Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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Caltech

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Project ID: ST120

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Overview

Timeline:

- Project Start Date: 08/01/15
- Project End Date: 07/31/18

Budget:

- Funds spent through 03/31/2016: $591,472
- Federal Share: $ 1M

Barriers

O. Lack of Understanding of Hydrogen Physisorption and Chemisorption.

- Reproducibility of synthesis and capacity measurements.
- Develop sorbent materials with increased binding energy and volumetric density.
- Develop cost-effective synthesis processes for promising materials.

Partners/Collaborations

- HySCORE (PNNL, Autrey, Bowden), Cealtech AS, Liox Power
- Project lead: Caltech

Relevance: Motivation for using graphene-based carbon

- High thermal conductivity
- Water and oxidative stability
- Strong interaction potential per unit mass
- Slit pore geometry near optimal for gas diffusion

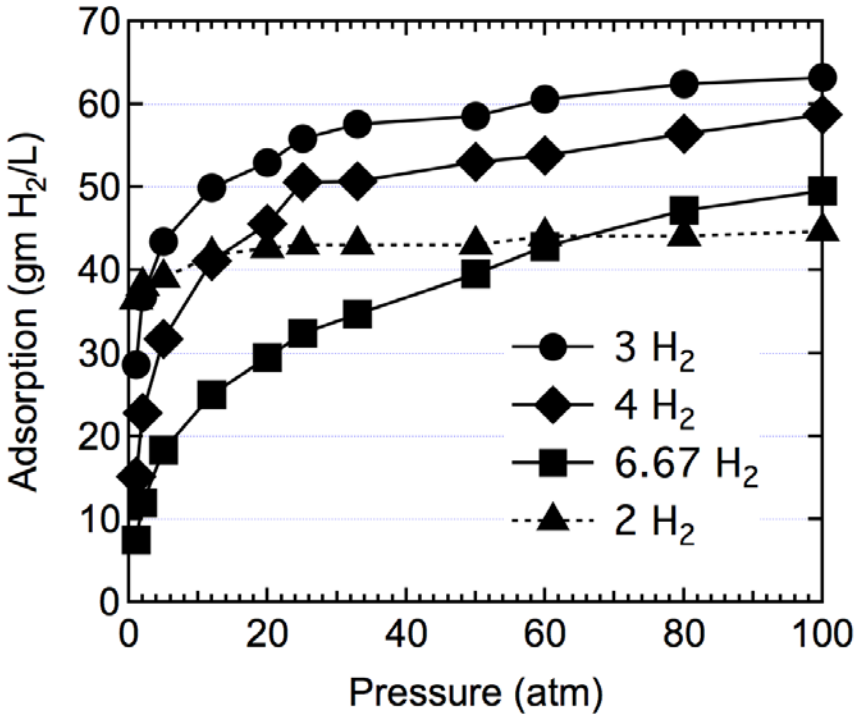
- But pore dimension tune-ability an issue so bottom up design using graphene chemistry

Relevance: Slit pore geometry offers high surface packing density

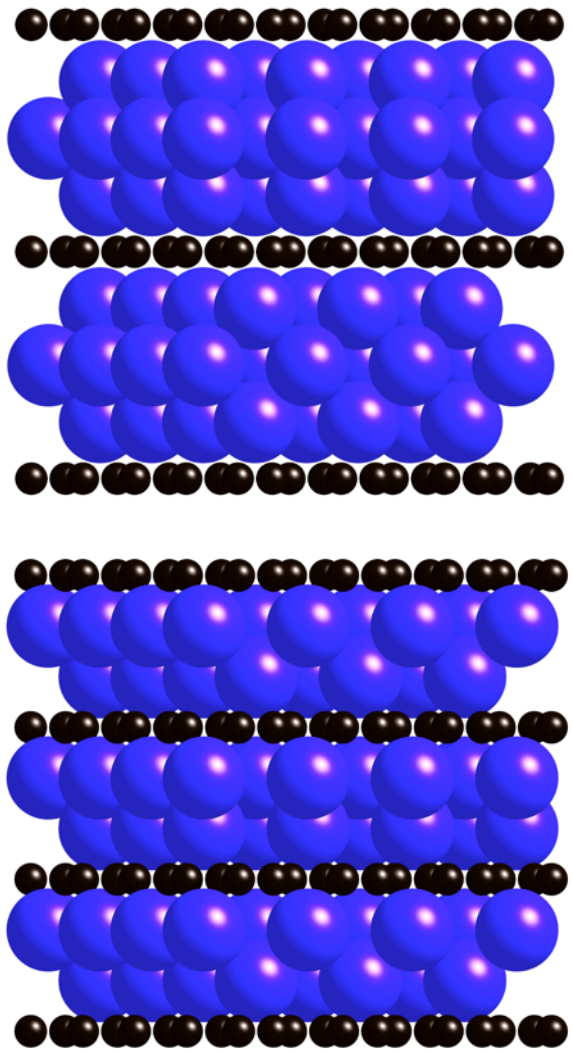
Goal is to:

a) Maximize surface area to micropore volume and

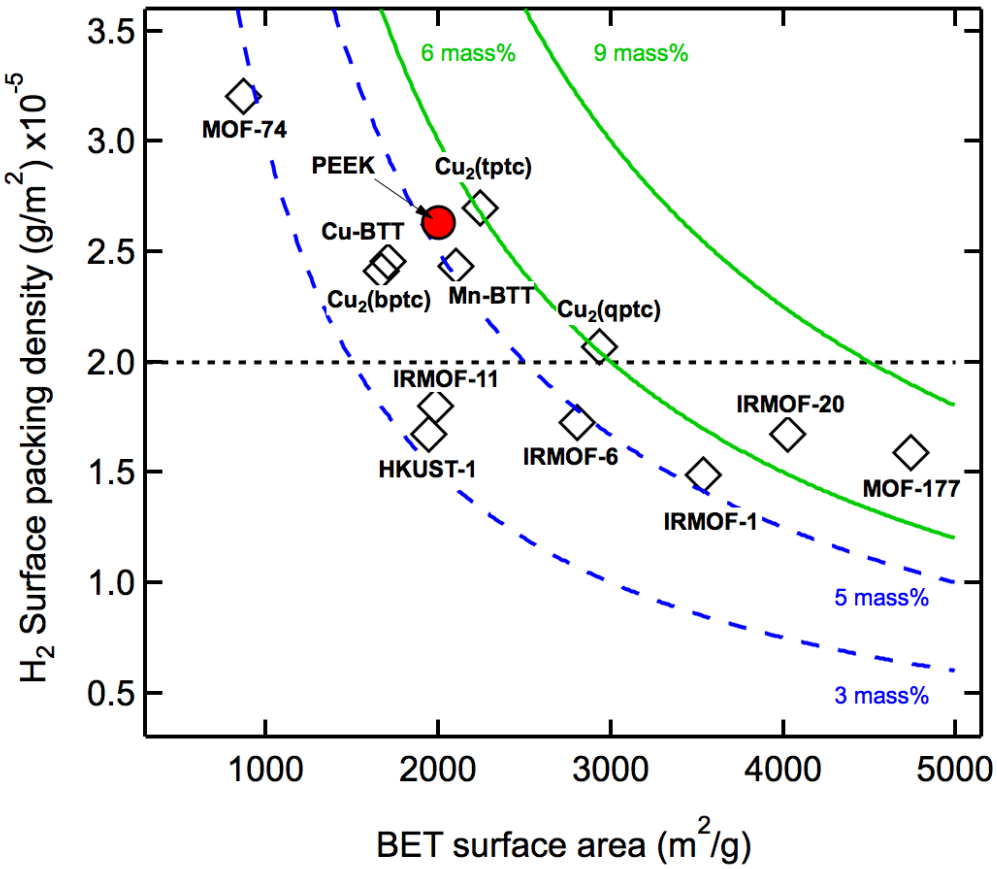
b) Functionalize surface to promote isosteric enthalpy



Q. Wang and J.K. Johnson, Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealized carbon slit pores, J. Chem. Phys. 110 (1999) p. 577.



Relevance: Maximizing surface packing density



Y. Liu, H. Kabbour, C. M. Brown, D. A. Neumann and C.C. Ahn, "Increasing the Density of Adsorbed Hydrogen with Coordinatively Unsaturated Metal Centers in Metal-Organic Frameworks," Langmuir, Vol. 24, No. 9, 2008.

Adsorbents can have high gravimetric density. 4 to 6 kJ/mol, a typical enthalpy range but enhancement by metal center sites to achieve high surface packing density observed.

Polyether-ether-ketone (PEEK) based activated carbon (no metal sites) an almost ideal starting material for high volumetric density improvements.

2000 m^2/g and 0.7 g/cc bulk density with 5.26 mass% uptake, > 40 g/l.

<u>But surface area of PEEK not optimized or functionalized</u>

T.P. McNicholas, A.M. Wang, K. O'Neill, R.J. Anderson, N.P. Stadie, A. Kleinhammes, P. Parilla, L. Simpson, C.C. Ahn, Y.Q. Wang, Y. Wu and J. Liu, "H_2 Storage in Microporous Carbons from PEEK Precursors," J. Phys. Chem. C 114 (32), 13902-8 (2010).

Approach: Graphene as the basis for bottom up platform

Motivated by potential to:

a) Improve surface area over that of PEEK (2000 m^2/g for PEEK vs 2630 m^2/g theoretical for graphene, 1400 m^2/g in LLNL graphene aerogels) and
b) Approach amenable to more simple functionalization routes.

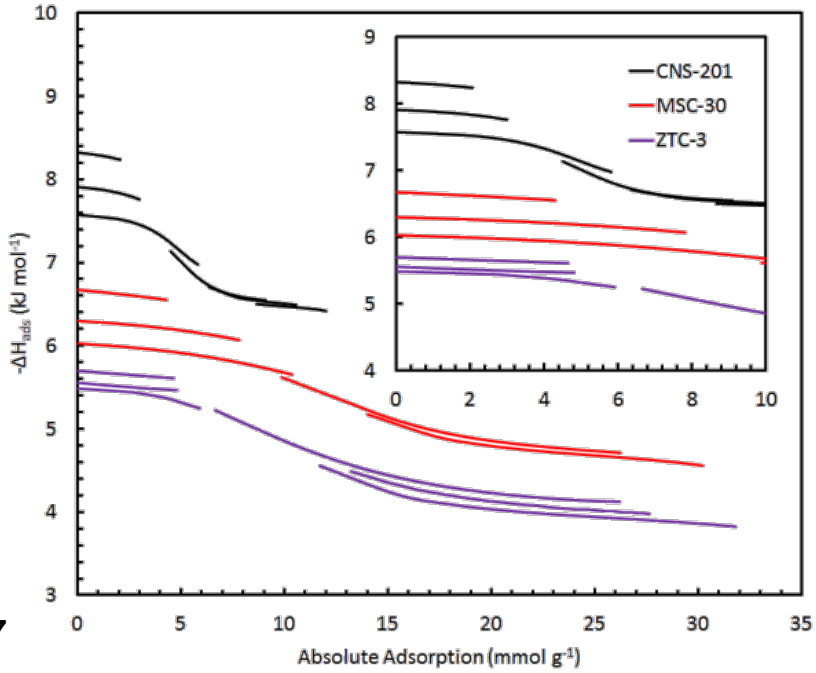
5 different synthesis routes explored;

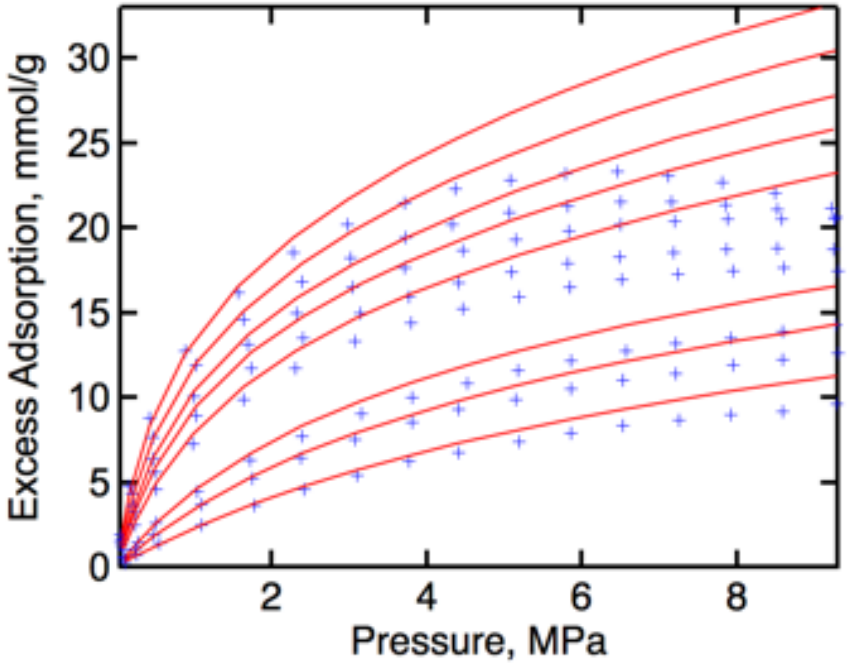
- Graphene oxide (GO) synthesized from graphite, followed by reduction to reduced graphene oxide and activation with KOH using:
  - Hydrazine hydrate
  - Microwave expansion
- Electrochemical exfoliation of graphite
- Activation of graphene with biomass
- Cold plasma synthesis/activation
- Vertically grown graphene

Approach: “Absolute” uptake data required for isosteric enthalpy determination

Enthalpy determination requires “absolute” uptake to apply Clausius-Clapeyron as with 2-site Langmuir model where we set $dq(p,T)/dT = 0$, and solve for $\partial P/\partial T$, where $dq/dT = 0$

Right: Solid lines from isotherms calculated absolute uptakes determined from experimental data (markers)



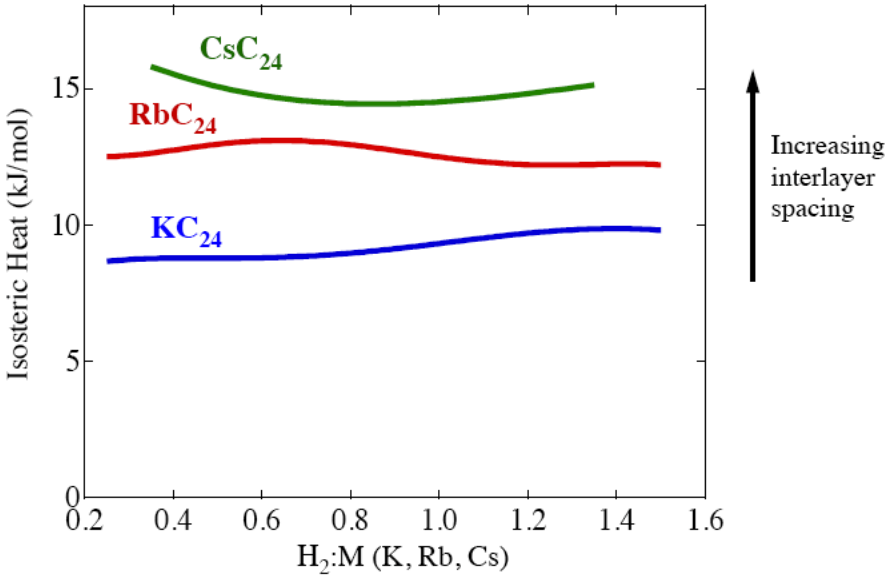


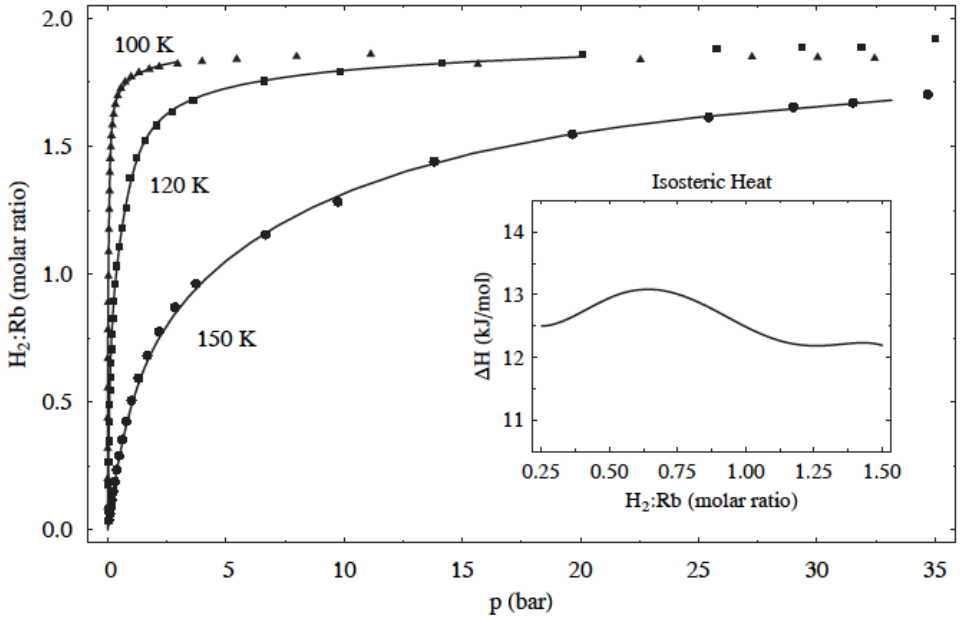
Two site Langmuir applied (left)* to relevant carbons; note isosteric enthalpy dependence on temp. range.

*From N. Stadie, “Synthesis and Thermodynamic Studies of Physisorptive Energy Storage Materials,” Ph.D. Caltech (2013).

Approach: Constant enthalpy in 2-d intercalated graphites as a model system

Constant enthalpy permits higher temperature desorption at moderate pressure and near lower temperature capacity with more useable H_2 (5 bar) at higher temperature.

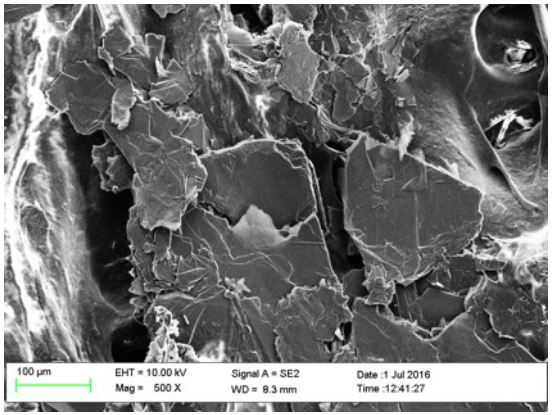




High constant enthalpy only seen so far in intercalated graphites.

From "Hydrogen Adsorption by Alkali Metal Graphite Intercalation Compounds," J. Purewal, Ph.D. Thesis, Caltech 2010.

Accomplishments/Progress: GO synthesis

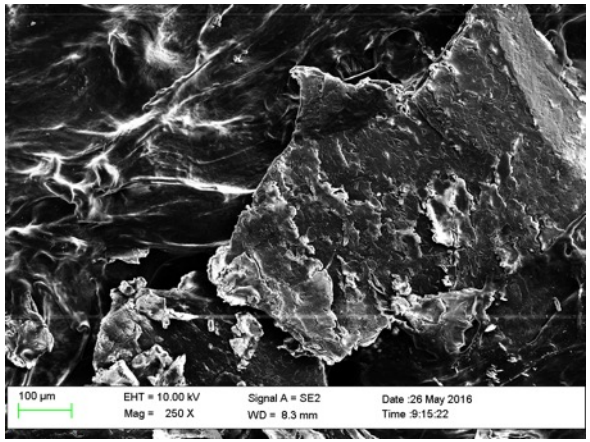


Graphite flakes (Madagascar) 3 g

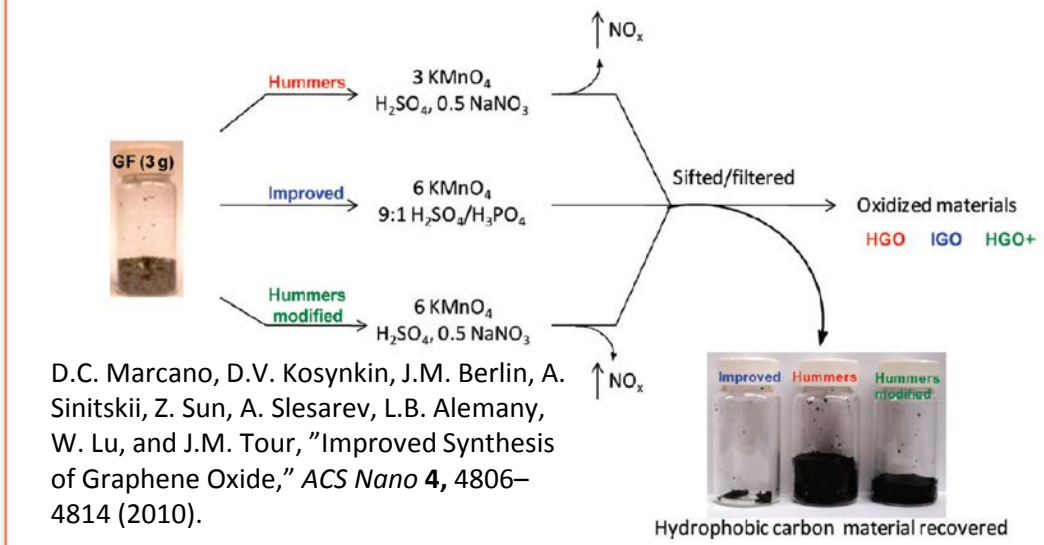
Improved Hummers Method

6 $KMnO_4$
9:1 H_2SO_4:H_3PO_4

centrifuged/ washed

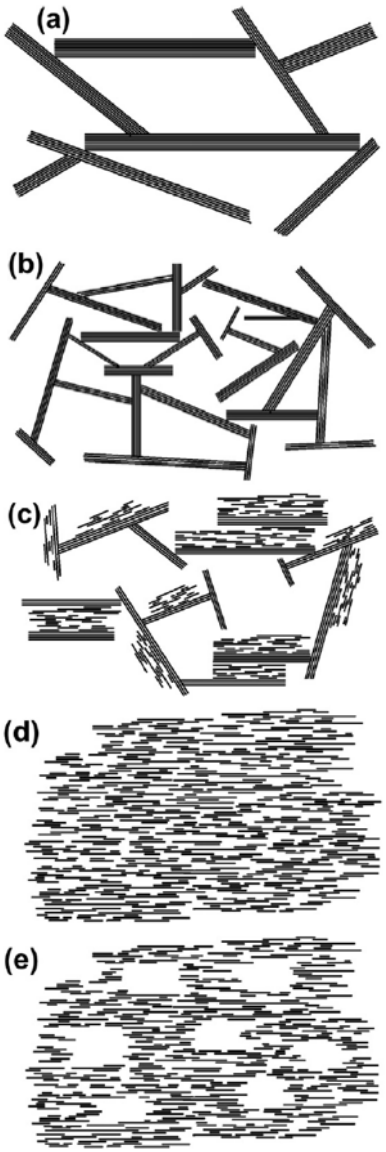


Graphene Oxide ~5 g

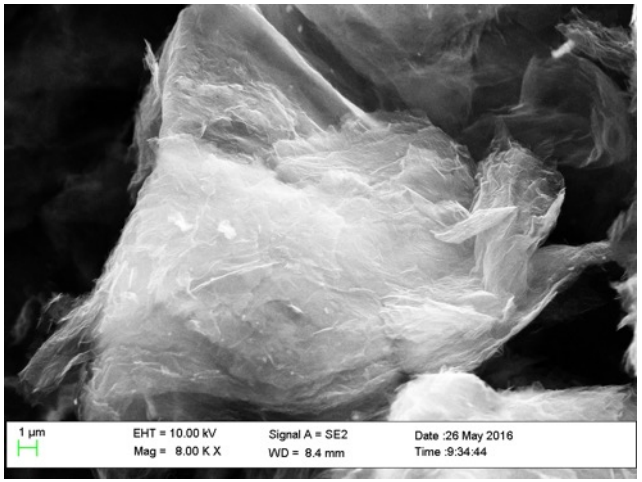


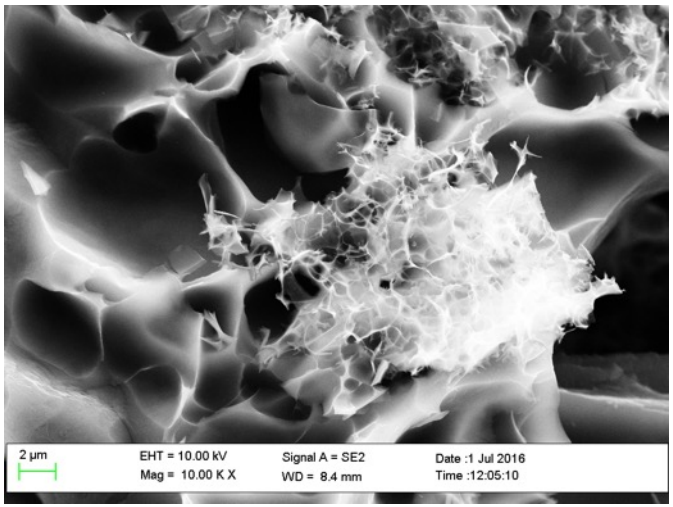
D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, and J.M. Tour, "Improved Synthesis of Graphene Oxide," *ACS Nano* **4,** 4806–4814 (2010).

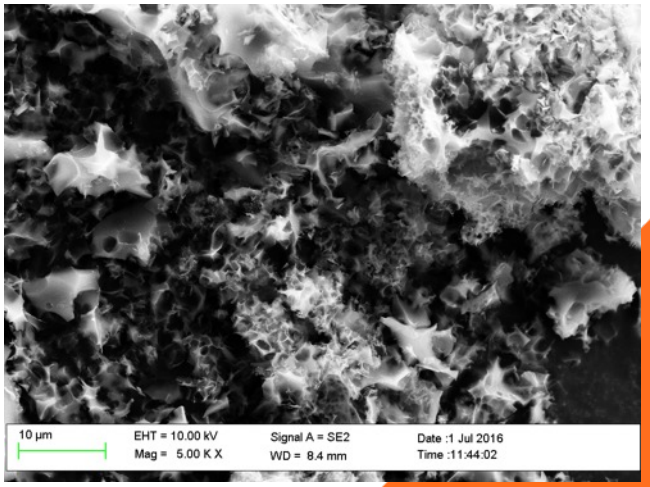
Accomplishments: Development of reduced graphene oxide (rGO) with activation



Schematic representation at left and SEM micrographs showing micro-structural development of high surface area graphene from graphene oxide.







Left schematic from: S. Wang, F. Tristan, D. Minami, T. Fujimori, R. Cruz-Silva, M. Terrones, K. Takeuchi, K. Teshima, F. Rodrıguez-Reinoso, M. Endo, K. Kaneko, “Activation routes for high surface area graphene monoliths from graphene oxide colloids“ Carbon 76 (2014) 220–231.

Accomplishments/Progress from Graphene oxide activation and compression -

Attempt No.	0	1	2	3	4	5	6	7	8	9	10	11
GO batch used	G.Super.	Madg. 3.3	Madg. 3.3	Madg. 3.3	Madg. 3.3	Madg. 3.3	Madg. 3.3	Madg. 3.2	Madg. 3.2	Sigma 4.1	GS A12	GS A12
pre-processing	micro.	micro.	micro.	micro.	micro.	micro.	micro.	micro.	micro.	N2H4	none	none
mass GO	40.2 mg	102 mg	97 mg	215 mg	128 mg	126 mg	162 mg	174 mg	207.5 mg	262.4 mg	207.5 mg	252.5 mg
conc. KOH used	7 M	7 M	7 M	7 M	7 M	7 M	3.5 M	3.5 M	7M	3.5 M	3.5 M	3.5 M
time stirred	4 h	4 h	4 h	4 h	4 h							4 h
time let sit	overnight	overnight	18 h	16 h	20 h							23 h
amt placed on filter						5 mL	5 mL	5 mL	6 mL	2 mL	3 mL	
time let sit						15 min	15 min	15 min	15 min	15 min	15 min	
amt used to rinse under vac						5 mL	11 mL	12 mL	14 mL	20 mL	22 mL	
total amount KOH (mL)	10 mL	20 mL	19.3 mL	20 mL	25.6 mL	10 mL	16 mL	17 mL	20 mL	22 mL	25 mL	25 mL
total amount KOH (mg)	3927 mg	7854 mg	7579 mg	7854 mg	10054 mg	3927 mg	3141 mg	3338 mg	7854 mg	4320 mg	4909 mg	4909 mg
ratio KOH/GO (mg/mg)	98	77	78	37	79	31	19	19	38	16	24	19
time in Buchi (125C)	3 h	overnight		19 h		18 h	12 h	22 h	16 h	26 h	26 h	24 h
gas flow tube furnace heating	under Ar flow, ramp 15K/min to 350C, hold 30 min, ramp 5K/min to 900C, hold 60 min, cool under gas											
acetic acid amt used	10 mL	20 mL	ruined (reacted with filter)	10 mL	?	< 3 mL	1-2 mL	~2 mL	nothing left after heating	~7 mL	~10 mL	~ 5 mL
water amt used	30 mL	?		20 mL	?	15 mL	~ 10 mL	~60 mL		~100 mL	100 mL	100 mL
time in Buchi (120C)	?	?			?		16 h	10 h		4 h	n/a	15 h
vacuum tube furnace heating	under vacuum, ramp 20 K/min to 900C, hold 60 min, cool under vacuum											
final product	1.3 mg			19.0 mg	5.0 mg	11.7 mg	49.9 mg	25.2 mg		93.7 mg	122.5 mg	137.4 mg
yield	3.20%			8%	4%	7%	31%	14%		36%	53%	54%
surface area	2300 m2/g			1730 m2/g		2600 m2/g	1170 m2/g	2200 m2/g		483 m2/g	42 m2/g	46 m2/g
% increase in surface area	1277%			936%		1457%	600%	1217%		45%	8%	18%

Accomplishments: Synthesis of graphene-based carbon in reasonable quantities

Attempt No.	1	2	3
Batch Name	sGO Batch 1	aligGO Batch 1	deligGO Batch 1
GO source	Sigma	Sigma	Sigma
biomass	sucrose	alkaline lignin	dealkaline lignin
GO sol'n	5 mg/mL	5 mg/mL	5 mg/mL
biomass sol'n	250 mg/mL	250 mg/mL	250 mg/mL
total amount	100 mL	50 mL	50 mL
GO:biomass	1:24	1:24	1:24
autoclave temp	180C	180C	180C
autocalve time	12 h	91 h	12 h
final collected mass	~ 8 g	8.9 g	7.4 g
surface area	<1 m^2/g		7.4 m^2/g

Table 1. Above: Synthesis parameters and yields for preparation of graphene- based carbon from biomass.

Attempt No.	1.1	1.1	1.2	1.4	1.3
source	sGO	sGO	sGO	sGO	sGO
batch	1	1	1	1	1
source mass (g)	1		0.5	0.5	0.5
total amount KOH (mL)				50 mL 7M	
total amount KOH (g)	4		2		2
ratio KOH/GO	4		4		4
mixing	hand		grinder	slurry	grinder
time stir				4 h	
time let sit				20 h	
time in Buchi (125C)				20 h	
gas flow tube furnace heating	under gas flow, ramp 5K/min to 800C, hold 60 min				
gas used	Ar		Ar	Ar	N2
flow rate	1 bbl/sec		1 bbl/sec	1 bbl/sec	500 mL/min
acetic acid used	10%		10%	10%	10%
vacuum tube furnace heating	no	yes	no	no	
final product	318 mg		44 mg		
yield	32%		9%		
surface area	1295	1180	1298	1080	
% increase in surface area	1294%	1179%	1297%	1079%	

Table 2. Above: Parameters, surface areas, and yields for activation of graphene-based carbon from biomass. All four activation attempts thus far show increases in surface area of over 1000%.

Figure 2. Left: Over 20 grams of graphene-based material was synthesized from reaction of graphene oxide with sucose, alkaline lignin, and dealkaline lignin, the parameters for which are given in Table 1.

Approach/Accomplishments: Etching of Pores in Graphene

Rationale to improve surface area and create active edge sites for functionalization.

- Plasma etching to modify monolayer and bulk materials:
- Direct and indirect oxygen and nitrogen plasmas produced holes in monolayer graphene and vertical graphene as evidenced by TEM and Raman
- Direct and indirect oxygen plasma produced changes in bulk samples of graphene nanoflakes and MSP20 activated carbon as indicated by BET surface area measurements and Raman.
- Also tested the effectiveness of a focused ion beam (FIB) for producing nanometer-scale holes in graphene (at right).

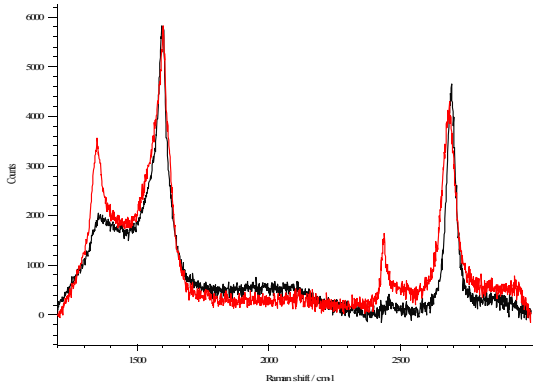
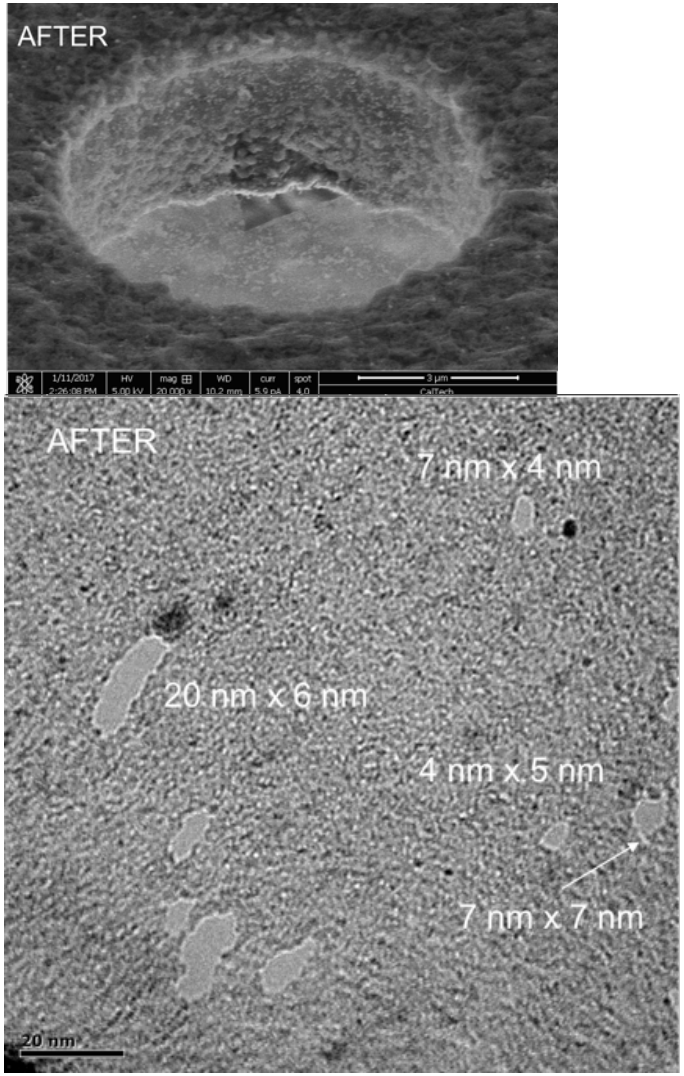
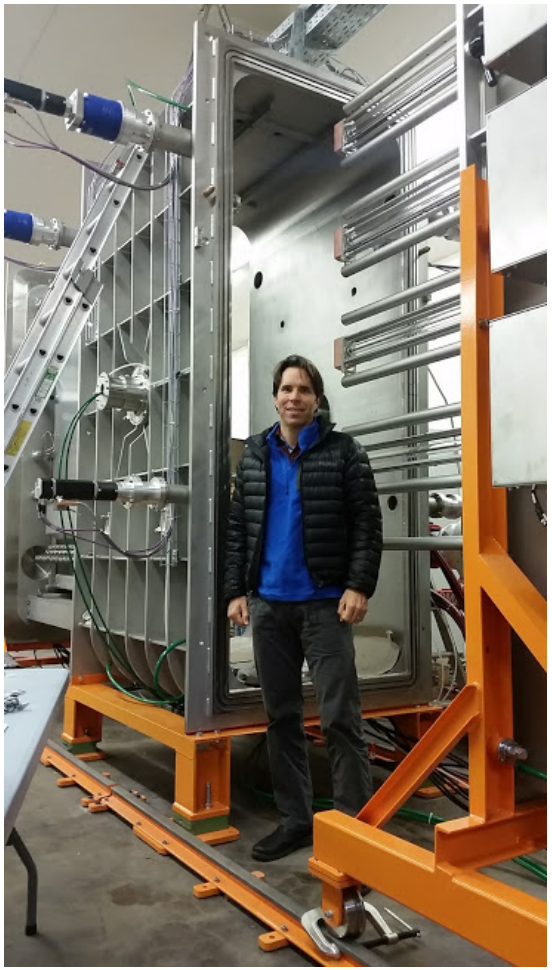


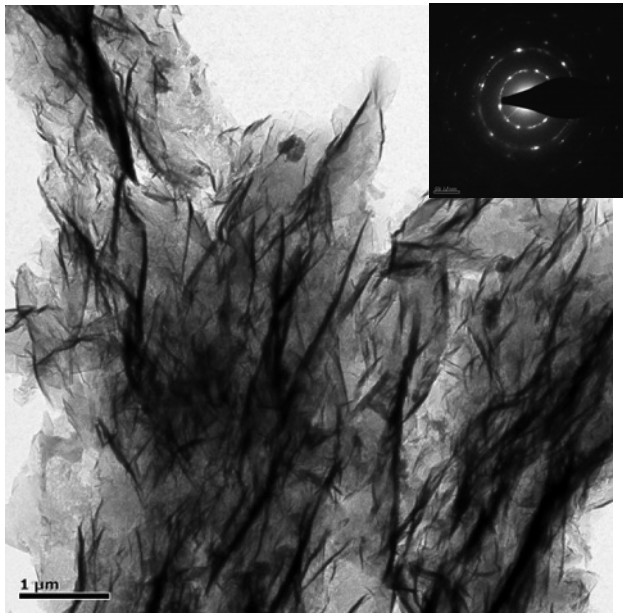
Fig. 1: Above: Raman spectra of monolayer graphene before (black) and after (red) treatment with nitrogen plasma shows sharp increase in the D band (~1350 cm^{-1}) consistent with the addition of holes in the graphene.

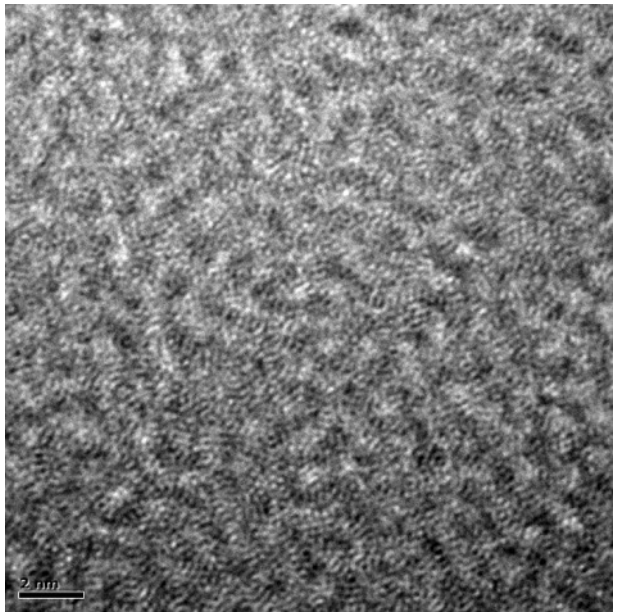


Right: SEM image of the graphene monolayer on copper grid after exposure to the FIB for 10s at 2kV and 4.3 pA. (Bottom) TEM images of holes formed near the large triangular hole after FIB exposure. Holes formed have a distribution of sizes.

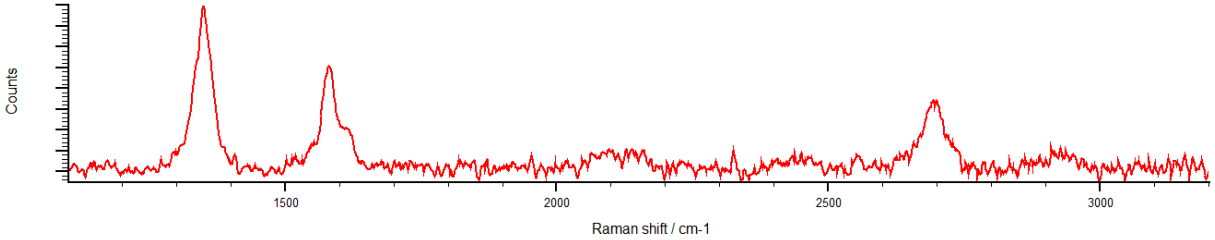
Accomplishments and Progress: Commercial continuous scale-up of plasma grown graphene







Above Left: Assembly of the plasma system for large-scale production of graphene. Cealtech AS, a Norwegian-based start-up has licensed Caltech technology to scale-up graphene growth. Above middle and right: TEM micrographs from pilot. Right: Initial graphene grown on plasma tube. Below: Raman spectrum showing large defect band at 1350. Turbostratic and not a-b stacked typical.



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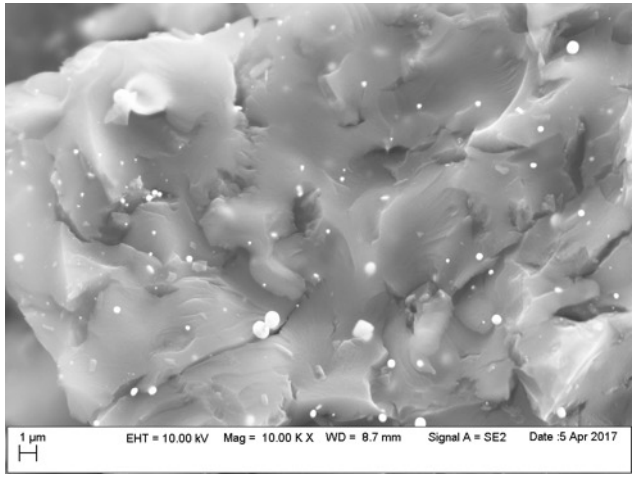
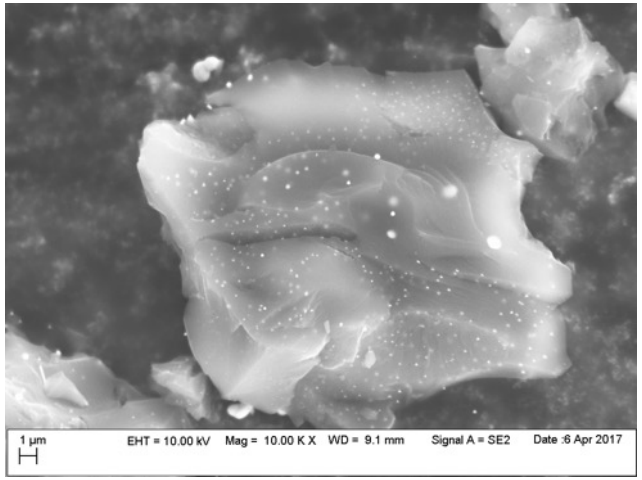
Accomplishments/Progress: Cu incorporation toward enthalpy modification Using $CuCl_2 \cdot 2H_2O$

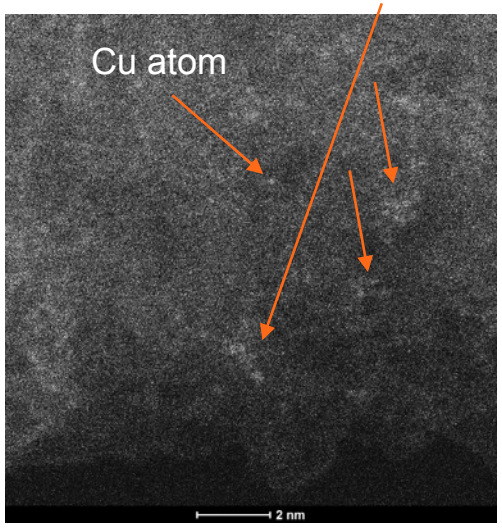


500°C under H_2, SSA 2323 m^2/g, heated

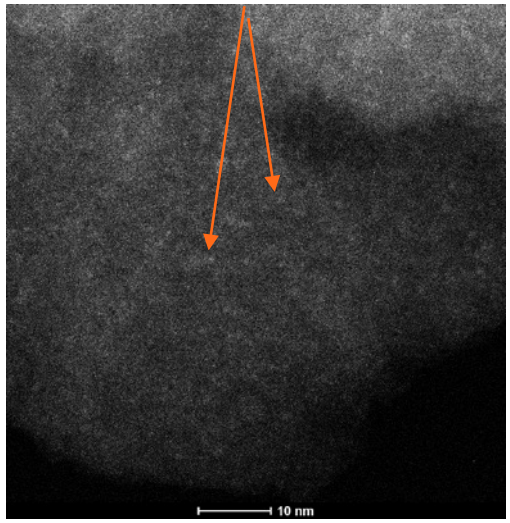


300°C under H_2, SSA 2425 m^2/g,

Cu cluster (5 atoms)



Cu clusters



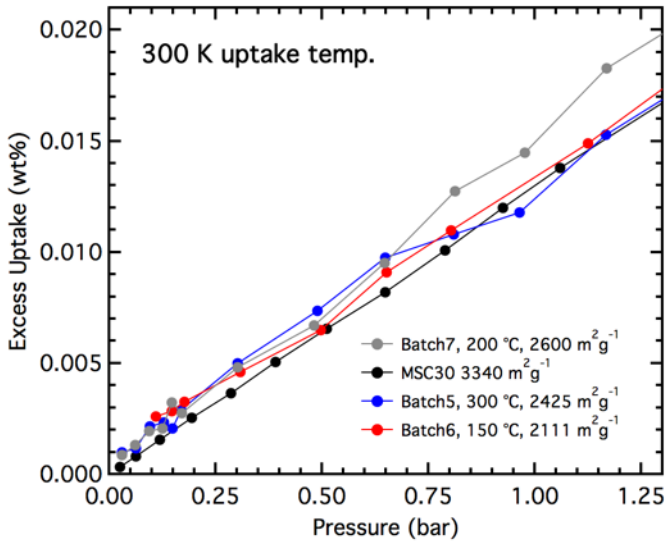
Left: 125°C under H_2, SSA 3006 m^2/g,

TEM High Angle Annular Dark Field micrograph from HySCORE collaborators (Bowden) at PNNL.

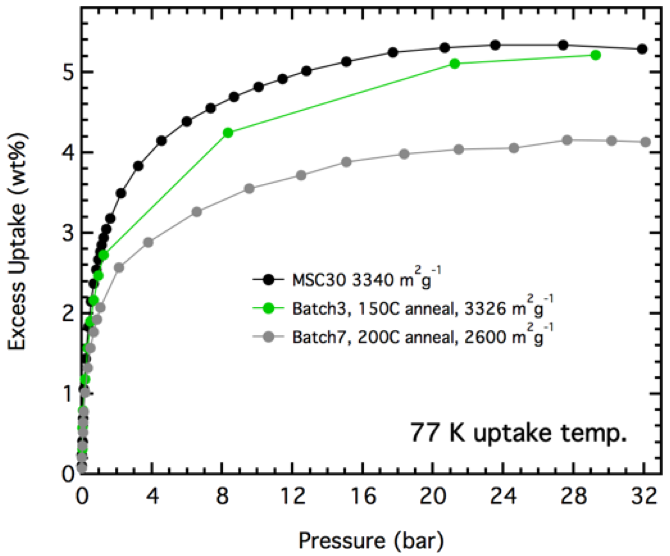
Accomplishments/Progress: Cu salt/reduction modifications

		C:Cu	salt conc.	Processing	Heat Treatment	Gas type	Surface Area	SEM?	Sieverts?	TEM?
		atom ratio	M				m^2/g			
Batch 1	$CuCl_2.2H_2O$	3366	0.012	stir 2h, filter, rinse with 100 mL water			1516	X	X	
Batch 2	$CuCl_2.2H_2O$	662	0.06							
Batch 3	$CuCl_2.2H_2O$	94*	0.44*	stir 24 h, (centrifuge, decant, rinse)x3 (orig. 16:1, 2.64M)	150C	10% H2 bal. Ar	3326	X	X	X
					125C	10% H2 bal. Ar	3006			X
Batch 4	$CuCl_2.2H_2O$	13	3.14	stir 24h, centrifuge 3000 RPM 1h, dry under vacuum overnight	150C	10% H2 bal. Ar	700	X		
					100C	vac. 42h	732			
					150C	10% H2 bal. Ar	773			
Batch 5	$CuCl_2.2H_2O$	62	0.67	stir 24h, centrifuge 3000 RPM 1h, evaporate overnight	300C		2425	X	X	
					500C		2323	X		
					O2 plasma 10 min		2014	X		
Batch 6	$Cu(NO_3)_2.2.5H_2O$	66	0.63	3000 RPM 1h, evaporate overnight	150C	H2	2111	X	X	
					175C	H2	1042*	X		
					200C	H2	2079	X		
Batch 7	$Cu(NO_3)_2.2.5H_2O$	120	0.35	3000 RPM 1h, evaporate overnight	200C	H2	2600	X	X	
Batch 8	$CuCl_2.2H_2O$	120	0.35	3000 RPM 1h, evaporate overnight						

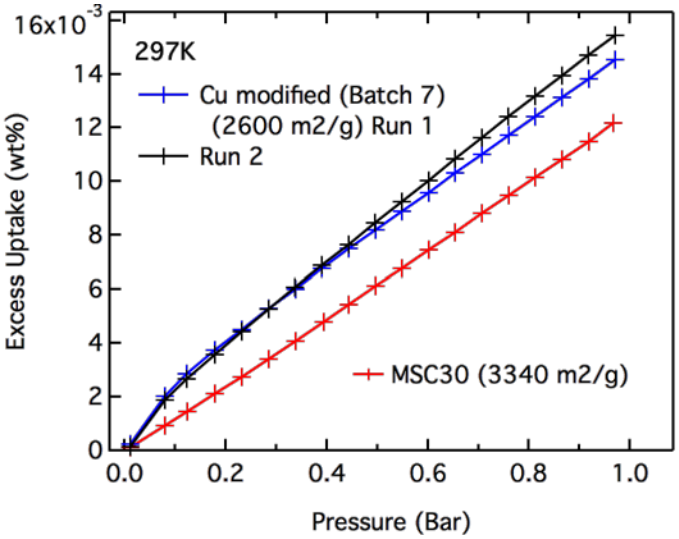
Progress to date on increasing isosteric heat and surface packing densities



Above: Initial ambient temp. low pressure Sieverts isotherm data indicating enhancement with Cu modification.

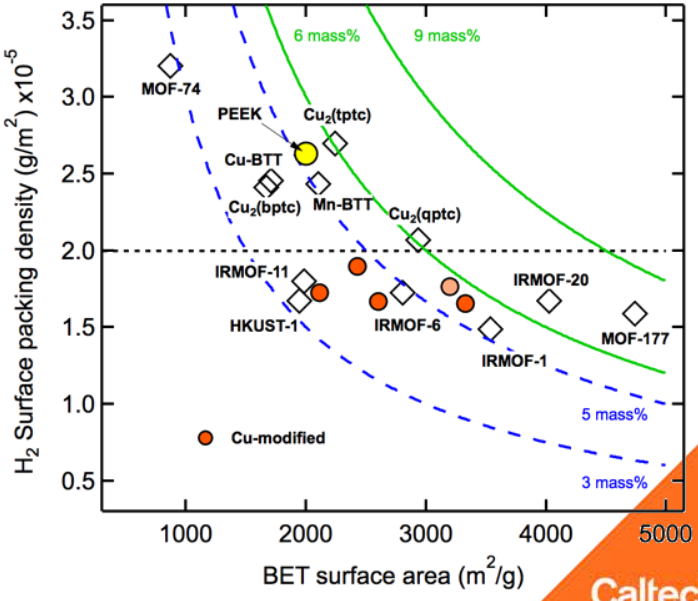


Above: 77 K isotherms showing surface area dependence.



Above: Validation of ambient temp. low pressure BET isotherm data indicating enhancement with Cu modification.

Right: Overlay of surface packing densities from Cu modified carbon from this work (red circles) compared to literature values.



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Accomplishments: Completed milestones since 2016 AMR

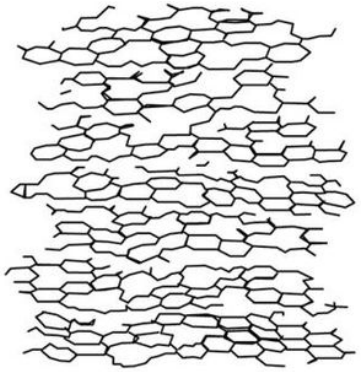
3	Develop Sieverts method for rapid turnaround by measuring fewer data points (able to measure 1 sample / day). Results should be comparable to full isotherms at 77 K and 87 K to within 5%. Method must 1) obtain parameters to check Chahine rule, and 2) obtain sorption at low coverage to measure isosteric heat (Henry's Law regime).	Milestone	4/30/16	100%	Completed.
4	Validation of graphene syntheses of Caltech graphenes and LLNL graphene oxide based graphenes, BN 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	Milestone	7/31/16	100%	Completed.
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.	Go/No-Go	7/31/16	✓	
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	Milestone	10/31/16	100%	Completed.
6	Scale up to 300 mg quantities with gravimetric and volumetric capacities within 5% of the performance observed for small batch material	Milestone	1/31/17	100%	Completed.
7	Deposit sub-nm clusters of metal atoms by plasma deposition on surfaces of two carbon materials, tentatively a carbon aerogel and MSC-30 while reducing the initial sample surface area by <10%. Alternative techniques may use wet chemistry. Assess the metal cluster sizes, and identify control parameters.	Milestone	4/30/17	100%	Completed.
8	Demonstrate an improvement in average isosteric heat, including an isosteric heat of adsorbption in the Henry's law regime of >10kJ/mole H_2	Milestone	7/31/17	50%	Started.

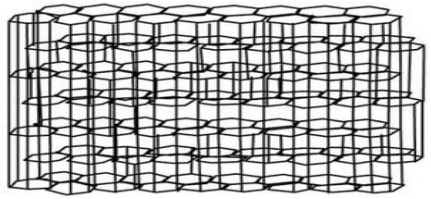
Remaining Challenges and Barriers

- Refinement of graphene syntheses and surface area modification to promote planar structures.
- Improvement to uniformity of Cu atom distribution within graphene microstructure.
- Increasing Cu (and Ni) concentration in a way that minimally diminishes gravimetric uptake.
- Validation/understanding of changes to isosteric enthalpy.

Proposed Future Work:

Emphasis on plasma synthesized graphene with vertical walls that have turbostratic stacking (and not a-b)





Refinement of metal functionalization with larger coverage of Cu (and Ni) incorporated with small size.

Greater interaction with PNNL for TEM analysis.

Validation of results with HySCORE facility.

Summary

- Objective: To promote high surface packing density and high constant isosteric enthalpy in graphene-based adsorbents.
- Relevance: Adsorbents take up, store and release H_2 in molecular form, minimizing activations barriers associated with bond breaking and/or solid state diffusion as required typically in other types of media, but typically low enthalpy of adsorption requires low temperatures.
- Approach: Use of graphene based structures to promote high volumetric and gravimetric density adsorbents and to serve as a platform for functionalization.
- Accomplishments: Syntheses of relatively large quantities of graphene-based materials and initial functionalization efforts toward appropriate dimensions.
- Collaborations: HySCORE, Cealtech AS, Liox Power, Inc.

Technical
Backup Slides

Accomplishments and Progress:
Responses to Previous Year Reviewers' Comments

"Overall, the project was not well defined."

Slides 3-6

…"why specific metals are under consideration"

Slide 5

"major problems: the lack of defect sites in graphene"

Slide 12-13

Relevance: Prior Cu-H_2 interaction studies

Studies from the late 70's and early 80's note unusual Cu-H_2 interactions with activation barriers not seen with other transition metals.

Typical adsorption energies from Cu surfaces a relatively weak ~2.3 to 3 kJ/mol.

Spectra at right indicate high thermal desorption temperatures (>ambient) possible from H_2 and D_2 on Cu surface.

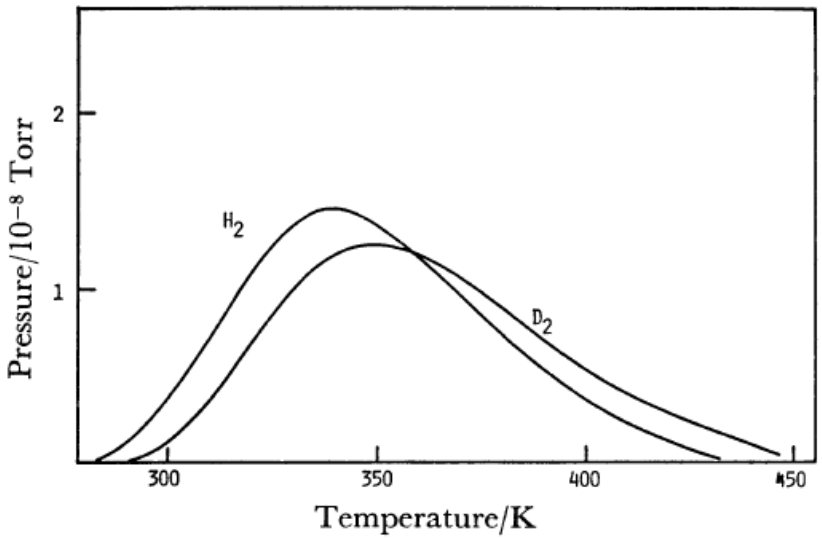
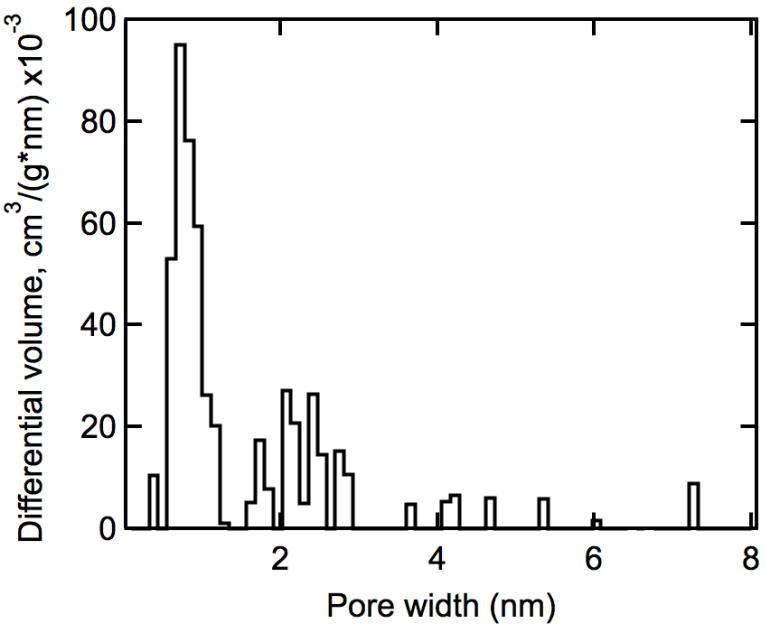


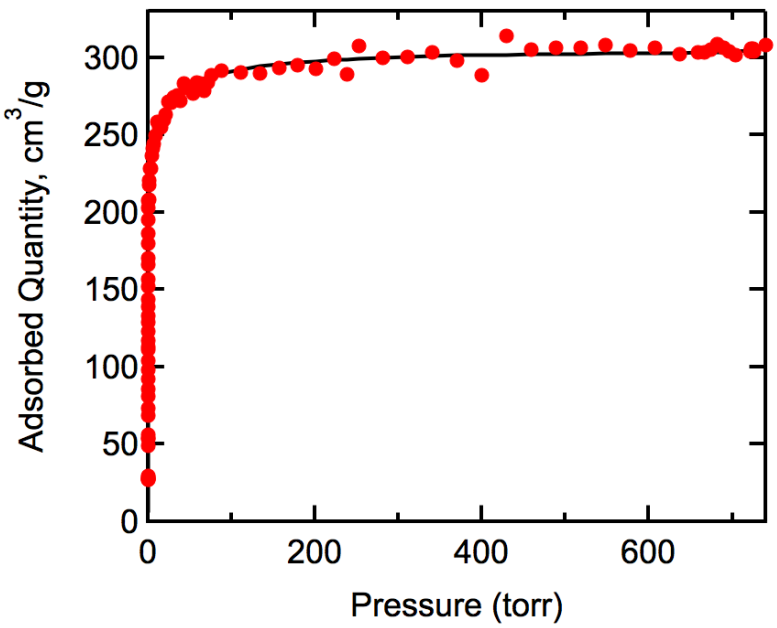
Fig. 2. Thermal desorption spectra of hydrogen and deuterium on copper surface.

"Thermal desorption of hydrogen adsorbed on Copper Surface," I. Kojima, M. Kiyomiya and I. Yasumori, Bull. Chem. Soc. Jpn, 53, 2123-2127 (1980).

Approach/Accomplishments: Pore distribution data analysis

Horvath-Kawazoe analysis of commercial packages inadequate[1].
We have adopted modified Kelvin approach adopted to account for finite pore dimensions[2].

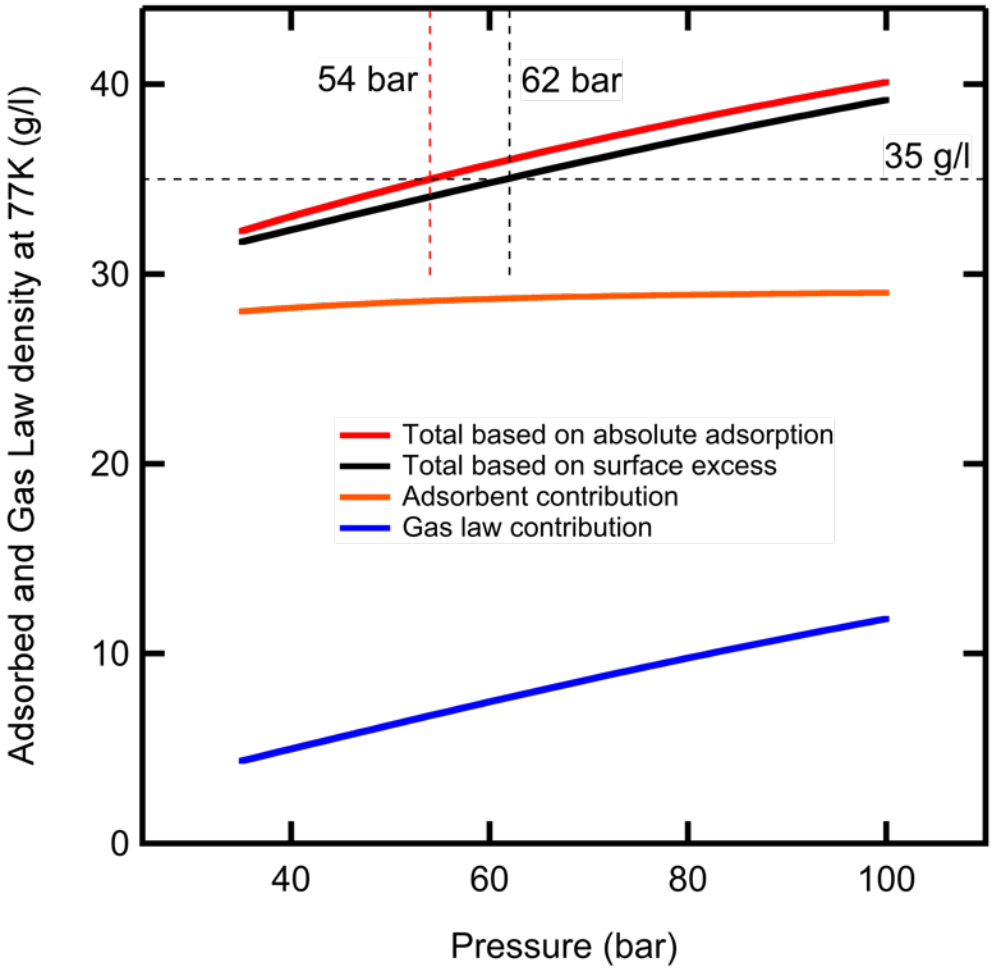




[1] G. Horvath and K. Kawazoe, "Method for the calculation of effective pore size distribution in molecular sieve carbon," J. Chem. Eng. Japan, 16, 6 (1983).
[2] C. Nguyen and D.D. Do, "A new method for the characterization of porous materials," Langmuir 15, 3608-15 (1999).

Accomplishments: Year 1: Project Summary

Go/No-Go



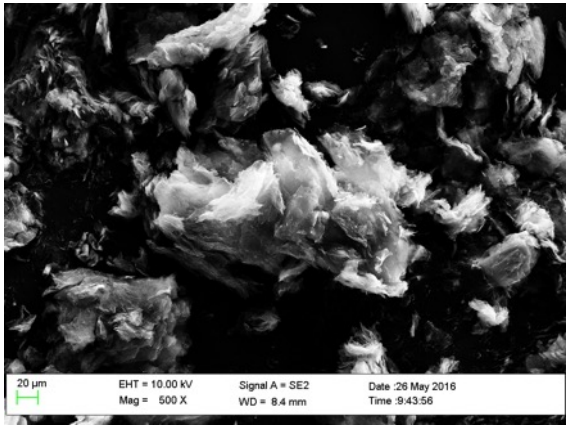
This plot summarizes the various contributions to the overall density of a one liter container at 77K over a pressure range of 35 to 100 bar. The gas law contribution as calculated from the equation of state is shown at the bottom in blue for a 0.378 liter volume. The contribution to the gas density from the adsorption of H_2 is shown in orange (calculated on the basis of absolute adsorption using a two site Langmuir model) and the total density is shown in the upper trace in red. The 35 g/l Go/No-Go target is achieved at 54 bar pressure under these conditions.

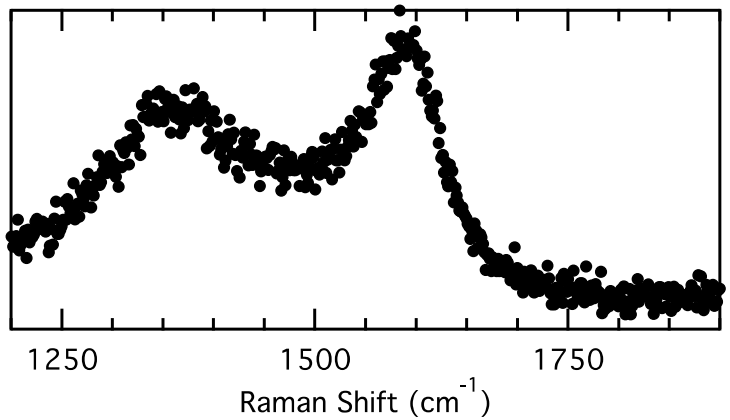
Accomplishments: Year 1: Project Summary

Bulk GO Modification needed to achieve high surface areas.

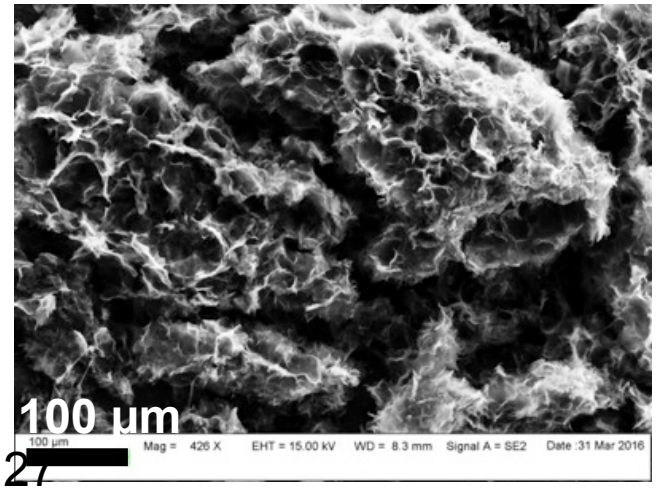
- Microwave processing “reduces” GO
- High temp KOH activation to complete surface area enhancement.

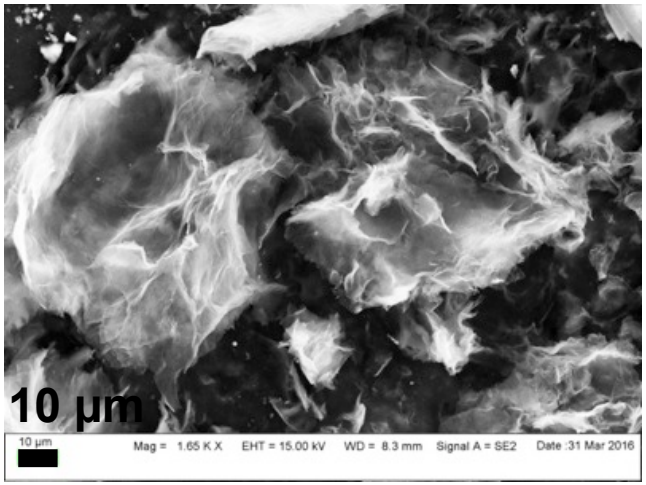
Microwave processed GO:





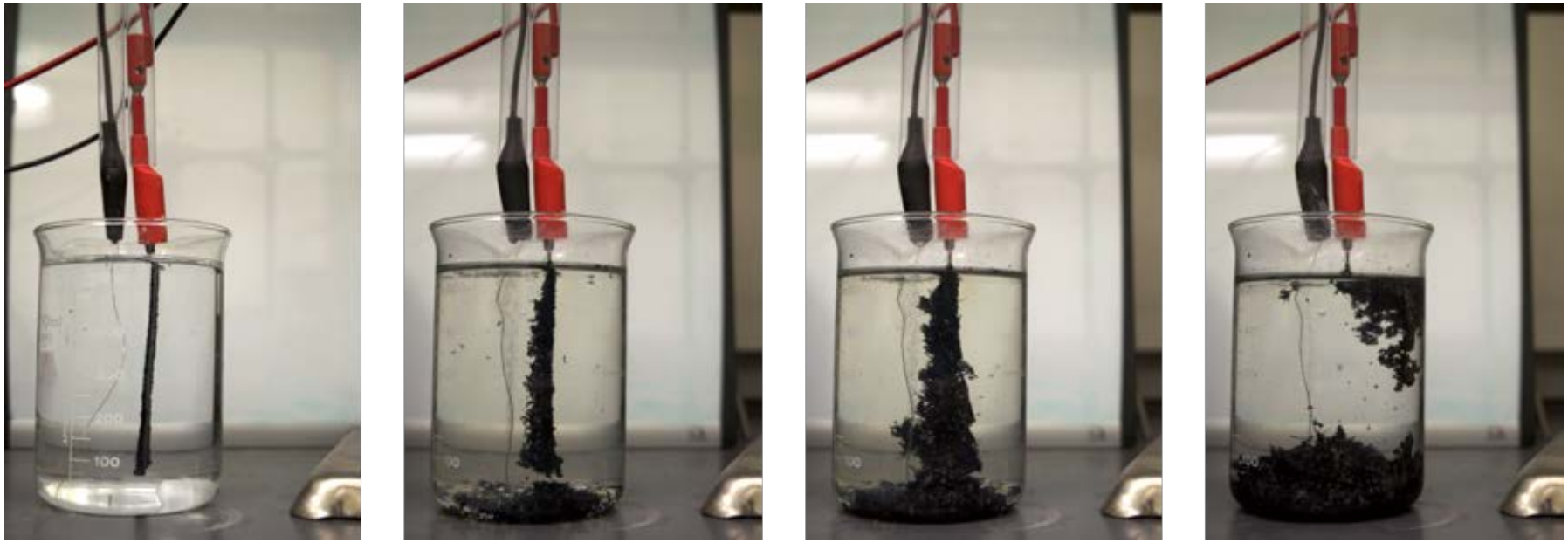
KOH activation of microwaved GO:





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

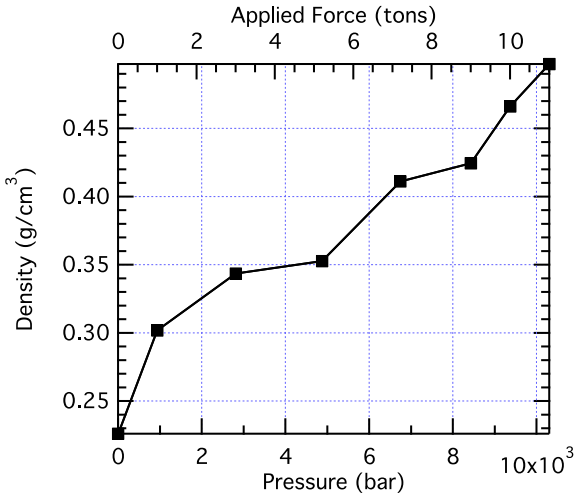
Approach/Accomplishments: Electrochemical synthesis of graphene-based carbon

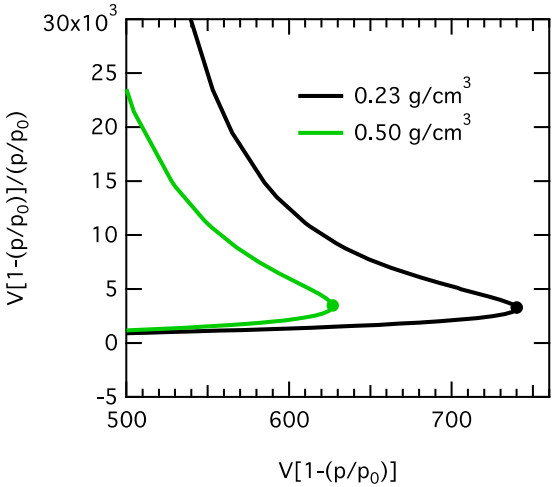


Time lapsed sequence (over 20h) of the exfoliation of graphite foil in ammonium sulfate solution against Pt wire at 5V.

Accomplishments: Year 1: Project Summary

Materials Compression to increase bulk density to 0.5 to 0.7 g/cc





Caltech

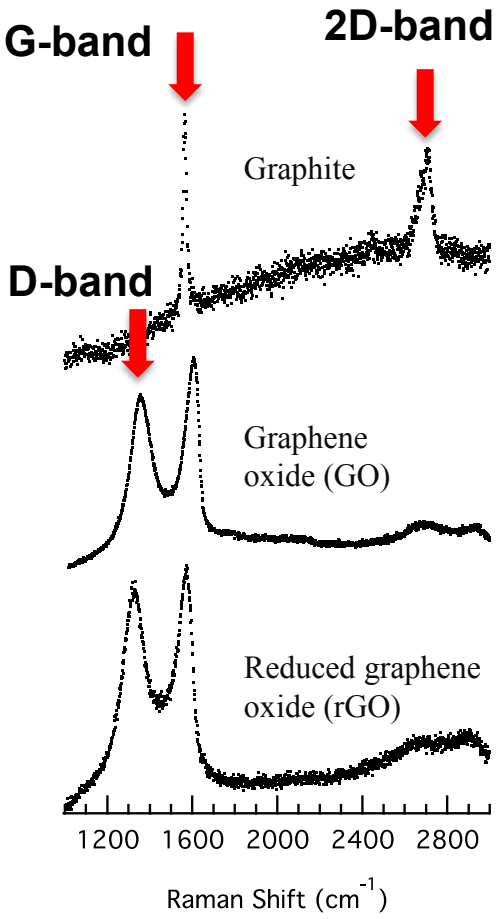
Approach/Accomplishments: Materials Characterization Library

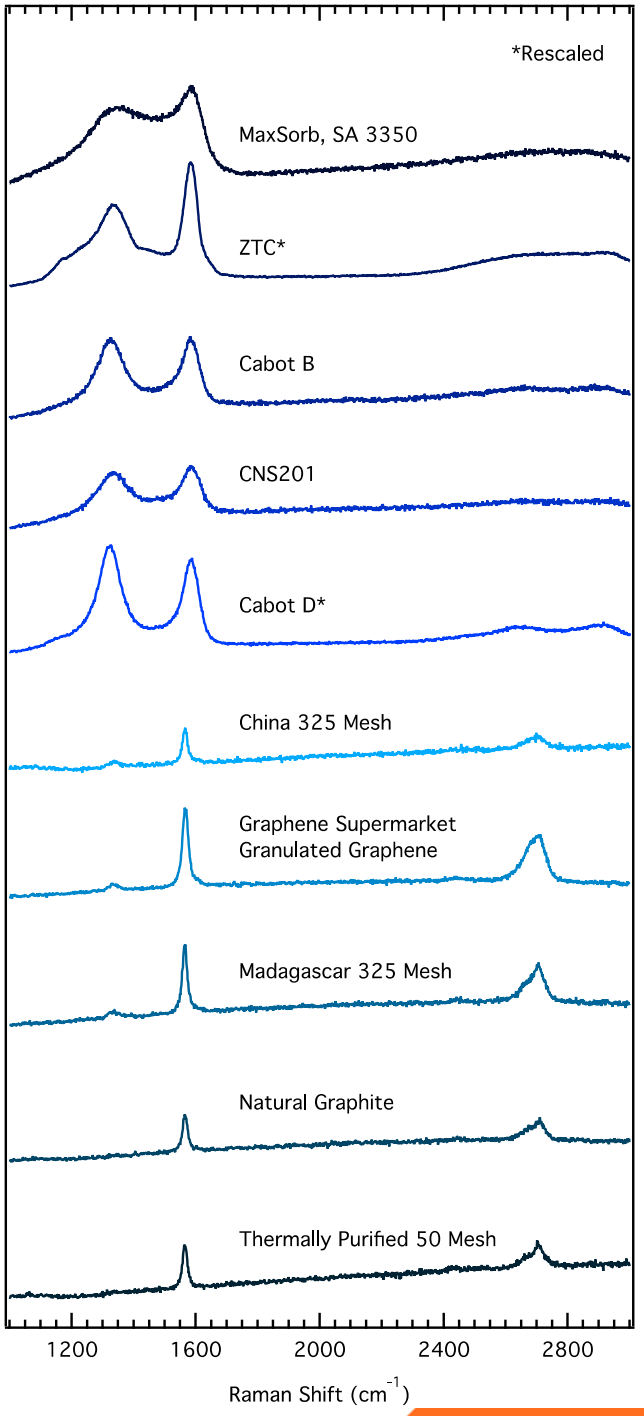
Enables baseline understanding of processing and measurement approaches

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:

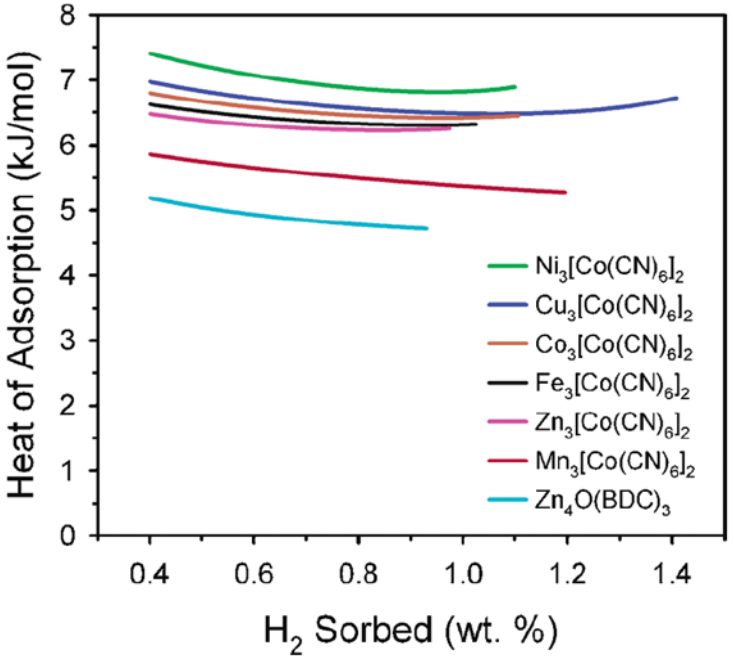




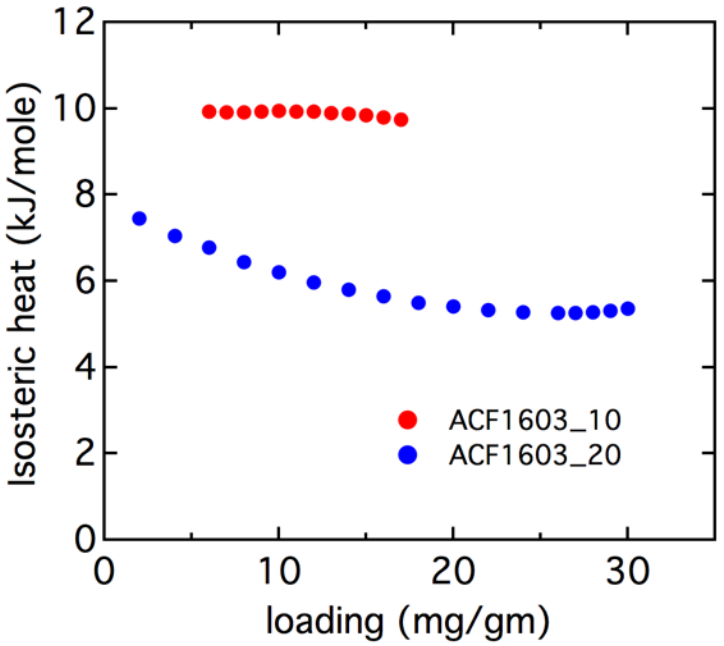
Approach: "Absolute" uptake determination to gauge functionalization effort

The "isoexcess" enthalpy typically derived from measured surface excess data but application of Clausius-Clapeyron for actual isosteric heat determination requires "absolute" data.

Isosteric enthalpy typically decreases with increasing density. Retrograde behavior due to use of "isoexcess" data.

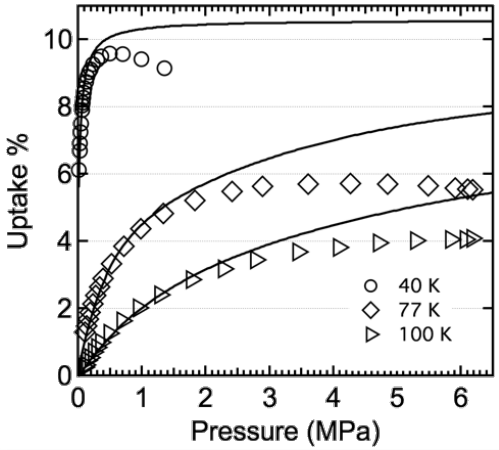


Kay, S. S.; Long, J. R. *J. Am. Chem31. Soc.* **2005**, 127, 6506.



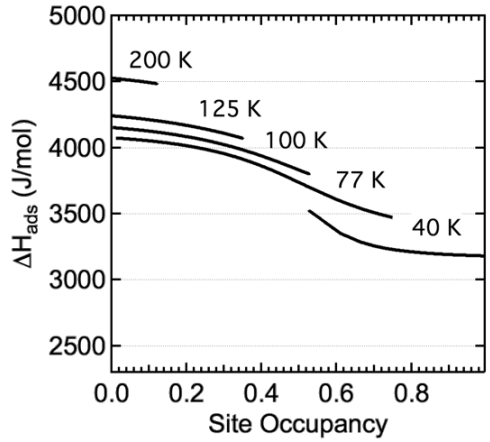
Ahn, CC, DOE Annual Merit Review ST23, 2008.

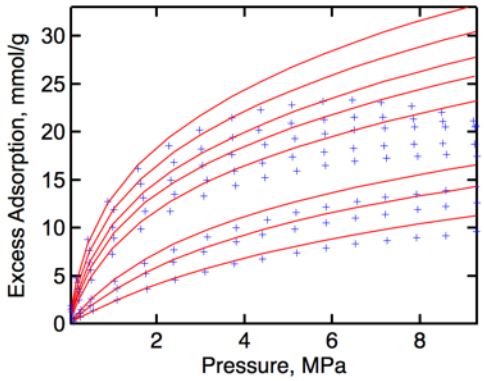
Approach: Two site Langmuir approach[a] to obtain absolute uptake



Algorithm requires us to set $dq(p,T)/dT = 0$, and solve for $\partial P/\partial T$, where $dq/dT = 0$

[a]From: F.O. Mertens, "Determination of absolute adsorption in highly ordered porous media", Surf. Sci., 603, 1979-1984 (2009).



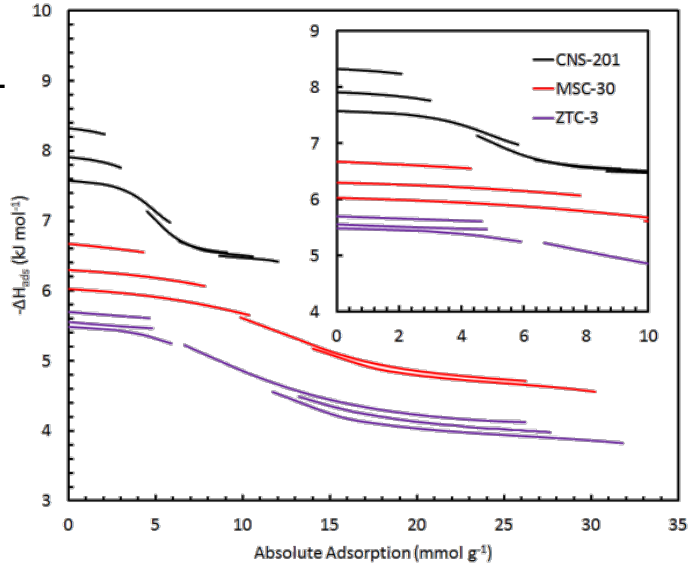


Solid lines from isotherms above are calculated absolute uptakes determined from experimental data (markers)

Algorithm implemented using Igor procedure with 3 command-line instruction set shown below with data intercept values.

gotoIsothermFit(material, gas)
gotoAbsoluteVsExcess(material,gas)
gotoIsostericheat(material, gas)
Aadith Moorthy (Caltech 2018)

(253 K) = 12.7964 kJ/mol
(263 K) = 12.8326 kJ/mol
(274 K) = 12.8181 kJ/mol
(283 K) = 12.9044 kJ/mol
(297 K) = 12.9975 kJ/mol
(349 K) = 13.1297 kJ/mol
(376 K) = 13.4175 kJ/mol
(423 K) = 13.6633 kJ/mol



Two site Langmuir applied above[b] to relevant carbons; note isosteric enthalpy dependence on temp. range.

[b] From N. Stadie, "Synthesis and Thermo-dynamic Studies of Physisorptive Energy Storage Materials," Ph.D. Caltech (2013)