Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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Caltech

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Overview

Timeline:

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

Budget:

- Funds spent through 03/31/2018: $897,341
- 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) (NREL, Gennett)
- Project lead: Caltech

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Relevance: Motivation for using graphene-based carbon

<u>Objectives</u>:

  a. Maximizing the surface-to-volume ratio of adsorbents to maximize hydrogen volumetric densities
  b. Use of metal additives to effect electron transfer to graphene substrate to increase isosteric enthalpy of adsorption DH over typically low values of 4-6 kJ/mole.
  c. Graphene adsorbents have stability against water and oxidation
  d. Slit pore geometry near optimal for gas diffusion

<u>Impact</u>:

  a) Increases of ΔH in Henry's Law regime were achieved through transition metal incorporation.
  b) Bimodal ΔH, with higher ΔH compatible with 340 K sorption

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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 previously. Literature approaches inadequate for producing relevant microstructure and dropped by this effort.
- 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

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Approach cont'd: Vertically grown graphene as the basis for bottom up platform

D. Boyd standing in front of the Forza reactor for producing graphene, now in production in Norway. The reactor is open in the picture, revealing the belt (about 1m in width) covered in graphene, visible from the black regions.

1 µm   EHT = 10.00 kV   Mag = 25.00 K X   WD = 7.8 mm   Signal A = InLens   Date :11 Aug 2017
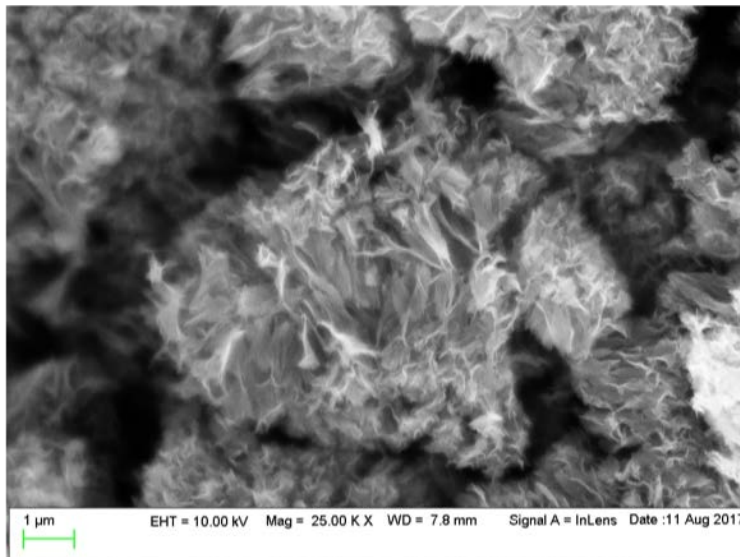
Progress continues towards scale-up of graphene production at the company using Caltech-licensed technology. (Above right) The magnitude of quantities produced is visible from the material (black) being scraped off the belt (silver). (Left) SEM images shows vertical graphene without the fibrous material seen in earlier batches.

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Accomplishments: Transition metal incorporation

Copper

Batch	Salt	C:Cu (atom ratio)	Cu:C (atom ratio)	salt conc. (M)	Processing	Heat Treatment	Gas type	Surface Area (m2/g)	XRF	SEM	EDS	BET 77K	BET 240K	BET 300K	BET 320K	Sieverts 77K	Sieverts 240K	Sieverts 300K	Sieverts 320K
Batch 1	$CuCl_2\cdot2H_2O$	3366	0.0003	0.012	stir 2h, filter, rinse with 100 mL water			1516	X	X	X					X			
Batch 2	$CuCl_2\cdot2H_2O$	662	0.0015	0.06															
Batch 3	$CuCl_2\cdot2H_2O$	94*	0.0106	0.44*	stir 24 h, (centrifuge, decant, rinse)x3 (orig. 16:1, 2.64M)	150C	10% H2 bal. Ar	3326	X	X	X					X		X	
						125C	10% H2 bal. Ar	3006											
Batch 4	$CuCl_2\cdot2H_2O$	13	0.0769	3.14	stir 24h, centrifuge 3000 RPM 1h, dry under vacuum overnight	150C	10% H2 bal. Ar	700	X	X	X								
						100C	vac. 42h	732											
						150C	10% H2 bal. Ar	773											
Batch 5*	$CuCl_2\cdot2H_2O$	62	0.0161	0.67	stir 24h, centrifuge 3000 RPM 1h, evaporate overnight	300C		2425	X	X	X			1		X		X	
						500C		2323	X	X	X								
						O2 plasma 10 min		2014		X	X								
Batch 6*	$Cu(NO_3)_2\cdot2.5H_2O$	66	0.0152	0.63	3000 RPM 1h, evaporate overnight	150C	H2	2111	X	X	X	2		5					
						175C	H2		X	X	X								
						200C	H2	2079	X	X	X					X		X	
Batch 7	$Cu(NO_3)_2\cdot2.5H_2O$	120	0.0083	0.35	see Batch 6	200C	H2	2600	X	X	X	2		4		X		X	
Batch 8	$CuCl_2\cdot2H_2O$	120	0.0083	0.35	see Batch 5														
Batch 9	$Cu(NO_3)_2\cdot2.5H_2O$	178	0.0056	0.23	see Batch 6	200C	H2	2943	X	X	X	2	4	8	1	X	X	X	X
Batch 10	$Cu(NO_3)_2\cdot2.5H_2O$	235	0.0043	0.18	see Batch 6	200C	H2	3177	X	X	X	1	1	5	1				
Batch 11	$Cu(NO_3)_2\cdot2.5H_2O$	117	0.0085	0.35	see Batch 6	200C	H2	2135	X	X	X	2		9					
Batch 12	$Cu(NO_3)_2\cdot2.5H_2O$	150	0.0067	0.28	see Batch 6	200C	H2	2174	X	X	X	2		8					

Nickel

Batch	Salt	C:Ni (atom ratio)	Ni:C (atom ratio)	Processing	Heat Treatment	Gas type	Surface Area after H2 annealing (m2/g)	Surface Area after 12h in vac.	Percent Change	XRF	SEM	EDS	BET 77K	BET 240K	BET 300K	BET 320K	Sieverts 77K	Sieverts 240K	Sieverts 300K	Sieverts 320K
Batch 1	$Ni(NO_3)_2\cdot6H_2O$	59	0.0169	stirred ~24h	275C 2h	H2	1951			X	X	X	X	X	X	X				
Batch 2	$Ni(NO_3)_2\cdot6H_2O$	62	0.0161	sonicated 180 min	cont.	H2														
Batch 3	$Ni(NO_3)_2\cdot6H_2O$	60	0.0167	sonicated 180 min	275C 2h	H2	1844			X	X	X			X					
Batch 4	$Ni(NO_3)_2\cdot6H_2O$	130	0.0077	sonicated 180 min	275C 2h	H2	2325	2453	5.51	X	X	X	X	X	X	X				
Batch 5	$Ni(NO_3)_2\cdot6H_2O$	120	0.0083	stirred ~24h	275C 2h	H2	2150	2330	8.37	X	X	X	X		X					
Batch 6	$Ni(NO_3)_2\cdot6H_2O$	110	0.0091	stirred ~24h	275C 2h	H2	1868			X			X		X					
Batch 7	$Ni(NO_3)_2\cdot6H_2O$	140	0.0071	stirred ~24h	275C 2h	H2		2458		X										
Batch 8	$Ni(NO_3)_2\cdot6H_2O$	150	0.0067	stirred ~24h	275C 2h	H2		2463		X										

Accomplishments/Progress:

Cobalt

		C:Co atom ratio	Co:C atom ratio	Processing	Heat Treatment	Gas type	Surface Area (m2/g) after H2 annealing	XRF	SEM	EDS	77K	240K	300K	320K
Batch 1	$Co(NO_3)_2 \cdot 6H_2O$	60	0.0167	stirred ~24h	290C 2h	H2	1598	x	x		x		x	
Batch 2	$Co(NO_3)_2 \cdot 6H_2O$	120	0.0083	stirred ~24h	290C 2h	H2	2285	x			x		x	
Batch 3	$Co(NO_3)_2 \cdot 6H_2O$	150	0.0067	stirred ~24h	290C 2h	H2	2289	x	x		x		x	

Zinc

		C:Zn atom ratio	Zn:C atom ratio	Processing	Heat Treatment	Gas type	Surface Area (m2/g) after H2 annealing	XRF	SEM	EDS	77K	240K	300K	320K
Batch 1	$Zn(NO_3)_2 \cdot 6H_2O$	94	0.0106	stirred ~24h	300C 2h	H2		x	x					
Batch 2	$Zn(NO_3)_2 \cdot 6H_2O$	189	0.0053	stirred ~24h	300C 2h	H2		x						
Batch 3	$Zn(NO_3)_2 \cdot 6H_2O$	236	0.0042	stirred ~24h	300C 2h	H2		x	x					

Gold

		C:Au atom ratio	Au:C atom ratio	Processing	Heat Treatment	Gas type	Surface Area (m2/g) after H2 annealing	XRF	SEM	EDS	77K	240K	300K	320K
Batch 1	$HAuCl_4 \cdot 3H_2O$	123	0.0081	stirred ~24h	110C 2h	H2	1841	x	x		x		x	
Batch 2	$HAuCl_4 \cdot 3H_2O$	628	0.0016	stirred ~24h	110C 2h	H2		x	x					

Silver

		C:Ag atom ratio	Ag:C atom ratio	Processing	Heat Treatment	Gas type	Surface Area (m2/g) after H2 annealing	XRF	SEM	EDS	77K	240K	300K	320K
Batch 1	$AgNO_3$	60	0.0167	stirred ~24h	377C 2h	H2								
Batch 2	$AgNO_3$	120	0.0083	stirred ~24h	377C 2h	H2	1445	x	x		x		x	
Batch 3	$AgNO_3$	180	0.0056	stirred ~24h	377C 2h	H2	2084	x	x		x		x	

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Accomplishments/Progress: Transition metal incorporation toward enthalpy modification at the nanoscale
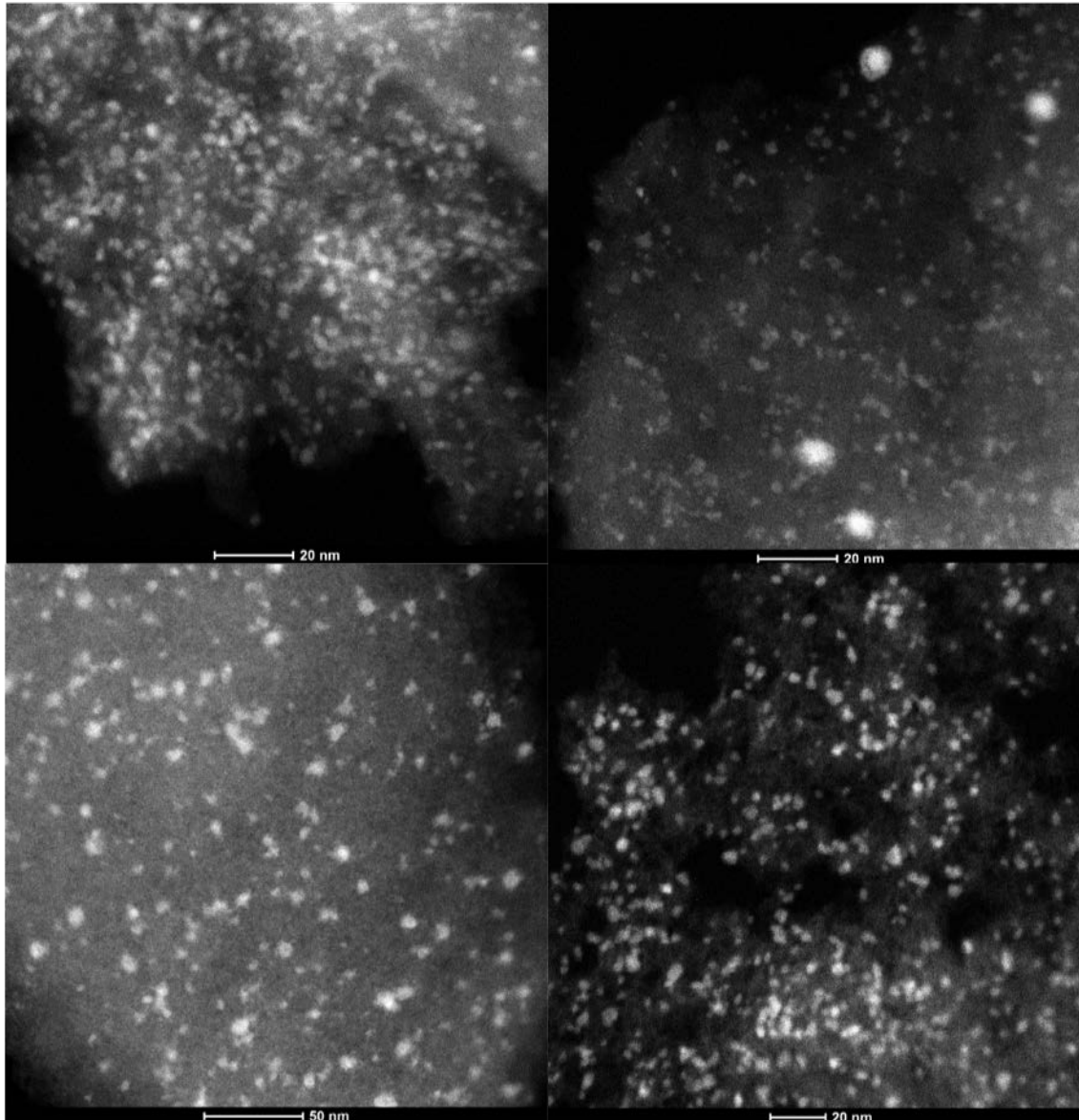
- Some results of transition metal salt incorporation validating nano-scale dimensions of metal species.
- Samples had oxidized during storage, transport and handling before micrographs (courtesy of M. Bowden, PNNL, HYSCORE) were taken.
- All metal incorporated samples showed enhanced Henry's Law enthalpy except for the Zn sample.

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Accomplishments: Establishing metal incorporation concentration via TGA
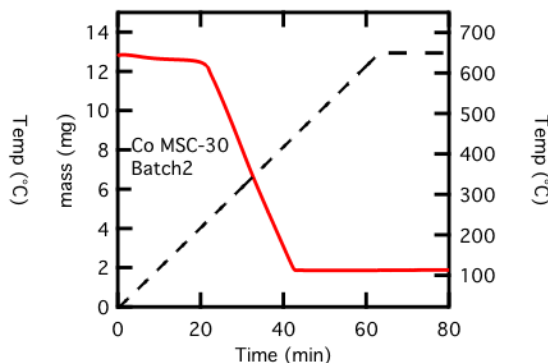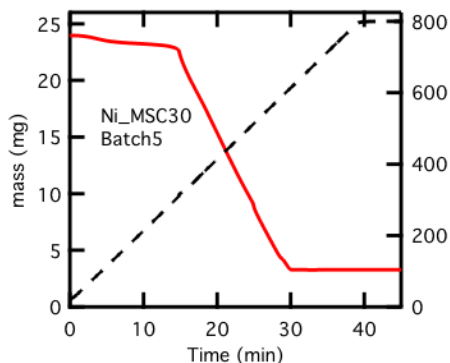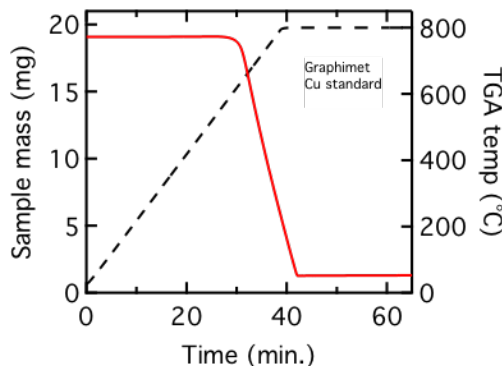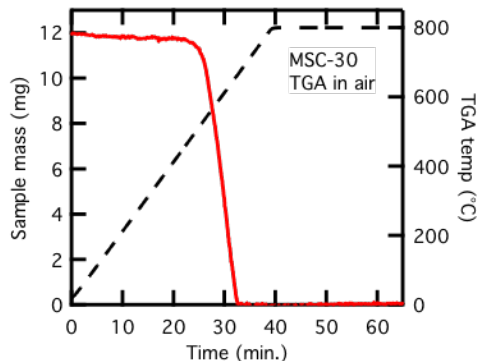
Prior x-ray fluorescence (XRF) data gave semi-quantitative metal concentrations.

"Burning" the sample in air to convert the carbon into CO_2 and oxidize the metal via Thermogravimetric analysis (TGA) resulted in reliable quantification of metal concentrations of the as-synthesized material.

Thermogravimetric Analysis (TGA) results for the heating of pristine carbon (upper left) and metal-functionalized materials in air. Continuous heating of the samples to at least 650°C in air causes complete loss of the carbon matrix, leaving behind fully oxidized metals. Metal funtionalized quantities were 11 wt% (2.5 at%) for the Ni containing sample (lower left), 5.4 wt% Cu in a commercial "graphimet" test sample (manufacturer specified 4.53% (upper right) and 11 wt% (2.2 at%) Co in the lower right. Results can be normalized for quicker XRF analysis.

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Accomplishments: Sieverts measurements
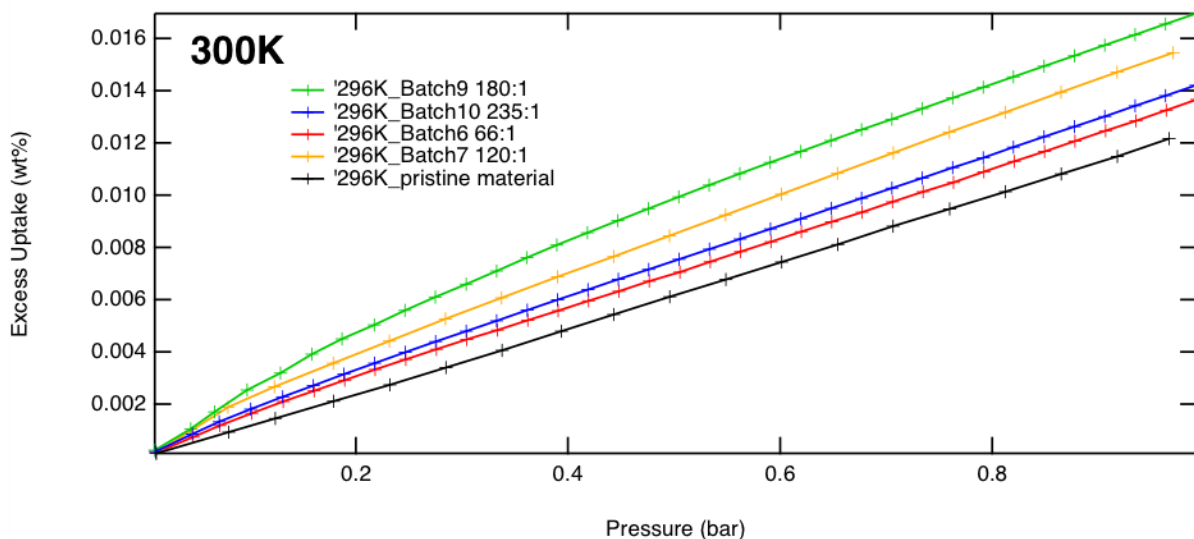
Left: Excess hydrogen uptake as a function of pressure at 300K for several difference concentrations of Cu metal all show an enhanced uptake compared to pristine material.

Below: Hydrogen adsorption measurements at 77K and up to 30 bar for materials with varying metal concentrations as compared to unmodified MSC30. The top plot shows the excess uptake, and the bottom plot shows the same results normalized by the specific surface area.
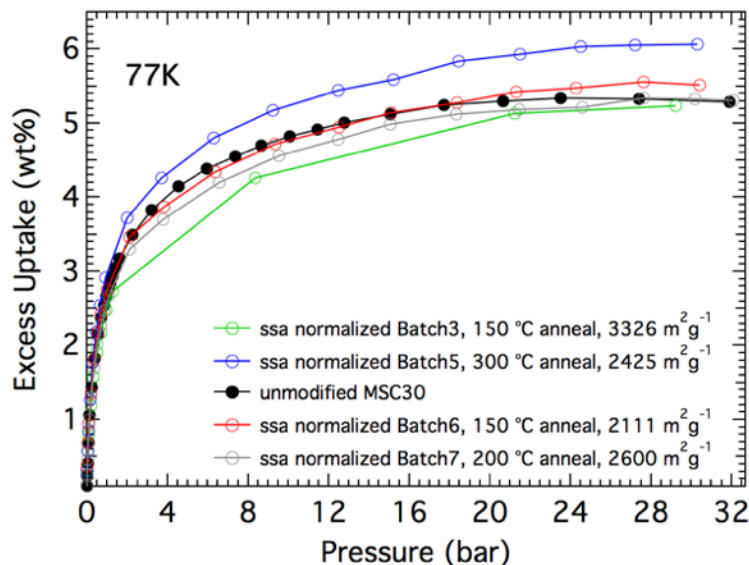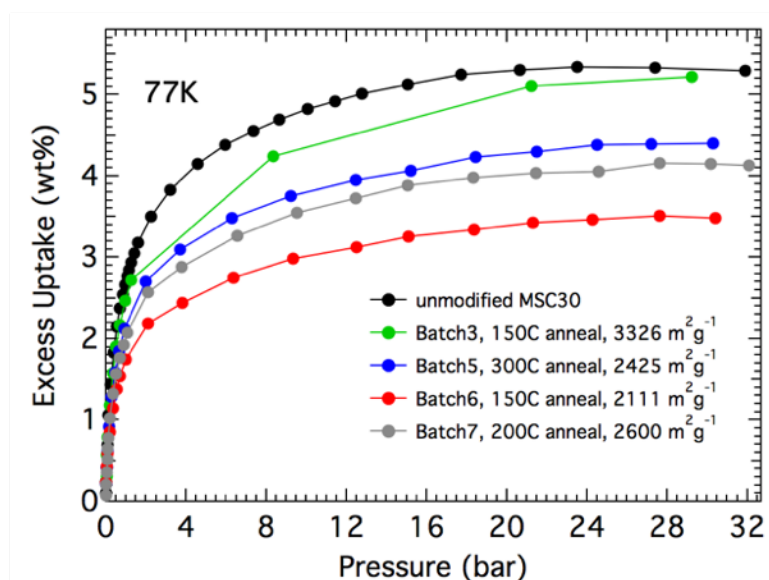
Accomplishments: Isosteric Heat Enhancement from transition metal incorporation
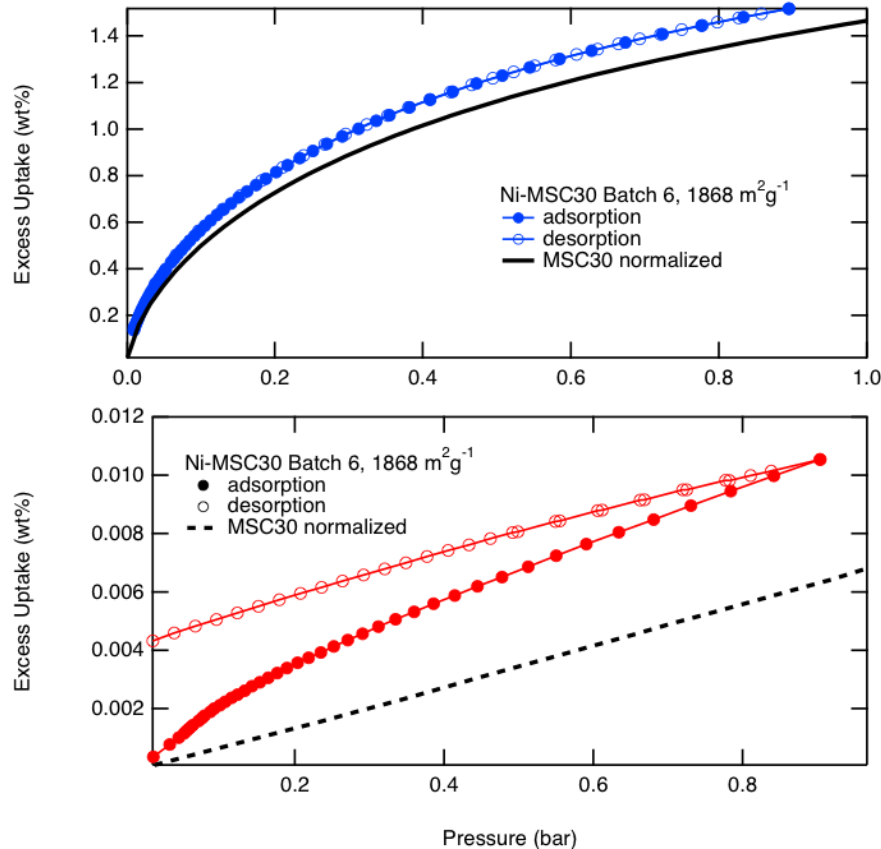
Enhancement seen with Ni (and Cu and Co containing samples)
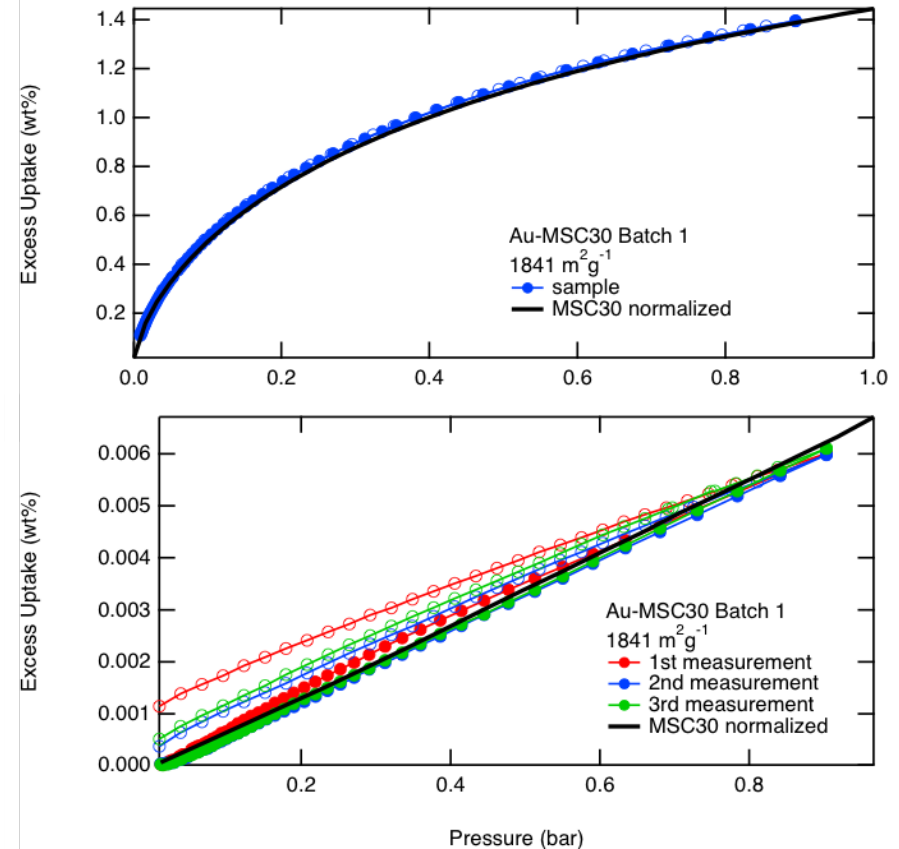
Enhancement not seen in Au

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Accomplishments: Summary of synthesis and characterization of metal-functionalized material and uptake enhancement
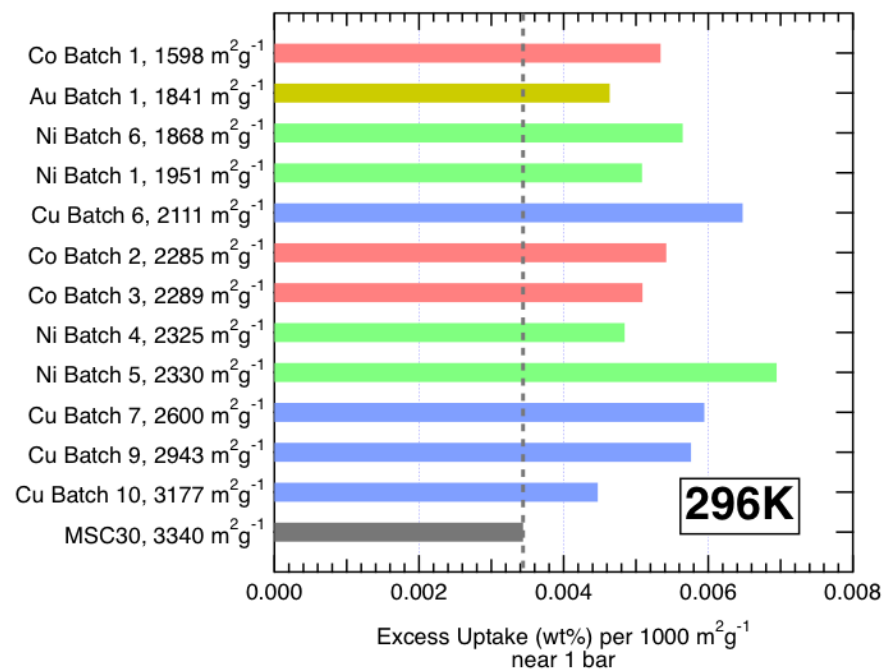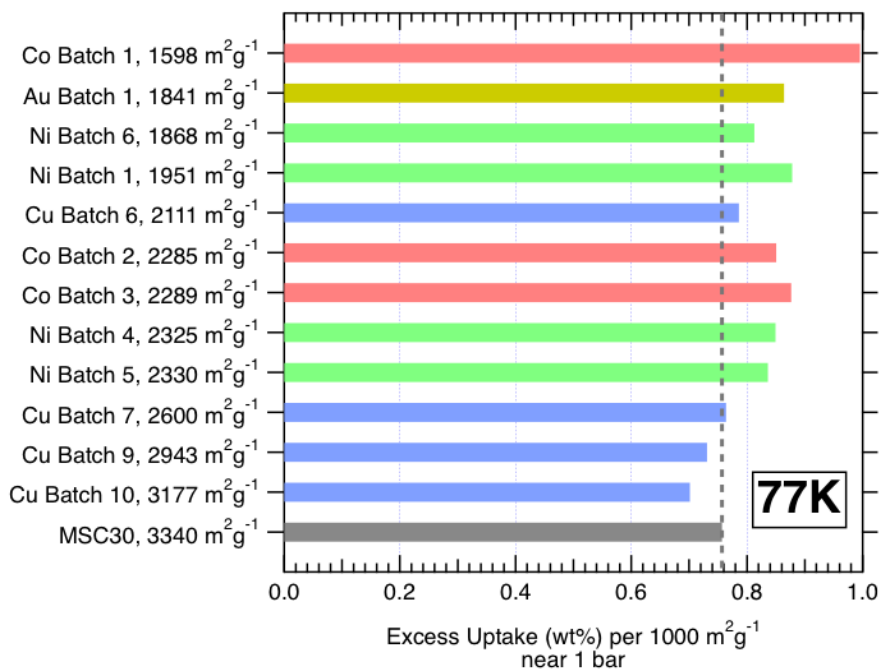
Many metal functionalized materials show higher excess uptake per unit surface area than pristine materials at both 77K and 296K

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Henry's Law analysis

Improvement to isosteric heat of adsorption in Henry's Law analysis, or a "differential enthalpy of adsorption at zero coverage" as developed by Cole et al [1]

Above right: shows the uptake for Batch 9 material at three temperatures over a range in pressure suitable for Henry's Law analysis.

Values are extracted from the slope of the plot in figure at right, which plots the parameter k_H as a function of inverse temperature, for which k_H is defined as:

$$k_H H = \lim_{p \to 0}(n/p)$$

ΔH of -10.8 kJ for 240 and 296K,
ΔH of -14.4 kJ for 319K data.
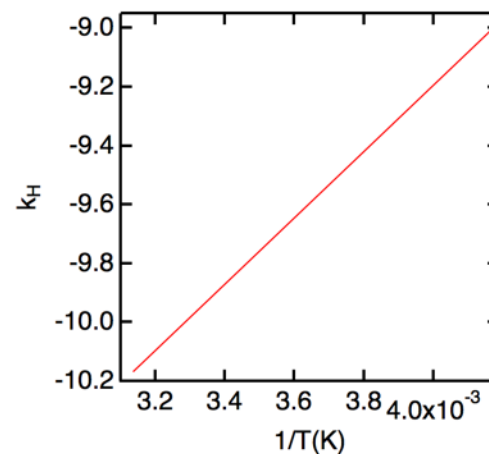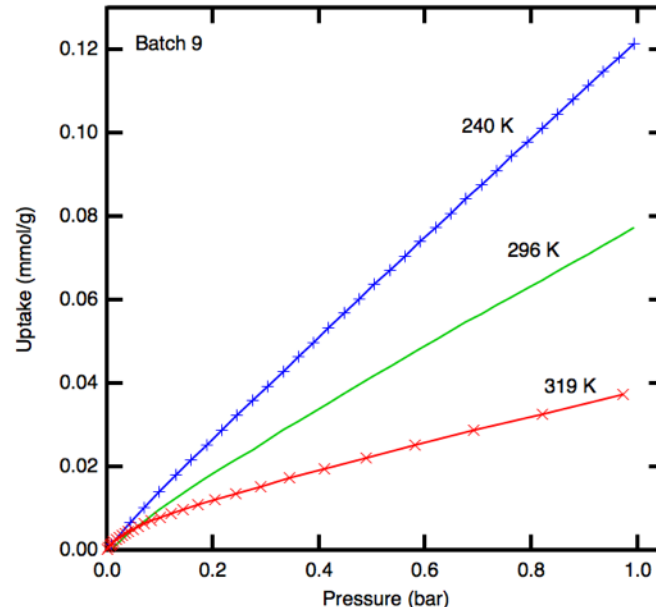
[1] J.H. Cole, D.H. Everett, C.T. Marshall, A.R. Paniego, J.C. Powl and F. Rodriguez-Reinoso, "Thermodynamics of the High Temperature Adsorption of some Permanent Gases by Porous Carbons," J. Chem. Soc. Faraday Trans. I 70, 2154 (1974).

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Accomplishments/Initial TPD results courtesy of NREL (Gennett, HYSCORE)
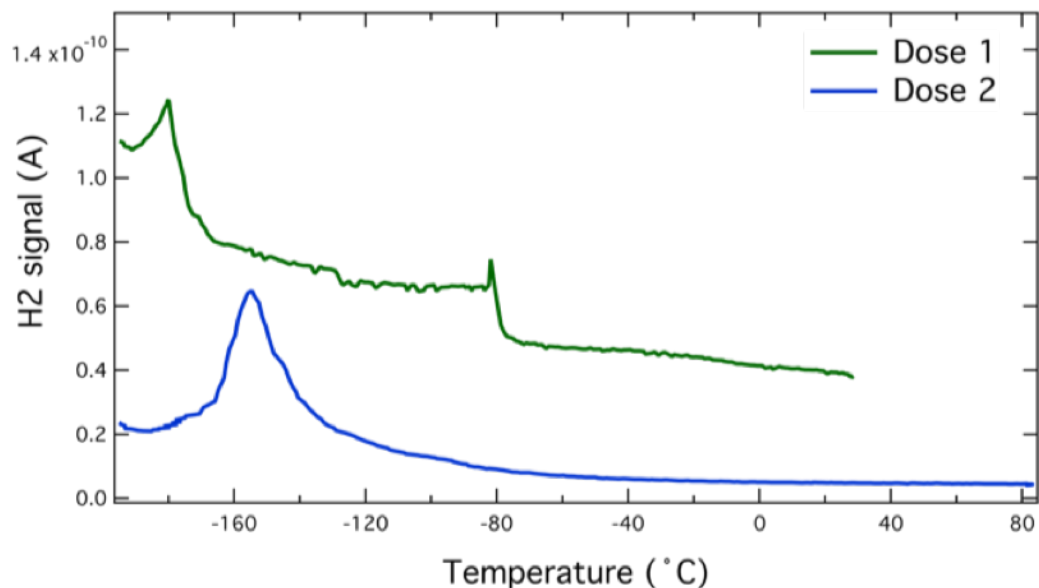
Above: Thermal programmed desorption measurements (TPD) showing the hydrogen signal from a Ni-containing sample. The sample was measured twice- green and blue represent the first and second runs, respectively. Sample was pumped to base pressure 10^{-8} Considerable water in sample, due presumably to atmosphere exposure. The first dose without degas showed very little hydrogen. Second dose after a 3 hr degas at 80 $^\circ$C. Physisorption peak, possible one small peak at approx -100 $^\circ$C. The peak intensity is about 100x less than expected for the surface area quoted.

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Accomplishments/Initial Caltech TPD results
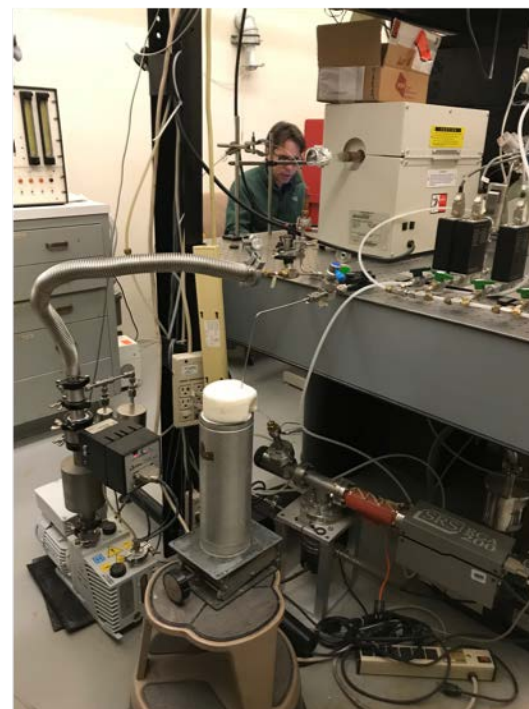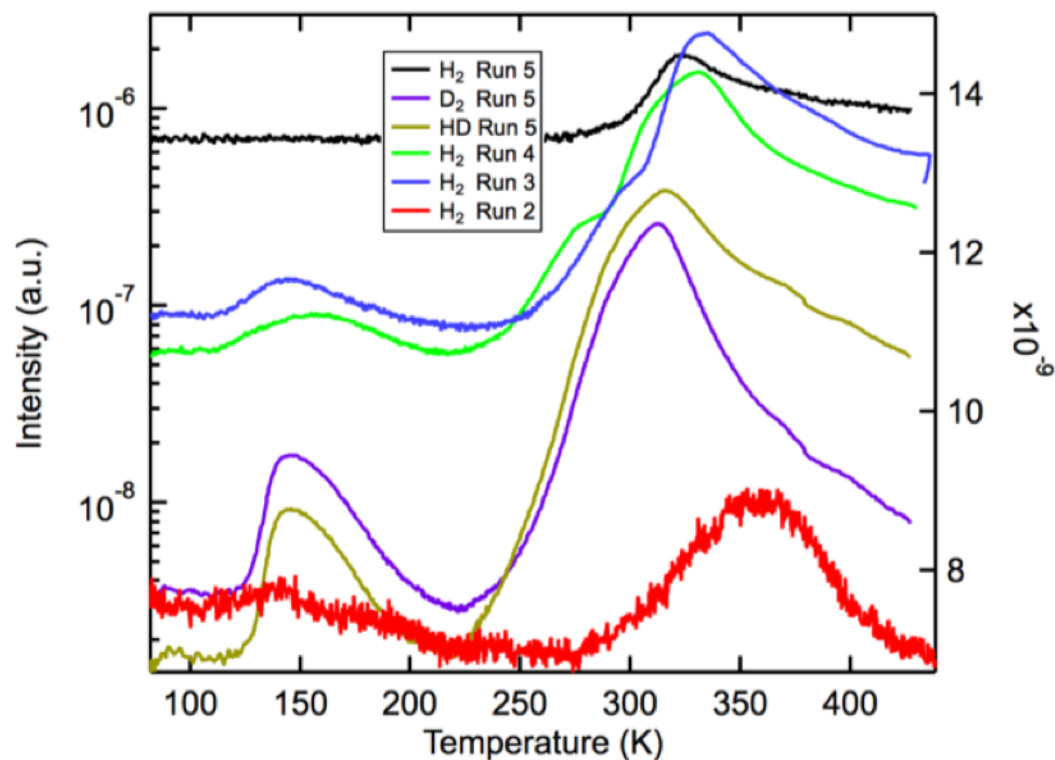
Left: To improve turnaround, a Caltech TPD system adopted in D. Boyd's lab. H_2 release at 140 K and 340 K likely physisorption or Kubas type binding. Initial tests on Cu nano-particles show H_2 and D_2 results with evidence of isotope mixing using generic TPD processing conditions, as above.

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.

- Measure $H_2 + D_2 \rightarrow HD$ for different Cu, (Ni (Co) depositions on graphene related carbons.

- Evaluate conversion for 140 K and 340 K hydrogen release.

- Validation of changes to isosteric enthalpy.

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Proposed Future Work:

Continued emphasis on optimized 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 another analysis facility.

Any proposed future work is subject to
change based on funding level

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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 transition metal functionalization efforts toward appropriate dimensions.

- Desorption observed at 340 K

- Collaborations: HySCORE

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