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

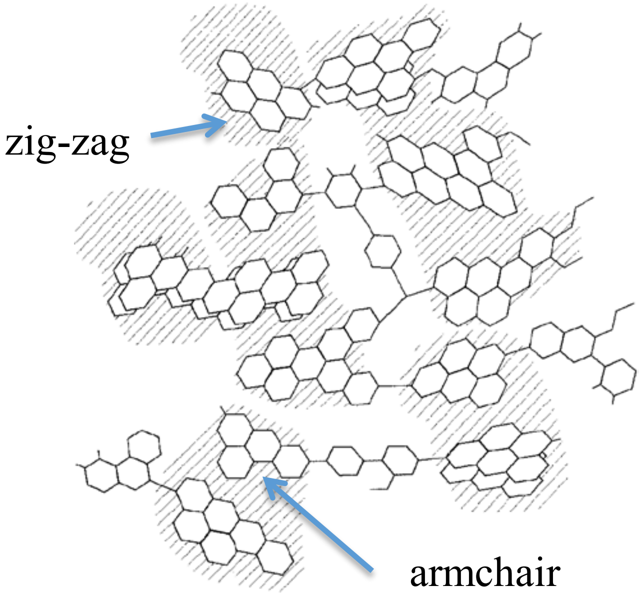
Interactions/collaborations

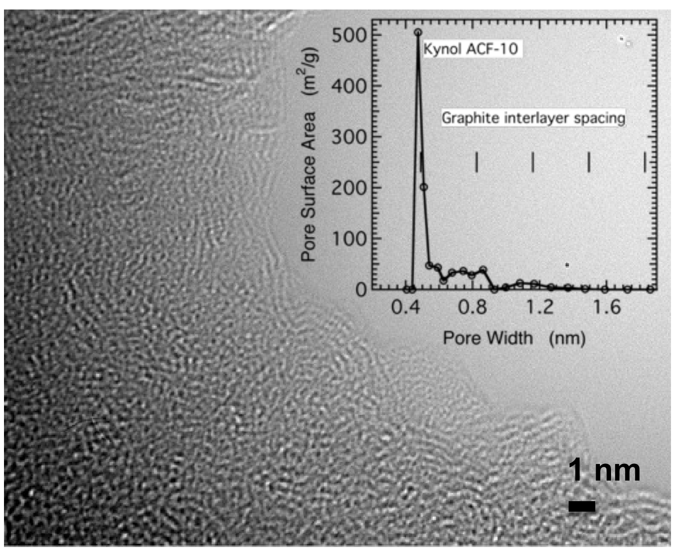
T. Baumann, LLNL

R.C. Bowman, Jr.

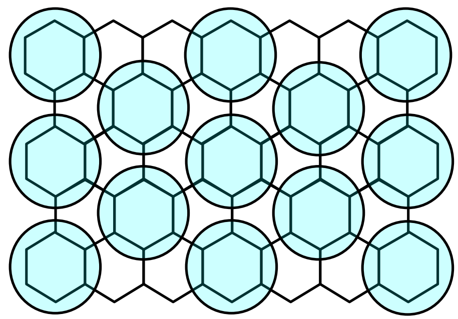
Why graphene instead of activated carbon?

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.

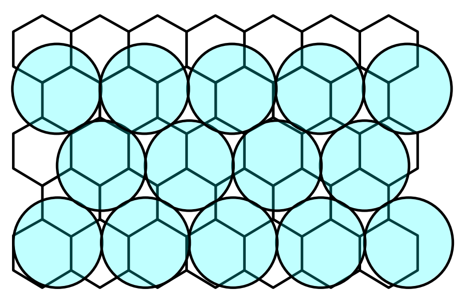




Graphene has a lower theoretical surface area (2630 m^2/g), but more regular for functionalization.



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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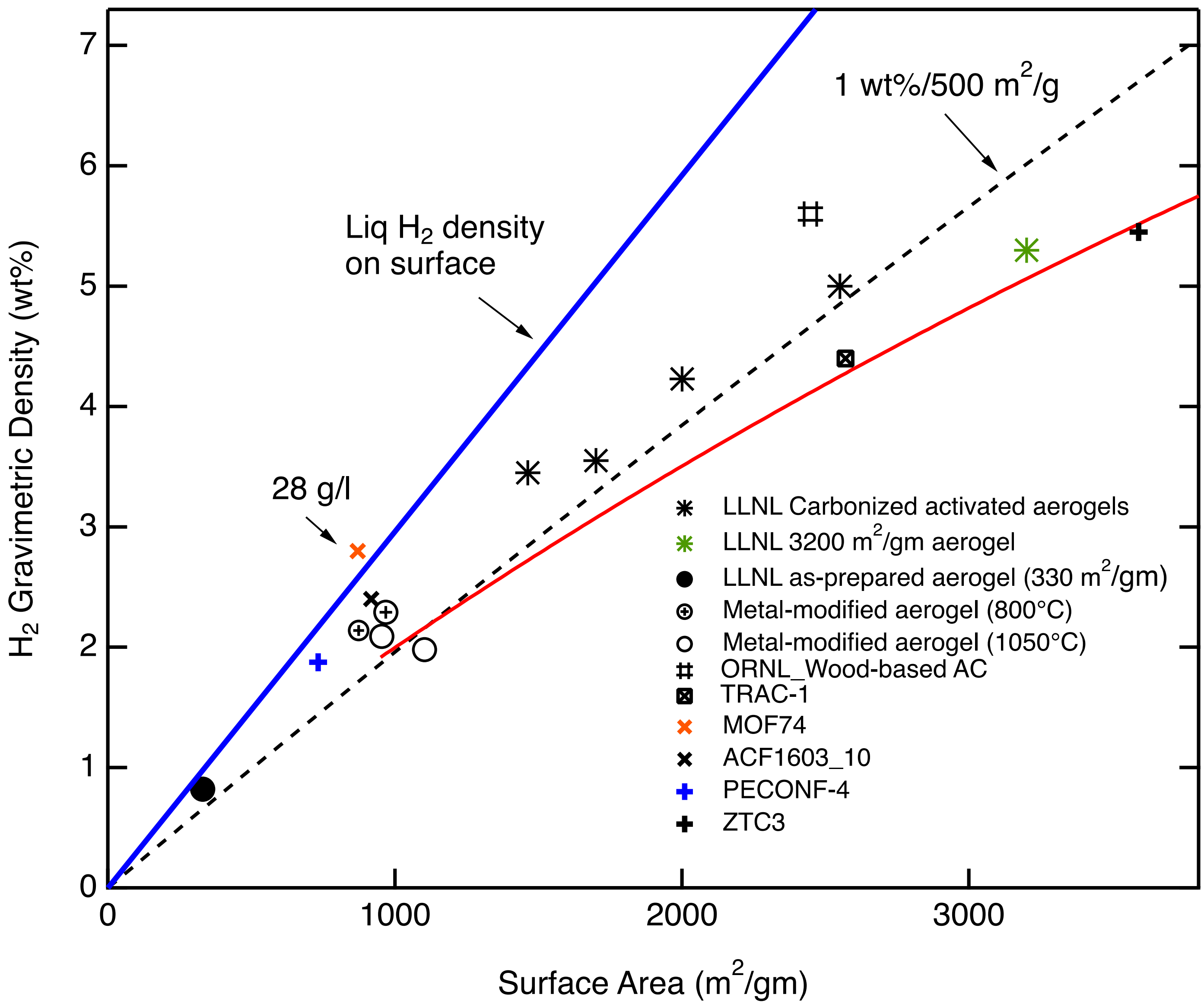
Capacity of Conventional Carbons



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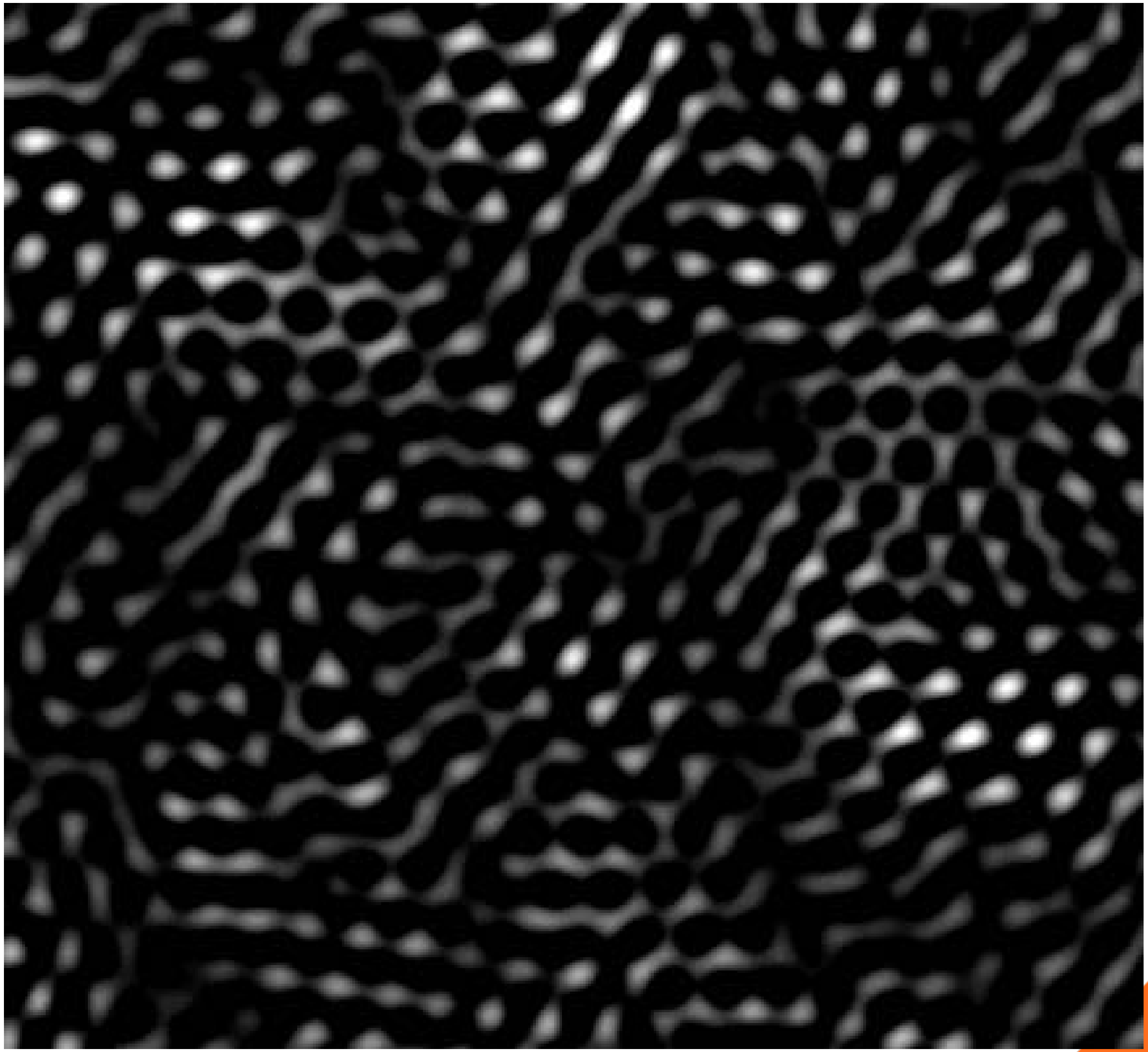
Rationale

- 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



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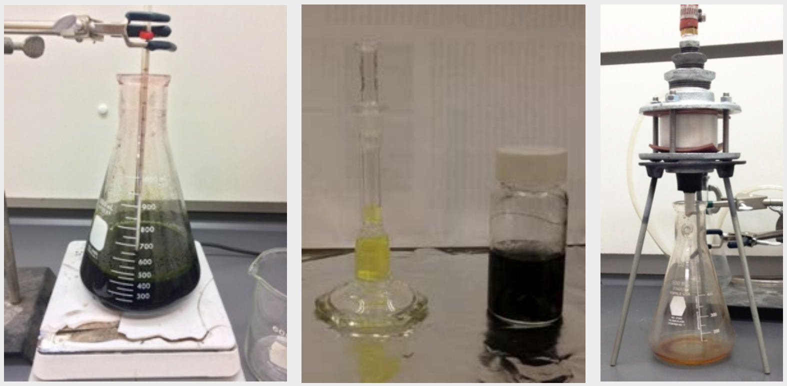
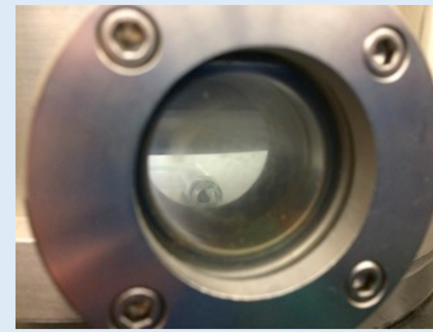
Synthesis and Preparation

Chemical Synthesis

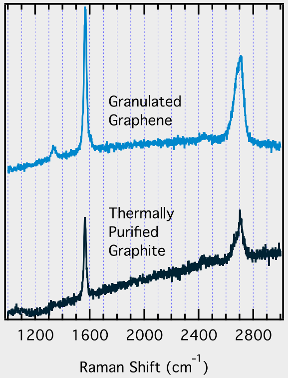


Oxygen Plasma Etching

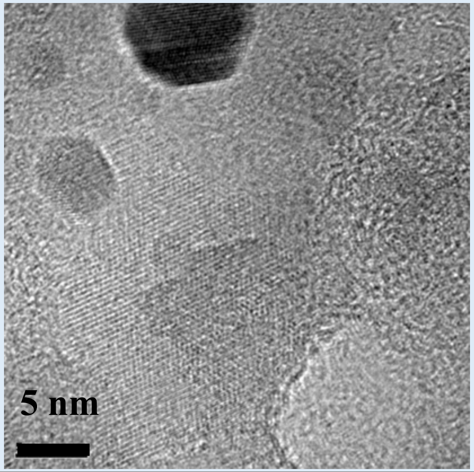


Materials Characterization Infrastructure

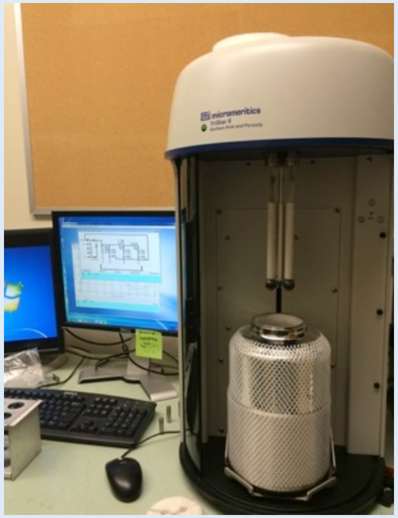
Raman Spectroscopy

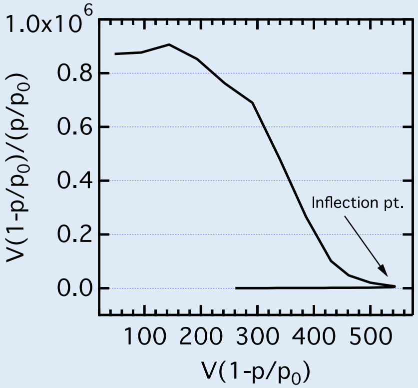


TEM

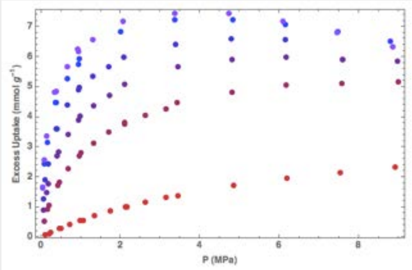


BET System





Sieverts Apparatus



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

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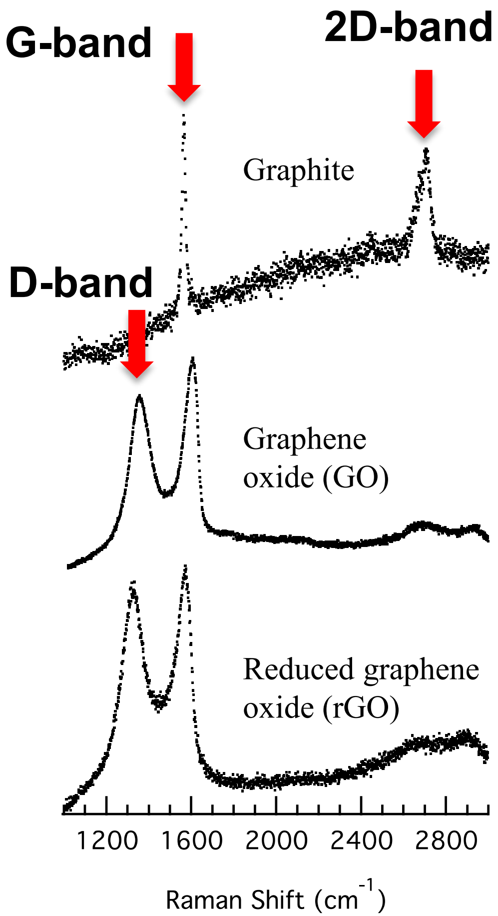
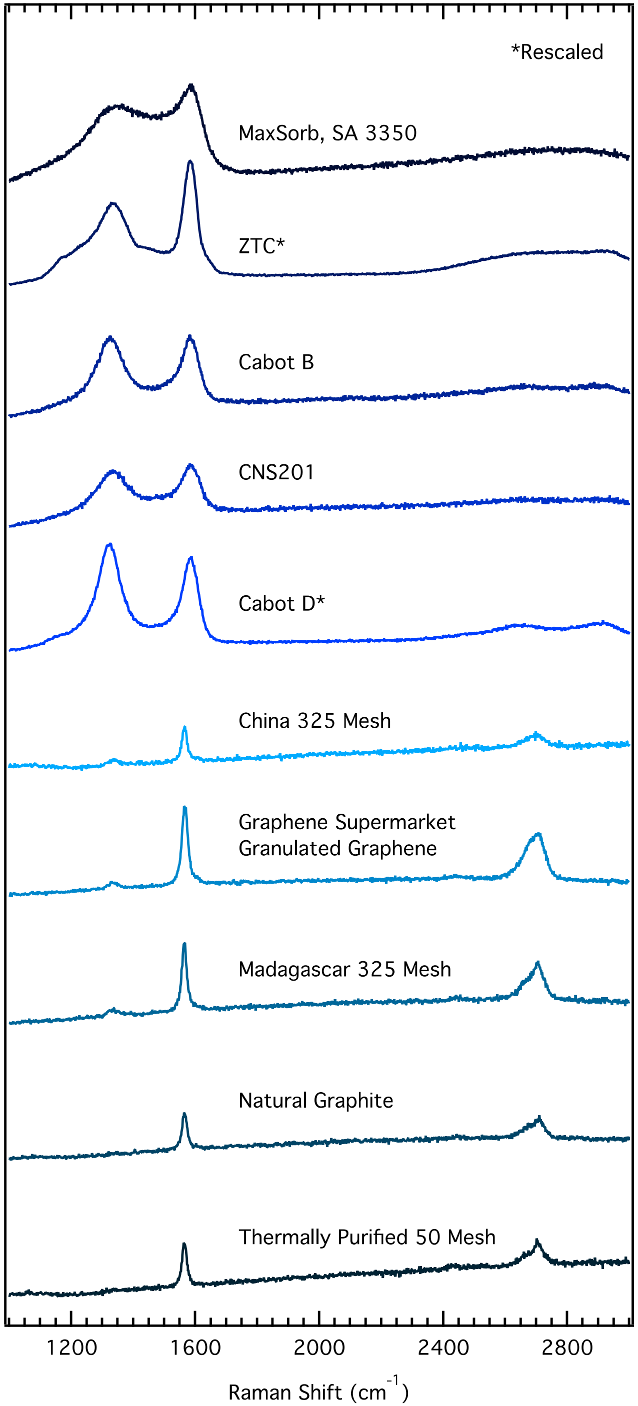
Materials Characterization Library

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

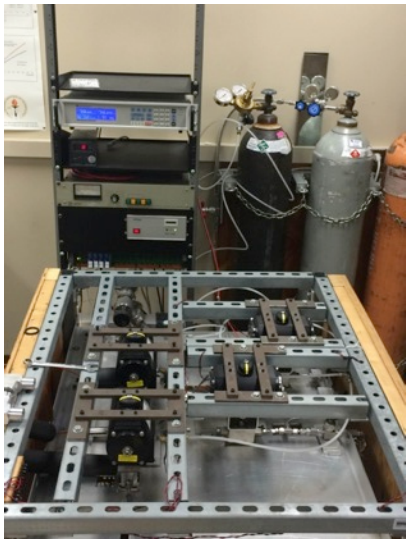
Raman Spectra:

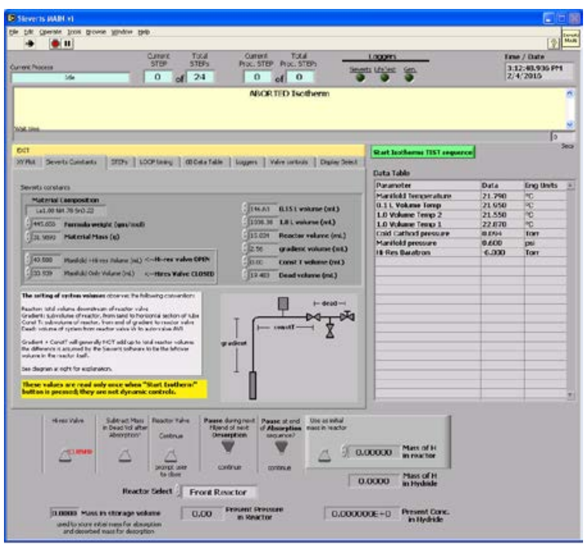


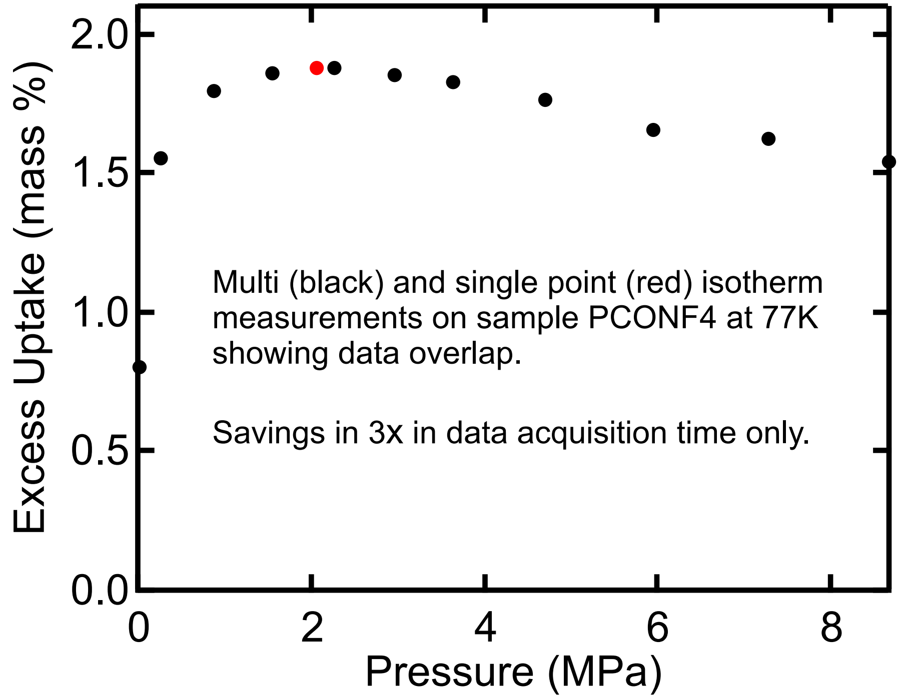


Sieverts Measurements

Sieverts Instrumentation at Caltech







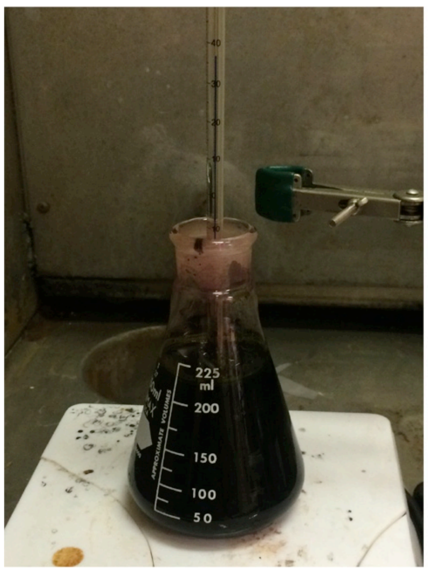
(Above): A Sieverts method for rapid screening of samples by measuring fewer data points require 1/3rd the time for a full isotherm measurement. A single point measurement at 77K (red) agrees with a full isotherm measurement (black) on a test sample, PCONF4.

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

Graphene Synthesis

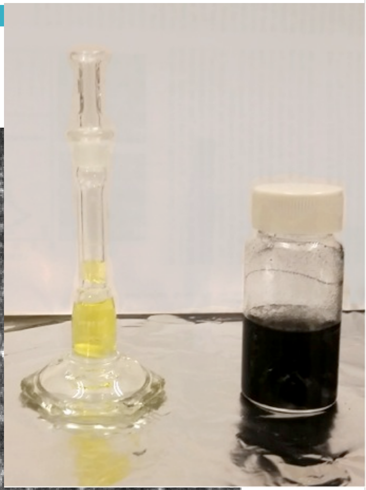
- Our synthesis of graphene oxide and graphene using a modified Hummers method.
- Optimizing the synthesis process for further modification and functionalization:
  - Analyzing the effects of starting with different types of graphite materials (Superior Graphite, Sigma-Aldrich, Graphene Supermarket,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

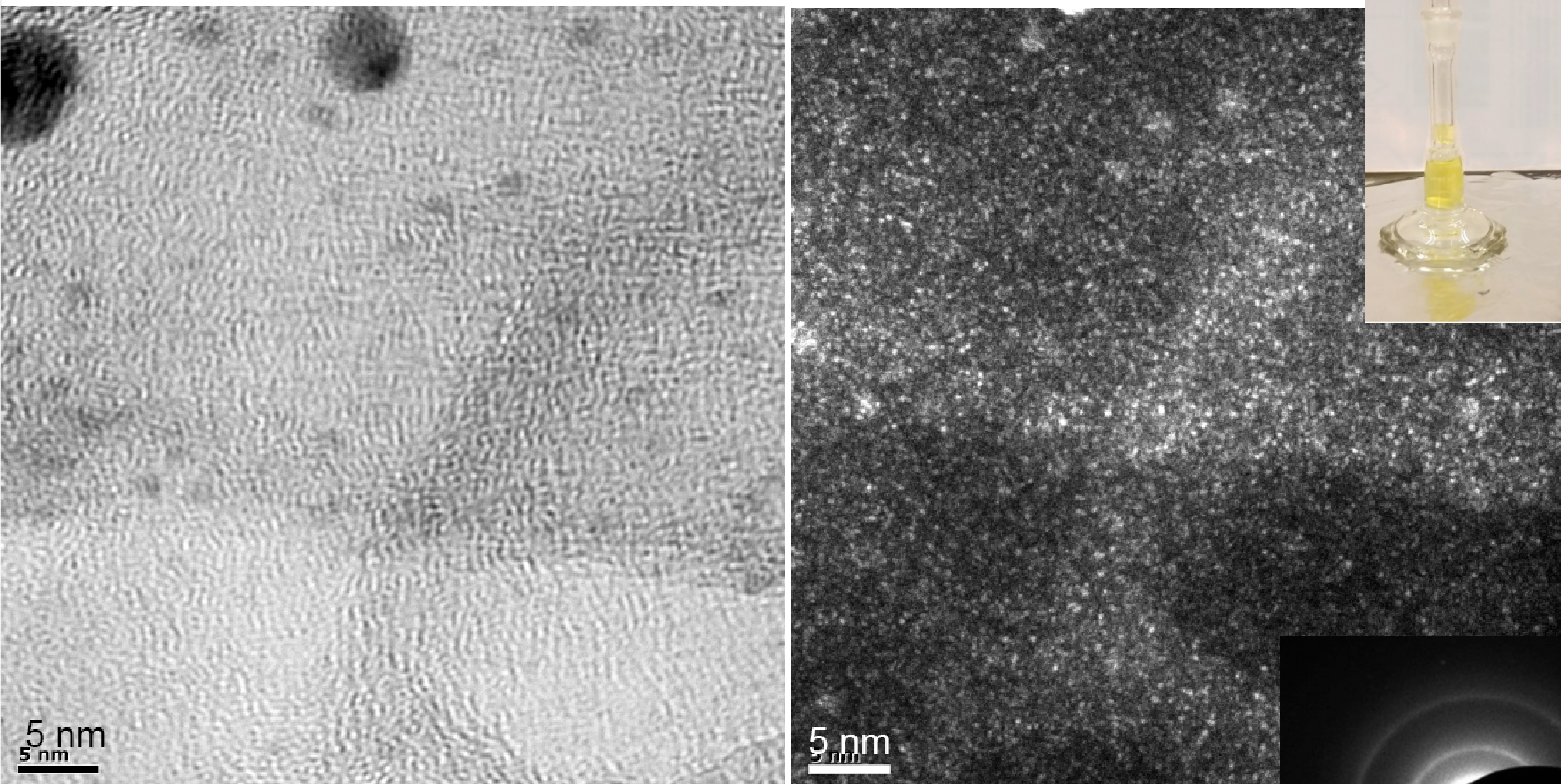
Modified Hummers Method (Tour, et al.):

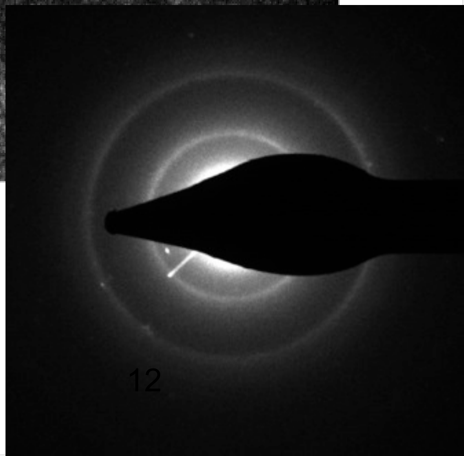


D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, Improved Synthesis of Graphene Oxide. *ACS Nano* **4,** 4806–4814 (2010).

Metal Functionalization: Chemical Deposition of Au

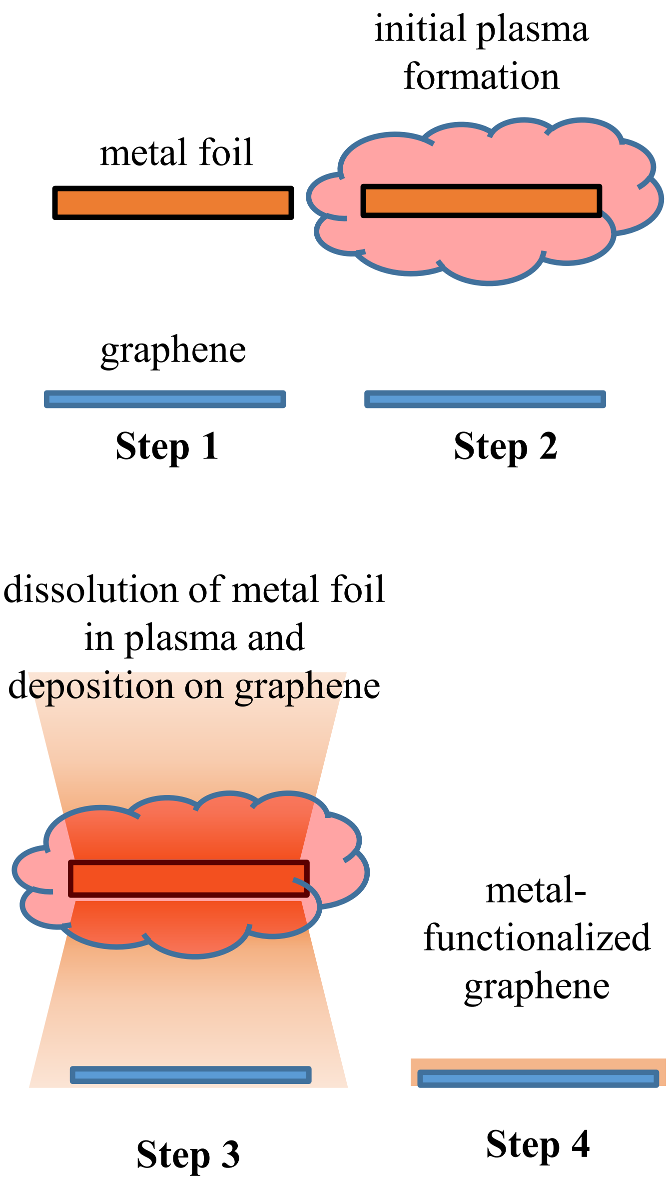




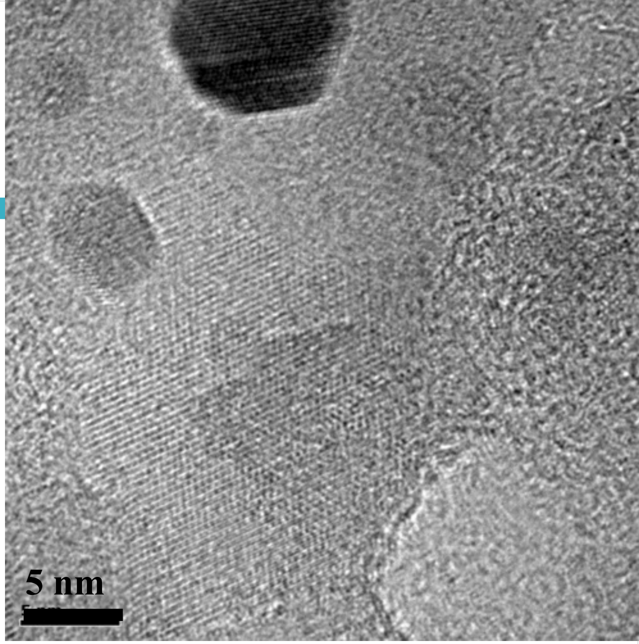


Bright field (left) and dark field (right) TEM images of Au nanoparticles deposited on graphene. Some larger particles ~1nm are visible in the BF image, while individual gold atoms decorating the surface are visible in the DF image.

Metal Functionalization: Plasma Deposition

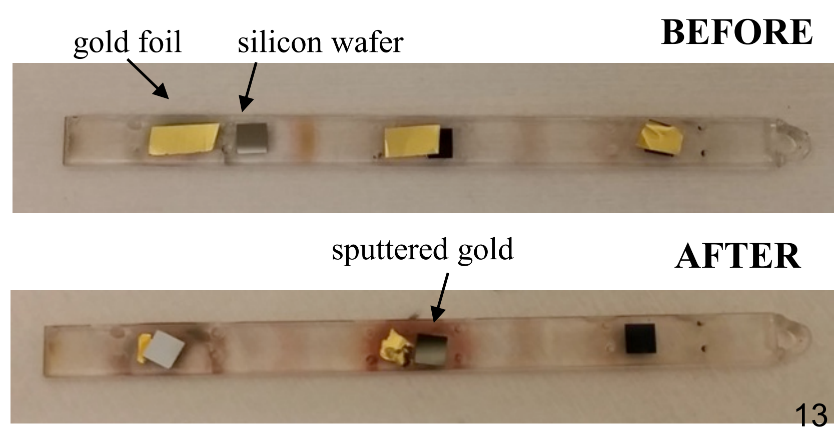


A plasma deposition approach for depositing nanoparticles from metal foil is being optimized (schematic at left).



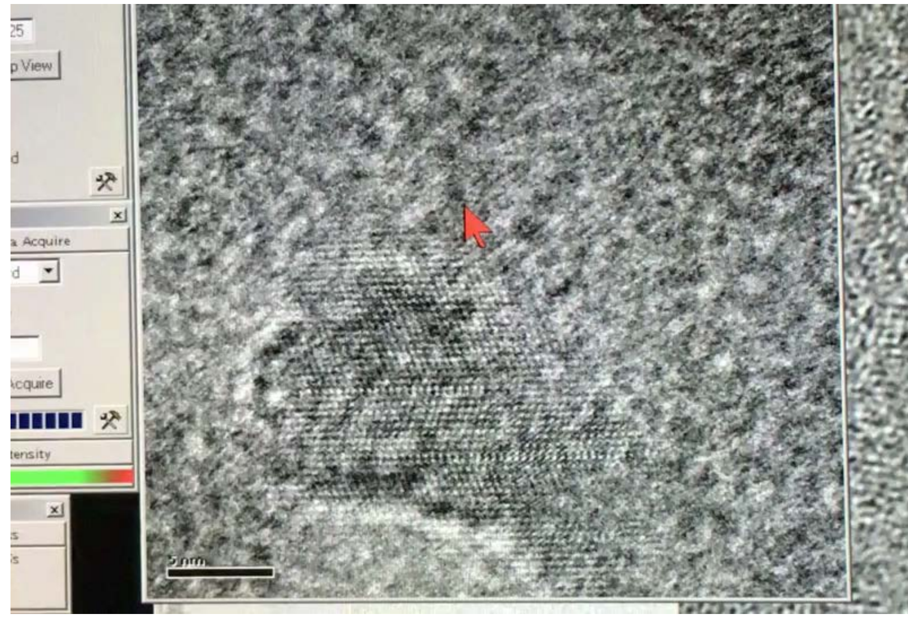
(Above): TEM images show ~5 nm Au particles (dark spot, upper middle) are visible on the graphene surface.

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



Functionalization with metals

Plasma Deposited Gold Particles on Monolayer Graphene:

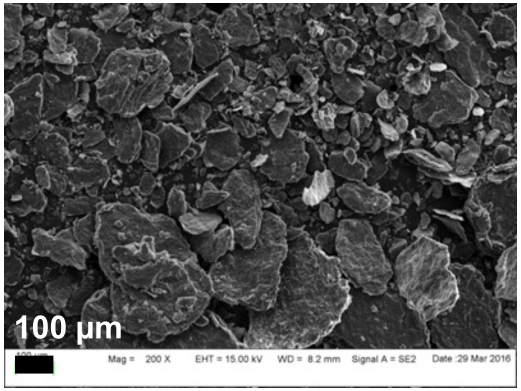


Au particle moving across surface

Au particle shrinking

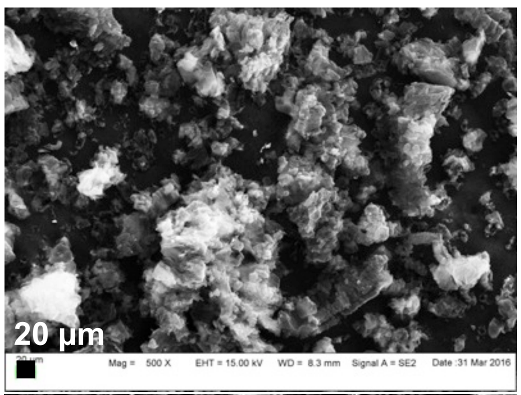
Bulk Modification

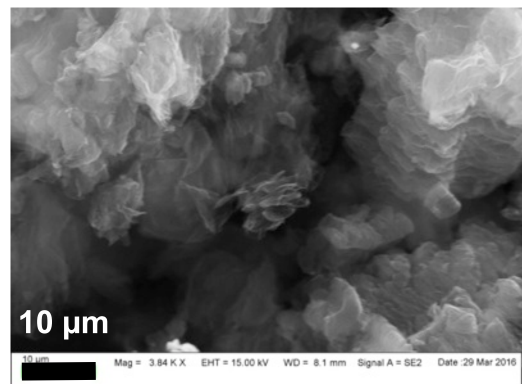
GO as prepared:



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

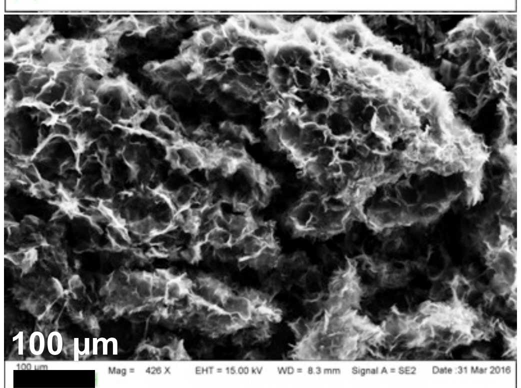
Microwave processed GO:

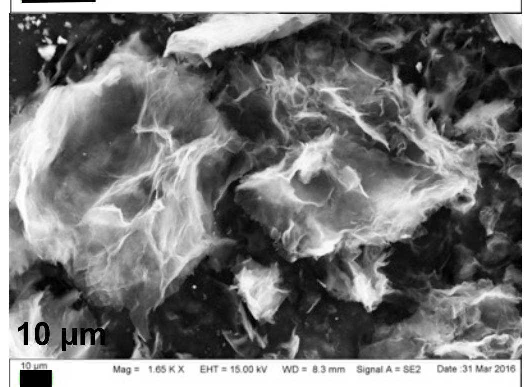




BET measurements indicate a more than 6x increase in surface area after activation

KOH activation of microwaved GO:





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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)

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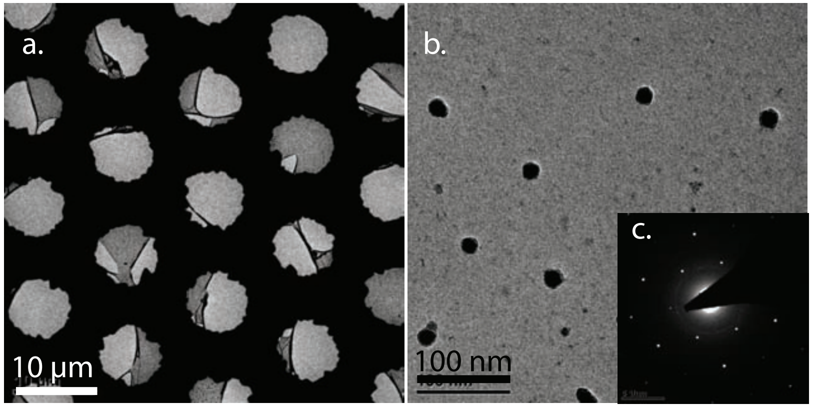
SUPPLEMENTAL SLIDES

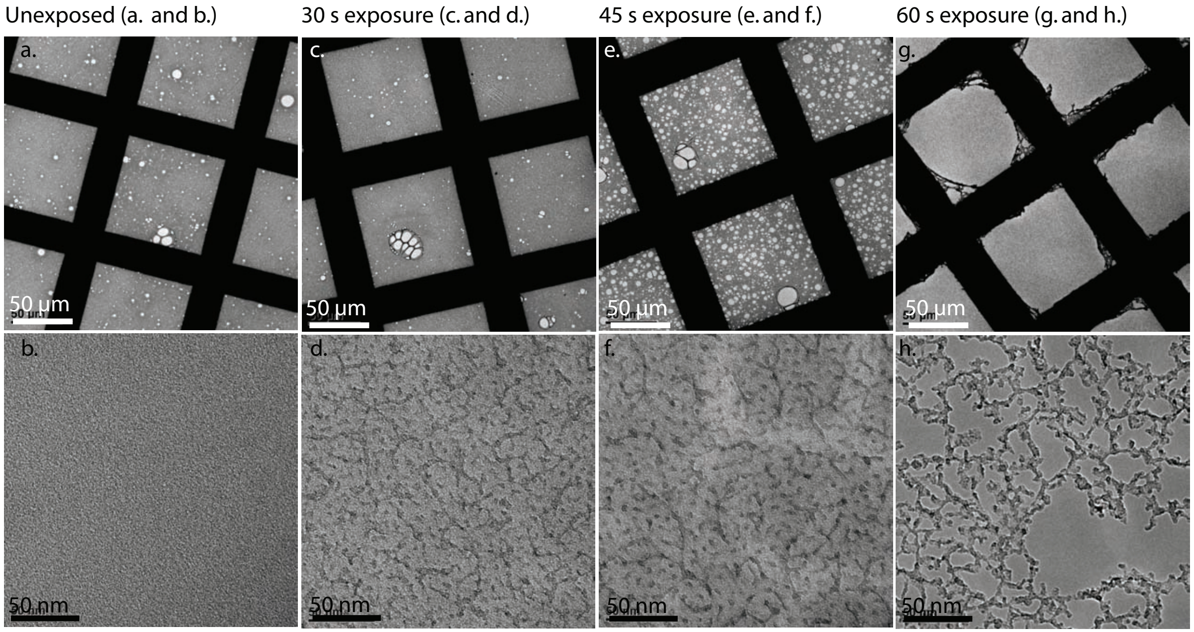
TEM Imaging of Metal Deposition and Plasma Exposure

Monolayer graphene on Cu mesh grid:



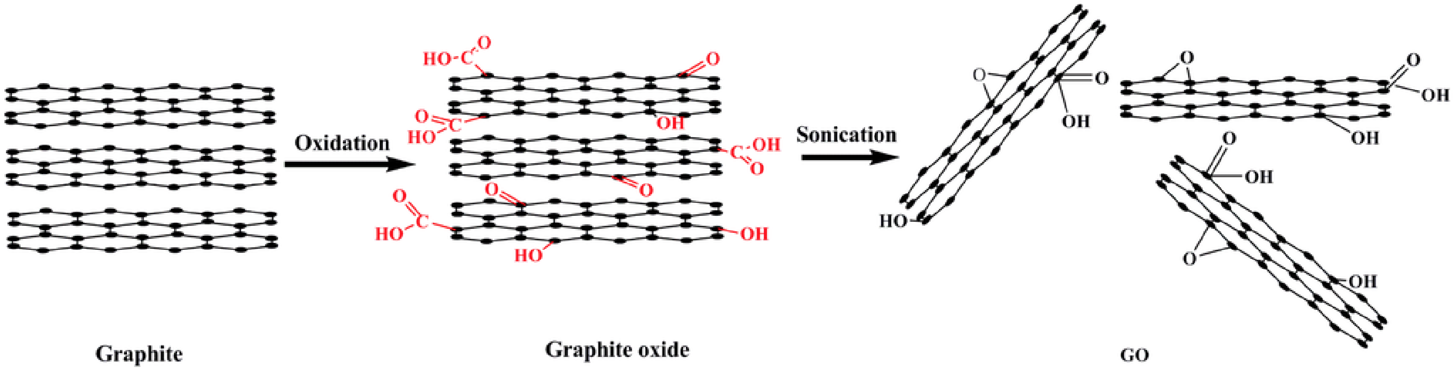
Monolayer graphene on copper mesh grid obtained from Ted Pella, Inc. (a) Shows a wide-field image. (b) Shows a region in more detail, revealing surface contaminants (black dots). (c) The SAD obtained with a 40 µm aperture for the region in (b).

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.

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)

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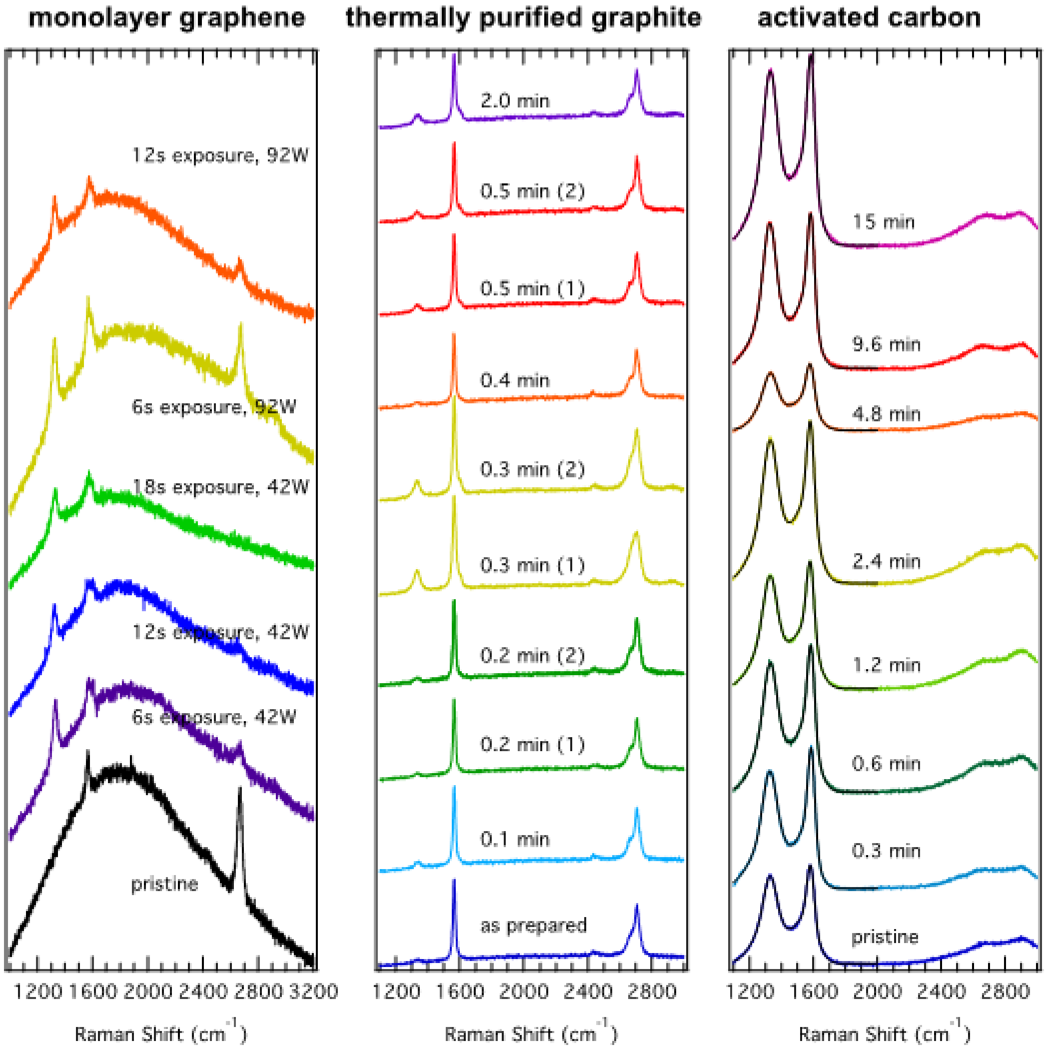
Oxygen Plasma Etching as Preparation for Functionalization

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: