. Counter and reference electrodes were graphite rod and Ag/AgCl respectively. Potentials for hydrogen evolution were extrapolated at 200µA/cm^2 from these voltammograms.

GUITAR electrodes have a

- 3 V potential window in 1 M H_2SO_4 and
- Excellent electron transfer kinetics

1 M H_2SO_4	GUITAR potential Limits (V)		(n = 15)
	Anodic ± σ	Cathodic ± σ	ΔEp 1mM $Fe(CN)_6^{4-/3-}$, 1 M KCl
	2.10 V ± 0.03	-0.90 V ± 0.11	73 mV ± 5

GUITAR electrodes have the largest reported aqueous potential windows

material	condition	cathodic	anodic	Total window	Ref.
GUITAR	**1M H_2SO_4, ± 0.2mA/cm^2, SHE**	**-0.9**	**2.1**	**3.0 V**	This work
Platinum		-0.1	1.4	1.5	
HOPG	0.1M H_2SO_4, ± 0.2mA/cm^2, SHE	-0.4	1.7	2.1	1
GC		-0.5	1.5	2.0	
BDD		-0.5	2.1	2.5	
DLC		-0.9	2.0	3.0	

- **HOPG and graphene are not good electrodes**
- **$Fe(CN)_6^{4-/3-}$ ΔEp > 500 mV**

Ultracapacitors & Energy Storage

- $E = \frac{1}{2} CV^2$
- Energy Storage
  - Increased Capacitance
  - Increase Cell Voltage, V
  - Aqueous Systems Preferred
    - $H_2SO_4(aq)$

Capacitance Studies

- GUITAR has much higher capacitance than other materials - DOS ?

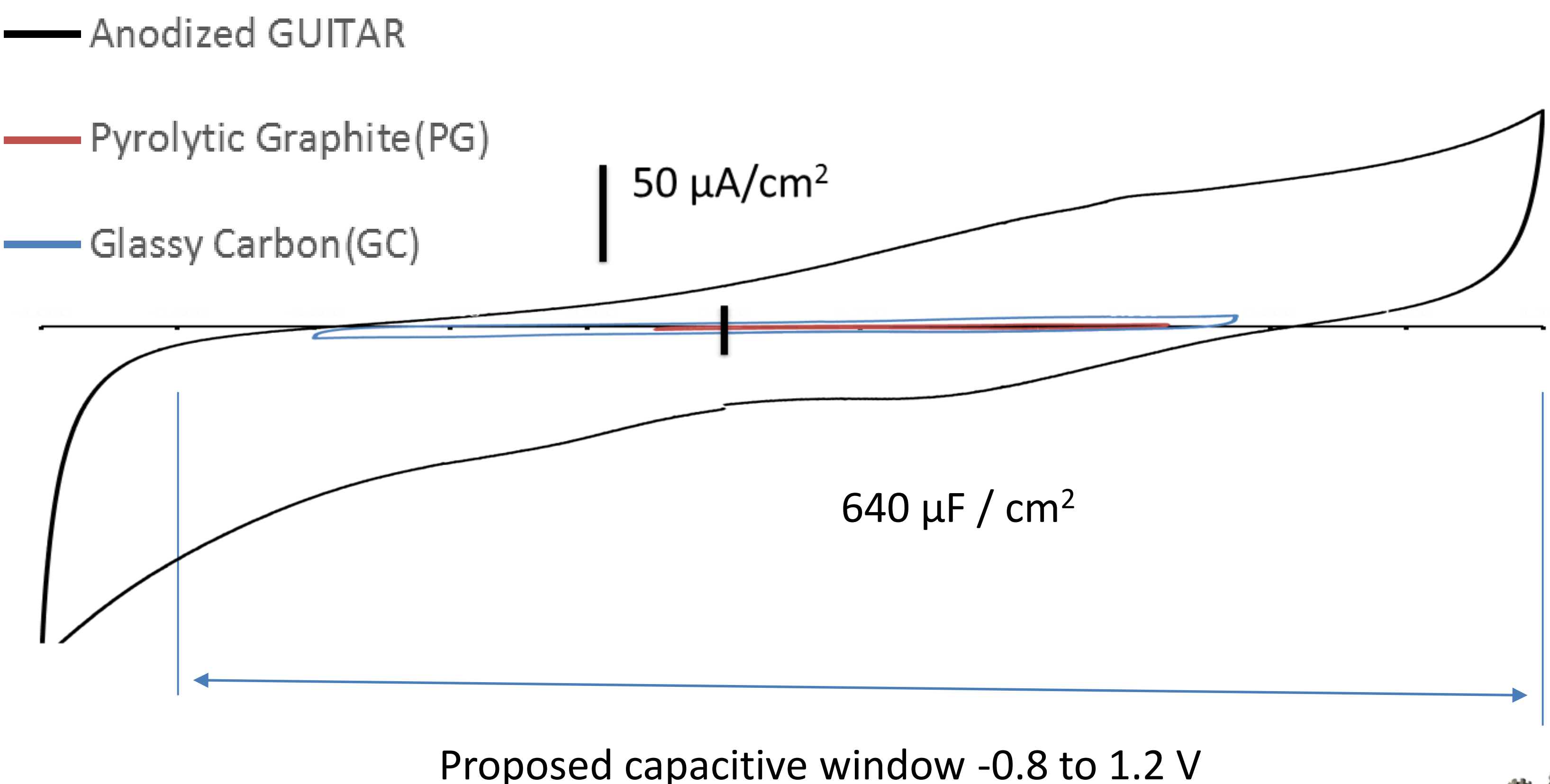
- Capacitors Applications Require Zero Faradaic current

    - Narrower potential window than 200 $\mu A/cm^2$ limits

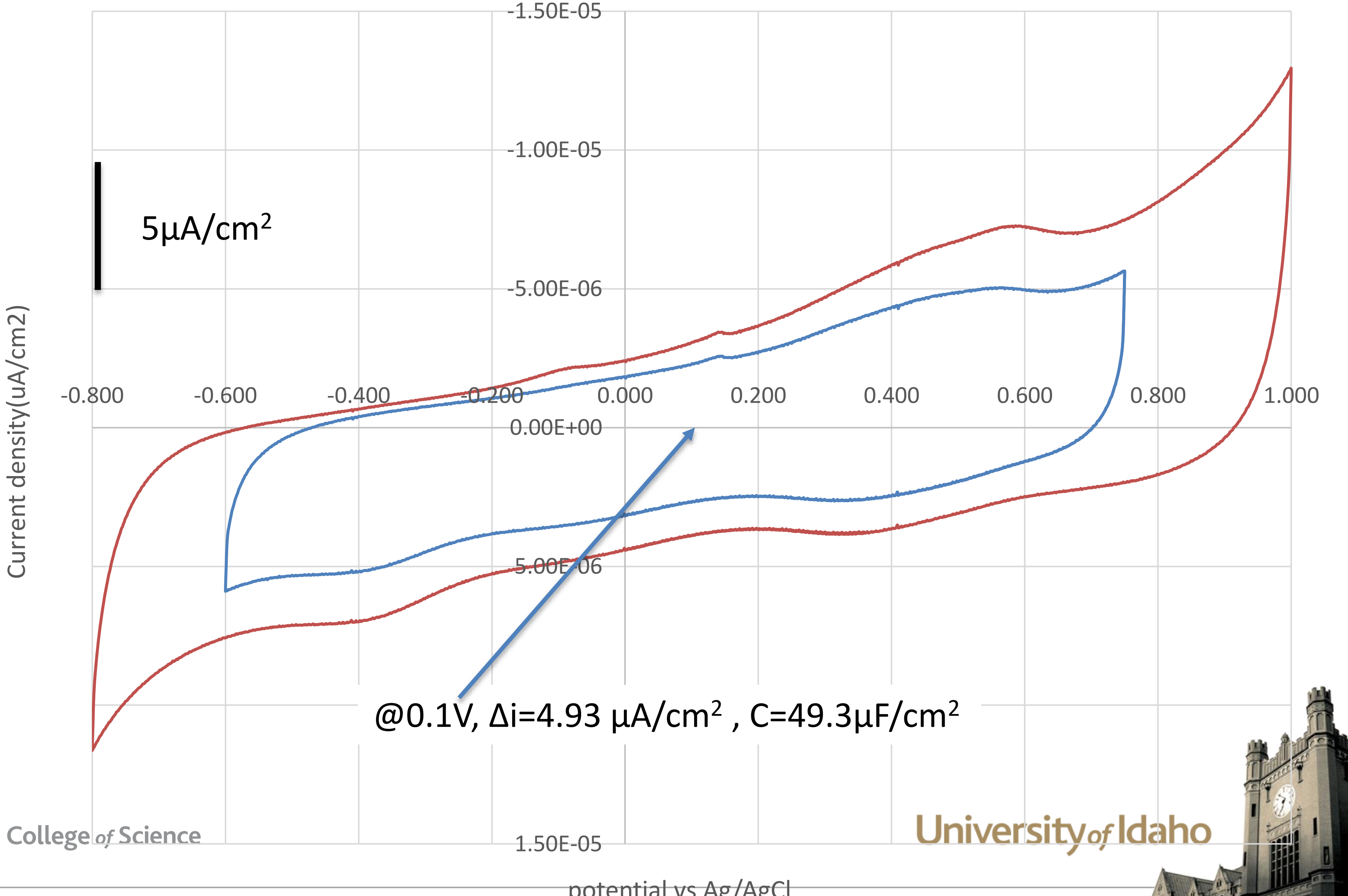
- Cyclic voltammetric measurements

$$C = \frac{i}{dV/_{dt}}$$

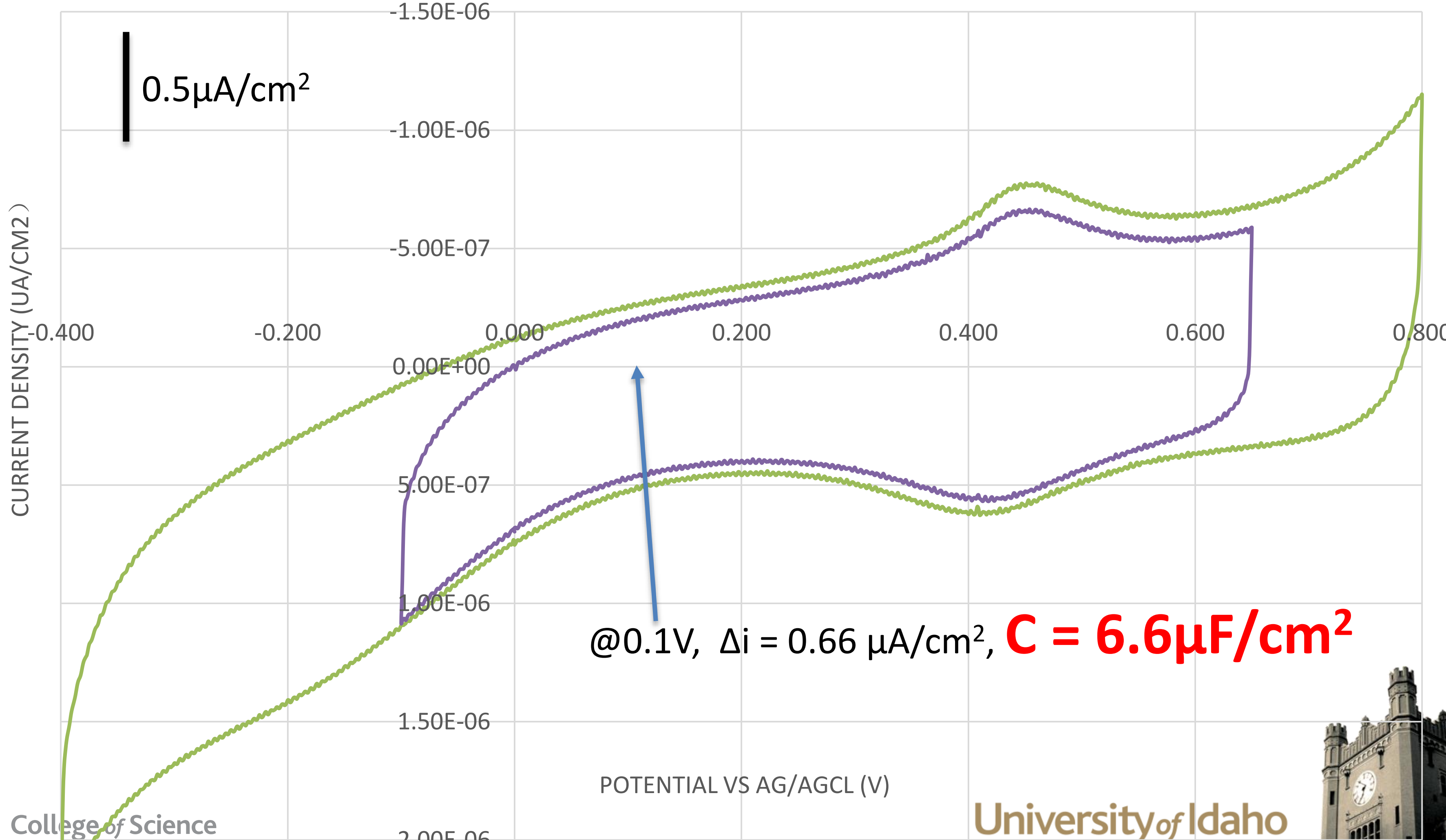
Capacitors Applications Require Zero Faradaic Current



Capacitance of Glassy Carbon electrode in 1M H_2SO_4, dV/dt = 50mV/s



Capacitance of pyrolytic graphite electrode in 1M H_2SO_4, dV/dt = 50mV/s



Material	Cathodic Limit (Volts)	Anodic Limit (Volts)	Capacitive Window (Volts)	Capacitance ($\mu F/cm^2$) @ 0.1 V
GUITAR	-0.8	1.2	2	640
Glassy Carbon (Bioanalytical Systems)	-0.6	0.7	1.3	50
Pyrolytic Graphite	-0.1	0.65	0.75	7

- GUITAR has more capacitance per unit than other carbon electrodes
- GUITAR has a wider capacitive window than other carbon electrodes

GUITAR vs. Activated Carbon (AC)

- AC -- the predominate material in UC's. Low Cost & High Surface Area

- Potential Window, & Capacitance,
  - C = 10 μF/cm^2
  - V = 0.8 V

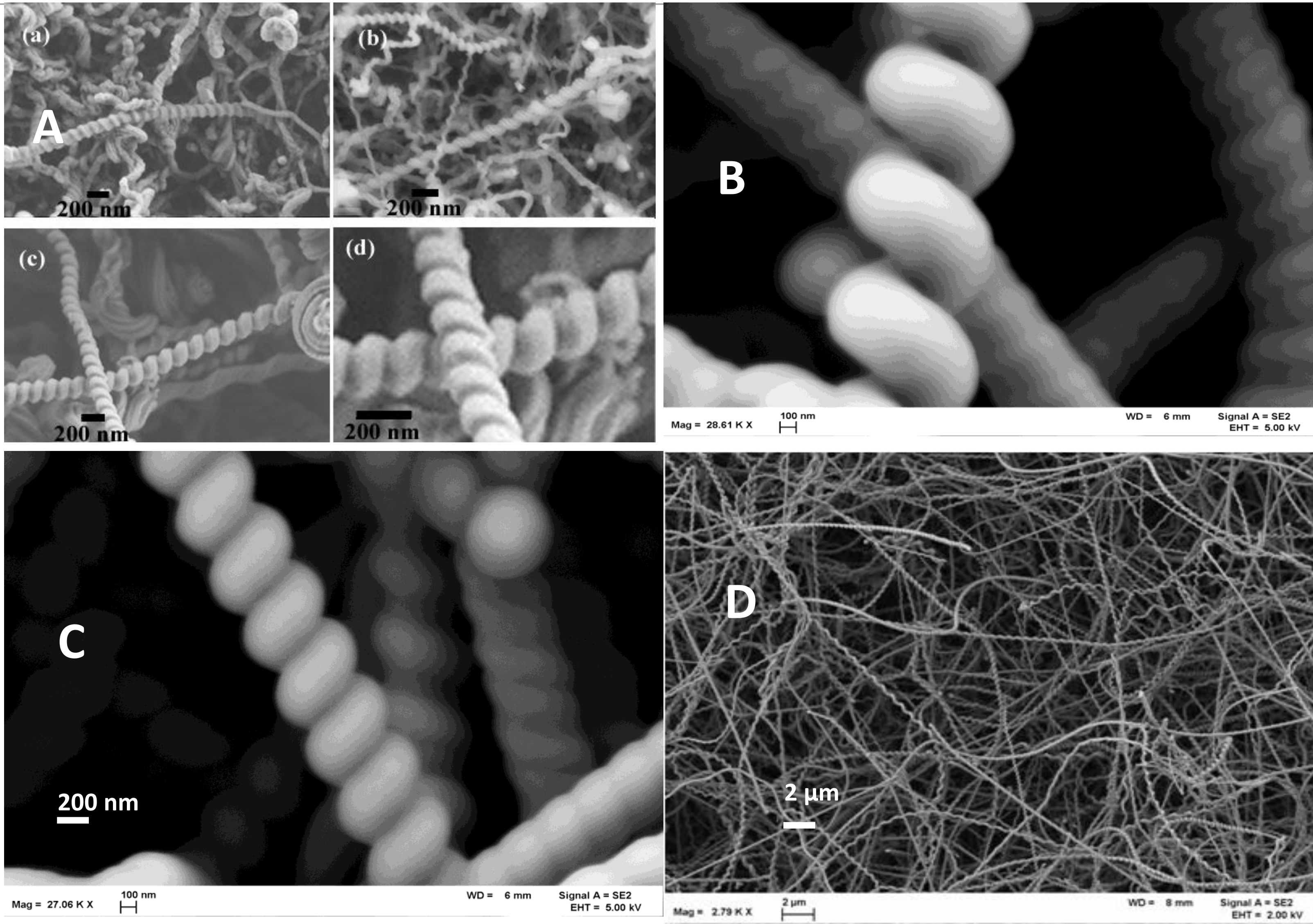
- Expected Performance:

- **AC)** **Energy = ½ CV^2 = 3 μJ/cm^2**

- **GUITAR)** **Energy = 1300 μJ/cm^2**

GUITAR vs. Activated Carbon (AC)

- AC surface area ≅ 1000 m^2/g
  - Specific Energy = 30 J/g
- GUITAR – produces conformal coatings
  - On McIlroy Nanosprings, surface area = 200 m^2/g
  - Specific Energy = 2600 J/g
  - Excluding nanospring mass



A – Bare silica McIlroy nanosprings. **B – D** Silica nanosprings coated with G-UI-TAR.

High Surface Area GUITAR Electrodes

- **Water Purification**
  - Wide potential and excellent electrode
  - Hydrophobic surface adsorption
- **Ultra-capacitors**
  - Aqueous Ucaps limited to 1.5 volts
  - GUITAR Ucaps > 2.0 V
  - Higher capacitance based on DOS?
- **V Redox Flow Batteries**
  - Requires high H_2 overpotential and, e- transfer kinetics
- **Enhancing Lead-Acid Battery**
  - Requires corrosion resistance, high O_2 and H_2 overpotential, conformal coatings on microporous materials, and electrochemical conductivity.
- **CNT Replacement in Fuel Cells**
  - GUITAR on nanosprings

Summary - GUITAR

- A new material
  - – Not HOPG, Graphene Paper
  - – Sulfur a key component to formation
    - Low T (800 ^{0}C), economical
  - – Atomically Smooth with nano-size grains
- Fast Electron Transfer
    - High DOS?
- Large Aqueous Potential Window
    - 3 Volts in 1 M H_2SO_4 exceeds almost all other electrode materials.
- Ability to create conformal coatings

Future

- 1450 cm^{-1} intermediate
- Electrical and Thermal Conductivities
- Hypotheses for
  - Anodic Limit
  - Cathodic limit (hydrophobicity)
- Pursue Applications

Conformal coatings on high surface area substrates.

- Nanosprings
- Halloysite nanotubes
- Diatomites
- Porous hollow glass microspheres

Acknowledgements

Yuqun Xie

Isaiah Gyan

Haoyu Zhu

Dr. Nolan Nicholas

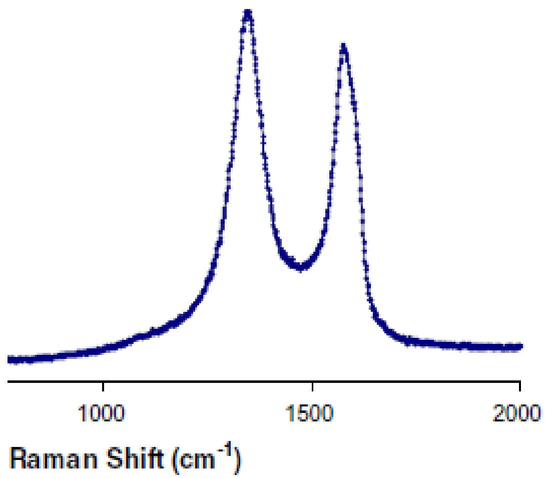
Jeremy Foutch

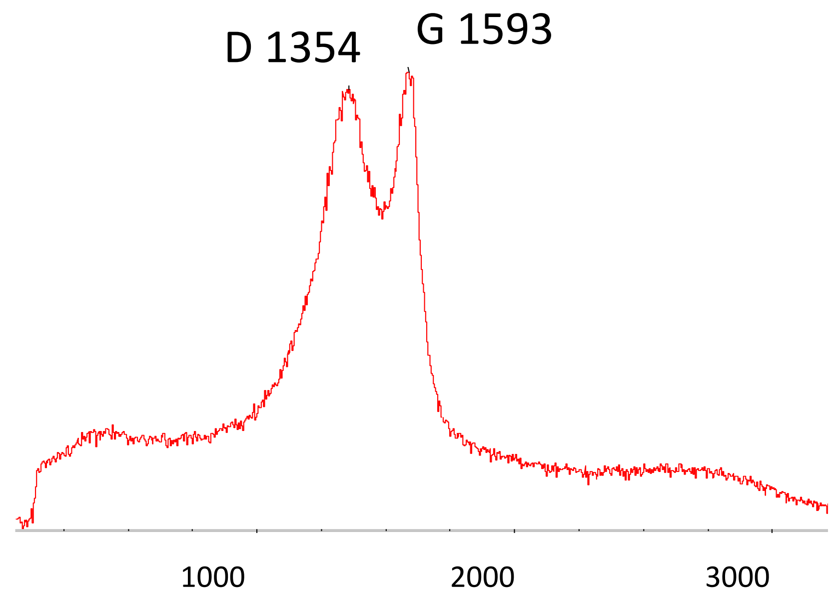
Prof. David McIlroy UI-Physics

Prof. Peter Griffiths UI-Chemistry

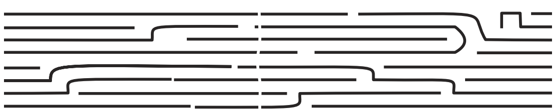
Prof. Eric Aston UI-Chem. E.

Raman Spectrum of UI Carbon





r-GO Paper



UI Carbon

I.F. Cheng, et al. Carbon. 2011,(49), 2852-2861
S. Stankovich, et,al. Carbon. 2007, (45), 1558-1565

Ferrari Amorphization Trajectory

1594

0.93

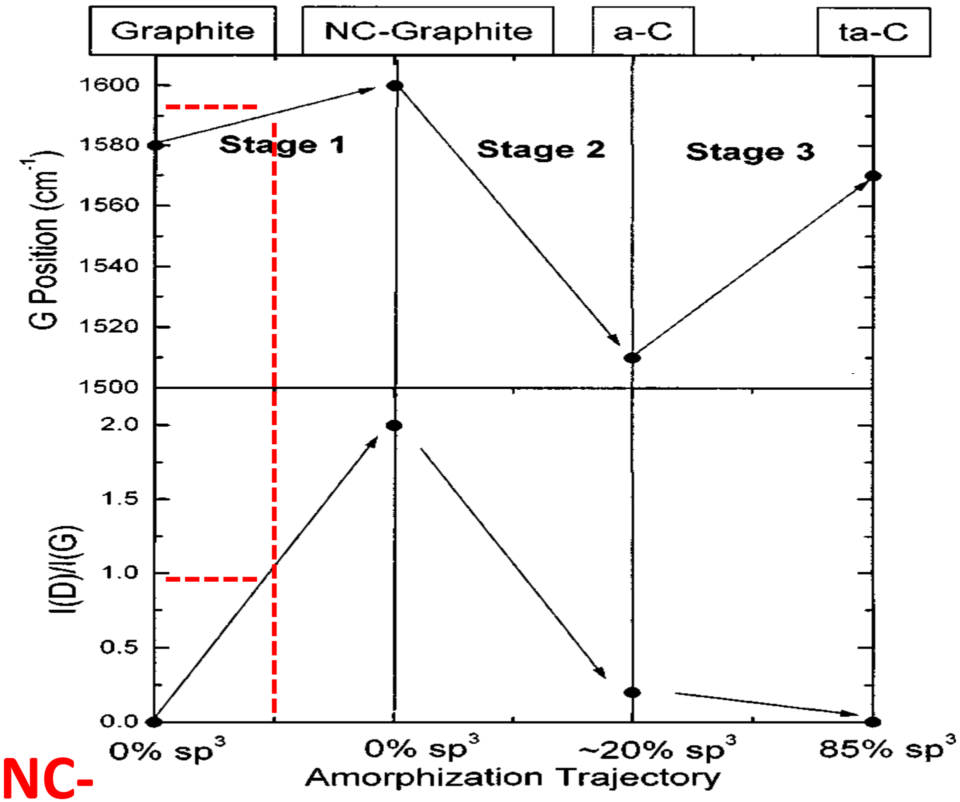
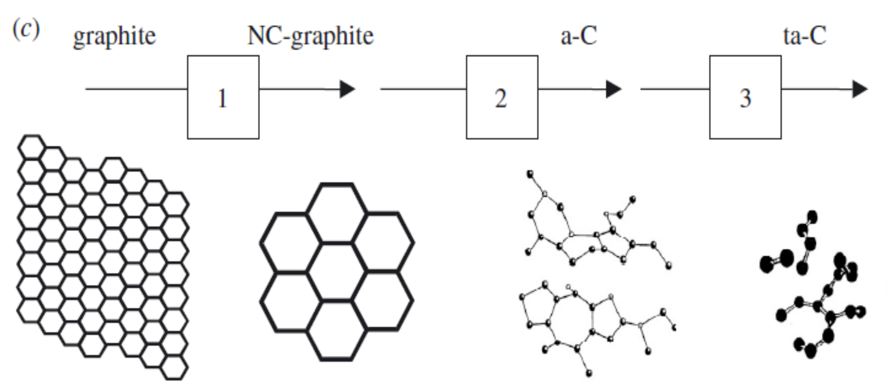
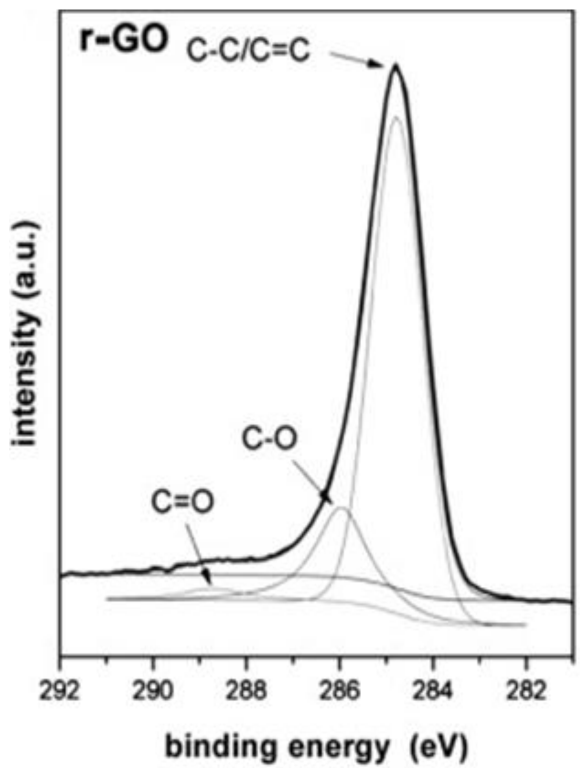


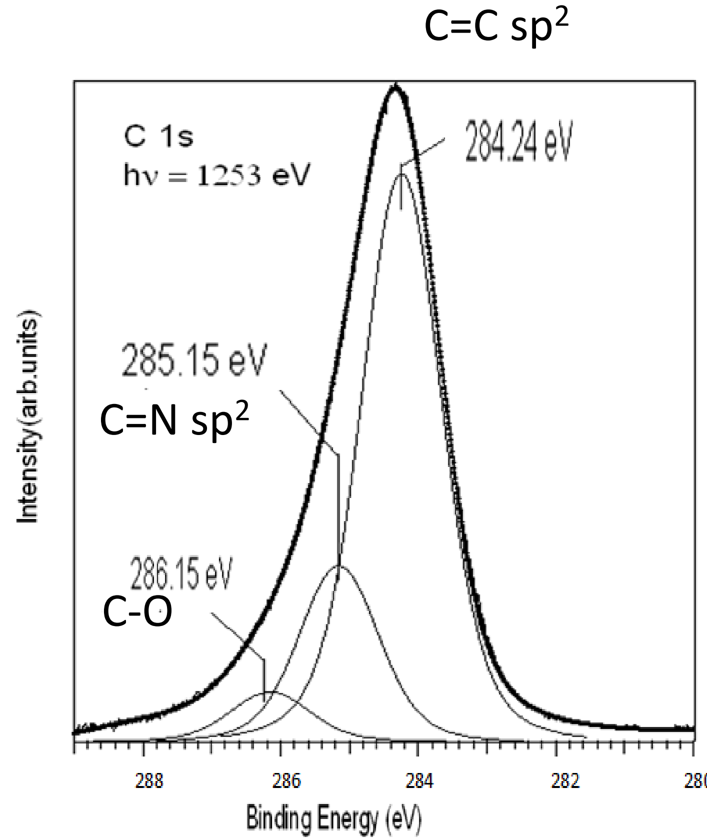
Figure 10 from Ferrari, Robertson. Phys Rev. 2000, (B61), 14095-14107



- ➢ **Between Graphite to NC-graphite**
- ➢ **0% sp^3 hybridization**

XPS – GP and UI Material are Nearly Pure Carbon





Reduced Graphene Oxide Paper

Pei, et al. Carbon. 2010, (48), 4466-4474

UI Carbon

Cheng, et al. Carbon. 2011,(49), 2852-2861