Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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Project ST120

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Overview

Timeline

- Project start date
  August 1, 2015
- Project end date
  July 31, 2018
- Percent complete: 22%

Barriers

- Weight and volume of on board hydrogen storage systems
- Low temperature and low enthalpy of adsorption

Budget

- Total project funding
  $1M (3 yrs)
  Federal share $1M
- Funding for FY16
  DOE share $333k

Partners

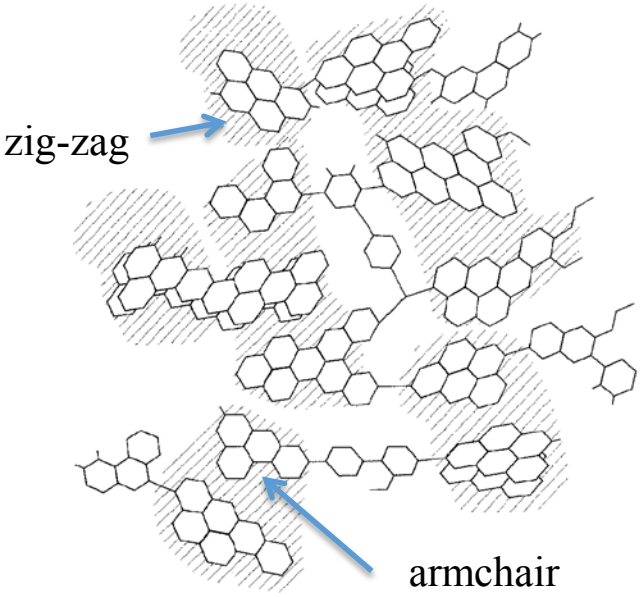
Interactions/collaborations

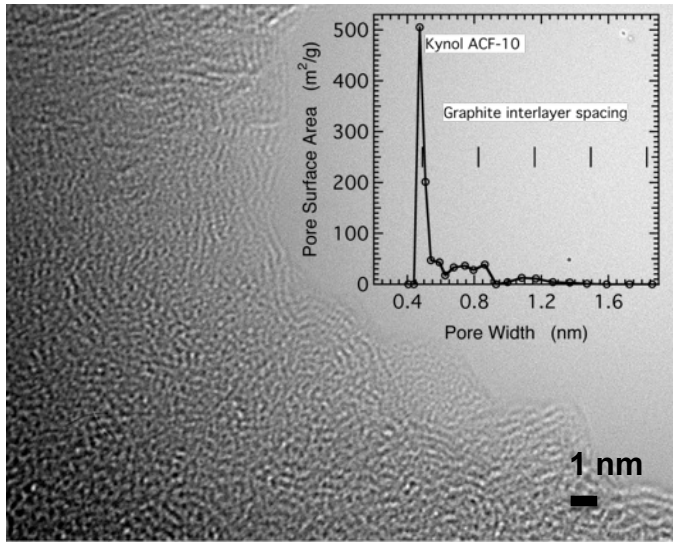
T. Baumann, LLNL

R.C. Bowman, Jr.

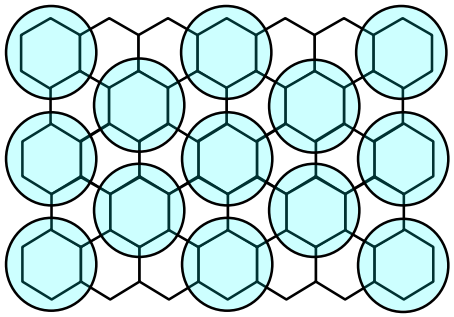
Why graphene instead of activated carbon?

Activated carbon can have higher surface areas (>3100m^2/g) but… zig-zag and armchair edge terminations have weaker binding sites than graphene surface. Functionalization possible but less well-defined geometrically so less easy to interpret.

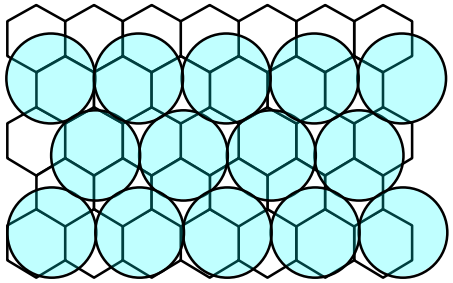




Graphene has a lower theoretical surface area (2630 m^2/g), but more regular for functionalization.



Commensurate √3 structure (LiC_6) or HC_3 => ~5.3 wt%. (39 g/L)



Incommensurate solid H_2 on graphite => ~7.7 wt%. (54g/L)

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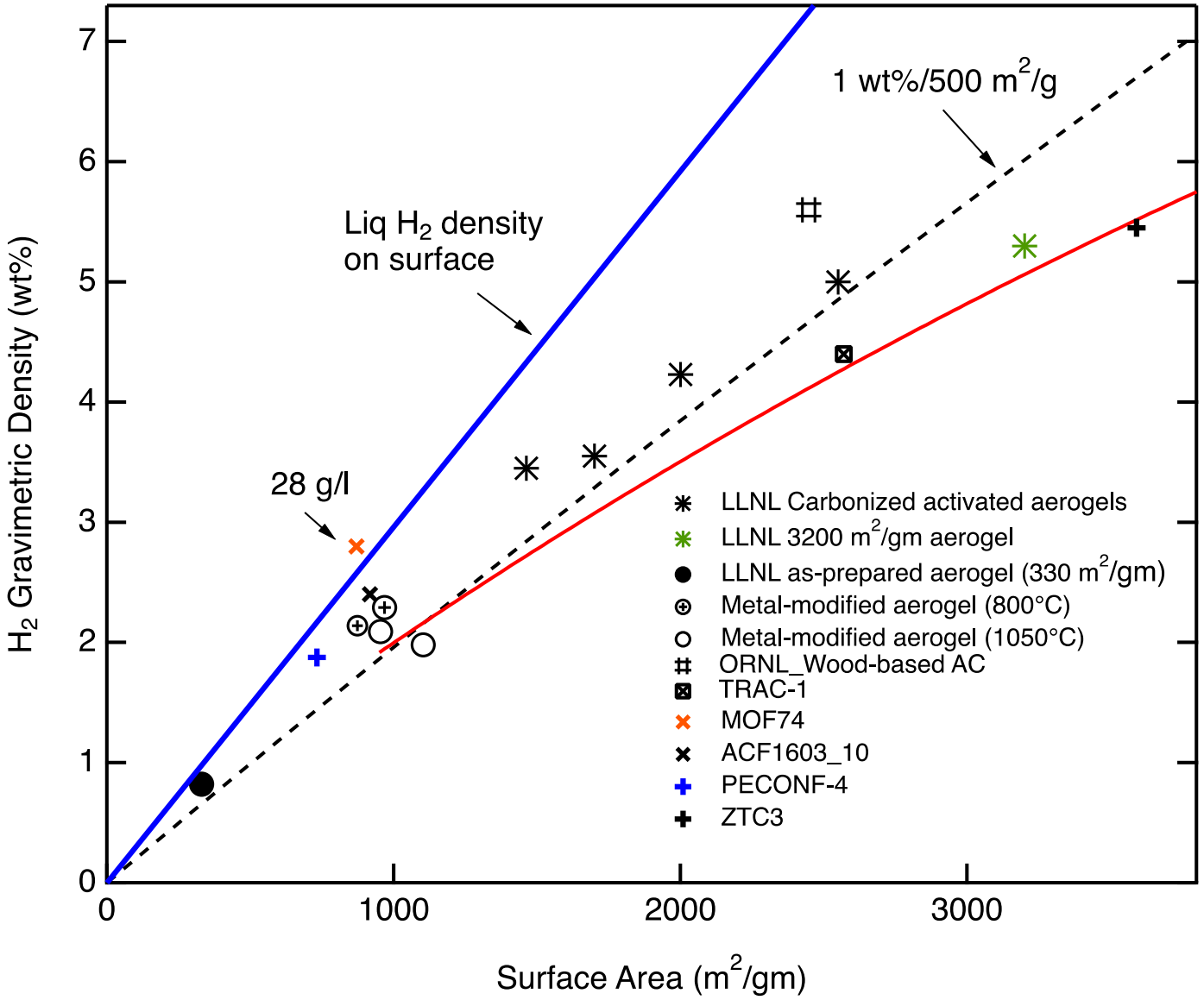
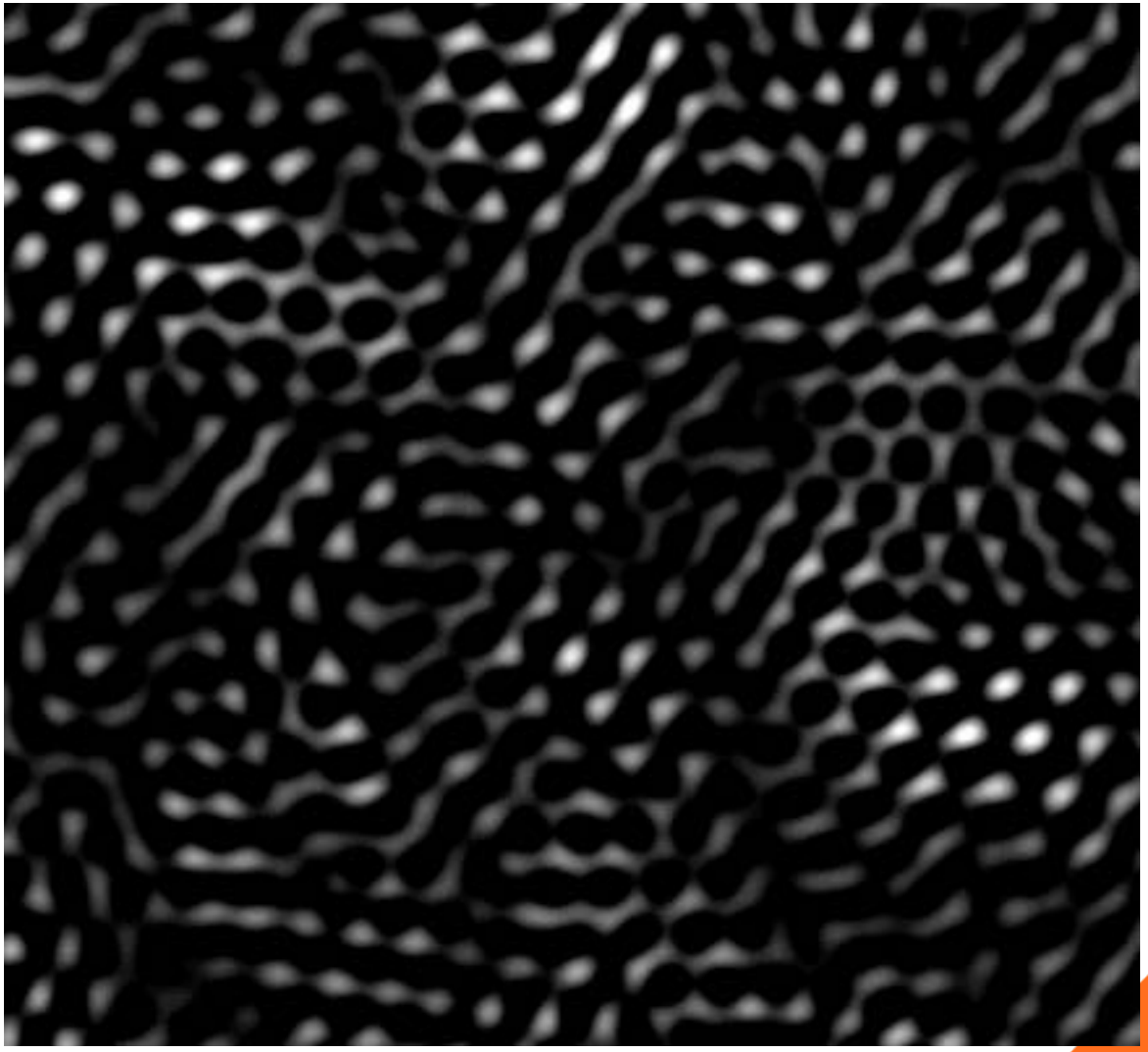
Capacity of Conventional Carbons



Rationale

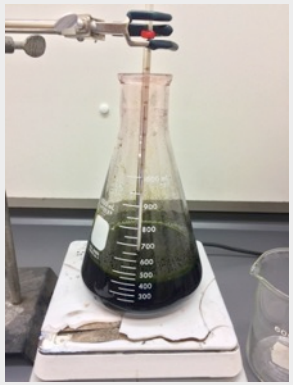
- Single layer graphene is a platform with excellent surface-to-volume ratio -- functionalize it.

- Synthesis and functionalization using
  - graphite oxide chemical routes
  - plasma physical approaches

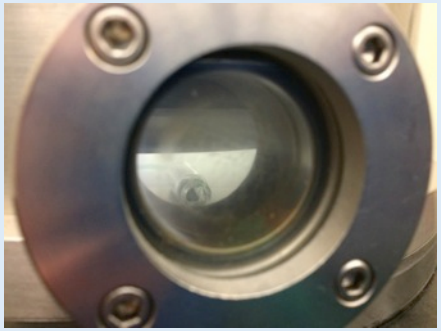


Synthesis and Preparation

Chemical Synthesis



Oxygen Plasma Etching



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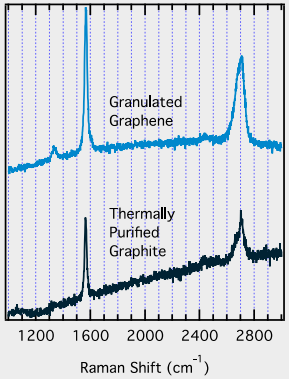
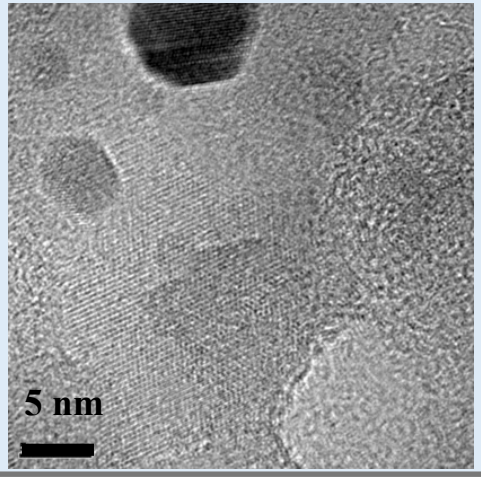
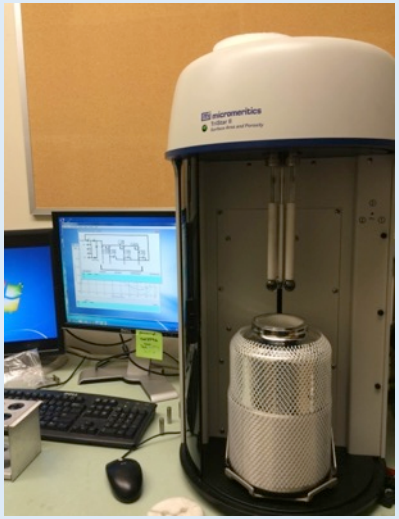
Materials Characterization Infrastructure

Raman Spectroscopy

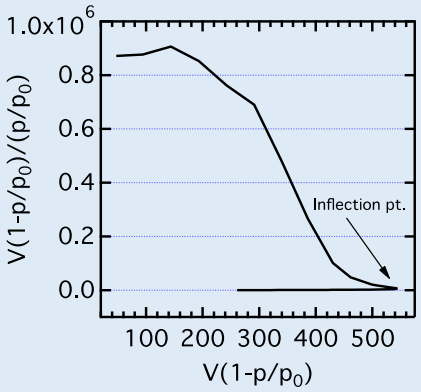


TEM

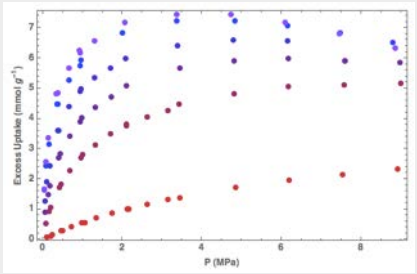




BET System



Sieverts Apparatus



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Detailed Project Plan

		SEM, Raman, XRD	TEM	FTIR	BET	Rapid Sieverts	Skeletal Density (He)*	Sieverts*	Ref.	Progress
O_2 plasma	graphene	×	×							80%
	bulk	×			×					
Au, Cu plasma	graphene	×	×							80%
	bulk	×	×		×	×				
Chemical Synthesis- graphite graphene oxide (GO)	modified Hummers	×	?						8	75%
	varying starting graphite	×	?							25%
Chemical Synthesis- GO to rGO/graphene	hydrazine hydrate	×	×		×					
	microwave	×	×		×				4	50%
Chemical Synthesis- modified graphene	KOH activation	×			×	×			4	50%
	compressed	×			×	×			2, 3	
Chemical Synthesis- metal incorporation	Au ($HAuCl_4$)	×	×			×			1	75%
	Cu ($CuCl_2$)	×	×			×			7	15%
	Co, Ni, Zn?	×	×			×				
ALD	TiO_2 (initial)	×	×	×	×	×			5	

* considered after evaulation of Rapid Sieverts

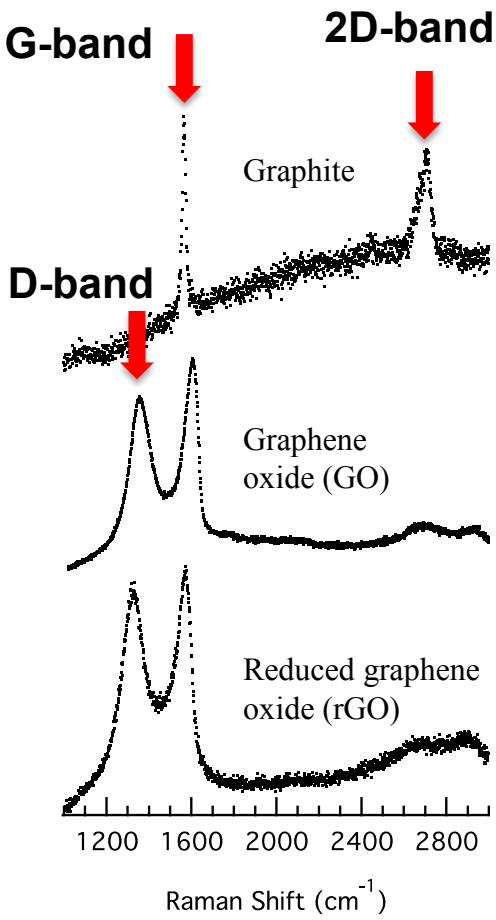
[1]Koo et al. J. Mater. Chem. 2012, 22, 7130, [2]Zhang et al. Carbon 2013, 54, 143, [3]Ghaffari et al. Adv. Mater. 2013, 25, 4879, [4]Kim et al. ACS Nano 2013 7 (8), 6899, [5]Tiznado et al. Powder Tech. 2014, 267, 201, [6]Wang et al. Carbon 2014, 76, 220, [7]Tien et al. Carbon 2011, 49, 1550, [8]Marcano et al. ACS Nano 2010, 4 (8) 4806

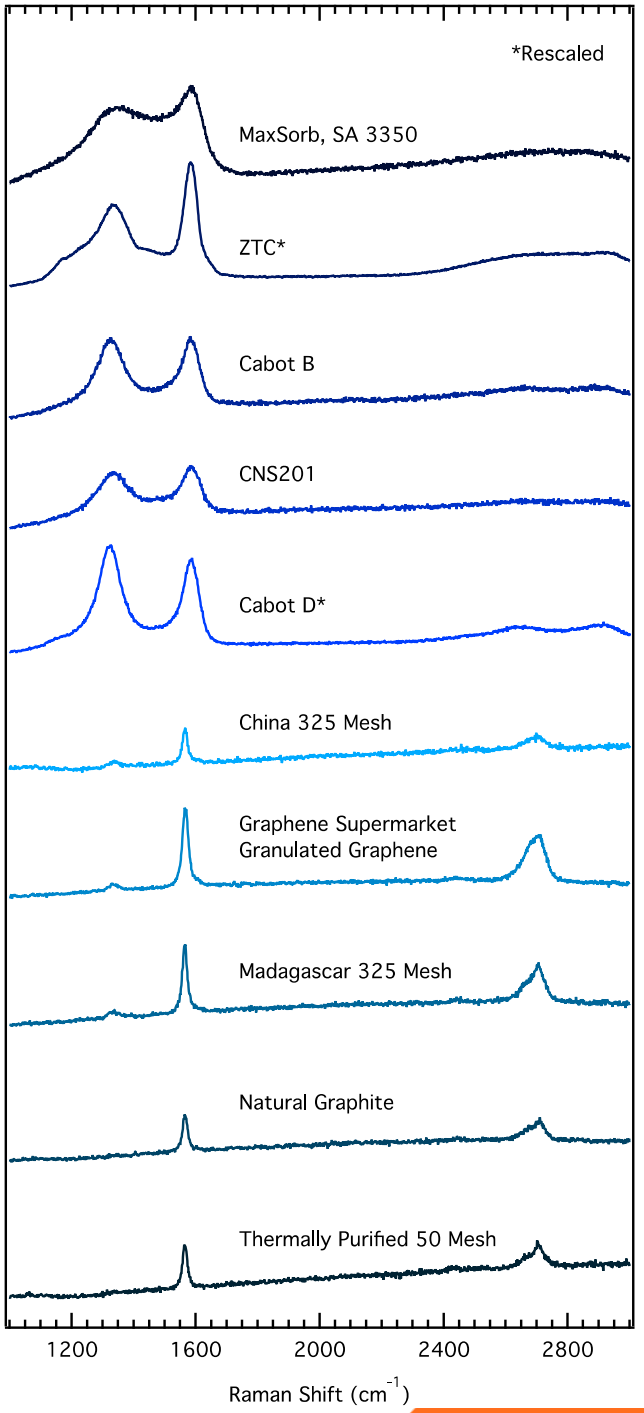
Materials Characterization Library

BET Surface Area:

Material	Surface Area (m^2/g)
MSP20	2300
CNS201	1147
SC2	1126
PCONF4	732
Thermally purified graphite	0.64
Graphene oxide	380

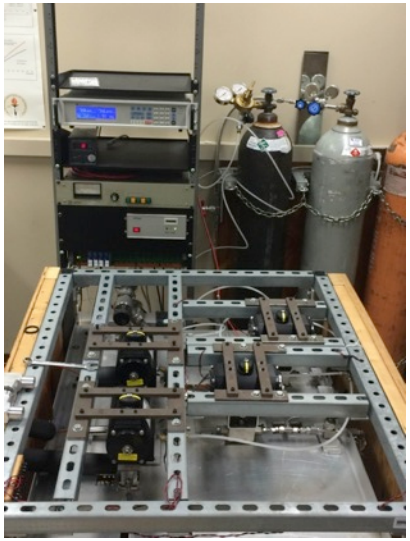
Raman Spectra:

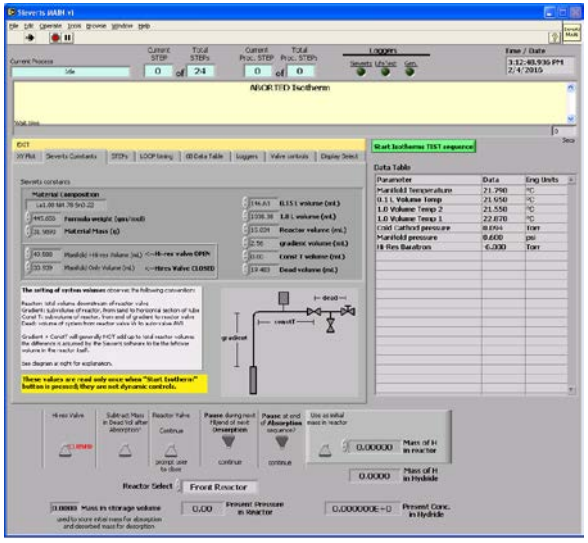


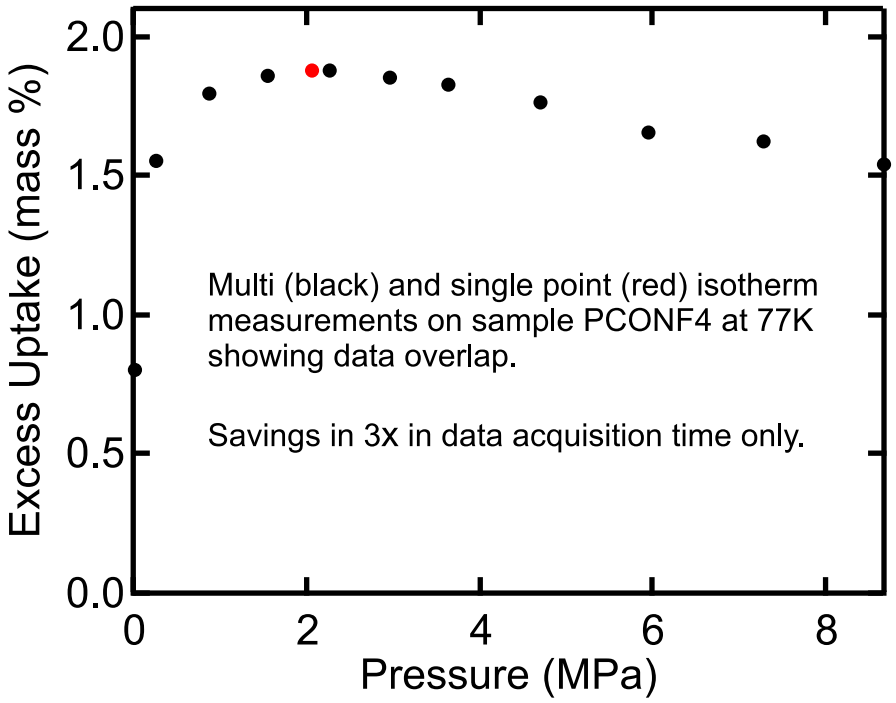


Sieverts Measurements

Sieverts Instrumentation at Caltech







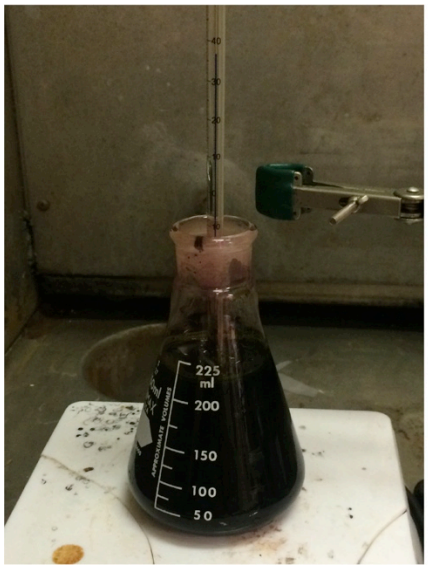
(Above): A Sieverts method for rapid screening of samples by measuring fewer data points require 1/3rd the time for a full isotherm measurement. A single point measurement at 77K (red) agrees with a full isotherm measurement (black) on a test sample, PCONF4.

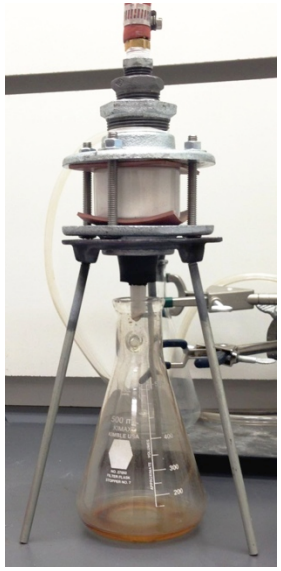
(Left): A third Sieverts system was obtained from JPL and brought to new lab-space at Caltech.

Graphene Synthesis

- Our synthesis of graphene oxide and graphene using a modified Hummers method.
- Optimizing the synthesis process for further modification and functionalization:
  - Analyzing the effects of starting with different types of graphite materials (Superior Graphite, Sigma-Aldrich, Graphene Supermarket, etc.).
  - Varying the technique for reduction of graphene oxide to graphene.

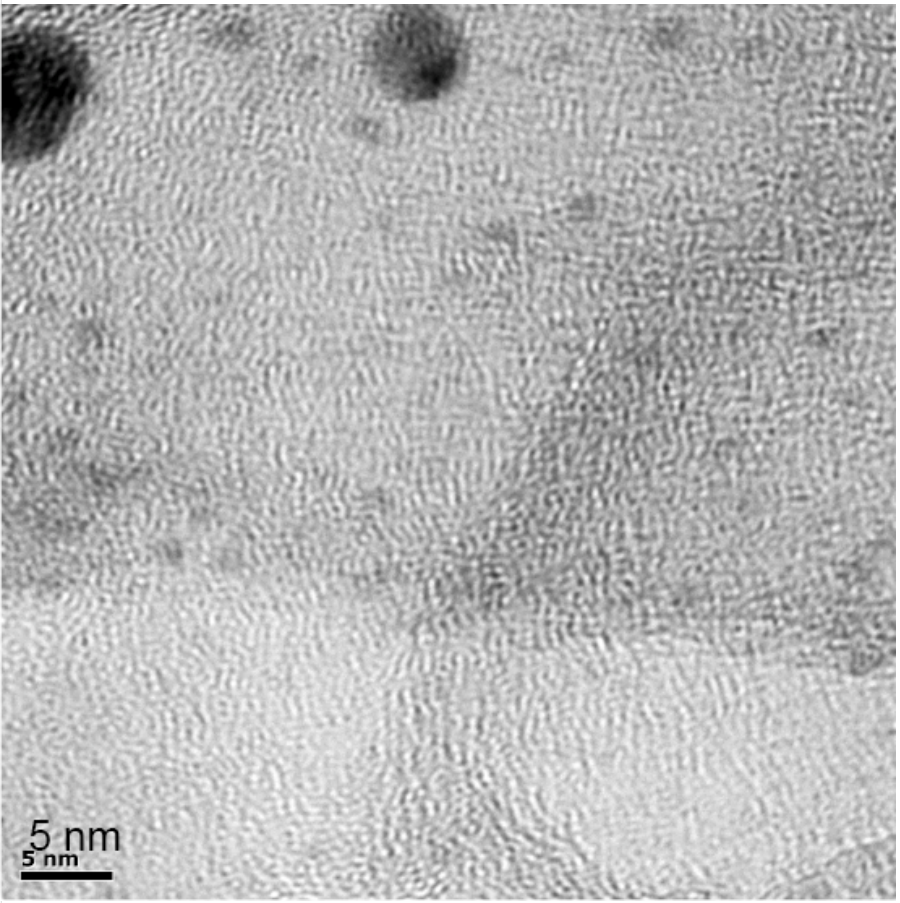
Modified Hummers Method (Tour, et al.):

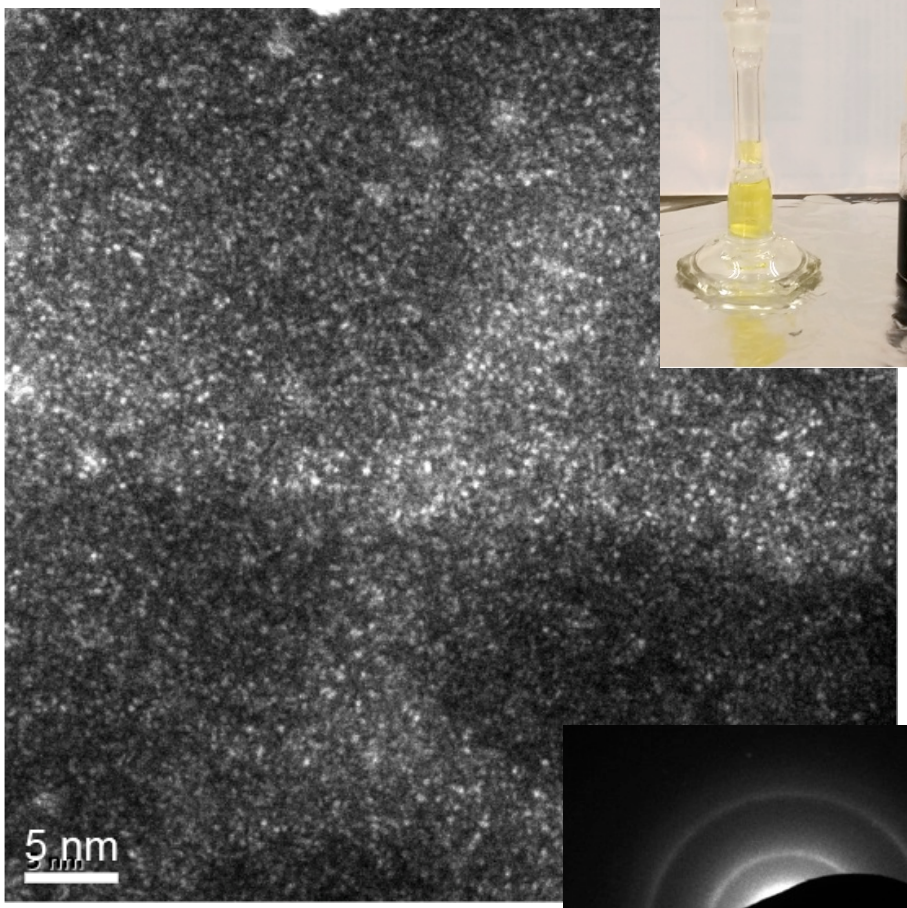


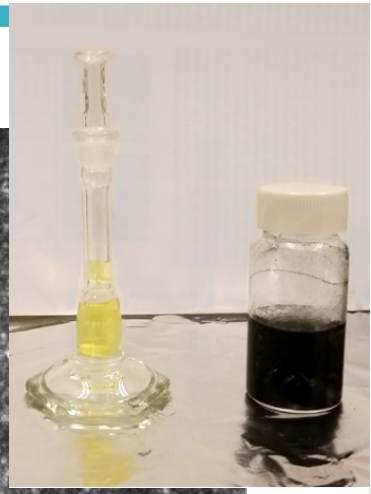


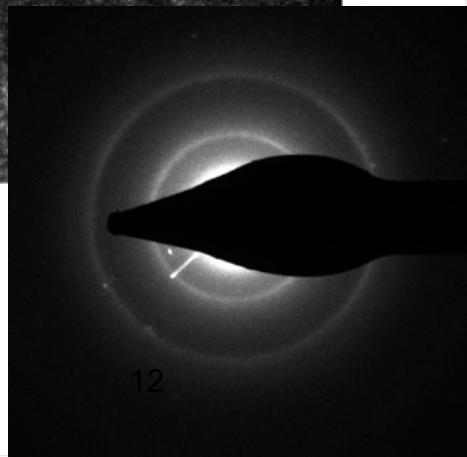
D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, Improved Synthesis of Graphene Oxide. *ACS Nano* **4,** 4806–4814 (2010).

Metal Functionalization: Chemical Deposition of Au



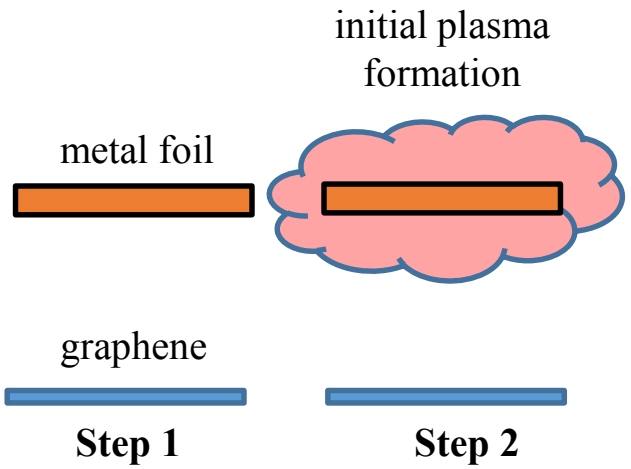




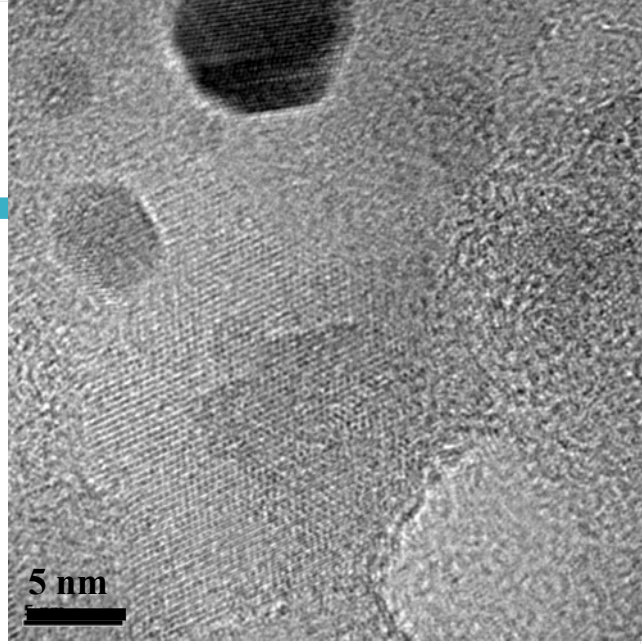


Bright field (left) and dark field (right) TEM images of Au nanoparticles deposited on graphene. Some larger particles ~1nm are visible in the BF image, while individual gold atoms decorating the surface are visible in the DF image.

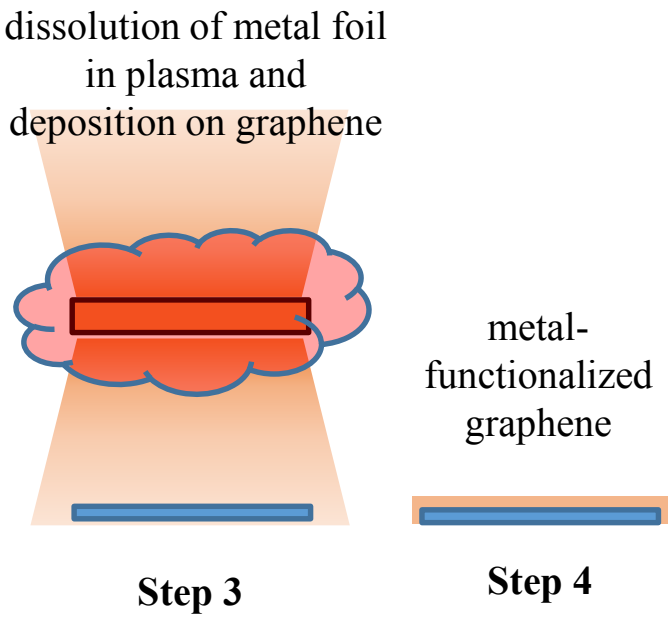
Metal Functionalization: Plasma Deposition



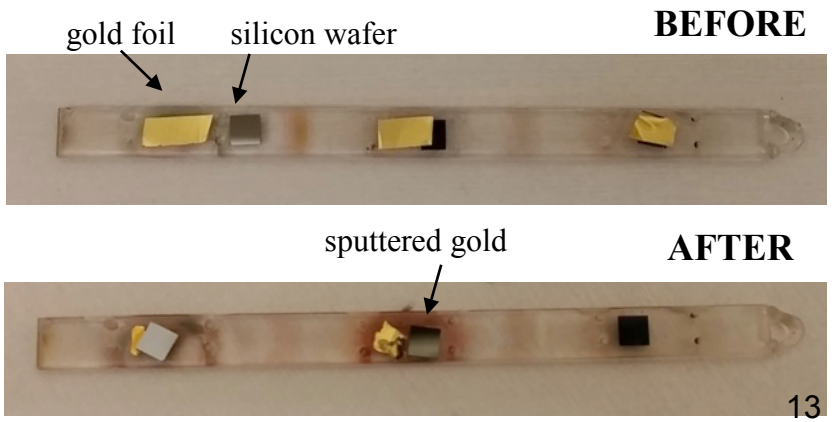
A plasma deposition approach for depositing nanoparticles from metal foil is being optimized (schematic at left).



(Above): TEM images show ~5 nm Au particles (dark spot, upper middle) are visible on the graphene surface.



(Below): Photos before and after plasma deposition of Au onto a silicon wafer.



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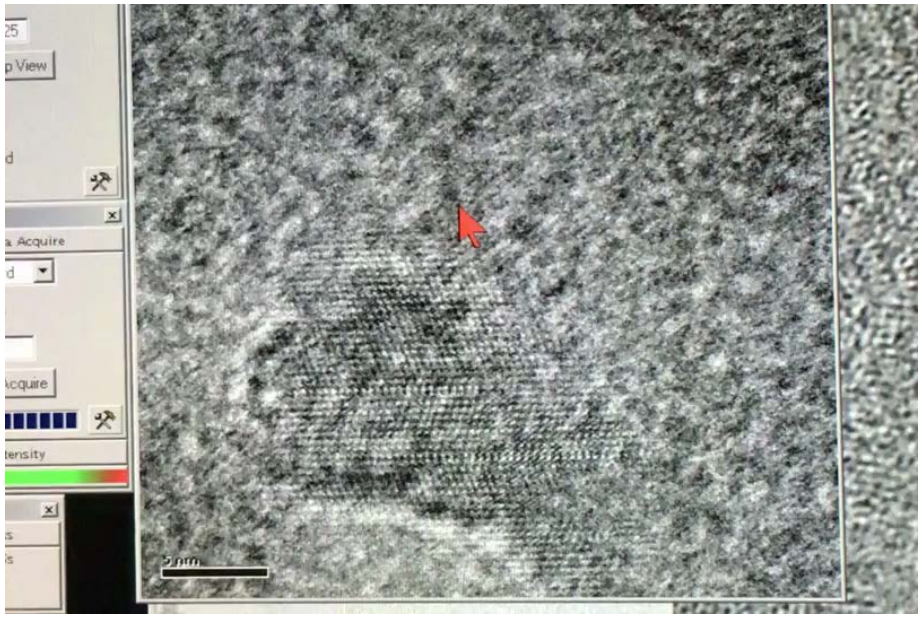
Functionalization with metals

Plasma Deposited Gold Particles on Monolayer Graphene:

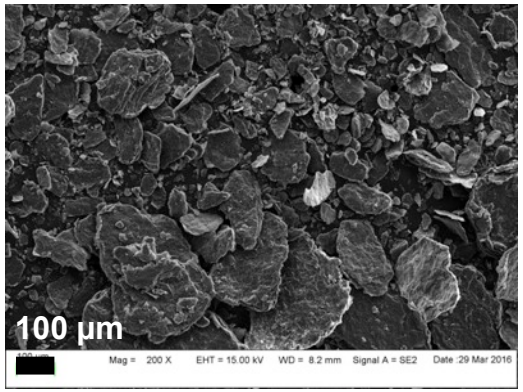
Au particle moving across surface



Au particle shrinking

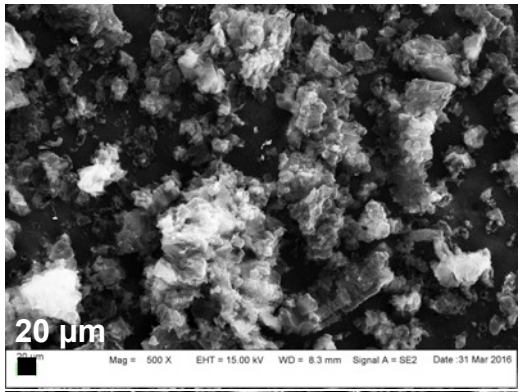
Bulk Modification

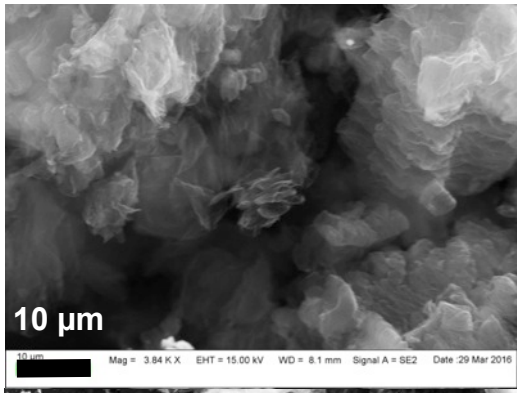
GO as prepared:



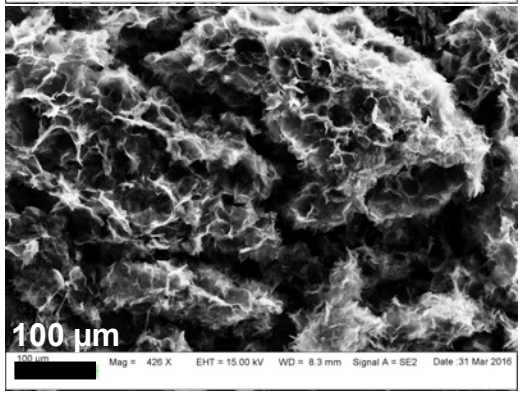
Surface Area Before Processing	Surface Area After Activation
380 m^2/g	2336 m^2/g

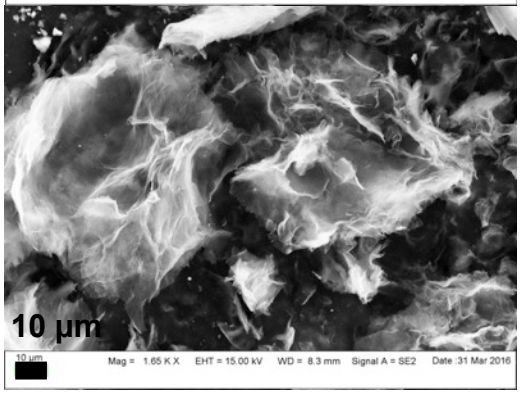
Microwave processed GO:





KOH activation of microwaved GO:





BET measurements indicate a more than 6x increase in surface area after activation

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Task #	Project Milestones	Task Completion Date	
		Original Planned	Percent Complete
Milestone 1	Specific surface area of carbon materials >1400m^2/gm.	10/31/15	100%
Milestone 2	Electron Microscopy analysis to determine metal distribution. Goal is metal clusters <1 nm on graphene.	1/31/16	100%
Milestone 3	Develop Sieverts method for rapid turnaround by measuring fewer data points (able to measure 1 sample / day). Results should be comparable to full isotherms at 77 K and 87 K to within 5%. Method must 1) obtain parameters to check Chahine rule, and 2) obtain sorption at low coverage to measure isosteric heat (Henry's Law regime).	4/30/16	100%
Milestone 4	Validation of graphene syntheses of Caltech graphenes and cycloparaphenylene. Analysis of graphene to bulk density of 0.5 to 0.7 gm/cc and that retain 80% of as-prepared surface areas. Bulk and skeletal density using He pychnometry	**7/31/16**	50%
Go/No-Go 1	**Meet or exceed present capabilities of carbon sorbents. Exceed 5 wt% excess and 35g/L total adsorption at 77K at P<100bar. Ensures that we can meet the best of the unmodified dense carbons before functionalization.**	**7/31/16**	
Milestone 5	Use oxygen plasma etching to induce 1-2 nm pores in sheet structures. Measure changes in specific surface area and hydrogen adsorption capacity. Determine if the pores are contributing >10% to BET surface area and to sorption characteristics	10/31/16	20%

Summary

- Acquired a BET system and second Sieverts system and installed them in new lab space in 204 Keck Laboratory
- Demonstrated surface area of a micro-porous carbon >1400 m^2/g (2300 m^2/g) using our BET system and single inflection point analysis of N_2 isotherm data (1^{st} quarter milestone)
- Functionalized graphene with Au clusters <1 nm in diameter via a chemical route, and demonstrated plasma deposition of metal clusters (2^{nd} quarter milestone)
- Developed rapid turnaround Sieverts method for screen materials without collection of full isotherms (3^{rd} quarter milestone)
- Prepared graphene oxide and graphene at Caltech, and characterized H_2 uptake in cycloparaphenylene and PECONF4 (progress towards 4^{th} quarter milestone)
- Observed a change in surface area from plasma exposure of a high surface-area carbon (progress towards 5^{th} quarter milestone)

SUPPLEMENTAL SLIDES

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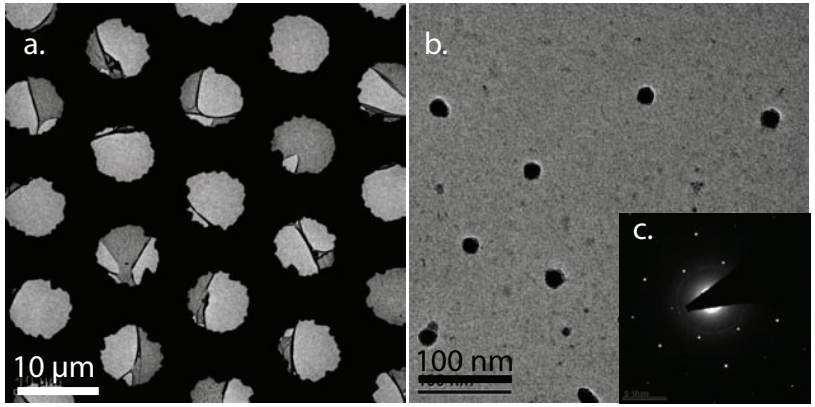
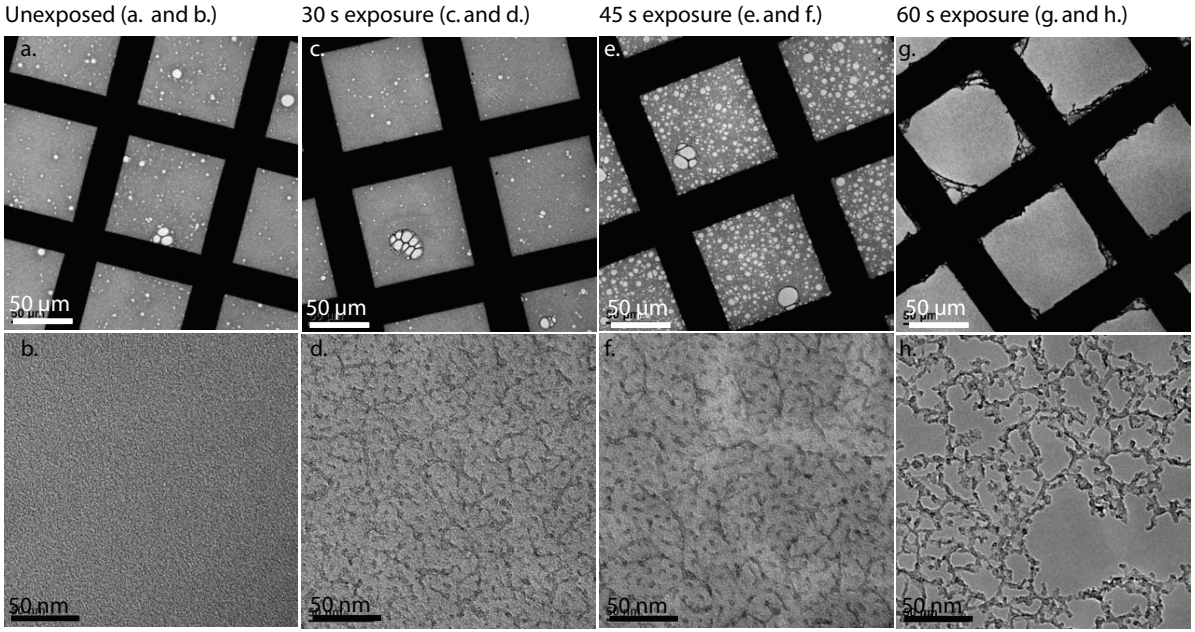
TEM Imaging of Metal Deposition and Plasma Exposure

Monolayer graphene on Cu mesh grid:



Monolayer graphene on copper mesh grid obtained from Ted Pella, Inc. (a) Shows a wide-field image. (b) Shows a region in more detail, revealing surface contaminants (black dots). (c) The SAD obtained with a 40 µm aperture for the region in (b).

Amorphous Carbon exposed to oxygen plasma:



TEM images of amorphous carbon spanning a copper grid at low and high magnifications. An unprocessed samples is shown in (a) and (b). The sample was then exposed to oxygen plasma for varying times (c-g) as indicated at the top of the figure.

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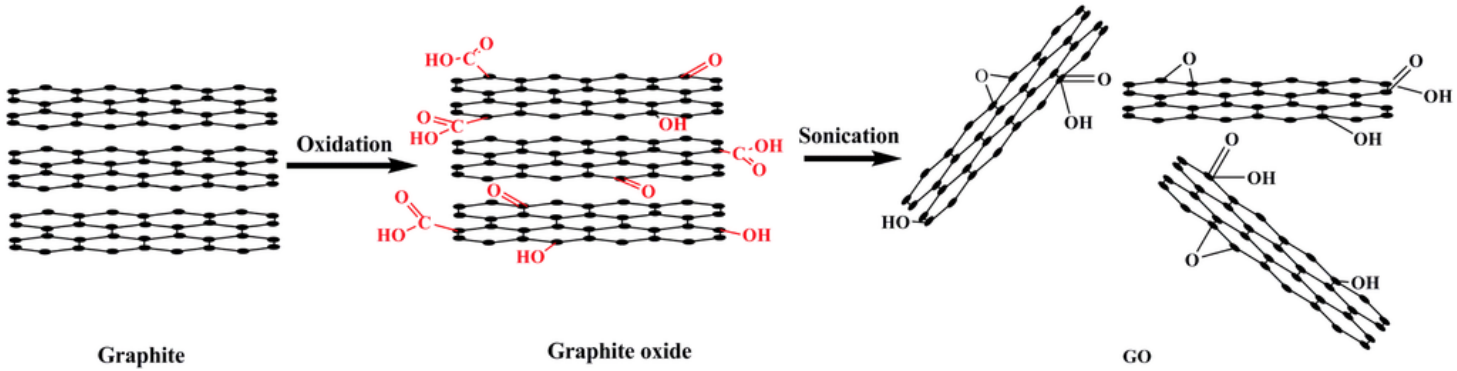
Graphite, graphene, graphite oxide, graphene oxide, GO, rGO . . .



Abbreviated guide:

Graphite – multiple layers of graphene

Graphite Oxide – multi-layer graphene with additional oxygen atoms, often used interchangeably with graphene oxide

Graphene – a single layer of carbon packed in a hexagonal lattice with a C-C distance of 0.142nm

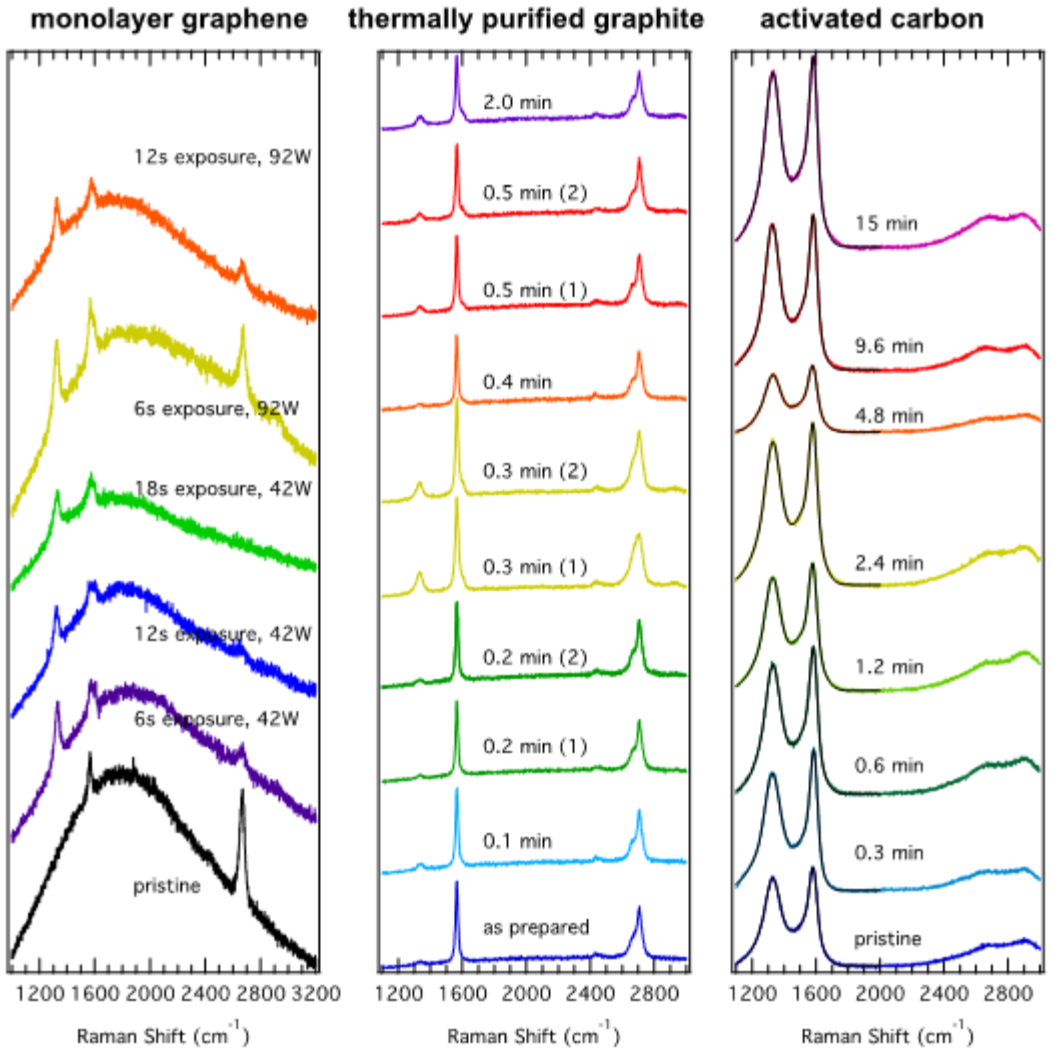
Graphene oxide (GO) – graphene with additional epoxides, alcohols, ketone carbonyls, and carboxylic groups

Reduced graphene oxide (rGO) – treated* graphene oxide that intends to remove oxygen and produce pristine graphene

Treatment includes hydrazine, hydrazine hydrate, hydrogen plasma, heat treatment (>1000° C)

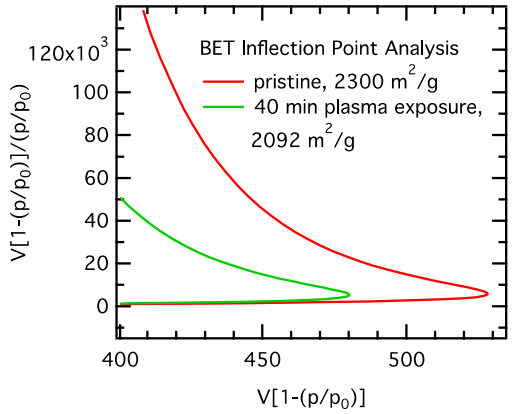
Oxygen Plasma Etching as Preparation for Functionalization

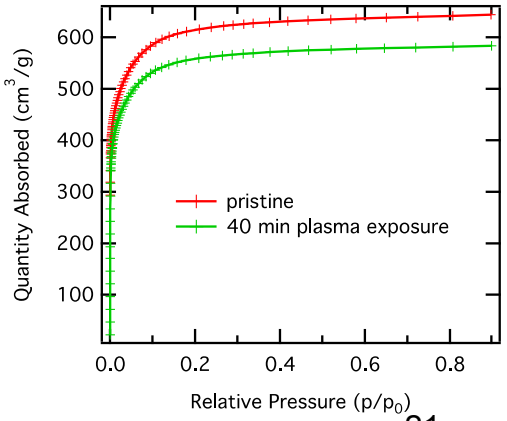
Changes in Various Carbon Samples with Oxygen Plasma Exposure Monitored with Raman:



Plasma etching induces changes in the material as a function of exposure time, though an increase of surface area is not yet demonstrated

Change in Surface Area with BET:





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