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Cross-cutting High Surface Area Graphene-based Frameworks with Controlled Pore Structure/Dopants

The goal of this project is to enhance the performance of graphene-based materials by manufacturing specific 3D architectures. The materials have global applications regarding fuel cell catalysts, gas adsorbents, supercapacitor/battery electrodes, ion (e.g., actinide) capture, gas separation, oil adsorption, and catalysis. This research focuses on hydrogen storage for hydrogen fuel cell vehicles with a potential transformational impact on hydrogen adsorbents that exhibit high gravimetric and volumetric density, a clean energy application sought by the Department of Energy. The development of an adsorbent material would enable broad commercial opportunities in hydrogen-fueled vehicles, promote new advanced nanomanufacturing scale-up, and open other opportunities at Savannah River National Laboratory to utilize a high surface area material that is robust, chemically stable, and radiation resistant.
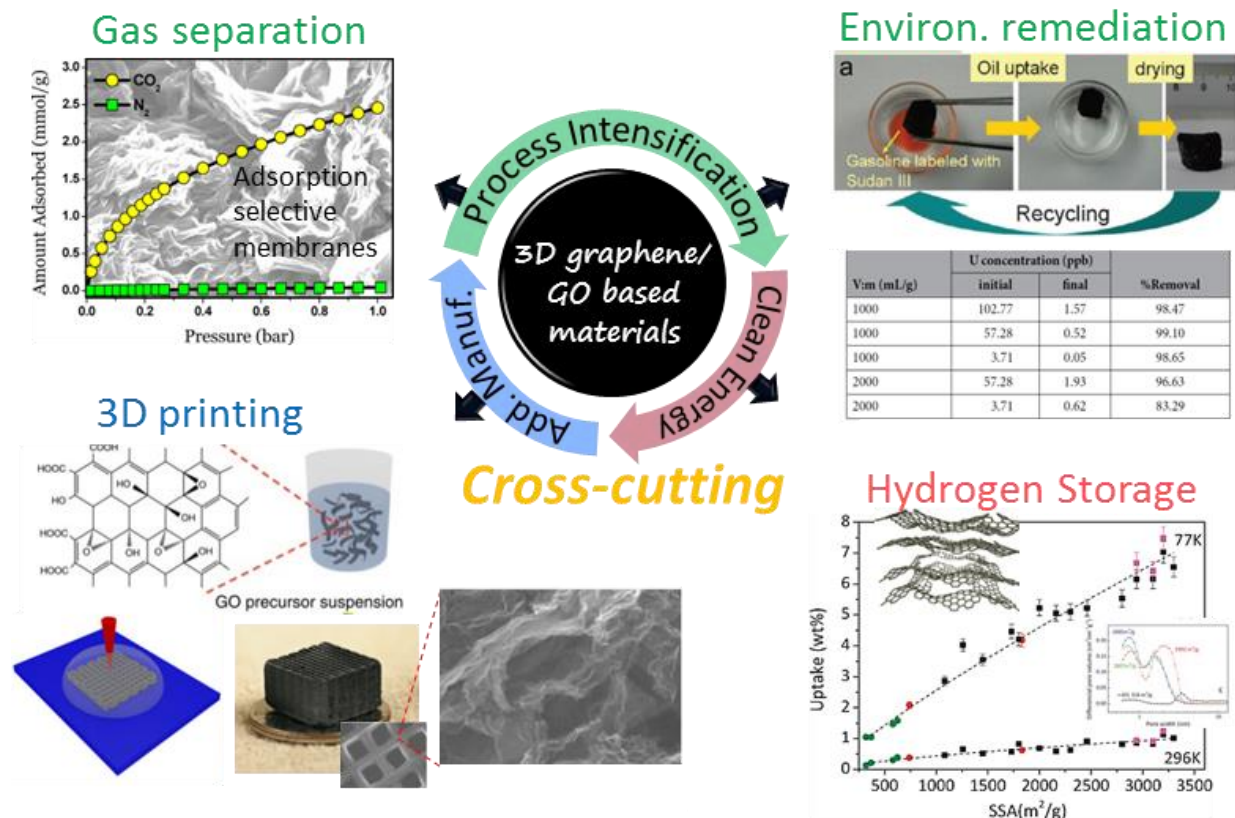

Figure 1: The need for 3D graphene optimization is ubiquitous across multiple applications.[1-4]

Awards and Recognition

Provide a concise (100 words or less) description of any awards and/or recognition achieved due to participation in a FY17 LDRD project.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature	**Date**

Cross-cutting High Surface Area Graphene-based Frameworks with Controlled Pore Structure/Dopants

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Subcontractor:
University of Texas at Dallas
NanoTechLabs, Inc.

Project Start Date: October 1, 2016
Project End Date: September 30, 2018

The proposed research seeks to enhance SRNL's materials innovation portfolio by developing novel 3D graphene-based frameworks that apply to applications in process intensification, advanced manufacturing, and clean energy with a specific focus on hydrogen storage. Our objective is to enhance the hydrogen adsorption properties of graphene and graphene nanoribbons (GNR) by optimizing pore structure and increasing hydrogen binding energy at adsorption sites. Initial activated graphene has reached specific surface area values of 2600 m^2/g with a pore volume of 1.88 cm^3/g and hydrogen uptake (77K) of 5.3 wt%. Similar experiments have been performed on GNRs with comparable results. Our goal at project end is to achieve SSAs >3400 m^2/g and >9 wt% H_2 uptake at 77 K and >3 wt% near room temperature for GNRs.

FY2017 Objectives

Prepare High Surface Area 3D Graphene Structures

- Prepare 3D graphene frameworks with a high surface area (>2500 m^2/g) and > 5wt% H_2 uptake.
- Develop methods for the microwave/thermal exfoliation of graphene that is activated either by chemical (KOH) or gas phase activation (CO_2).

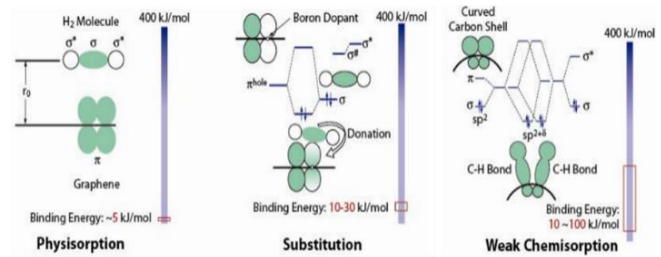**Prepare High Surface Area GNRs doped with Heteroatoms**

- Prepare high surface area (>2500 m^2/g) GNRs with substitutional doping.
- Synthesize GNRs with varied geometric architecture (UTD)
- Measure hydrogen uptake of high surface area activated GNRs.

Introduction

DOE's Fuel Cell Technologies Office (FCTO) has set a goal to enable widespread commercialization of hydrogen, which requires adequate hydrogen storage media for onboard vehicles and portable power applications. Graphene-based framework's multifunctional properties provide potential to meet all DOE targets for hydrogen storage. SRNL is teaming with the University of Texas at Dallas (UTD) to use a facile rationally designed approach to enhance the hydrogen adsorption properties of high-aspect ratio graphene nanoribbons (GNRs), which contain remarkably high graphene-edge content and more easily accessible basal planes than its competitor, graphene. In a 3-phase, 2-year research approach, these unique structures will be constructed into macroscopic functional 3D architectures followed by perforation, corrugation and heteroatom (i.e., B, N) doping on the graphitic planar surfaces in order to significantly increase surface area (>3300 m^2/g) and hydrogen binding energy (>10 kJ/mol) to increase uptake at room temperature. The objective is to optimize the adsorbents with a ~9wt% gravimetric and

40 g/liter volumetric capacity at 77K with a subsequent primary objective of increasing H_2 uptake near room temperature.

A few material development approaches essential for the advancement of graphene-based H_2 adsorbents have been suggested: optimize pore structure[5], increase binding energy[5] with substitutional atoms and localized curvature, and high-density edge decoration[6]. The addition of heteroatom dopants to the graphene planar surface has shown[7] to increase localized binding energy (Figure 2). Recent models on edge decoration have shown promise as a means to meet DOE H_2 storage targets[8], but that success

Figure 2. Illustration of three types of sorbent binding mechanisms: the two on the right enhance dihydrogen binding via substitution and curvature[8].

applies more for GNRs due to their inherently high edge content. The outcome of this work is to prove feasibility of the synthesis of a carbon-based hydrogen adsorbent that stores hydrogen at higher loadings than predicted by the Chahine rule[9] in which a linear dependence of the hydrogen uptake is related directly to surface area. Our proposed design will increase the hydrogen affinity relative to surface area and seek to obtain uptake values that are ~2X the storage based on the Chahine rule alone.

Approach

In a 3-phase, 2-year research approach, the GNRs will be constructed into macroscopic functional 3D architectures followed by perforation, corrugation and heteroatom (i.e., B, N) doping on the graphitic planar surfaces in order to significantly increase surface area (>3300 m^2/g) and hydrogen binding energy (>10 kJ/mol), to increase uptake at room temperature. The objective is to optimize the adsorbents with a ~9wt% gravimetric and 40 g/liter volumetric capacity at 77K with a subsequent primary objective of increasing H_2 uptake near room temperature.
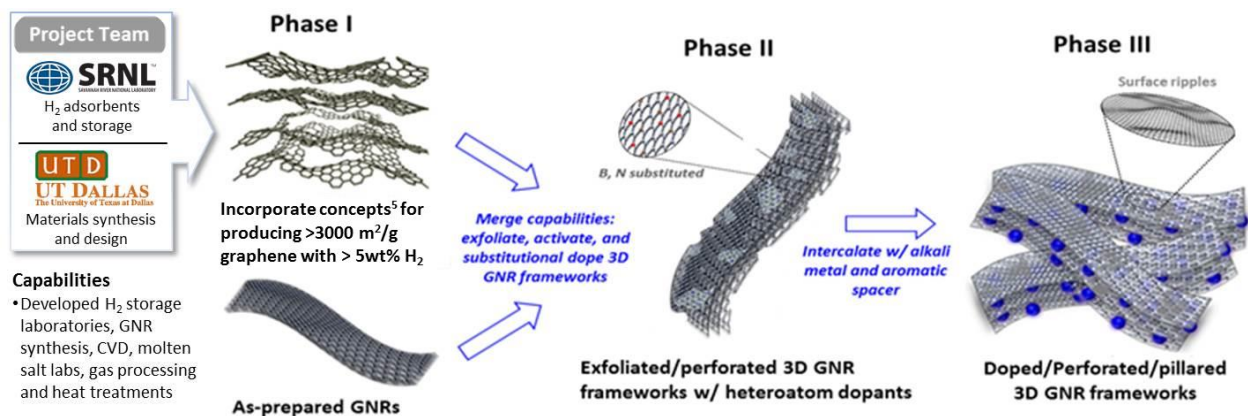
Figure 3. Flow schematic of material development shown in three phases. From left to right, Phase I) development of capabilities to produce high surface area 3D graphene frameworks and parallel synthesis of GNRs, Phase II) exfoliation, activation, and substitutional B, N doping, and Phase III) plane separation with alkali metals and aromatic spacers in addition to imparting surface ripples for increased binding energy.

The specific scientific approach is to produce:

➢ 3D graphene nanoribbon frameworks with high surface area and optimal binding energies due to the heteroatom doping of narrow, high aspect ratio GNR structures with optimized and accessible pore structure (0.6-1.3 nm interplane),

> corrugation and plane separation that provides additional enhancement to H_2 adsorption capacity and performance due to curvature induced binding sites, accessible interplanes, and metal induced charge gradients.

SRNL's proposed multiple post-treatment steps is necessary to meet DOE performance targets where application of only one approach (i.e., perforation, substitution, plane separation) would fall short. The innovation of the approach comes from first developing scientific principles for GNR base materials with: 1) ribbons of various dimensions (i.e., widths and lengths controlled by CNT starting material) where SRNL currently, in collaboration with NanoTechLabs, can synthesize CNTs with incremental diameters and lengths by carefully controlling growth parameters, and 2) controlling stacked (unzipped, but not fully exfoliated) and single layer architectures while understanding their role in hydrogen adsorption. The developed base materials will be thermal or microwave exfoliated and perforated using recently improved KOH activation[1] to significantly increase surface area near or above 3000 m^2/g. As mentioned, further innovation is expected from taking advantage of the high graphene edge content.

Results/Discussion

To establish a greater than 3000 m^2/g surface area with > 6wt% hydrogen uptake at 77K, we have produced scaffolded[2] graphene using thermal exfoliation to produce reduce graphene oxide (rGO) followed by KOH activation. Graphene oxide is produced by chemical oxidizing graphite using the Hummers[10] method. Briefly, graphite flakes, NaNO3, H_2SO_4 (98%) are mixed in an ice bath to prevent premature reaction, stirred for 2 hours followed by slow addition of $KMnO_4$. After stirring for 2 days at 35°C, The suspension is heated to 98°C with effervescence for 10 minutes. As shown in Figure 4, the
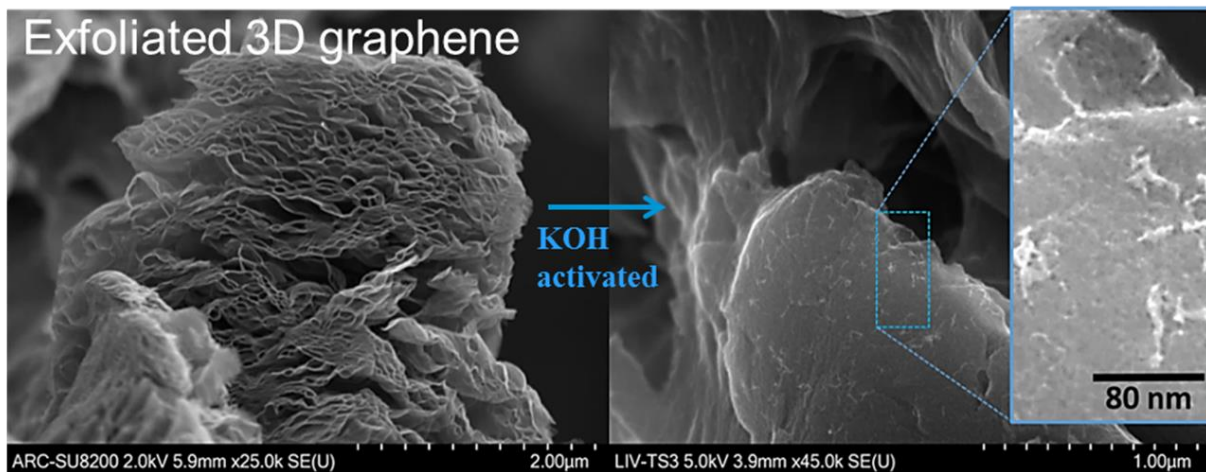
Figure 4. (left) Thermally exfoliated GO and thus rGO produced at SRNL. (right) KOH activated rGO that exhibits higher density and typical perforation on the surface.
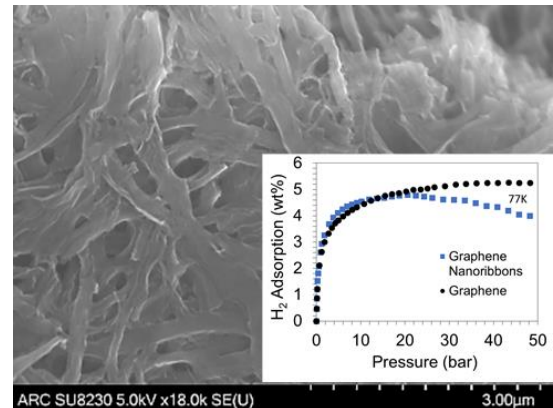
graphene forms a highly porous structure after thermal exfoliation. It then densifies after a KOH/methanol solution is mixed with the thermally exfoliated GO, vacuum dried, and heated at 800°C for 1 hour. Initial activated graphene reached specific surface area (SSA) values of 2600 m^2/g with a pore volume of 1.88 cm^3/g and hydrogen uptake (77K) of 5.3 wt%. The thermally exfoliated GO yielded a SSA of 250 m^2/g before the activation. Several factors that need further development to increase surface area are:

1) Using thermal exfoliation versus microwave exfoliate is crucial to creating a chemically compatible surface for KOH wetting and reaching high surface areas after KOH activation.
2) A surface area after thermal exfoliation is needed above 350 m^2/g, but too high can lead to lower surface areas following KOH activation.

3) The optimal thermal exfoliation temperature[11] is 70-90°C above the first mass loss measured by thermogravimetric analysis (typical at ~225°C). These values change for graphene nanoribbons.
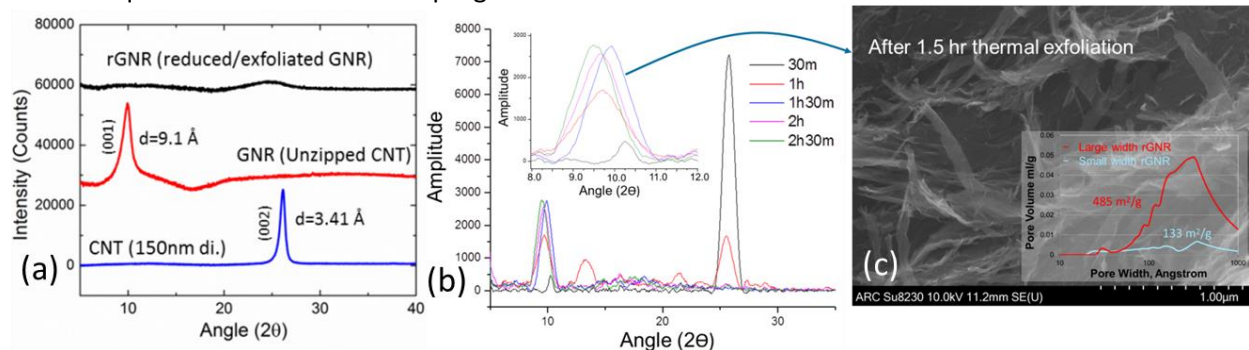
To these points, we have used several approaches to optimize thermal exfoliation to reach >350 m^2/g: 1) ball milling the graphite before oxidation to impart defects, 2) HCL acid incorporation into the graphene oxide step to increase interlaminate pressure, and 3) increasing the effervescent reaction time at the end of the oxidation step. Methods 1 and 2 failed to provide sufficient final high SSAs, but method 3 was successful in increasing the SSA after thermal exfoliation to ~380 m^2/g for graphene. We have KOH activated these materials and are currently in process of measuring the final SSA and performing hydrogen uptake measurements.

For graphene nanoribbons, we produce large width (~800 nm) and small width (~150nm) GNRs (LWGNRs and SWGNRs, respectively) by chemically oxidizing carbon nanotubes with different diameters using the Tour[12] method. The LWGNRs (shown in Figure 5) were found to fully unzip as discerned from the XRD data in Figure 6a. Following the unzipping, thermal exfoliation easily occur with a complete disappearance of the graphene oxide peak seen in the XRD data. EDS and FTIR also confirmed reduction of the oxygen functionalities. The thermal exfoliation step was found to produce an SSAs of 485 m^2/g followed by KOH activation SSAa of 2726 m^2/g with a total pore volume of 2.07 ml/g. The same sample was split in half for which we sonication the LWGNRs during the KOH activation step. This sample gave an SSA of 2465 m^2/g with a 1.66 ml/g total pore

Figure 5: SEM image of large-width GNRs. Insert shows hydrogen uptake at 77K of graphene and LWGNRs with ~2400 m^2/g SSAs.

volume. The smaller surface area sample was activated first and subsequently tested for hydrogen uptake which showed ~4.8 wt% (insert, Figure 5). Testing of the larger SSA sample is in progress in addition to further increasing the final surface area. The SWGNRs were difficult to thermally exfoliate which led to a study shown in Figure 6b, which involves an oxidation reaction time study versus XRD peak shift. The materials produced after a 1.5 hr reaction was successfully thermally exfoliated as shown in Figure 6c; however, the SSA was low due to a needed longer exfoliation time. The further exfoliation and subsequent KOH activation is in progress.

Figure 6. (a) Results show the loss of the large diameter CNT peak (26°) and the appearance of the LWGNR oxidation peak (9.1 Å). (b) The disappearance of the small diameter CNT peak (26°) occurs 1st at 1.5 hrs and shows a significant SWGNR oxidation peak (~9.5°) indicating full unzipping without over oxidation. (c) A larger batch of the 1.5hr recipe was produced and thermally exfoliated to produce well-structure SWGNRs, as seen in the SEM image. The insert compares the pore structure of the LWGNR to the SWGNR. The small SSA for the SWGNR is likely due to incomplete exfoliation.

FY2017 Accomplishments

- Graphene and graphene nanoribbon adsorbents with an average SSA of 2400 m^2/g had ~5.0 wt% H_2 uptake. The graphene and graphene nanoribbons has been further optimized, with measurements pending. Intial boron and nitrogen doping has proven successful up to full conversion of the carbon to BN. This research is ongoing for controlling the dopant content.
- XRD analysis showed the 100% conversion from carbon nanotube to GNRs.
- Small diameter GNRs were difficult to thermally exfoliate, but after an XRD aliquot study versus reaction time, optimized structures did thermally exfoliate.
- The hydrogen test cell was modified to be able to measure reduced sample sizes (from 200 mg to 100 mg) to help reduce the need for large sample batches.

Future Directions

- Utilize the expertise at UTD to develop new techniques to increase hydrogen uptake at room temperature for the GNRs.
- Focus on pore structure, volumetric capacity, and increasing binding energy (increase uptake temperature).
- Publish work in collaboration with UTD. The work for the two different sized GNRs will be finished and published in FY18.

FY 2017 Publications/Presentations

Presentation: Clean Energy Portfolio review for FY17 LDRDs, HTRL facilities, 07/27/2017

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Acronyms

SRNL –   Savannah River National Laboratory
UTD –   University of Texas at Dallas
GNR –   Graphene nanoribbon
CNT –   Carbon nanotubes
MWNT –   Multi-walled nanotubes

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None