

IV.C.14 Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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Overall Objectives

- Develop a carbon-based, functionalized material prepared by new methods (graphene) or old (exfoliated graphite) with a capacity for hydrogen storage by physisorption of 11 wt% excess and 40 g/L total (near 77 K and <100 bar), a near-constant isosteric heat of adsorption, excellent kinetics, and long cycle life. Understand how far hydrogen physisorption capacity can be extended beyond the present rules of thumb for carbon materials (e.g., 1 wt% excess per every 500 m²/gram). The goal is achieving >1.5 wt% excess per every 500 m²/g.
- Demonstrate a near-constant isosteric heat of adsorption, excellent kinetics, and long cycle lives.

Fiscal Year (FY) 2017 Objectives

- Achieve at least 1.3 wt% excess H₂/500 m²/g in graphene based material with >3,000 m²/g specific surface area and 45 g/L total volumetric capacity at pressures less than 100 bar and 77 K.
- Etch 1–2 nm pores in graphene sheet structures and determine if pores contribute <10% to Brunauer–Emmett–Teller (BET) surface area and to hydrogen sorption characteristics.
- Produce 300 mg quantities of material with demonstrated gravimetric and volumetric capacities within 5% of smaller scale material performance.
- Deposit sub-nanometer clusters of metal atoms on surfaces of two carbon materials and demonstrate a reduction in surface area of <10%.

- Demonstrate an improvement in average isosteric heat, an isosteric heat of adsorption in the Henry's law regime of >10 kJ/mole H₂.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) System Weight and Volume
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is developing functionalized graphene materials to maximize hydrogen uptake and increase temperatures of operation. These materials are intended to meet the 2020 DOE hydrogen storage targets for high hydrogen gravimetric and volumetric capacity.

- System gravimetric capacity: 1.5 kWh/kg (4.5 wt% H₂)
- System volumetric capacity: 1.0 kWh/L (30 g H₂/L)

FY 2017 Accomplishments

- Used direct and indirect oxygen and nitrogen plasma as well as focused ion beam exposure to produce holes in monolayer graphene, vertical graphene, graphene nanoflakes, and activated carbon, resulting in holes observed with Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).
- Synthesized and characterized graphene-based carbon in gram quantities. Received initial batches of large-scale plasma grown graphene from a start-up company using Caltech-licensed technology.
- Functionalized materials with varying amounts of copper clusters, achieving surface area reduction of <5% for low copper concentration.
- Demonstrated an improvement in isosteric heat of adsorption in Henry's law regime for copper-functionalized materials at 300 K.



INTRODUCTION

One of the advantages of adsorbents as a storage medium is that dihydrogen retains its molecular form throughout the adsorption/desorption cycle, and the cycle requires minimal activation energy. The primary disadvantage of sorbents is that typical adsorption enthalpies are relatively weak, compared to bond formation with chemical hydrogen, or to interstitial atomic hydrogen in metal hydrides. Additionally, the van der Waals dimension of molecular hydrogen is large in comparison to atomic hydrogen, putting limits on the overall volumetric density that systems based on dihydrogen can achieve.

Graphene-based materials offer an excellent starting platform for hydrogen sorption owing to their high surface area for dihydrogen adsorption. The key step is to optimize functional groups on the graphene for maximizing the volumetric density of dihydrogen adsorption. Part of the effort at Caltech is directed toward this optimization. While prior work on physisorbents has illustrated the importance of high surface area in achieving gravimetric uptakes of relevance to the program, volumetric densities have recently been recognized as a critical metric. Under many conditions, the nature of the adsorption process can still offer volumetric density advantages over the use of compressed gas storage, although not as high as intermetallic hydride densities. For dihydrogen that adsorbs onto a substrate, the London dispersion forces that can be regarded as transient dipoles in polarizable substances are a major contributor to physisorption processes. We are designing metal functionalizations for carbon surfaces that should optimize these attractive forces, enabling higher heats of adsorption, higher temperatures of operation, and higher capacities per surface area of material.

APPROACH

Previous work at Caltech has shown that alkali metal-intercalated graphites, which have pore dimensions similar to the graphene geometries we seek, can result in constant isosteric enthalpies of adsorption. These specialized structures had the advantage of electron back donation from the alkali metal to the graphitic planes, but these observations motivate the addition of metal atoms substitutionally in the graphene or on graphene surfaces. These local centers could increase both the isosteric heat of adsorption and the number of active sites for dihydrogen adsorption. We also note that for H_2 on metal surfaces, adsorption and desorption typically occurs above room temperature.

This project aims to promote high surface packing density of hydrogen and high constant isosteric enthalpy in graphene and graphene-based materials. Specific key goals are to attain a high volumetric density of hydrogen, a near-constant heat of adsorption, rapid kinetics for adsorption and desorption, and long cycle life. We have altered the

carbon surfaces by incorporating metal centers to increase the strength of the dispersion forces. The incorporation of these metal centers will continue to be optimized to gain better understanding of hydrogen physisorption and to reach technical targets for system gravimetric and volumetric capacity.

RESULTS

Efforts for the second phase of this project occurred in three primary areas: (1) synthesis of graphene and graphene materials, (2) modification of graphene via pore formation and metal functionalization, and (3) hydrogen adsorption measurements.

Two pathways have been employed to synthesize graphene-based carbon in reasonable quantities. Caltech has licensed its technology for plasma grown graphene to Cealtech AS, a Norwegian-based start-up [1,2]. Caltech has assembled a large-scale plasma system for continuous graphene growth. Figure 1a shows team member David Boyd standing next to the plasma chamber during assembly in Germany. A TEM micrograph in Figure 1b and corresponding selected area diffraction plot in Figure 1c indicate that this plasma approach for graphene synthesis yields high quality graphene. Raman spectroscopy confirms a large defect band at $1,350\text{ cm}^{-1}$ and indicates that the graphene planes stack turbostratically. Parallel efforts have used a traditional synthesis and activation route to produce graphene-based carbon from reaction of graphene oxide with biomass including sucrose and lignin. These materials can be easily obtained in large quantities (5–10 g per reaction), and show an increase in surface area of over 1,000% after activation.

Modification of graphene and graphene-based carbons is at the core of our plan to reach DOE hydrogen storage targets for high volumetric density of hydrogen. The second phase of the project has focused on the modification of materials by introduction of pores and functionalization with metals. The rationale for etching of pores in graphene is to improve surface area and create active edge sites for functionalization. Plasma etching was employed to modify monolayer and bulk materials. SEM, TEM, Raman spectroscopy, and BET surface area measurements indicate the successful introduction of nanometer-scale holes. Figure 2a shows an SEM image of a graphene monolayer suspended over a copper grid with a large triangular hole resulting from focused ion beam exposure. Nanometer-sized pores were observed near the large triangular hole by TEM, as shown in Figure 2b.

Functionalization with metals is central to our approach of increasing surface packing density of hydrogen. In the first phase of the project, we demonstrated the deposition of Au and Cu metal nanoclusters $<1\text{ nm}$ by both chemical and plasma deposition routes. In the second phase of the

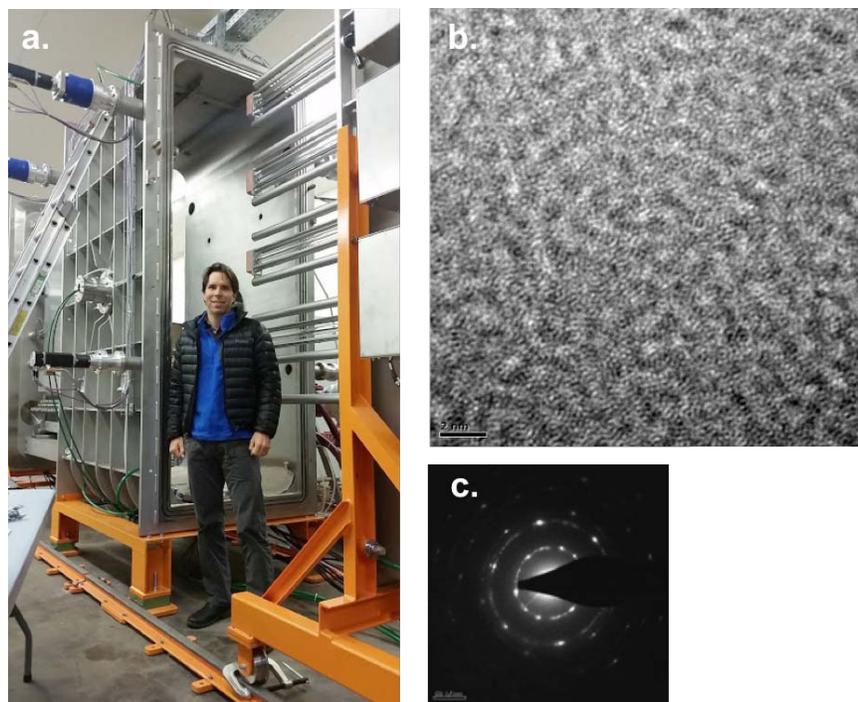


FIGURE 1. (a) Caltech team member David Boyd standing next to the plasma reactor for large-scale graphene synthesis, (b) TEM image of plasma-grown graphene, and (c) Selected area diffraction indicating that this plasma approach for graphene synthesis yields high quality graphene.

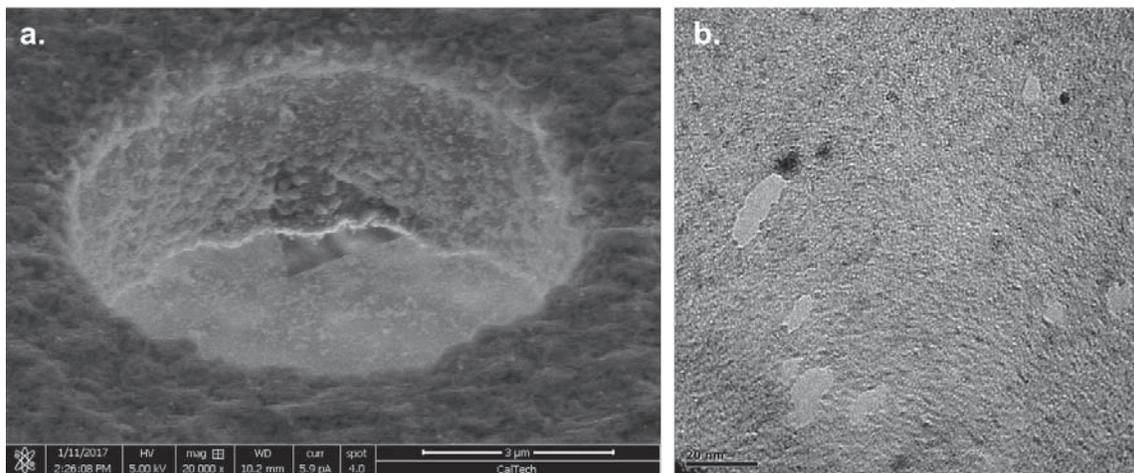


FIGURE 2. (a) SEM image of a graphene monolayer suspended over a copper grid with a large triangular hole resulting from focused ion beam exposure, and (b) nanometer-sized holes near the large hole observed with TEM.

project, these functionalization efforts were scaled-up to produce sample quantities sufficient for hydrogen adsorption testing. Figure 3 shows a high angle annular dark field TEM images of Cu atoms and Cu nanoclusters, as evidenced from the small white dots. Images were obtained by Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) collaborators at Pacific Northwest National

Laboratory. This material, with a surface area of 3,006 m²/g, was functionalized from CuCl₂ · 2H₂O salt and annealed under hydrogen gas at 125°C. This material is one example of more than a dozen large-batch samples prepared from various metal salts that resulted in materials with varying metal concentrations, metal cluster sizes, and surface areas. Functionalization results in a decrease in surface

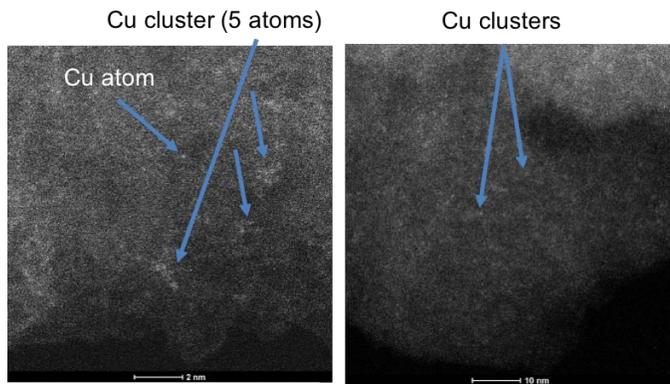


FIGURE 3. TEM high angle annular dark field image of graphene functionalized with Cu nanoclusters (appearing in bright white regions).

area ranging from 0.5–40% compared to pristine material, however this may be overcome by increased hydrogen packing density on the surface, as discussed below.

Hydrogen adsorption measurements using the Sieverts method are critical to characterization of the materials we develop. In the first phase of the project, a second Sieverts apparatus was commissioned to mitigate data acquisition constraints, and a “Rapid Sieverts” screen method to assess materials using a single data point at 77 K and 20 bar. In the second phase of the project, the screening of materials has been further streamlined by adaptation of the BET system used for surface area measurements to also obtain hydrogen isotherms (<1 bar) at 77 K, 242 K, 300 K, and 322 K. Initial ambient temperature low pressure isotherm data indicate an enhancement with Cu modification, an example of which is shown in Figure 4. This figure compares pristine material (black dashed lines) with its functionalized counterpart at 296 K and 319 K. The functionalized material, containing 1.65 at% Cu, has a surface area of 2,943 m²/g. This represents a reduction in surface area of 12% from the pristine material. However, at 296 K and 1 bar, the uptake of hydrogen by the functionalized material is 131% of the pristine material. This is a positive indication of how metal centers increase the enthalpy of adsorption, indicating a promising pathway for the practical use of adsorbents.

CONCLUSIONS AND UPCOMING ACTIVITIES

As this project reaches the end of its second phase, several conclusions can be drawn:

- Relatively large quantities of graphene-based materials can be produced and functionalized with metals.

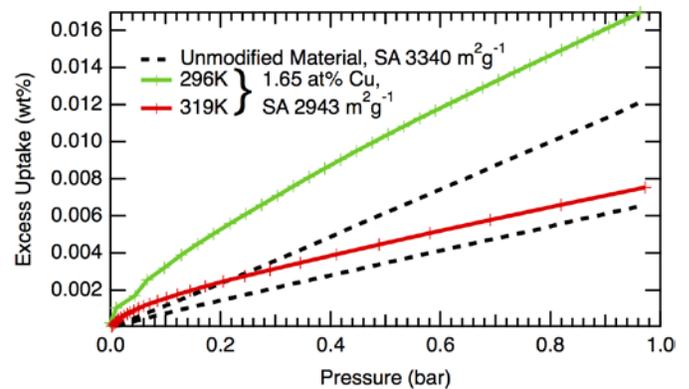


FIGURE 4. Isotherm data for functionalized material indicating an enhancement in uptake (colored curves) over pristine material (black lines) at 296 K and 319 K.

- Chemical functionalization of materials with metals can produce varying sizes and concentrations of metal clusters.
- Ambient temperature low pressure isotherm data show an enhancement of hydrogen adsorption with Cu modification, indicating an increased enthalpy of adsorption in metal-functionalized materials.

Goals for work in the third phase of the project are:

- Identification of the role of low dimensional structure, and validation of >40 g/L total adsorption; multi temperature analyses over 77 K to 160 K for isosteric heat validation >10 kJ/mole.
- Achieve ≥ 1.5 wt% excess H₂/500 m²/g in material with >3,000 m²/g specific surface area at pressures <100 bar and 77 K.
- Achieve net adsorption of ≥ 6 wt% H₂ at any temperature or pressure. Achieve net adsorption of ≥ 1 wt% H₂ at 30 bar and 300 K.
- High gravimetric and volumetric density analysis. Gravimetric density meeting or exceeding 11 wt% H₂ and volumetric capacities exceeding 40 g/L total at 77 K and 40 bar pressure.

REFERENCES

1. Boyd, D.A., et al. (2015). Single-step deposition of high-mobility graphene at reduced temperatures. *Nature Communications*, 6. <http://doi.org/10.1038/ncomms7620>
2. Issued US patent 9,150,418.