FROM THE LAB BENCH TO THE FUEL TANK: DEVELOPMENT AND ANALYSIS OF NOVEL ADSORBENTS FOR HYDROGEN AND NATURAL GAS STORAGE

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DEVELOPMENT AND ANALYSIS OF NOVEL ADSORBENTS FOR
HYDROGEN AND NATURAL GAS STORAGE

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DEDICATION

To my parents, Susan and Gary, and my sister, Melissa: your endless support has kept me motivated and allowed me to succeed.

To Ayita: your constant companionship provided me peace in the times I needed it, and smiles in the times I didn't.

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ABSTRACT

Hydrogen and natural gas offer a promising avenue towards reducing greenhouse gas emissions in the transportation sector; however, storage poses a non-trivial challenge, with current systems requiring prohibitively large and bulky hardware. Adsorbent media, notably nanoporous activated carbons, have seen significant development towards making such solutions viable, but none have yet to demonstrate the performance necessary to supplant existing technologies.

Presented here is the synthesis and optimization of two materials designed to be especially competitive, as well as the techniques implemented to characterize them. Boron doping of nanoporous carbons, with the incorporation of carrier gas assisted deposition, is proposed to enhance the surface's binding potential while maintaining the integrity of the inherent pore space. This process explicitly demonstrates complete infiltration of the carbon's internal volume and facilitates boron substitution to a greater extent relative to other similarly-produced materials. Carbon nitrides, specifically the graphitic isomer $g\text{-C}_3\text{N}_4$, are theorized to produce adsorbents with surface areas and binding energy in excess of activated carbons via facile synthesis. Crystallographic investigation reveals the previously-reported synthesis methods instead produce a polymeric structure; this results in a highly-aggregating bulk that strongly resists exfoliation.

CHAPTER 1 – Introduction and Motivation

Man-made climate change has emerged as an existential threat to the survival and long-term well-being of our species. The dramatic rise in global temperature, which has seen steady year-over-year increases since the industrial era, is subsequently well correlated with CO₂ emissions associated with fossil fuel consumption (Fig 1.1); this has contributed to atmospheric CO₂ levels that will exceed anything recorded within the last 800,000 years[1].

Fig 1.1. (left) Global temperature anomaly relative to 1951-1980[2], [3]. (right) Cumulative yearly global CO₂ emissions for the predominant sources, during the same time period[4], [5].

The United Nations' Paris Agreement[6] seeks to limit the rise in global temperature to 2°C above preindustrial levels, a benchmark level that's considered to herald catastrophic consequences to global ecosystems. Already at three-quarters this limit, it may be unavoidable given current consumption and policies[7]. Indeed, some of

the less optimistic models predict global temperature increases as high as 4.8 °C by 2100[8]; to put this figure in perspective, this is similar to the warming that superseded the Last Glacial Maximum over the period 20-10,000 BCE[9], whereby global ice coverage was reduced by 60% and resulting in a 120 m rise in sea level[10].

The implementation of greener energy sources, such as nuclear, solar, wind, etc, have made strides towards addressing this. However, while these renewables continue to account for an increasing share in global energy production, they currently only comprise just over 15% altogether. Further, the transportation sector, which makes up 28% of total U.S. energy consumption (and 25% globally), is especially reliant on fossil fuels, with biofuels constituting the only meaningful contribution from renewable sources (~5% of transportation sector consumption[11]).

Fig 1.2. *Left*: Evolution of global energy consumption by source[12]. *Right*: Global (ca. 2012,[13]) and U.S. (ca. 2019,[11]) energy consumption across the major sectors. Approximately 5% of the U.S.'s transportation-sector fuel is generated via renewable sources.

Hydrogen and natural gas powered vehicles provide one pathway towards a greener transportation infrastructure, with natural gas currently accounting for 3% of the

transportation sector consumption[11]. Vehicles running on natural gas generate 6-11% lower levels of greenhouse gasses compared to traditional gasoline[14]; hydrogen fuel cells offer an even more attractive incentive in that the only direct byproducts consist of water and heat.

While examples of consumer-grade natural gas vehicles can be found (e.g. *Honda Civic GX*), the vast majority exist at the industrial and municipal level: long-haul trucks, city busses, refuse trucks, etc. This is a direct result of the challenges associated with storage. As a gas, the *gasoline-gallon equivalent* (GGE) of methane, i.e. the quantity of methane required to equal the energy content of one gallon of gasoline, occupies 3.6 m³ of volume (~950 gallons) at STP[15]. This is naturally compounded for hydrogen – 1 GGE is 10.1 m³ (~2700 gallons). Overcoming this constraint involves extensive modifications to existing storage systems; as such, current vehicles store natural gas either as highly compressed (CNG), requiring large, bulky cylinders that reduce cargo/passenger space, or as liquified (LNG), which necessitates the incorporation of cryogenic instrumentation both onboard and from the filling station. In the previously mentioned Honda Civic GX, the storage tank occupies a significant amount of what would otherwise be available trunk space. Contrast this with current electric vehicles, whereby the absence of a traditional combustion engine produces *additional* storage space for the consumer (Fig 1.3).

Fig 1.3. *Left:* Trunk space of the CNG Honda Civic GX is severely reduced by the large storage tank[16], [17]. *Right:* Without the need for a conventional combustion engine, EV's such as the Tesla Model Y are capable of providing additional storage space[18].

In order to make natural gas (and ultimately hydrogen) vehicles viable in the consumer market, it is imperative to address the issues involved with storage. The U.S. Department of Energy's Office of Energy Efficiency & Renewable Energy (DOE-EERE) is spearheading one such initiative. As part of this, they have outlined a number of targets regarding system cost, H_2 delivery, and storage efficiency: in particular are the mandates of 65 g H_2 per kg system mass and 50 g H_2 per L system volume[19]. Such goals require densification to levels approaching liquid H_2 ($\rho = 71 \text{ g/L}$) under the constraint of a not-unlimited total system mass. For instance, to achieve 25 GGE requires 25 kg H_2 [20], which must then be stored by a system not exceeding 360 kg in mass and 0.5 m^3 in total volume.

Adsorption provides one such means towards potentially meeting these goals. During adsorption, the molecules of a gas or liquid *adsorbate* adhere to the surface of a solid *adsorbent*; this results in a high density film of the adsorbed material. Impressively, it has been shown that a number of C-based substrates are capable of generating adsorbed films significantly in excess of liquid H_2 ($>100 \text{ g } H_2/\text{L sorbent at } 77\text{K}$ [21]). When coupled

with the exceptionally high surface area native to many materials, adsorption proves exceptionally competitive.

In the H₂ storage community, metal-organic frameworks (MOFs) have been the subject of particularly intense interest[22]. MOFs are coordination polymers comprised of metallic clusters linked via organic ligands; these systems are highly tunable, generating inter-connected 3D skeletons whose unique structures result from the particular precursor materials used. MOFs are notable for their extraordinary surface areas, with values as high as 7000 m²/g reported and upwards of 14000 m²/g theorized[23]. However, the labor and cost involved in the synthesis currently limits production to the laboratory scale, posing a significant challenge to any industrial implementation[24]. Further, despite considerable study, MOF materials have been unable to consistently meet DOE H₂ storage benchmarks[25].

Activated carbons do not suffer from the same drawbacks. For one, they can be readily produced from a number of organic precursors; notably, this includes several that are otherwise considered waste materials, such as olive stones[26], coconut shells[27], peach pits[28], and corncob[29]. Further, the processing of such materials typically requires simple and inexpensive exfoliation and activation treatments, making them quite amenable to industrial scaling.

Chahine's rule demonstrates that the adsorption performance in carbonaceous materials improves directly with surface area[30]; given that activated carbons are renowned for their naturally high surface areas, they would be expected to be correspondingly competitive storage media. However, high surface area activated carbons have consistently failed to meet the aforementioned targets[31]. As activated carbons can

be characterized as disordered individual graphene sheets[32], (with a known ideal surface area, 2965 m²/g[33]), this may imply a maximum uptake threshold.

Thus, to improve the storage capabilities of graphene-based materials requires augmentation of the H₂-solid interaction, resulting increased density within the adsorbed film. Such an effect may be induced via surface functionalization[34]–[36], and the efficacy of two such attempts will be described here.

CHAPTER 2 – Adsorbent Metrics and Characterization

2.1. Basic metrics of porous media

The most analytically simple model of a porous material is binary, with constituent solid and void phases (V_{solid} and V_{pore} , respectively). Various volume fractions provide the natural language upon which the groundwork of more refined analyses will be built.

First, the bulk density ρ_{bulk} assumes the traditional definition of total mass to total occupied volume:

$$\rho_{bulk} \equiv \frac{m_{solid}}{V_{pore} + V_{solid}} \quad (2.1)$$

This density varies based on the specific morphology of the material. The absolute density of the material itself (the so-called ‘skeletal’ density ρ_{skel}) excludes any available intrastitial void space within a unit:

$$\rho_{skel} \equiv \frac{m_{solid}}{V_{solid}} \quad (2.2)$$

By and large, the skeletal density is function of the particular chemistry and crystalline basis present. Various graphene-based structures have been reliably measured via He pycnometry in-house to $\rho_{skel} = 2.0 \text{ g/cm}^3$ [37], consistent with the values associated

with amorphous carbon (1.8-2.1 g/cm³) and lower than pure graphite (2.3 g/cm³)[38]. This difference is due to including gas-inaccessible voids ('closed pores') intrinsic to the definition of the bulk solid.

The total volume of the pore space contained within a sample, normalized to sample mass, is a crucial characteristic of porous media and is measured directly via N₂ uptake at just below the saturation pressure P_0 (specifically, 0.995 P/P_0) at 77K. Under these conditions, liquid N₂ fills the entire pore space via capillary condensation. Analytically, the specific total pore volume (TPV) represents the quantity:

$$TPV \equiv \frac{V_{pore}}{m_{solid}} \quad (2.3)$$

Or, in terms of the previously defined densities:

$$TPV \equiv \frac{1}{\rho_{bulk}} - \frac{1}{\rho_{skel}} \quad (2.4)$$

The gravimetric dependence inherent to the total pore volume constrains universal comparison. Thus, the porosity (or pore fraction) ϕ is introduced:

$$\phi \equiv \frac{V_{pore}}{V_{pore} + V_{solid}} \quad (2.5)$$

This value, which represents a structurally- and compositionally-independent characteristic quantity, reflects the fraction of the individual unit medium (particle, grain, sheet, etc) consisting of voids available to gas and naturally is constrained to the domain $0 \leq \phi \leq 1$. ϕ is determined analytically from TPV measurements via:

$$\phi \equiv \frac{1}{1 + (TPV * \rho_{skel})^{-1}} \quad (2.6)$$

The porosity serves as one of the paramount quantities in the characterization of porous media as it represents the space physically accessible to a gas. However, adsorption is ultimately a surface-based phenomenon and thus relies on the availability of sample surface as well. This characteristic is quantified via the specific surface area, Σ , which is determined by applying the Brunauer-Emmett-Teller (BET) theory[39] to N₂ sorption measurements in the pressure range 0.01-0.03 P/P₀.

Porosity and surface area are the associated characteristics of the phases that define the binary sorbent system: pore and solid, respectively. As such, they are largely independent. However, both are crucial towards the development of a material capable of storing sufficient quantities of gas: too low of a porosity and gas is unable to adequately permeate the sorbent, while too low of a surface area yields minimal adsorption (Fig 2.1).

Fig 2.1. Illustration highlighting the independence of porosity and surface area. Removing large sections of volume results in increased ϕ with minimal change to Σ , while removing many smaller non-continuous sections yields the inverse.

2.2. Van der Waals Interactions

The gas solid interaction is mediated by two opposing interactions:

1. A steep, Pauli-like repulsive potential
2. A smoother, attractive London dispersion (dipole-dipole) potential

The net of these forces is known as the Van der Waals interaction. Many mathematical models exist to describe this phenomenon, perhaps most notably the 12-6 Lennard-Jones potential. While computationally and analytically accessible, it holds up less well under especially rigorous scrutiny when applied to specific systems above monomolecular ones in complexity [9]; Steele's 10-4 potential (eq. 2.7) has been demonstrated to more reliably describe the short-range repulsion of a solid-fluid interaction, particularly with regards to methane adsorbed onto graphite [10].

$$\Phi_{10-4} = E_b * \left[\frac{2}{5} \left(\frac{\sigma}{r} \right)^{10} - \left(\frac{\sigma}{r} \right)^4 \right] \quad (2.7)$$

Here, E_b (the binding energy of the system) refers to the depth of the potential well (minima) (Fig 2.2) formed via the superposition of the repulsive and attractive interactions; a particle found at this position (R_{eq}) is in equilibrium. σ represents the distance at which the net potential is zero, equivalent to the sum of the van der Waals radii of the interacting atoms.

Fig 2.2. Potential schematic of a representative system, using $E_b = -6.5$ kJ/mol, $\sigma = 2.5$ Å, and equilibrium distance $R_{eq} = 2.9$ Å. This demonstrates the limited range of the Van der Waal interaction, as the potential is essentially nonexistent by 1 nm.

The preceding detailed the interaction of a gas molecule with a single solid surface; however, a gas molecule residing in a 3-dimensional sorbent will naturally be subject to contributions from multiple sources. A graphite-like material is assumed to consist of slit shaped pores, i.e. a geometry defined by two $\sim$ infinite parallel sheets. The total binding potential in this configuration is thus calculated as the sum of the contributions from each opposing sheet (Fig 2.3).

Fig 2.3. Simulated potential plots from a left (black) and right (blue) pore wall along with the net (red), calculated using the 10-4 Steele potential[40] for a system with $E_b=6.5$ kJ/mol. Physical locations for each wall are represented by the y-axis and the vertical blue line, respectively. As the walls are brought closer together, the contributions from each will begin to superimpose, yielding a net binding energy that grows up to double each wall's individual binding energy (at a separation of twice the equilibrium distance R_{eq}).

For large pores (width $\gg 2R_{eq}$), the walls act essentially independently as the potential for each quickly decays for large r . As the walls close in, the potentials begin to overlap, ultimately yielding a value double that of the individual walls for a pore width double that of the equilibrium distance. In this scenario, the superpositioned equilibrium positions will cause gas molecules to form an ultra-dense monolayer in the center of the pore.

2.3. Excess Adsorption

The binding energy ultimately serves as the impetus driving the adsorption mechanism, whereby gas molecules attracted to the sorbent will overcome the intermolecular repulsive forces that mediate the gas's bulk density. This generates a dense

adsorbed film ($\rho_{ads} \geq \rho_{bulk}$) along the surface of the solid; the precise density of this film will vary by sample and isn't readily determined by any available analytical technique[21]. Because of this non-characterized second phase in the system (along with the bulk gas that matches the inlet pressure), measurement of adsorbed gas storage is notably non-straightforward.

Quantified characterization of the pore structure facilitates this analysis. Theoretically, determination of the pore space available to the gas (via measurement of the specific total pore volume using N_2 sorption) allows for the calculation of gas molecules contained in a non-adsorptive system using basic principles: any quantity of gas molecules detected above this expected value is thus a reflection of the extent of adsorptive effects present. This quantity is referred to as the *Gibbs excess adsorption*, and is the only adsorption metric capable of direct measurement[41]. Normalization to the sample mass, as would be required for an apples-to-apples comparison between samples, returns the *gravimetric excess adsorption* (G_{ex}).

Fig 2.4. Cartoon depicting arrangement of gas molecules in a typical compressed system (left) and in a sorbent-based system (right). In the compressed tank, gas molecules fill the volume uniformly at the prescribed inlet pressure. In the adsorbed tank, the adsorbent occupies some volume; however, this loss in accessible volume may be offset by the formation of an adsorbed film (yellow) that stores gas at a much higher density than the bulk. The mass of gas molecules in this film above what the bulk gas density predicts is defined as the excess adsorption (red).

There are two techniques commonly used to determine excess adsorption:

1. Gravimetrically: A sample with a known pore structure is outgassed and weighed. It is then exposed to a gas source at a given pressure, allowed to equilibrate, and

- weighed. The difference in the two masses represents the total gas contained in the sample; subtracting the calculated gas uptake from this yields the excess.
2. Volumetrically: A sample with a known pore structure is outgassed in a cell of known volume and weighed. Next, a second known volume is filled with gas and isolated from the source. The sample is then exposed to this dosing volume, allowed to equilibrate, and isolated again. Pressure and temperature measurements collected before and after dosing allow for calculation of the number of gas molecules transferred to the sample; comparing this to the calculated gas uptake yields the excess.

Fig 2.5. Sorption instrumentation in the ALL-CRAFT lab: gravimetric instrument (*left*), and manual (*middle*) and automated (*right*) volumetric instruments.

The gravimetric method has the advantage of measuring excess adsorption with minimal assumptions, but the mass measurements required for each data point is non-trivially user/time intensive. In addition, it is typically not capable of measuring H_2 reliably, as the small mass of H_2 relative to the sorbent (as well as the vessel) introduces prohibitive error in the measurement.

The volumetric method has the advantage of being readily automated, as all measurements may be digitally collected. However, because the measurements are successive, errors continuously propagate and become quite large at high pressures. Further, due to the nature of the measurement, it is not possible to determine uptake at a particular pressure of interest; instead, data is fitted to a model and interpolated to the desired value.

The principle of excess adsorption hinges on the adsorbed film existing at a higher density than the bulk gas. However, at high enough pressures, the pressure of the gas is able to oppose the intermolecular repulsions more effectively than the binding energy with the solid, and the density of the gas of the bulk matches that in the film. At this point, the system is said to be in *saturation*, which coincides with the plot of excess adsorption vs pressure dropping to zero (Fig 2.6).

Recently, it has been demonstrated that the saturation density of several different carbon-based samples of varying morphologies were universally similar (100-115 g H₂/L sorbent at 77K), and remarkably, greater than that of liquid hydrogen (71 g/L at 20K)[21]; this can be interpreted as support for the integral role the unique Hydrogen-Carbon London dispersion interaction plays in mediating the adsorption process.

Excess adsorption measurements yield invaluable insight into the storage properties of a material. Adsorption, as a surface phenomenon, is mediated by two main material properties: the total surface available (Σ) and the strength of the surface-gas interaction (E_b). It has been well documented that excess adsorption scales linearly with surface area (1 wt% maximum H₂ excess adsorption per 500 m²/g at 77K[30]), so normalization of an excess adsorption plot to the surface area (*aerial excess adsorption*) thus represents an indirect measure of a sample's effective binding energy.

Ultimately though, while tremendously useful in characterizing and comparing sample uptake properties, excess adsorption on its own ultimately gives little information regarding its true capability as a storage medium.

2.4. Gravimetric and Volumetric Storage Capacity

Total uptake of a material, which gives more applicable information from an engineering standpoint, requires quantification of both gas phases: excess and bulk. Therefore, the total *gravimetric storage capacity* (G_{st}) is calculated through the addition of the quantity of gas in the bulk non-adsorbed phase to the previously determined gravimetric excess. While the excess has been previously defined as the quantity of gas molecules found in the adsorbed film above what would exist in a raw, compressed state, it may be extrapolated to incorporate any arbitrary (but consistent) volume. For this purpose, the total pore volume may be conveniently applied, with the total mass of gas in the bulk state within the pores represented by the product of the specific total pore volume and the gas density. In general, ϕ is a more preferable metric as it defines the pore space independent of sample structure and composition. Therefore, after applying eq 2.6, the gravimetric storage capacity may be expressed as:

$$G_{st} = G_{ex} + \frac{\rho_{gas}}{\rho_{skel}} \left(\frac{\phi}{1 - \phi} \right) \quad (2.8)$$

Similarly, the total uptake may be normalized to the total volume of the system, rather than the mass of the sorbent, resulting in a quantity known as the *volumetric storage capacity* (V_{st}). The volumetric storage capacity is often the preferred reported value over the gravimetric for a number of reasons, among them:

- In automotive applications, the addition of additional tank mass is generally not an issue. However, as space is a finite commodity (particularly in personal vehicles), volumetric efficiency is paramount.

- While G_{st} is a quantity that may only be compared to other sorbent materials, V_{st} , representing uptake having been normalized to a given storage tank, may be readily plotted against and compared to analogous systems, notably the raw compressed gas.

The volumetric storage capacity V_{st} is expressed thus:

$$V_{st} = \rho_{skel}(1 - \phi)G_{ex} + \phi\rho_{gas} \quad (2.9)$$

Fig 2.6. Plots of gravimetric excess adsorption (*left*), gravimetric storage capacity (G_{st} , *middle*), and volumetric storage capacity (V_{st} , *right*) of representative MU nanoporous carbon 3K-0079 at 77K. Data are represented by black squares, with applied Ono-Kondo fits in red. Plotted along V_{st} is the bulk gas density reported from NIST[42].

As an analogue to the total storage capacity of a material, the total amount of gas in the adsorbed phase can be calculated in a similar fashion. This quantity can yield unique insights into the nature of the kinematics within adsorbed films. However, determination of the total adsorption within a material is a non-trivial endeavor as it relies on precise knowledge of film thickness, a characteristic which isn't robustly understood and is subsequently up to significant debate[21], [37]. Various methodologies exist which attempt to resolve this question, each with their own set of assumptions, and often culminating in conflicting results. Because this work isn't dedicated to the study of the aforementioned nanoscale kinematics, total adsorption as a storage metric will not be discussed further here.

2.5. Adsorptive vs Compressed Storage

At first glance, one might be tempted to deem an adsorbent system superior to compression in the domain of nonzero excess adsorption. However, this fails to take into account volume occupied by the sorbent, which would otherwise be available to the gas. Therefore, the objective by which a sorbent system may be ultimately judged is given by $V_{st} > \rho_{gas}$. Past this limit, compression becomes a more efficient storage technique. Applying this metric to eq. 2.9 yields the following, rather satisfying relation:

$$G_{ex} > \frac{\rho_{gas}}{\rho_{skel}} \quad (2.11)$$

Simultaneous plotting of ρ_{gas}/ρ_{skel} , the quantity of gas displaced by the sorbent material, subsequently yields the effective domain in which adsorptive storage exceeds that of compressed gas.

Fig 2.7. $G_{ex}(\text{CH}_4)$ of MU carbon monolith Br-0311 with high pressure linear extrapolation. Simultaneous plotting of eq. 2.11 (using $\rho_{skel} = 2.0 \text{ g/mL}$) yields the domain in which adsorptive storage performance exceeds compressed gas capabilities.

2.6 Powder packing fraction

As defined, each of the aforementioned storage metrics relied, in some way, on the porosity determined from N₂ sorption. This value reflects the fraction of void space within a grain of material, explicitly excluding any interparticle voids that exist. While useful from a materials standpoint, it fails to accurately represent true behavior within a tank where these interparticle voids account for a significant portion of the available volumes. To this end, the packing fraction f (analogous to the formal crystallographic definition) is introduced:

$$f \equiv \frac{V_{occ}}{V_{tank}} \quad (2.12)$$

In this formulation, V_{occ} (the volume occupied within a tank) includes all intraparticle volumes (solid, as well as open and closed pores) – sorbent grains are each considered uniformly space-filling. From here, a new porosity ϕ_f that represents the true void fraction of a tank, is generated:

$$\phi_f = f * \phi_1 + (1 - f) \quad (2.13)$$

The first term refers to the tank void volume contributed by intraparticle pores, with ϕ_1 representing the “crystalline porosity” of the material, i.e. the porosity of the grains as determined by N₂ sorption. The second term then refers to interparticle void space. In this representation, using $f = 1$ returns the crystalline porosity (useful for applications regarding storage efficiency of the material itself, or for consideration of truly completely space filling materials such as monoliths), while $f = 0$ gives a tank porosity corresponding to an

empty (compressed) tank. For a filled tank, constituent grains may be approximated as monodisperse spheres, random close packing of which gives $f = 0.63$; this value represents the highest possible particulate density, as the theoretical maximum of $f = 0.74$ (coordination number 12) is unattainable for powders[43].

The tank porosity (eq. 2.13) may be implemented within eq's 1.8 and 1.9 to yield the gravimetric and volumetric storage capacities within a packed sorbent tank. Through the additional void volume now accounted for, $\phi_f \leq \phi_1$; because of this, the tank gravimetric storage is expected to be greater than that within the individual grains, while the volumetric storage would be expected to demonstrate a decrease.

Fig 2.8. Tank gravimetric and volumetric CH₄ storage capacities (open squares) calculated from the crystalline values (closed squares) using a packing fraction associated with random close packing of uniform spheres ($f = 0.63$) for representative MU powder 3K-0046 ($\phi_1=0.82$, $\Sigma=2700$ m²/g).

Using $G_{ex,f} = G_{ex,1}$ (as additional void space has no effect on excess adsorption), these quantities, relative to the performance within individual grains, can be analytically expressed via:

$$G_{st,f} = G_{st,1} + (f^{-1} - 1) \frac{\rho_{gas}}{\rho_{bulk}} \quad (2.14)$$

$$V_{st,f} = f * V_{st,1} + (1 - f) \rho_{gas} \quad (2.15)$$

$G_{st,f}$ and $V_{st,f}$ represent the gravimetric and volumetric storage capacities of a packed tank at some packing fraction f ; $G_{st,1}$ and $V_{st,1}$ are the analogous intragranular values.

The tank G_{st} features an additive term that corresponds to surplus gas storage for a fixed sorbent mass, the effect of which is greater for greater ρ_{gas} . As expected, this value increases to ∞ in the limit $f \rightarrow 0$, the case of an empty, compressed tank.

The tank V_{st} is composed of two terms: $f \cdot V_{st,1}$ corresponds to adsorptive storage within grains, while $(1-f)\rho_{gas}$ corresponds to nonadsorptive storage between grains. $V_{st,f}$ decreases with f due to the increased contribution of storage within this ‘dead volume’, ultimately mirroring ρ_{gas} in the limit $f \rightarrow 0$. At sufficiently high pressure (as dictated by eq. 2.11) and for all f , $V_{st,f}$ equals and is subsequently exceeded by ρ_{gas} .

Table 2.1. CH₄ tank vs crystalline storage capacities of 3K-0046 at 24°C (from Fig 1.8)

Pressure	$G_{st,f} / G_{st,1}$	$V_{st,f} / V_{st,1}$
35 bar	1.15	0.72
100 bar	1.30	0.81
250 bar	1.52	0.96

CHAPTER 3 – Morphological and Chemical Characterization of Activated Carbons and their Precursors

3.1 Chemical activation of biomass

Activated carbons are nanoporous materials synthesized via chemical and/or physical treatment of various biomass media. They are attractive for a number of reasons, not least of all because of the ultra-high surface areas (approaching 3000 m²/g) that are attainable via processes that are both inexpensive and labor non-intensive. Relative to other nanoporous media (metal-organic frameworks, zeolites, etc), activated carbons represent exceptional efficiency in the yield per cost.

Integral to this is the range of available starting materials, as essentially any carbonaceous biomasses are capable of generating activated carbons. This includes products that are otherwise considered waste: olive stones[26], coconut shells[27], and peach pits[28], just to name a few. The US-midwest-based ALL-CRAFT team subsequently selected corncob as a precursor material[29].

The optimal synthesis determined by the MU team involves two distinct steps: carbonization and activation. During carbonization, the parent biomass is soaked in phosphoric acid (H₃PO₄) to isolate and break down the major organic components;

subsequent pyrolysis and washing yields a graphitic-like material, designated as *Char*. This step alone dramatically augments the pore space (Fig 3.1 and Table 3.1)

Further pore development occurs during potassium hydroxide (KOH) activation. Here, hydroxyl groups react with non-graphitized carbon to generate new porosity, while intercalation of metallic potassium expands existing pores. This process has been shown to be exceptionally controllable, with variations in temperature and KOH concentration offering tunability to particular pore modalities.

Fig 3.1. Evolution of the nanoporous space of biomass corncob as native, after acid charring, and after chemical activation[44]. With each step, the total pore volume increases dramatically, propagated via the introduction of distinct 7 and 15 Å pore populations.

Table 3.1. Quantitative pore space comparison during each stage of activated carbon production

Lot #	Σ (m ² /g)	ϕ
Corncob	7	0.04
Charred Biomass	1200	0.59
Activated Carbon	2500	0.78

3.2 Corncob precursor

The starting material for MU's activated carbon synthesis is *Grit-O'Cobs 4060*, produced by The Andersons corporation. This series is produced from the woody ring of the corncob, which comprises its bulk by mass, yielding a high density, granular material that's highly sorbent, durable and contains a low ash content[45].

Fig 3.2. Diagram of the different parts of the corncob[45]. MU activated carbons are produced via the woody ring portion, which generates higher density grains, as opposed to the flakes produced by the pith and the chaff.

This particular grade (4060) is so named due to being comprised primarily (~85%) of grains sieved between 40 and 60 mesh (425 μm and 250 μm , respectively)[45]. SEM analysis (Fig 3.3) confirms this: rudimentary size analysis finds that the short dimension of almost all grains (n=52) to be between 200-500 μm . There is wide variability in the aspect ratio, with the longer dimensions ranging from square to double (A.R. 1.00-0.5); some were even longer, with several grains approaching 1 mm in length.

Fig 3.3. Particle analysis of the raw corncob material used in production of MU's activated carbons. Particle sizes are in line with the manufacturer specifications (250-425 μm sieve)

EDS chemical analysis (Fig 3.4 and Table 3.2) confirms a product that is largely free of significant unwanted contaminants. Measurement across several grains returns a minimum of 96 wt% of C and O (and implicitly, H). There are a number of additional elements clearly visible in the spectra that are consistent with components expected of corncob ash[46]; with the exception of K, all of which comprise well below 1 wt% in the sample.

Fig 3.4. EDS chemical analysis of several grains of raw corn cob; quantification given in Table 3.2. Each location was predominantly C & O with similar contaminants that are consistent with ash.

Table 3.2 Composition of raw corn cob precursor, as indicated in Fig 3.4.

Wt%	#1	#2	#3	#4
C	50	51	52	53
O	47	48	44	45
K	1.5	0.5	2.3	1.6
Cl	0.5	0.2	0.2	0.5
P	0.1	0.1	0.6	0.3
Si	0.1	0.1	0.5	0.1
Cu	0.2	0.2	0.1	0.2
Mg	0.1	-	0.4	0.1
Al	0.1	0.1	0.1	0.1

SEM imaging of the surface reveals a porous, cellulose-like microstructure. This is inline with what would be expected, given its reduced listed density (0.35 g/cm^3) relative to granular activated carbons ($\rho_{\text{crys}}=2.00 \text{ g/cm}^3$, $\rho_{\text{pack}}=1.26 \text{ g/cm}^3$).

Fig 3.5. Cellulose-like microstructure representative of precursor corncob.

3.3 Charring and Activation

Each step in the activation process (corncob, char, and activated carbon) is compared below in Figs 3.6-8. Along the reaction pathway, the average size of a ‘large’ grain decreases from approximately $450\ \mu\text{m} \rightarrow 350\ \mu\text{m} \rightarrow 250\ \mu\text{m}$. In addition, while the char appears largely relatively uniform, the activated carbon exhibits a significant variance, including diameters well below $100\ \mu\text{m}$.

The considerable porosity of activated carbons is most immediately evident via the large ($\sim 10\text{-}50\ \mu\text{m}$) macropores that riddle individual grains. Examination of the precursor reveals these to be products of the initial charring. While certainly not negligible, the N_2 results reported in Fig 3.1 and Table 3.1 indicate them to be far from the sole contributors to the exceptional pore space of activated carbons.

Fig 3.6. Macrostructure comparison of corn cob precursor (left), its product after charring (middle), and final activated carbon (right). Each stage is shown to result in a decreasing particulate size; representative markers for 450 μm , 350 μm , and 250 μm help demonstrate this.

Fig 3.7. Microstructure comparison of a char before and after activation. The large ($\sim 10\text{-}50\text{ }\mu\text{m}$) voids observed in MU activated carbons are demonstrated to form during the initial carbonization process.

Fig 3.8. Nanostructure comparison of the three stages of activation, at 10kx (left) and 40kx (right). At these length scales, the effects of the chemical activation are apparent via the increased surface roughness of the final product.

Higher magnification imaging (Fig 3.8) facilitates differentiation of the charring and activation products. Upon examination, the surface of the char is very smooth and not especially unlike the corncob. In contrast, the surface of the activated carbon is much more textured, representative of the significant disruption of the matrix induced by the KOH intercalation and consumption.

3.4 Fe contamination during activation

Backscattered (BSE) imaging reveals further information. The intensity of the BSE signal is dependent on local chemistry: regions of higher density will appear brighter. Thus, it would be expected that BSE imaging of activated carbons would yield very little contrast, especially when mounted to carbon tape. However, BSE imaging of 3K-0079 demonstrates a remarkable amount of high contrast. In addition to sporadic particulates, which may be attributed to contamination introduced anytime between synthesis to imaging, there are discrete regions within otherwise normal individual grains that generate high backscatter contrast (Fig 3.9).

Fig 3.9. In addition to minor contamination via sporadic high-density particulates, backscattered electron (BSE) images of 3K-0079 show large regions of chemical alteration of the grains themselves.

This feature is examined further via EDS in Fig 3.10. Aside from the expected C and O signals, the only other significant element present is Fe. Interestingly enough, analysis of the opposite end of the same grain returns a much reduced, but still present Fe signal; a scan of a separate grain that is free from this localized incursion returns an essentially indistinguishable spectrum, suggesting this presence to be potentially widespread, if not ubiquitous.

Fig 3.10. (Top) Chemical analysis of a contaminated grain indicate a strong inclusion of iron; this is shown to persist past where it is visible, albeit to a more limited extent. (Bottom) This same signal is present in an otherwise visibly-clean grain. This indicates potentially wide-scale contamination, most likely from the reaction vessel.

This then elicits the query as to whether the iron is introduced during activation or charring; both the acid wash (H_3PO_4) and basic activation (KOH) are similarly aggressive to stainless steel, especially at elevated temperatures[47], [48]. A similar analysis is carried out on a grain from the precursor char-0069, with the backscatter imaging exhibiting uniform contrast throughout the observed grains. Furthermore, EDS from the bare surface (Fig 3.11) is devoid of any Fe. Similar high-density particulates can be seen throughout, with EDS confirming them to be stainless steel.

Fig 3.11. EDS chemical analysis of char-0069 (the precursor of 3K-0079 from Fig 3.12) is devoid of Fe, indicating contamination likely occurred during activation.

This also helps to provide some additional context into the nature of the contamination, as all instances from the activated carbon yielded solely Fe, as opposed to the Ni, Cr, etc that would be expected to be accompanying in the case of stainless steel. It can thus be reasonably concluded that the observed contamination may be most likely attributed to leaching iron from the walls of the stainless steel reaction vessel – an issue that would be expected to compound, with each successive ‘etching’ continually weakening the material.

During large-scale production, discrete steel particulates could be fairly easily separated out by sieving or a magnetic trap; a reacted product that has interacted with an unknown quantity of material poses a much more significant concern. In addition to the unpredictable effect this would have on the adsorption potential, this would likely result in a sorbent that is considerably more susceptible to oxidation, contributing to a hastened degradation across sequential fill cycles.

To this end, the MU team explored alternative materials. Monel, a nickel copper alloy, has been long touted for its corrosion resistance[49], and has thus found emergent applications in refining and marine engineering. Charring and activation vessels were produced from monel; samples produced in these vessels were indistinguishable from those using the ‘traditional’ stainless steel vessels in both pore space measurements and morphological characterization.

Crucially, BSE imaging reveals a consistently uniform granular contrast (Fig 3.12), with the only high-density regions constrained to discrete particulates. This is confirmed via EDS, with both the char and the activated carbon consisting solely of C and O. Analysis of the particulates are consistent with typical byproducts of a large-scale processing of biomass material (steel, silicates, etc).

Fig 3.12. Backscattered electron (BSE) images of a char (left) and subsequent activated carbon (right), both produced in monel reaction vessels; dashed boxes indicate the regions used for EDS analysis (Fig 3.13). While both contain sporadic high-density particulates, none demonstrate the intragranular Fe contamination seen with the steel-synthesized samples (Fig 3.9).

Fig 3.13. EDS analysis of 1.6K-0081 activated carbon (bottom) and its precursor Char-0070 (top), both of which were synthesized in monel reaction vessels and subsequently devoid of the previously observed iron contamination. Higher density areas from BSE imaging are shown to be discrete silica and steel particulates.

CHAPTER 4 – Boron Doping via Flow Deposition

4.1 Background

Motivation

In an adsorbed gas system, storage is predicated by a number of surface phenomena.

Its ultimate efficacy is thus mainly contingent on two main factors:

1. The total surface area available to the gas
2. The strength of the gas-solid interaction

The large surface areas and microporosities generated through the activation process have long made activated carbons an attractive medium for various applications, such as water filtration[50] and as a medical treatment for ingested poisons[51]. Due to the carbon's native ability to reversibly trap materials within its porous network, many groups have investigated its potential as a hydrogen and methane fuel storage system[31], [52], [53]. A major advantage is the ability to tune the parameters of the pore space through varying activation parameters to achieve desired porosities, pore size modalities, etc[54], [55] (Fig 4.1).

Fig 4.1. The porous structure of carbons is highly controllable via the various activation parameters. Here, it's shown that the pore modality, and consequently the total porosity, increases with the concentration of the activation agent (potassium hydroxide, KOH); the sample name is indicative of the initial mass ratio of KOH to C[55].

Despite this controllability, carbonaceous-based sorbent systems have been unable to meet requisite storage targets outlined by the U.S. Department of Energy for on-board systems[56]. To that end, significant efforts have been directed toward improving the binding energy of the material via surface functionalization[31]. One such approach has focused on the direct incorporation of boron into the graphitic lattice; Monte Carlo simulations for systems impregnated with 5-10 wt% B predict an increase in H_2 binding energies from 4-8 kJ/mol[57] to as high as 13.5 kJ/mol and storage capable of meeting 2010 DOE goals[36].

Fig 4.2. Left: Graphical representation of the theoretical binding energy landscape of carbonaceous systems doped to 1 and 5 wt% B. Right: Calculated gravimetric and volumetric storage capacities of hydrogen in B-doped carbon systems to various concentrations in room and cryogenic temperatures. Both figures taken from[36].

Initial doping efforts

The MU team have undertaken extensive studies on the efficacy of such a procedure. Decaborane ($B_{10}H_{14}$) has been utilized as the doping agent as it contains a large quantity of boron with a relatively small volumetric footprint, making it a good candidate for infiltrating the microporous network of the activated carbons. Further, it is very volatile, decomposing into diborane (B_2H_6) and elemental boron at 300 °C[58].

Fig 4.3. Chemical structure of decaborane ($B_{10}H_{14}$)[59]. It's compact octadecahedral structure makes it an efficient B carrier to the micropores of activated carbons.

There are two main components to the doping procedure[37], [60]. First, crystalline decaborane is vaporized and allowed to fill the pore space. This is carried out by loading

requisite quantities of decaborane and carbon into an alumina reaction vessel under argon atmosphere, and heating the mixture to 120 °C at 2 °C/min. This rate was based on the manufacturer's recommendation: alumina is capable of withstanding high temperatures (up to around 1750 °C), but is susceptible to cracking under thermal shock[61]. Finally, the sample is heated to high temperatures (600 °C or 1000 °C, typically) to decompose the decaborane for incorporation into the matrix. Initial methods allowed the system to cool to room temperature after deposition[60], while later iterations proceeded immediately to annealing[37].

A selection of results are shown below in Table 4.1 and Fig 4.4. The concentration of boron in each produced sample is determined via prompt gamma neutron activation analysis (PGAA). The ease of analysis and the remarkable sensitivity to boron, allowing for detection as low as 10 ppb, make it an ideal technique for routine characterization.

The aforementioned doping methods are shown to be effective in delivering boron to the carbon, with concentrations between 5 and 10 wt% repeatedly achieved. Elevated concentrations (as high as 30 wt%) have been measured in samples produced with increased quantities of initial decaborane. However, this uptake is revealed to not be without cost: as the concentration of boron increases, the surface area from N₂ sorption is shown to have a corresponding decrease of about 50 m²/g for each weight percent added (Fig 4.4).

Table 4.1. Comparison of surface areas from precursor and liquid-doped carbons

Precursor Doped Samp	B Conc [wt%]	Σ [m ² /g]	$\Delta \Sigma$ [m ² /g]	ΔH [kJ/mol]
2K-0286	n/a	1940	n/a	—
2K-0248	1.7	1670	-270	—
3K-250C	n/a	2700	n/a	—
3K-H30(I,A)	8.4	2300	-400	—
3K-600C	n/a	2600	n/a	—
3K-H60(I,A)	8.6	2100	-500	—
3K-H60(I,B)	6.7	2100	-500	—
3K-H75(I,A)	1.8	2400	-200	—
3K-0079	n/a	2660	n/a	7.42
3K-0201	8.0	2030	-630	8.38
3K-0202	5.8	2300	-360	—
3K-0205	9.7	2260	-400	7.76
3K-0207	12.4	2000	-660	—
3K-0208	13.7	1950	-710	—
3K-0209	14.8	1700	-960	—
3K-0211	6.2	2180	-480	7.76
3K-0212	7.4	2100	-560	—
3K-0226	3.4	2300	-360	—
3K-0227	4.0	2400	-260	—
3K-0285	n/a	2590	n/a	—
3K-0219	8.7	1980	-610	—
4K-0288	n/a	2790	n/a	—
4K-0240	1.5	2530	-260	7.32
4K-0244	1.6	2460	-330	7.61
4K-0245	3.9	2490	-300	7.62
4K-0246	4.1	2370	-420	7.38
4K-0747	3.6	2350	-440	7.07
4K-0748	5.6	2390	-400	8.27
4K-0749	5.9	2250	-540	7.22
4K-0750	6.9	2190	-600	8.09
4K-0751	5.9	2490	-300	7.38
4K-0752	9.1	2060	-730	7.24
5K-0280	n/a	2700	n/a	—
5K-0215	8.0	1950	-750	9.64
5K-0742	3.9	2350	-350	—

Fig 4.4. Results of boron doping via liquid deposition of decaborane ($B_{10}H_{14}$). Left, Bottom: Surface area is shown to decrease by around $50 \text{ m}^2/\text{g}$ for each wt% boron added to the sample. Left, Top: The same samples (where available) demonstrate a negligible increase to the enthalpy of adsorption, well short of the 13.5 kJ/mol predicted at $10 \text{ wt\%}$. Right: Pore size distribution of doped samples shows that the decrease in surface area is correlated to a reduction in the nanoporous volume.

A brief examination of the corresponding pore size distributions demonstrates a reduction in the nanoporous volumes within the samples as boron concentration increases. This decrease can thus be most likely attributed to pore blockage. As the decaborane melts, it may condense at pore entrances, preventing uniform deposition. This is supported by the marginal increases in enthalpy of adsorption observed for most doped samples, indicating the lack of widespread boron substitution throughout the sample.

To avoid this, samples were produced in which the decaborane was kept separate from the carbon, mitigating any direct incidence of liquid decaborane on the pore space. This method proved to be ineffective, yielding only a small fraction of the boron concentration found in samples doped via the original procedure. It's possible that some quantity of decaborane deposited on the reaction vessel, but as there is considerably more available surface area within the sample, this effect is likely minimal.

Table 4.2. Comparison of samples doped with and without exposure to liquid decaborane. All samples produced from sample 3K-0079 preoutgassed to 600 °C and using a quantity of decaborane equivalent to 6.6 wt% B.

Sample	Deposition Method	Outgas Temp	B conc (PGAA)
3K-0201	Liquid (Stationary)	600 °C	8.0 wt%
3K-0202	Liquid (Stationary)	1000 °C	5.8 wt%
3K-0203	Vapor (Stationary)	600 °C	0.3 wt%

As will be discussed in the following section, decaborane is strongly interacting with carbon; the more likely candidate is adsorption to the immediate (i.e. top) carbon surface, prior to infiltration of the pore space. Thus, after annealing, the bulk of the boron would have either outgassed from the system or been highly localized.

To overcome this, a carrier gas will be introduced to aid diffusion. Ar was selected as it is highly inert and matches the glovebox storage environment of both the precursor and produced samples. As with gas chromatography, the performance of a carrier gas depends on a number of different factors: temperature, flow rate, etc. These will be discussed below.

Flow Deposition Viability

As has been shown, the initial deposition of decaborane into the pore space is crucial to the doping mechanism. In stationary doping, crystalline decaborane is mixed directly with powdered carbon. This proximity facilitates decaborane uptake within the pore space, something that flow doping lacks by design.

Instead, with vaporized decaborane limited to flowing across the surface of the carbon, the deposition relies on its active adsorption. The decaborane-graphene interaction is quite strong, on the order of ~70 kJ/mol[62]; when considered along with the much

weaker decaborane-decaborane interaction and relatively small molecular footprint, it is expected to generate strong uptake.

This uptake can be modeled using theoretical Langmuir isotherms[63], which are viable in the low-pressure regime expected for strong adsorbers. The curve is described by:

$$\theta[T, p] = \frac{\chi[T] * p}{1 + \chi[T] * p} \quad (4.1)$$

where $\chi[T]$ is the localized Langmuir constant:

$$\chi[T] = \frac{e^{-Eb/kT}}{\prod_{i=1}^3 \sinh\left(\frac{h\nu_i}{2kT}\right)} \left(\frac{h^6}{(8\pi M_{DB}/N_A)^3 (kT)^5} \right)^{1/2} \quad (4.2)$$

The Langmuir model describes molecular interactions in terms of surface coverage, i.e. the fraction of available ‘sites’ occupied by the adsorbed molecule. To express this in terms of gravimetric adsorption G_{ads} :

$$G_{ads}[T, p, \Sigma] = \frac{m_{ads}}{m_{samp}} = \left(\frac{M_{DB} * \Sigma}{N_A * \alpha_{DB}} \right) * \theta[T, p] \quad (4.3)$$

Finally, converting to the weight percent of boron:

$$w_B[T, p, \Sigma] = \frac{m_B}{m_{samp}} = \frac{G_{ads}[T, p, \Sigma]}{\left(M_{DB}/10M_B \right) + G_{ads}[T, p, \Sigma]} \quad (4.4)$$

Langmuir curves using temperatures 100-150 °C are shown Fig 4.5, expressed in units of gravimetric adsorption of decaborane as well as boron weight percent. As

expected, the strong decaborane-carbon interaction produces large uptakes at low pressures. Further, phase information can be incorporated via decaborane's liquid-gas coexistence curve[60], given by:

$$\ln(p[T]) = -9.38 * 10^{-5}T^2 + 0.06T - 8.89 \quad (4.5)$$

For a given isotherm, pressures above the coexistence limit yields liquid decaborane. Thus, consideration of this behavior helps define the upper limit of uptake possible within the sample. As demonstrated in Fig 4.5, at 120 °C (the temperature used for deposition during both stationary and flow doping) a porous carbon with a surface area of 2700 m²/g (a typical value for MU-produced '3K' activated carbons) allows for up to the equivalent of ~70 wt% B to be deposited on the surface before liquefaction. Indeed, it is apparent that 10 wt% B is readily achievable across all temperatures.

Fig 4.5. Adsorption curves for decaborane on carbon, based on the Langmuir model. The right axis displays the conversion to weight percent boron. The liquid-gas coexistence point is plotted for each curve, which correlates to the upper bound of decaborane that may be deposited in the gas phase. The dashed green line indicates the adsorption required for 10 wt% B uptake to be well below the point of liquification.

Table 4.3. Values incorporated as parameters in Equations 4.1-5 when generating Fig 4.5[62]

$v_{x/y}$ [Hz]	v_z [Hz]	E_b [kJ/mol]	α [m ²]	Σ [m ² /g]
6.59×10^{12}	11.9×10^{12}	-71.3	12.25×10^{-20}	2700

4.2 Experimental Setup

Hardware

A custom apparatus was developed and built in-house to perform this synthesis. (Fig 4.6). The central component is a long (≥ 40 cm) quartz tube (1 in. OD) that serves as the reaction vessel. The tube houses two quartz boats (10cm long) that to hold the decaborane and carbon in the upstream and downstream ends, respectively. The decaborane section of the tube is heated via heating tape; an initial design had the carbon encased within a bead bath ('2-step flow'), but this was eventually replaced with a split tube furnace to facilitate immediate annealing ('1-step flow'). Both heating elements are regulated with programmable temperature controllers to specific rates. An alumina block sits at the far downstream end of the tube to protect the gaskets from radiant heat damaging the gasket.

From upstream, an Ar source is fed directly into an analog flowmeter which modulates the incoming flowrate of the carrier gas. The flowmeter is fed into the common port of a T-valve; this allows the line to be purged prior to directing flow into towards the reaction vessel, which is isolated by a second valve. An analog pressure gauge monitors the pressure of the carrier gas immediately prior to the decaborane. A ball valve isolates the reaction vessel on the downstream side, which leads to a dry ice cold trap to prevent any escaping decaborane. Finally, an analog pressure regulator is used to modulate the pressure in the reaction vessel (measured via the upstream gauge).

Fig. 4.6. ALL-CRAFT-designed and -constructed instrument to produce boron doped samples under Ar flow. Flow direction is left to right. $B_{10}H_{14}$ and C are loaded into separate quartz boats and placed inside the reaction vessel, with the entirety of the hardware between the hoses assembled and sealed inside the glovebox.

Procedure

Appropriate quantities of $B_{10}H_{14}$ and C are measured and loaded into the reaction vessel, and the adjoining valves are assembled and sealed inside the glovebox so as not to introduce atmospheric contamination. The vessel is transferred to the fumehood where the reaction will take place, and the peripheral components attached. With the t-valve venting to the hood, Ar flow is initiated and the upstream pressure set with the flowmeter; this also serves to flush the line. The t-valve is then reversed, with flow incident upon the closed valve.

To begin the reaction, the carbon boat is first brought to temperature (120 °C) and allowed to equilibrate; during this time, the decaborane is cooled with a dry ice bath. This serves to eliminate any thermal gradient within the bulk carbon that the vaporized $B_{10}H_{14}$ might condense onto. After 30 minutes, the dry ice bath is replaced with heat tape and

flow is initiated. The desired pressure, measured with the upstream gauge, is adjusted with the backpressure regulator to the desired level. The decaborane is heated at 2 °C/min (so as to be consistent with the stationary doping) and held for 1 hour. For ‘1-step’ doping, the furnace is directly ramped to the annealing temperature; for ‘2-step’ doping, the system is cooled, sealed, transferred into the glovebox, and annealed in a separate vessel.

Fig. 4.7. Temperature and pressure profiles used for the flow doping apparatus. The dotted line at ~500 min. in the 2-step annealing process references the unspecified time to transfer the system to a separate annealing vessel in the glovebox.

As will be discussed further, boron was eventually discovered to substitute into the matrix (as designed) at a fairly poor rate, with generally over 90% of deposited boron found to exist as unreacted species. To combat this, an additional ‘massive annealing’ was implemented, whereby samples would be ramped to 1200 °C in alumina (at 2 °C/min), held at that temperature for 16 hours, and ramped back down at the same rate. The product of this treatment was subsequently assigned a separate, unique lot number.

Parameters

The following parameters offer variability within the reaction procedure:

- a. Reaction temperature, via the tube furnace
- b. Carrier gas flow rate, via the upstream flowmeter
- c. Ambient pressure, via the downstream regulator
- d. Initial B content, via the included mass of decaborane

Of the customizable parameters, the temperature is perhaps the most critical as it most directly governs the resulting gas kinetics; however, all syntheses were performed 120 °C (and using a ramp rate of 2 °C/min) so as to be consistent with prior methods ('stationary' doping).

Of the remaining, flow rate and pressure most directly contribute to the decaborane evaporation rate and, along with the initial quantity used, the overall exposure time.

Evaporation Rate

Calculation of a material's evaporation rate depends on a large number of parameters, many of which are dynamic, non-uniform, and/or interconnected; thus, reliable analyses are typically constrained to empirical observation[64]. One estimate, derived for the release of hazardous materials[65], approximates the evaporation rate E by

$$E[g/s] = \frac{18^{1/3}}{4} \frac{M^{2/3}}{RT} * A * P_{vap} * u^{0.78} \quad (4.6)$$

where M is the molar mass, $R=83.14 \text{ bar}\cdot\text{cm}^3/\text{mol}\cdot\text{K}$ is the gas constant, T is the reaction temperature in K, A is the surface area of the material in cm^2 , P_{vap} is its vapor pressure in bar, and u is the ambient air velocity in cm/s. Under this formulation, the power law of the air velocity u is indicative of the reduction of the mean due to turbulent flow[66].

The open face of the quartz boats containing the decaborane serves as the area ($100\text{mm}\times 17\text{mm}=17\text{cm}^2$). Using Matthew Beckner's decaborane phase model[60], the

vapor pressure of decaborane at 120°C is determined to be 59.16 mbar. With these values, the evaporation rate can be given by

$$E[\text{mg}/\text{min}] = 29.8 * u^{0.78} \quad (4.7)$$

Prior to the reaction vessel, the N₂ gas flow is governed by the analog flowmeter. The outgoing rate is measured in *standard cubic feet per hour* (SCF), the flow rate of the gas under IUPAC standard conditions: T_{std}=273.15 K and P_{std}=10⁵ Pa=1 bar[67]. Converting to the elevated temperature and pressure of the reaction volume (i.e., the ‘*actual*’ cubic feet per hour):

$$ACF = \left(\frac{P_{std}}{P_{rxn}}\right) \left(\frac{T_{rxn}}{T_{std}}\right) * SCF = \frac{1 + \frac{T_{rxn}[\text{°C}]}{T_{std}}}{P_{abs}[\text{bar}]} SCF \quad (4.8)$$

Normalizing this volumetric flow rate to the reaction vessel’s cross section (ID=20 mm) gives the Ar carrier gas flow velocity:

$$u[\text{cm}/\text{s}] = 3.60 * \frac{SCF}{P_{abs}[\text{bar}]} \quad (4.9)$$

Combining this with 4.7 gives the net result:

$$E[\text{mg}/\text{min}] = 81 * \left(\frac{SCF}{P_{abs}[\text{bar}]}\right)^{0.78} \quad (4.10)$$

Samples Produced

The installed flowmeter is capable of measuring output between 0.4-5.0 scfh. Higher flow rates are certainly possible, but not employed so as to avoid significant turbulence and displacement of the powder. 0.5 and 2.0 scfh were selected for this study.

Assuming all fittings and accessories are suitably rated, the pressure is limited by the overpressure allowable by the quartz reaction vessel. Using a design strength of 1000 Pa[68], this limitation, via the hoop strength[69], can be expressed as:

$$\left(\frac{(OD - t)^2 + t}{(OD - t)} \right) \frac{P}{2t} = \left(\frac{(ID + t)^2 + t}{(ID + t)} \right) \frac{P}{2t} < 70 \text{ bar} \quad (4.11)$$

where OD/ID are the outer/inner diameters, t is the tube's wall thickness, and P the absolute pressure inside the tube. With $OD = 25.4$ mm and $t = 1.5$ mm, the maximum allowable pressure is 8.75 bar. 1.2 and 2.5 bar were selected for this study, with the latter listed as the maximum pressure measurable by the gauge included with the cell assembly.

Lastly, 1 g of carbon (specifically, 3K-0079) was used for each sample to maintain a constant volume for the dopant to interact with. 0.125 and 0.5 g of decaborane were selected; these values correspond to ultimate boron concentrations of 10 and 30 wt%, respectively and assuming perfect efficiency.

Altogether, 4 samples were produced to study the effect of the various conditions; these are summarized below.

Table 4.4. Conditions utilized to deposit decaborane using Ar flow

Lot #	gDB/gC	SCF	P _{abs} [bar]	E[mg/min]
0230	0.125/1	2	2.5	68
0231	0.125/1	0.5	2.5	23
0234	0.125/1	0.5	1.2	41
0235	0.5/1	0.5	2.5	23

Sample 3K-0231 used a low flow rate and high cell pressure, thus serving as minimal evaporation baseline. Evaporation rate was increased via flow rate and pressure in samples 3K-0230 and 3K-0234, respectively. Finally, sample 3K-0235 used identical flow conditions as 3K-0231, but a greater amount of decaborane, thereby increasing the

carbon's total exposure. The normalized results for both evaporation rate and exposure time across all samples are summarized below.

Fig 4.8. Normalized evaporation rates and times for the parametric study of flow doping conditions. Minimum evaporation rate (and subsequently maximum exposure time) is represented by sample 0231, with an increasing rate provided by through increased flow rate and decreased ambient pressure for samples 0230 and 0234, respectively. Sample 0235 used the same conditions as 0231, but a greater initial decaborane mass, thereby increasing exposure time.

4.3 Results

Boron doping results

The results of the deposition are shown below in Table 4.5, and are compared to stationary doping in Fig 4.9. As shown, the ultimate B uptake of flow doped samples is significantly less than that of liquid doped samples; whereas the former routinely exhibits nearly perfect *uptake efficiency* (i.e., the measured B concentration relative to the stoichiometrically predicted value), the highest performing flow doped sample was about half. However, even the lowest measured flow-doping sample demonstrated significant improvement over the stationary-doping vapor counterpart. Further, there appears to be some consistency: samples 3K-0231 and 3K-0235 were produced under identical conditions, with varying degrees of initial decaborane content, and exhibited similar uptake

efficiency. This would seem to suggest the uptake is process-dependent (likely related to the aforementioned evaporation rates), with preference towards lower flow rates and cell pressures.

Table 4.5. B uptake of samples produced for parametric study of flow doping conditions

Lot #	B _{conc} (pred)	Flow	Pressure	Annealing	B _{conc} (PGAA)	Efficiency
0230	10 wt%	High	High	1000 °C	1.6 wt%	0.16
0231	10 wt%	Low	High	1000 °C	3.0 wt%	0.30
0234	10 wt%	Low	Low	1000 °C	5.2 wt%	0.52
0235	30 wt%	Low	High	1000 °C	10.8 wt%	0.35

Fig 4.9. Samples doped via flow-assisted vapor deposition (red hatched) under different conditions all demonstrate markedly improved deposition quantities compared to the non-flow-assisted (blue hatched).

B diffusion into C pore space

The above PGAA results confirm the successful delivery and deposition of decaborane to the carbon; however, in order to be considered a more effective doping method than stationary, it must be demonstrated to have efficiently diffused throughout the pore space. Vapor deposition of monolithic carbons (as explored in Chapter 5) is shown to be diffusion-limited, albeit on the ~cm scale whereas MU activated carbons feature

diameters well below 1 mm (and often 100 μm) across their narrowest dimension. Further, those samples were produced without preheating the carbon surface, providing a ‘cold’ surface upon which the decaborane could readily condense, especially given the now-quantified affinity between the materials.

Focused ion beam (FIB) milling provides a method for exploring this. Generally coupled within an SEM, the technique involves the impingement of high energy metallic ions onto a given surface. This is a naturally destructive procedure that is capable of milling to nm-level resolution.

Sample 3K-0235 was chosen for study because of its high B content (10.8 wt%, as measured by PGAA). As B is at the low end of the detection limits for even modern EDS systems, a higher concentration improves the likelihood of being able to deconvolute the B signal from the nearby C. Upon selecting a suitable particle and site, a 2 μm thick protective layer of Pt is deposited. This serves to protect the integrity of the milled face by minimized ‘curtaining’ by stray ions. A cross section is exposed first by high-current milling to remove the bulk material, followed by a lower current milling that polishes the face for analysis. This process can be seen in Fig 4.10.

Fig 4.10. Preparation of a analyzable cross-sectional face from a single grain of sample 3K-0235. A layer of Pt is deposited directly above the section to be exposed to serve as a protective barrier. Bulk material is then removed by high-current Ga ion milling. Finally, a low-current polishing yields a bulk face suitable for analysis.

Imaging of the exposed cross-section (Fig 4.11) reveals an amorphous structure with areas of varying visible porosity, the diameters of which range from ~ 10 -100nm. EDS hypermapping exhibits, in addition to uniform C throughout the face, a high concentration of B located uniformly at the periphery. This indicates a large degree of the deposition occurs on the surface of the grains.

However, a significant amount of B is also detected across the face itself, and specifically in regions correlated to the visible porosity. This result confirms that the vaporized decaborane has full access to the carbon's porous network and deposits throughout. Further, the localization of the observed B serves to mitigate the concern of the detected counts resulting from surface-deposited B having been displaced during the milling process.

Fig 4.11. Boron diffusion through the bulk. Top left: Cross-section of a single grain of B-doped sample 3K-0235 (10.8 wt% B, via PGAA), prepared via FIB-SEM milling. Right: Inset demonstrating regions of localized exposed porosity. Bottom left: B elemental map (via EDS) of the interior – the regions of high B concentration correlate well with the visible porosity, providing evidence of diffusion throughout the entirety of the pore space.

Observation of the surface boundary reveals an additional aspect of the doping mechanism. When imaged in backscatter (bottom right in Fig 4.12), an amorphous layer (approximately 200-400 nm thick) is visible at the immediate boundary. The reduced intensity of this area indicates that it is of lower mass density; this would seem to correlate well with the observed B boundary layer observed in the EDS map from Fig 4.12. However, a secondary image collected simultaneously (bottom left in Fig 4.12) denotes little distinction between the two regions, perhaps aside from somewhat reduced porosity, refuting that this could be a separate structure and instead possibly directly demonstrating B diffusion through the C matrix itself.

Fig 4.12. High magnification inset of FIB-exposed cross-section of 3K-0235 (10.8 wt% B, via PGAA) at the surface boundary under secondary and backscatter imaging (T2 and T1 detectors, respectively). The high-density layered structure visible at the top of the cross-section is a protective Pt layer. The Pt-C boundary (annotated in yellow) is clearly visible in the secondary image (bottom left), with the C appearing fairly uniform in structure. A backscatter image (bottom right, collected simultaneously with secondary) shows a region of lower density extending >500 nm into the bulk. It's reasonable to assign this to B (see the ring of B from the elemental map in Fig 4.11), and thus may serve as a measure of the extent of boron intercalation through the C matrix.

Effect on pore space via N₂ porosimetry and BET

The pore space of flow-doped samples are shown to be similarly affected by the introduction of B as those doped via the stationary method. In Fig 4.13, both the cumulative as well as differential pore volumes demonstrate an analogous, uniform decrease with increasing B content.

Fig 4.13. Cumulative (top) and differential (bottom) pore volumes for flow-doped samples

Both the BET surface area and porosity also experience appreciable decreases with increasing B content (Table 4.6), with the surface area in particular exhibiting a similar loss rate as stationary doped samples ($\sim 50 \text{ m}^2/\text{g}/\text{wt}\%$, Fig 4.14). The smallest pore volumes are perhaps the most pertinent to investigate; in addition to contributing the greatest absorptive potential (Fig 2.3) and thus shouldering much of the low-pressure storage, they would naturally be the most susceptible to clogging. However, analysis of the sub-nm pore fraction, defined as the fraction of total pore volume contributed by pores of width $\leq 10 \text{ Å}$, demonstrates minimal difference in reduction of these pore geometries, especially

compared to the effect demonstrated by the high temperature annealing alone (Fig 4.14, right).

Table 4.6. N₂ porosimetry measurements for samples produced for parametric study of flow doping conditions

Lot #	Method	B _{conc} [wt% B]	Σ _{BET} [m ² /g]	φ	V _{pore} (<1nm)/ V _{pore} (total)
0079	<i>Precursor</i>	n/a	2680	0.785	0.275
+OG 1000°C	<i>Precursor</i>	n/a	2530	0.782	0.260
0227	Stationary	4.0	2440	0.776	0.258
0201	Stationary	8.0	2030	0.742	0.260
0208	Stationary	13.7	1950	0.739	0.247
0230	Flow	1.62	2320	0.780	0.230
0231	Flow	2.96	2230	0.753	0.273
0234	Flow	5.2	1880	0.724	0.266
0235	Flow	10.8	1620	0.702	0.254

Fig 4.14. Left: Flow doped samples exhibited a similar decrease in surface area as noted in Fig 4.3. Right: Flow doped samples demonstrate a loss of sub-nm pore space at a similar rate as stationary doped samples.

H₂ binding energy

The gas-solid interaction strength can be determined via application of the Clausius-Clapeyron relation to isothermal measurements at adjacent temperatures[70]:

$$\Delta H(\theta) = \frac{RT_1T_2}{T_2 - T_1} \ln \left(\frac{p_2(T_2, \theta)}{p_1(T_2, \theta)} \right) \quad (4.12)$$

In Eq 4.12, p_1 and p_2 represent the pressures of each isotherm at some constant coverage θ . This presents a challenge when working with experimental data, as the volumetric method doesn't allow for collection at specified pressures; rather, it's required to fit one of the isotherms, which isn't always straightforward (Appendix 3), in order to interpolate to an associated value from the other. On top of this, calculation of the absolute adsorption from the experimentally determined excess adsorption requires knowledge of the absorbed film thickness, an exceptionally nontrivial endeavor[21].

Fig 4.15. Representations of 77K and 87K H_2 absolute adsorption curves across the full isotherm (left) and in the low-pressure (“Henry’s Law”) regime (right). Calculation of the gas-solid binding energy via eq 4.12 requires fitting a wide range of points and interpolating (left); doing so via 4.14 only requires the determination of the slope from the linear low pressure regime (right).

At very low pressures ($\ll 1$ bar), gas adsorption can be modeled via the linear Henry’s Law:

$$m_{\text{abs}} = k_H * p \quad (4.13)$$

As the contribution from the bulk is essentially non-existent in this regime, the gravimetric excess is a more than suitable approximation for the absolute adsorption. Thus,

upon substituting 4.13 into 4.12, the enthalpy of adsorption can be determined by linear fitting of low-pressure sorption data (Fig 4.15, right), and inputting the generated slopes k_H into:

$$\Delta H(\theta) = \frac{RT_1T_2}{T_2 - T_1} \ln \left(\frac{k_H(T_1)}{k_H(T_2)} \right) = \left(5.59 \frac{\text{kJ}}{\text{mol}} \right) \ln \left(\frac{k_H(77\text{K})}{k_H(87\text{K})} \right) \quad (4.14)$$

The results of the fitting area shown below in Fig 4.16, and summarized in Table

4.7.

Fig 4.16. H₂ isotherms of the undoped precursor (left) and boron flow-doped samples (right) in the low pressure limit. In this regime, strong adsorbers demonstrate linear behavior and excess adsorption approximates total adsorption; analysis of the resulting slopes can be used to calculate binding energies.

Table 4.7. Enthalpy of adsorption measurements for flow-doped samples

Lot #	Method	B _{conc} [wt% B]	Slope (77K)	Slope (87K)	ΔH [kJ/mol]
0079	<i>Precursor</i>	n/a	573	146	7.7
0201	Stationary	8.0	613	93	10.6
0230	Flow	1.62	617	131	8.7
0231	Flow	2.96	444	119	7.4
0234	Flow	5.2	478	89	9.4
0235	Flow	10.8	271	94	6.0

Using this method, a representative stationary-doped sample (3K-0201, 8.0 wt% B) is determined to have an enthalpy of adsorption ΔH of 10.6 kJ/mol, a demonstrable improvement over the undoped precursor's 7.7 kJ/mol. By comparison, the samples doped via flow exhibit a much more modest improvement, with the greatest value, 9.4 kJ/mol, measured for 3K-0234 (5.2 wt% B); as uncertainties >1 kJ/mol are not uncommon[37], this doesn't indicate an especially remarkable improvement.

This is supported through high-pressure ($p < 200$ bar) H_2 sorption measurements (Fig 4.17) where uptake in the doped sample is observed to be significantly reduced compared to its undoped precursor. This can be most likely attributed to its dramatically decreased surface area: 1900 m^2/g compared to 2700 m^2/g in the parent material. Normalizing the gravimetric excess adsorption (units: g sorbate / g sorbent) to the surface area (units: m^2 sorbent / g sorbent) yields the surface excess adsorption (units: g sorbate / m^2 sorbent), a metric that isolates the contribution of the material's binding energy as it pertains to its potential as an adsorption medium. The surface excess for the doped sample is shown to be only marginally greater than for the undoped parent, in agreement with the previous enthalpy measurements.

Fig 4.17. Gravimetric (black) and surface (blue) excess plots of flow-doped 3K-0234 versus its undoped precursor 3K-0079. The reduction in gravimetric excess in the B-doped sample is likely due to its heavily reduced surface area; this is confirmed upon normalization, with a slightly increased surface excess concentration indicative of a marginally more attractive sorbent.

4.4 Investigation of the B-C bonding environment

Achieving the proposed augmentation binding energy through doping[36] requires the incorporation of boron into the carbon matrix itself; adsorption and surface bonding would not see such improvements, rather would likely be deleterious through obstruction of pore space and adsorption sites. Therefore, characterization of the chemical environment of the deposited boron is of equal importance as its quantification.

This substitution generates minimal structural alterations to the lattice, with effects as minor as $>1 \text{ \AA}$ maximum out-of-plane deflection[71]. Therefore, chemically-based characterization techniques are required. Many of these, while readily available for analyzing bulk samples, don't offer any significant information past quantification (e.g. PGAA, EDX). NMR would seem to be a natural fit given the high receptivity of ^{11}B relative to ^{13}C [72]; however, the paramagnetism native to graphitic materials, as well as

the presence of a number of various magnetic contaminants due to their origins as waste biomass, result in peak broadening and background contributions that hindered higher-order analyses[73].

Chemical Analysis: FTIR

Fourier-transform infrared spectroscopy (FTIR) is a technique that's found applications across many disciplines. This is in large part due to its distinct conceptualization as an interferometry-based analysis that probes the constituent bonds directly. The resulting spectral data is representative of the various vibrational modes (e.g. stretching, bending, twisting, etc) characteristic of that bond, insight not typically attainable outside of synchrotron sources.

To that end, FTIR was employed in an attempt to confirm the presence of sp^2 bonded boron groups within doped samples[74]. A trough at 1020 cm^{-1} is assigned to B-C stretching vibration[75] and serves as the positive indicator. However, this falls inside the so-called fingerprint region, a set of frequencies (typically between $1500\text{-}500\text{ cm}^{-1}$), that contain a large quantity of absorption bands for organic compounds[76]; this typically results in a complex spectral pattern that is characteristic of that compound as a whole, but wherein individual features are difficult to analyze. An infrared microscope was implemented as a means to overcome this hurdle, which served to isolate the desired structures from the less-desirable surrounding environment. This resulted in dramatically improved resolution across all bands (Fig 4.18, left).

The results for sample 3K-H30 (8.4 wt% B via PGAA) are shown below, compared the undoped precursor. The results do demonstrate evidence of a B-C bonding, but the

corresponding signal is much too weak to be relied upon for anything further than qualitative confirmation.

Fig 4.18. FTIR analysis of B-doped nanoporous carbon. Left: the incorporation of a microscope to the FTIR system (green) dramatically improved the resolution compared to results from the native device (black/blue), allowing the signal from B-C stretching at 1020 cm^{-1} to become differentiable from the fingerprint region when analyzing boron carbide (B_4C) as a reference material. Right: measured FTIR absorption spectra for undoped (top) and doped (bottom) activated carbons.

Chemical Analysis: EELS

Electron energy loss spectroscopy (EELS) is another attractive candidate. EELS spectra are generated the deconvolution of the TEM signal as the beam is modulated via interaction with the sample's electron cloud, rather than its nucleus. As such, it is capable of delivering considerably more refined information. For example, graphite and diamond would be indistinguishable by most chemical-based analysis methods; however, EELS can readily differentiate the two by a sharp absorption peak correlating to the pi bonding present in the former that is absent in the latter. A similar distinction would be expected between the B signals of the native decaborane adsorbed to the pore wall and those substituted into the sp^2 bonding environment of the C matrix.

Sample 5K-0215 (8 wt% B via PGAA) was pressed into a KBr pellet as in the FTIR study. This helped minimize the exposure to atmosphere during transport prior to loading into the Helios FIB for milling. The pellet was loaded directly into the microscope, and a

partially exposed grain selected for analysis. FIB milling and polishing (Fig 4.19) produced a 200 nm thin lamella supported by thick KBr posts on either end.

Fig 4.19. FIB milling utilized to produce a thinned lamella suitable for TEM analysis. a. A partially exposed carbon grain protruding from the pressed KBr pellet. b. One side of the FIB milling that exposed the grain cross-section for analysis. c. Thinned and extracted lamella, mounted for transport. A large carbon cross-section can be seen in the upper left and a smaller section in the bottom right; the remaining material is interstitial KBr. d. Thinned lamella as seen from above.

The lamella was transported to MU-EMC and analyzed using the Tecnai F30 TEM and its associated Gatan imaging filter (GIF) to generate EELS data. Unfortunately, the main cross-section intended for imaging proved to be too thick to yield reliable data. Instead, a second, smaller particulate was analyzed; thickness mapping (Fig 4.20) confirmed this section was to be uniformly less than 1 electron mean free path in thickness, and thus suitable for analysis. However, collected EELS spectra failed to generate B counts appreciably above background, much less in quantities that would afford higher-order analyses.

Fig 4.20. a. TEM image of an electron-transparent region of the lamella. b. EELS thickness measurements confirm the sample to be uniformly less than 1 mean free path (200 nm at 300 kV for carbonaceous materials), and thus suitable for analysis. EELS scan of the region showed no appreciable B counts with which to analyze.

This highlights the main drawbacks native to this technique: it requires extensive and involved sample preparation, and is extremely localized in its scope. As seen in Fig 4.11, even a site confirmed to contain appreciable quantities of B demonstrated extensive regions of reduced concentration. Thus, effective utilization of EELS would clearly necessitate fairly thorough screening on top of the already required milling and liftout. This would be cumbersome for a single measurement, and completely impractical as a routine characterization tool.

Chemical Analysis: XPS

X-ray photoelectron spectroscopy (XPS) is a powerful and accessible technique for fine probing of a sample's chemical environment. A monochromated X-ray source impinges on the surface, with the resulting excitation generating the emission of photoelectrons; the measurable energy of each is subsequently representative of the characteristic binding energy. This is similar to the output spectra of EDS, although the direct measurement of the ejected electron itself (rather than the associated secondary x-ray emission) generates improved energy resolution: the unique bonding environment introduces measurable shifts in the binding energy, which may be distinguished via deconvolution of the resulting spectrum.

Samples of interest were analyzed on the Kratos Axis 165 at the Advanced Materials Characterization laboratory on the S&T campus using a monochromated Al- α source. First, a wide scan was collected across the full range: 0-1100 eV, using a step size of 0.5 eV. In addition to serving as a quality control check of the sample, it provides rough quantitative data via single-peak fitting of the features. Higher resolution scans (step size

0.1 eV) were also collected in the regions corresponding to the 1s orbitals of B, C, and O for deconvolution (Fig 4.21).

Fig 4.21. Example of XPS data collected for sample 3K-0205, doped via stationary deposition to 9.7 wt% B. Top: A full spectrum reveals the elements present; simple peak fitting yields a rough quantification. Bottom: High-resolution scans of the regions corresponding to the 1s component of B, C, and O (highlighted in top) allow for more refined deconvolution.

For this analysis, 6 unique bonding configurations are considered: C-C (graphene-like carbon in an sp^2 arrangement), B-C (boron substituted into the graphitic sheet), B-B (non-substituted boranes, e.g. deca-, di-, etc), C-H (terminal methyl/methylene groups from sheet peripheries), and miscellaneous oxides C-O and B-O. Some configurations are unique to a single element, however most would naturally be expected to contribute to the features of both constituent elements. This thus makes for 9 total peaks to be analyzed between the 3 individual elemental features:

Table 4.8. Peak positions and FWHMs used for deconvolution[77]–[79]

Signal	RSF	Bond	Position (eV)	FWHM (eV)
B1s	0.159	B-B	188.5	2.0
		B-C	191.0	2.5
		B-O	193.0	1.9
C1s	0.278	C-B	283.5	1.0
		C-C	284.4	0.8
		C-H	285.0	1.5
		C-O	286.5	1.5
O1s	0.780	O-B	531.8	1.8
		O-C	532.8	1.8

Included in Table 4.8 are each signals' *relative sensitivity factors (RSF)*, empirical scaling terms which compensate for the variation in signal intensity from different transitions; their incorporation is fundamental to performing accurate quantification. Peak deconvolution is remarkably non-straightforward and can yield dramatically different outputs for relatively minor variations in constraints. This is apparent when considering the proposed deconvolution for the B1s feature: the B-C peak is the primary focus, but is located in between two valleys observed for virtually all B1s regions of doped samples (Fig 4.22). This introduces a potentially high degree of high degree of ambiguity in the ultimate quantification of this feature (Fig 4.22).

Fig 4.22. Two potential deconvolutions for the B1s feature of sample 3K-0205, demonstrating possible extrema in determined B-C concentrations.

A set of relationships are thus established in order to aid in generating reliable quantification information. They are comprised of peak areas from deconvolution in addition to the aforementioned sensitivity factor, and serve to generate individual feature weights.

Table 4.9. Terms involved in peak deconvolution refinement

Parameter	Description
a_y^z	Area for each fitted peak of bond type z in the spectrum of element y
A_y	Total area of element y : $A_y = \sum_1^{all} a_y^i$
x_y^z	Fraction of bond type z in the spectrum of element y : $x_y^z = a_y^z / A_y$
X_y	Fraction (concentration) of element y within the sample: $X_y = (A_y / \sigma_y) / \sum_i^{all} (A_i / \sigma_i)$
σ_y	‘Relative sensitivity factor’ (i.e. scaling factor) of element y

The first set, labeled the ‘reciprocal equations’, require that signals from a single bond must comprise equal representation in each of the separate spectra:

$$\frac{A_B}{\sigma_B} x_B^{B-C} = \frac{1}{3} \frac{A_C}{\sigma_C} x_C^{C-B} \quad (4.15)$$

$$\frac{A_B}{\sigma_B} x_B^{B-O} = \frac{A_O}{\sigma_O} x_O^{O-B} \quad (4.16)$$

$$\frac{A_C}{\sigma_C} x_C^{C-O} = \frac{A_O}{\sigma_O} x_O^{O-C} \quad (4.17)$$

The next set, labeled the ‘consistency equations’, require that the total concentration of each element be accounted for via the individual features.

$$x_B^{B-B} X_B + \frac{1}{3} x_C^{C-B} X_C + x_O^{O-B} X_O = X_B \quad (4.18)$$

$$x_C^{C-C} X_C + 3x_B^{B-C} X_B + x_O^{O-C} X_O + x_C^{C-H} X_C = X_C \quad (4.19)$$

$$x_B^{B-O} X_B + x_C^{C-O} X_C = X_O \quad (4.20)$$

When used in conjunction with the CasaXPS fitting software, incorporation of these equations to the deconvolution process allows for a quantification that’s guided by physical rather than solely statistical significance. An example of such a protocol is given in Fig 4.23, wherein 3K-0205 is found to contain 0.9 wt% sp² bonded boron.

Fig 4.23. Example deconvolution for sample 3K-0205 for the B1s (left), C1s (top right), and O1s peaks (bottom right) after background subtraction. To aid in deconvolution, individual peaks are correlated across elements within the spectrum via the equations described in 4.15-20, e.g. the feature attributed to B-O bonding in the B spectrum is considered in conjunction with the feature attributed to O-B bonding in the O spectrum for consistency.

The results for the flow doped samples (using both standard and massive annealing) are shown Table 4.10 and Fig 4.24 below, along with representative stationary doped samples. In addition to containing comparable overall B content, they demonstrate similar sp^2 B content. Further, the massive annealing process is shown to improve the ‘efficiency’ of the doping process by significantly increasing both the total yield and the ratio of sp^2 -bonded B. The former is made apparent through each sample trending towards the solid line in Fig 4.24, which represents 100% of B in an sp^2 arrangement.

Table 4.10. Comparison of B-C weight percentages in vapor-doped samples vs liquid doped

Sample	Doping Method	B _{tot} (wt%)	B _{B-C} (wt%)	B _{B-C} /B _{tot} (%)	O _{tot} (wt%)
3K-0205	Liquid	7.5	0.9	12.5	9.0
3K-0208	Liquid	14.6	1.7	11.7	9.7
3K-0211	Liquid	7.6	0.6	8.5	10.9
4K-0240	Liquid	1.2	0.0	0.0	6.2
4K-0244	Liquid	1.7	0.0	0.0	7.8
4K-0245	Liquid	4.1	0.7	17.6	10.0
4K-0748	Liquid	5.2	1.0	18.6	7.9
5K-0215	Liquid	8.4	1.7	20.7	8.7
3K-0230	Vapor	2.5	0.1	3.2	4.4
3K-1035	Vapor	4.4	0.4	9.8	6.8
3K-0231	Vapor	6.9	0.9	13.1	8.3
3K-1036	Vapor	4.2	1.3	29.7	5.9
3K-0234	Vapor	5.4	0.7	13.0	6.5
3K-1037	Vapor	6.6	2.6	39.6	6.6
3K-0235	Vapor	27.3	1.5	5.4	10.4
3K-1038	Vapor	20.7	1.5	7.4	8.9

Fig 4.24. Samples doped via vapor deposition (blue) are shown to be comparable to those doped via liquid deposition (red) in both total and sp²-bonded B content. Samples produced via an additional 1200 °C annealing are tied to their parent sample via arrows. The solid line indicates the ideal B uptake scenario wherein all B is bonded to C; the dashed line indicates the observed trendline, which is closer to 1/6.

Sample 3K-1037 is especially notable: it is found to contain 2.6 wt% sp^2 B content, which is close to 40% of the total B of the sample. This greatly outpaces all other MU-doped carbons for both metrics, the values of which were confirmed via measurement of a separate aliquot (Fig 4.25).

Fig 4.25. B1s peak deconvolution for flow doped sample 3K-0234 (left) and its ‘massively annealed’ counterpart 3K-1037 (center/right). The sp^2 -bonded content increased substantially following the additional annealing, made apparent from the dramatic increase in counts in the region ascribed to B-C bonding across two separate aliquots.

4.5 Sample 3K-0235: an anomalous result

SEM examination of flow-doped sample 3K-0235 revealed a notable quantity of the carbon grains covered by a unique filament-like structure (Fig 4.26); these structures have not been observed on any of our other doped (or undoped) samples to date, and persisted through the high-temperature annealing that produced 3K-1038.

Fig 4.26. SEM of 3K-0235 (top left) and 3K-1038 (top right) showing the filament similarly present in both. The latter is the product of an additional 1 hour of heating at 1200 °C, indicative of a robust, likely crystalline structure. Bottom: High magnification backscatter image of 3K-0235 demonstrating the individual structures; the greater intensity of the cap regions indicates a higher density.

The filaments are 20-85 nm in diameter and long (many observed to be greater than 1 μm), and feature a more dense, roughly hemispherical cap. EDS revealed these structures to be primarily composed of B, confirming them to be most likely a product of the doping process. Additionally, the growth of these ‘B nanowires’ appeared to be correlated with localized Fe contamination. (Fig 4.27)

Fig 4.27. Left: Secondary electron image of a grain of 3K-1038 featuring an isolated filament population. Right: EDS of this region confirmed the filaments to be boron, radially distributed around a population of surface iron.

High resolution TEM (HR-TEM) was utilized to characterize these structures. A portion of 3K-0235 was suspended in an ethanol solution and sonicated for 5 minutes to isolate the filaments from the bulk carbon. After deposition onto a holey carbon TEM grid, SEM was used to identify candidate locations. HR-TEM imaging of these structures confirmed their high crystallinity (Fig 4.28). However, exposure to the beam generated fairly rapid amorphization of the structures, limiting more precise lattice measurements via electron diffraction.

Fig 4.28. Left: SEM image of individual filaments isolated on a holey carbon TEM grid after sonication. HR-TEM images confirm the increased density of the cap (middle) and the crystallinity of the body (right).

Sample 3K-0231 did not feature such filaments, despite having been synthesized under identical flow conditions; rather, the production of 3K-0235 was differentiated only by an elevated initial decaborane concentration. Instead, the surface of 3K-0231 was similarly contaminated, but with iron particulates. These particulates were considerably larger than the typical filament, ranging up to 200 nm in diameter (Fig 4.29).

Fig 4.29. SEM imaging of samples 3K-0231 (left) and 3K-0235 (right) at 5kx (top) and 20kx (bottom). Both samples were doped from the same precursor and using identical flow conditions, with the only difference consisting of a greater initial quantity of decaborane during the synthesis of 3K-0235. 3K-0231 did not feature the filaments seen in 3K-0235, but was instead found to have grains sporadically populated with Fe particulates.

These structures were most likely generated via ‘vapor-liquid-solid’ (VLS) deposition. First, a metallic catalyst is deposited onto the growth surface and formed into individual nucleation sites, typically via annealing. Then, the gaseous reactant is flowed across the surface, which has been heated above the catalyst’s melting point. The reactant is adsorbed to the liquefied catalyst, where it diffuses through the droplet. Supersaturation subsequently results in axial crystal growth from the substrate[80].

In this work, iron would serve as the catalytic site. Aside from the spatulas used for particulate transfer, iron was never directly in contact from initial receipt of the precursor carbon: the doping and first annealing were performed in quartz boats within a quartz tube, and the subsequent massive annealing was carried out in alumina. Therefore, any iron was most likely introduced during the carbon production: the parent material (3K-0079) was originally charred in stainless steel (char-0071), and iron contamination was indeed sporadically observed via XPS (Fig 4.30). Similar contamination concerns later catalyzed the implementation of a monel reaction vessel during charring and activation to improve quality control[54].

Fig 4.30. The higher-energy regime of XPS spectra of 3K-1038 (flow doped to 21 wt% boron, *red*) and 3K-0079 (undoped precursor, *black*), which was measured on two separate occasions (*black*). High degrees of iron contamination (~10 wt%, *middle*) were sporadically observed in the precursor carbon, while otherwise

being completely absent (*top*). The same contamination was observed in trace amounts in the subsequent doped sample (*bottom*).

The growth of a “1-D” boron structure is supported by evidence from the literature. Yang et al.[81] demonstrated growth of boron nanowires from VLS deposition of diborane at 900 °C (Fig 4.31); this is similar to the 1000 °C annealing performed for the synthesis of 3K-0235, with diborane an expected product of decaborane’s decomposition[58]. This work utilized Au catalysts, but Fe is commonly utilized in the VLS growth of carbon nanotubes[82], so the efficacy observed here is not overtly surprising. The propagation of these nanowires would explain the anomalously high concentration B-B bonds observed in this particular sample (Fig 4.25). Further characterization hasn’t been attempted as these structures are not expected to be advantageous for adsorption.

Fig 4.31. Left: TEM image of a cluster of filaments from 3K-0235. Right: TEM images of boron nanowires produced via VLS deposition at 900 °C demonstrating very similar structures[81].

CHAPTER 5 – Boron Doping of Nanoporous Carbon Monoliths

5.1 Background

As discussed previously, nanoporous graphite-like carbons are an attractive sorbent for a number of reasons, notably:

- a. They feature large surface areas, on the order of $2800 \text{ m}^2/\text{g}$, and
- b. They can be produced via a simple 2-step chemical washing/activation process, resulting in a material that is inexpensive and readily mass producible[83].

By varying synthesis conditions, the pore spaces of these materials can be optimized for storage through engineering specific pore sizes, porosities, and surface areas[44]. However, the binding energy of nanoporous carbon to H_2 ($\sim 6 \text{ kJ/mol}$ [36]) is prohibitively low towards meeting DOE storage goals. To this end, the ALL-CRAFT team have explored various modifications by which to improve uptake. Among these, two have proven especially promising:

1. Surface functionalization through the incorporation of B into the graphene lattice. This substitution creates an e^- deficient surface with strong binding

sites due to vacant p_z orbitals. Calculations predict an increase of upwards of 12 kJ/mol[36] on a graphene sheet doped to 10 wt% B.

2. Reduction of interstitial space via compaction. Sorption efficiency of powders is reduced by large intergranular volumes, whereby gas is stored in a compressed vs adsorbed state; the formation of a compacted monolith, wherein carbon grains approximate close-packed spheres ($\rho_{\text{packing}} = 0.63$), attempts to mitigate this. Further, binding the material serves to prevent large-scale elutriation of grains through the extended system.

All facets of sorbent production are generally tested and optimized separately, the scope of many being so great as to comprise entire dissertation projects[32], [37], [54], [60], [84]. However, an ultimate tank material would inevitably consist as an aggregation of the most promising and thoroughly investigated methodologies. To this end, we attempt to explore the logistics of implementing the two aforementioned techniques in tandem: a boron-doped monolith.

In producing such a material, a natural question arises: should boron-doped carbon be pressed into a monolith, or should a monolith be boron doped? The arguments tend to favor the latter. For one, the pressure and heat required to form the monolith may displace or otherwise disrupt the functional B groups; the localized high binding sites may also act as a sink for vaporized binder material. Further, in a hypothetical “assembly line”, an extruded monolith could be readily fed into a ‘doping-chamber’ to aid potential automation much more efficiently than loading a freshly-doped powder for compaction.

Monolith fabrication ubiquitously causes reductions in both BET surface area and porosity (Table 5.1). This can be attributed to some level of pore blockage/filling from the

binding agent *polyvinylidene chloride* (PVDC, $(C_2H_2Cl_2)_n$). While much study has been dedicated to minimizing the amount of binder required to form a viable, solid briquette[84], this effect has been unavoidable. However, while significant H_2 uptake measurements of carbon monoliths indicate that extensive pore networks remain available, it remains to be seen if the same holds true for the larger decaborane molecule. Therefore, it is prudent to evaluate the viability of boron-doping within this reduced pore space.

Table 5.1. N_2 structural characterization of representative monoliths and precursor powders.

Sample	Σ_{BET} [m^2/g]	ϕ	V_{pore} [g/cm^3]
2.5K-0086	2400	0.72	1.29
Br-0162 (Briq 15)	1900	0.71	0.58
MWV-0260	2600	0.76	1.54
Br-0311	2300	0.74	0.52

5.2 Small scale: 1 cm pellet

As a preliminary effort, a core sample, 1 cm in diameter by 2 cm in length, was cut from Br-0162 and doped following Method 1[60] to a theoretical 10 wt% B. The pellet was cut in half lengthwise, finely ground, and mixed. A PGAA measurement of this powder returned a B content of 4.51 wt%. While this is promising in terms of B yield, it gives no indication of the thoroughness of the decaborane intercalation into the monolith.

To explore the distribution, the remaining half section was segmented radially and laterally. First, it was cut into 4 cross-sectional slices; the endcap was kept intact, while the rest were roughly separated into inner and outer sections. The dimensions of each section (both thickness and radial) were determined algebraically based on the masses.

Table 5.2. Calculated dimensions and measured B content of segmented doped pellet.

Section	Mass	Thickness	Radius	B _{PGAA}
1 _{inner}	99.5 mg	3.6 mm	4.0 mm	1.64 wt%
1 _{outer}	54.6 mg		1.0 mm	3.37 wt%
2 _{inner}	63.7 mg	3.7 mm	3.1 mm	2.32 wt%
2 _{outer}	97.6 mg		1.9 mm	4.77 wt%
3 _{inner}	39.7 mg	1.8 mm	3.6 mm	4.20 wt%
3 _{outer}	38.5 mg		1.4 mm	4.85 wt%
4	38.4 mg	0.8 mm	5.0 mm	4.85 wt%

Fig 5.1. Pictorial representation of the spatial distribution of B within half of a 1 cm x 2 cm doped pellet (precursor: Br-0162). The bottom half of the pellet was initially characterized as a single unit to contain 4.5 wt% B, in good agreement with values later determined for the peripheries of the top half.

While PGAA measurements indicate B is more likely to be found in the peripheral sections, there were no sections completely vacant, indicating some level of intercalation past the immediate pellet exterior. Looking at the difference between the endcap and the innermost section (4 and 1_{in}, respectively) allows for the calculation of a rudimentary gradient of B loss through the pellet: 4.12 wt%/cm. This is a non-trivial amount of B loss,

especially in the context of our full, 3.5 inch monoliths – to dope the briquette thoroughly would require decaborane to penetrate through 4.5 cm of material, at the least.

5.3 Macro scale: 2 inch monolith

The experiment was repeated on a larger scale using well-formed briquettes extracted from the Kansas City test tank. Doping was performed in a 2 inch quartz tube, with the decaborane (to an amount equivalent to 10 wt%) in the bottom below the suspended monolith. Two monoliths were doped in different orientations: with the face parallel (“flow-through”) and perpendicular (“dispersion”) to the cross-section face of the tube (Fig 5.2).

Fig 5.2. Cartoon depicting the orientation of the ‘dispersion’ (left) and ‘flow-through’ (right) deposition samples. The side nearest the decaborane in the dispersion briquette formed a beige film after deposition (middle).

The flow-through briquette (Figure 5.2, right) was 20.50 mm tall and cut to a diameter of 43.43 mm – just wide enough to fit into the tube. For analysis, it was first cut into 3 equal cross-sections; each of these cross-sections were then cut into concentric rings

using standard 1 1/4" and 13/16" hole saws (effective blade thicknesses of ~2.5 mm) and a custom built ~7 mm hole saw (effective blade thickness of ~1.5 mm).

Fig 5.3. Left: Diagram of the segmented ‘flow-through’ B-doped briquette, identifying the 12 individual sections subjected to PGAA testing. Right: Plot of the associated B concentrations, with consecutive segments from a cross-section denoted with individualized markers and connected by lines. Note: the points attributed to the left/right of the briquette in fact refer to a single measurement, plotted twice for the sake of symmetry.

As expected, the bottom of the briquette (the side nearest the decaborane) yielded the greatest B uptake, essentially double what was measured for the top. The middle segment, with the exception of the peripheral piece, was found to contain no boron. There was a very mild radial dependence, with decreasing B content towards the center. Note: while the graph shows data points for both the ‘left’ and ‘right’ of the briquette, this is strictly cosmetic for the sake of the figure, as there was no differentiation between the sides.

The dispersion briquette (Figure 5.2, left) was cut to 33.00 mm tall and a diameter of 38.30 mm. It was sliced into 3 equal cross-sections as well, and these cut using a 7/8" hole saw (thickness of ~2.5 mm) and the same 7 mm hole saw. Upon doping, the dispersion briquette had developed a beige film (presumably some boron polymer) on the side facing the initial decaborane powder reservoir. It's assumed that this is indicative of a much greater concentration of decaborane on the side nearest the source, and is thus further segmented into top and bottom sections.

Fig 5.4. Left: Diagram of the segmented 'dispersion' B-doped briquette, identifying the 15 individual sections subjected to PGAA testing. Right: Plot of the associated B concentrations, with consecutive segments from a cross-section denoted with individualized markers and connected by lines.

As seen with the flow-through briquette, the sections nearest the decaborane (red) yielded a greater quantity of B, although not nearly to the extent that the visible film would seem to indicate. The left and right sides of the briquette (l/r in orientation, bottom/top in terms of the briquette faces) had essentially identical measurements in all regions. Tellingly, the side furthest from the decaborane (blue) generated greater concentrations than the middle (yellow). The middle segment mirrored what was seen from the flow-through briquette, in that there was no observed B in non-peripheral segments. As such, it is not possible to calculate deposition gradients since, based on these values, a system that contained B only at the extremities would be indistinguishable from one that had a linear decrease across the full length.

Fig 5.5. All sections entirely isolated from the pellet exterior, across both monoliths, demonstrated no measurable quantities of B. As such, calculation of B deposition gradients is impossible.

CHAPTER 6 – Synthesis and Characterization of Graphitic Carbon Nitride

6.1 Motivation/Prior Work

As described in Chapter 4, the incorporation of B atoms into the graphitic lattice of activated carbons holds significant potential for augmenting their performance as H₂ sorbent materials: substitution of 5-10 wt% B into the graphitic lattice is predicted to enhance the binding energy by as much as 240% [36]. In practice, however, the fraction of surface sites with fully substituted boron (bonded to neighboring carbon atoms by sp²-bonds) and accordingly high binding energies was generally limited to $\leq \sim 1$ wt%, too small to make the surface uniformly and globally a high-binding-energy surface. Further, only about one in six boron atoms was shown to be properly sp²-bonded; rather, the boron tended to aggregate in clumps (demonstrated via considerable quantities of sp³ B-B bonds) rather than fully incorporate into the matrix. These groups do not only fail to enhance the system's binding energy, but also ultimately reduce the number of total adsorption sites by clogging pores and diminishing the available surface area. Values up to ~ 2 wt% sp²-bonded B were demonstrated for select samples, but these were accompanied by an increasingly higher concentration of non-sp²-bonded B.

Fig 6.1. Weight percent of sp^2 -bonded B atoms as a function of total B weight percent of a representative sample of MU B-doped C, as determined from fine peak deconvolution of the associated XPS spectra. Sp^2 -bonded B made up less than 2 weight percent of the total sample, too low to make an appreciable improvement to global binding energies. Increasing the amount of total B present served to only result in increasing aggregates of B-B clusters.

To this end, we considered alternative adsorbent materials outside of purely graphene-based systems. Graphitic carbon nitride (g-CN) is one such potential platform for high binding energy and surface area storage of H_2 . Well-established for a variety of semi-conductor applications, most notably as a photocatalyst of H_2 from H_2O [85], its adsorbent capabilities are largely unexplored[86].

g-CNs are a particular class of carbon nitride structures that take the form of parallel sheets comprised of alternating N and C atoms with composition C_3N_4 . The valence structure within individual sheets hosts regular patterns of in-plane voids, which contribute to high surface area by way of surface area across voids. The promise is that with successful exfoliation of g-CN, resulting in high edge-to-in-plane surface ratios, materials with surface areas $4000-6000 \text{ m}^2/\text{g}$ and elevated binding energies can be manufactured.

Fig 6.2. Structural representations of the two accepted possible configurations for graphitic carbon nitride (C_3N_4), using triazine (*left*) and heptazine (*right*) repeating bases. Examples of the additional pore space afforded by the native in-plane voids are highlighted in red.

In addition, this molecular configuration, which natively gives rise to alternating partial charges on the constituent atoms, is expected to result in strong dipole interactions (and therefore high binding energies) with adsorbed H_2 molecules. Electronic structure calculations predict an increase in binding energy from 4.5 kJ/mol on an individual graphene sheet to 6.5 kJ/mol[73] on an adsorption site on an individual sheet of g-CN (Fig. 6.3), a ~50% improvement in binding energy relative to carbon.

Fig 6.3. Comparison of electronic structure calculations of H₂-to-substrate potentials showing an improved potential, in both depth and equilibrium position, of graphitic carbon nitride over coronene[73]. Inset shows the heptazine unit and H₂ position used for calculation.

6.2 Synthesis of graphitic carbon nitrides (g-CN)

Many synthetic routes to g-CN have been described; routes to laboratory-scale synthesis include both solvothermal reactions in high boiling organic solvents and solid-state metathesis reactions[87]. Of particular interest though are routes involving polymerization of inexpensive bulk industrial precursors, such as cyanamide, dicyandiamide, or melamine, as these could be most readily scaled for widespread application[88].

There exists significant variation in the conditions and precursors proposed to produce viable and verifiable g-CN materials[89]–[91]. Each of these, while responsible for incorporating various synthetic nuances into the reaction, adhere to a common general pathway, whereby simple carbon nitride compounds are successively condensed into more complex oligomers at increasing temperatures via reduction of amine functional groups. One such representative example is demonstrated below in Fig 6.4; it should be noted

though that the actual reaction would be significantly less discretized, with many of the intermediate structures expected to coexist (such as the melam and melem groups, *d.* and *e.* respectively).

Fig 6.4. Example of a possible reaction pathway in the production of graphitic carbon nitride. Melamine (*c*) can be produced in a number of ways, most commonly via the decomposition of urea ($\text{CO}(\text{NH}_2)_2$); as shown here, dicyandiamide (*b*) (and it's precursor, cyanamide (*a*)) is another such candidate. Thermal treatment of melamine leads to a cascade of successive condensations. First, an initially formed dimer (melam, *d*) will rapidly form a 3-ringed planar structure known as melem (*e*). These will themselves link to form staggered chains (melon, *f*), followed by a low-density plane (poly(heptazine imide), *g*), and ultimately graphitic carbon nitride (*h*).

Melamine ($\text{C}_3\text{H}_6\text{N}_6$, *c.* from Fig 6.4), a heterocyclic trimer of cyanamide ($\text{HN}=\text{C}=\text{NH}$), is one such attractive parent compound. Melamine is known to readily produce a number of assorted crystalline structures that take various forms and dimensionalities, many of which have facilitated extensive industrial and household applications. For instance, in the presence of formaldehyde, temperatures as low as 75°C are sufficient to induce robust cross-linking of melamine units[92]; the resulting resin has seen widespread application as dinnerware and laminates (e.g. *Formica*)[93]. Further, emulsifications of these resins with a blowing agent (such as pentane, etc) produces a highly porous 3-dimensional foam[94]. In addition to thermal and acoustic insulation, melamine foams have recently found repurpose as a “non-chemical” household cleaner (e.g. *Magic Eraser*).

Fig 6.5. Comparison of the microstructure of commercially-available melamine resin bowls (*top*) and melamine foam scouring pads (*bottom*) at 500x (*left*) and 10kx (*right*), demonstrating the dramatic variation in microstructure capable through modification of synthesis conditions.

As such, melamine has demonstrated significant promise as a readily polymerizable precursor material for g-CN synthesis and was thus implemented as the primary substrate in the reaction in the present work according to the procedure outlined by Yang[95]. First, 1.25 g of melamine (suspended in 50 mL dimethylformamide, *DMF*) was mixed with 4.8 mL pyridine (in solution with 20 mL *DMF*) in a two-neck round bottom flask and flushed with nitrogen. Separately, 3.58 g of cyanuric chloride was dissolved in 50 mL of *DMF*; upon color change (indicating the formation of Gold's reagent), this solution was added dropwise to the melamine/pyridine. This mixture was stirred for 6 hours at 0 °C via an ice bath, followed by another 6 hours at room temperature. The aminoalkylation of the reagents is performed through heating the mixture at 120 °C under reflux for 24 hours, followed by concentrating the reacted product in-vacuo. Finally, the sample was extracted via centrifugation at 25,000 g, and placed in a vacuum oven at 105 °C for 24 hours to drive off any remaining solvent.

Preliminary characterization is shown below in Figs 6.6-8. The final product exhibits the pale yellow color characteristic of graphitic carbon nitrides (Fig 6.6). Evidence of some degree of condensation can be observed through the formation of many large particles (>1 mm in some cases). Most of these can be easily reduced with moderate grinding, as SEM imaging demonstrates the largest grains to be largely aggregations of disparate particulates <~5 μm (Fig 6.7). EDS analysis of a representative structure confirms the sample to be comprised solely of C and N, as expected, along with a minor quantity of surface O (Fig 6.8). Crucially, the spectra lacks any observable Cl from unreacted cyanuric chloride, likely indicative of successful aminoalkylation as intended from Gold's reagent.

Fig 6.6. Image of precursor melamine before (*left*) and after (*right*) thermal synthesis. The heated product demonstrated the pale yellow color characteristic of graphitic carbon nitride.

Fig 6.7. *Top Left*: Low magnification SE image of GCN-1001, produced via the polymerization of commercial melamine; the formative condensation is exemplified by the resulting wide granule size distribution, with many observed particles $>1\mu\text{m}$. *Top Right*: SE image of the disparate surface of a typical grain. *Bottom*: High magnification images of neighboring regions of the previous particle demonstrating the extremely varied topography of MU-synthesized g-CN particles.

Fig 6.8. EDS spectra of a representative particle confirms the resulting material is comprised entirely of C and N, as well as minimal O. Cl (peak location 2.6 keV) is notably absent from the spectrum, indicating no residual unreacted cyanuric chloride present.

g-CN's predicted performance as a storage medium hinges on formation of specific structures. Perhaps most notable (and distinct) is the condensation of the six-membered heterocyclic *triazine* into the more complex *heptazine*, as demonstrated in steps *d.* to *e.* of Fig 6.4. However, the aforementioned analyses offer only a cursory overview of the synthesized product, and lack the resolution required to differentiate the almost-tautomeric intermediate structures by a considerable margin. As such, more specialized techniques are explored, in the hope that a more comprehensive understanding of the reaction mechanisms will facilitate production of materials fully optimized for hydrogen storage.

6.3 Characterization of crystalline structure

Analysis of carbon-nitride samples poses a non-trivial challenge. As demonstrated in Fig 6.9, the greatest variation along the reaction pathway is the reduction in H; direct measurements of hydrogen is generally limited to highly specialized instrumentation (e.g. neutron scattering). Subsequently, analysis is limited to measurements contingent on the C and N species present. Investigation of the composition alone is likely to be insufficient as the ratio of the two is fairly invariant throughout (Fig 6.9), and would be especially

susceptible to various potential organic contamination. Thus, more specialized techniques are required.

Fig 6.9. Ternary diagram of the C/N/H atomic percentages for the structures shown in Fig 6.4. (a-c share a common stoichiometry of the form $C_nN_{2n}H_{2n}$). The series of reactions are largely driven by elimination of ammonia and subsequent linking of the functional amine groups, demonstrated here as the pathway is characterized by the successive reduction of H accompanied by uniform increases in both C and N.

XPS

XPS was proven to be an indispensable tool in characterizing the boron environment of doped activated carbons (Ch. 4.4), a notably difficult task due to the challenge involved in distinguishing the acute variations in chemistry of neighboring elements. Nitrogen-containing compounds introduce many analogous difficulties, making XPS similarly attractive. However, this investigation involves the evolution of the N-C chemical species, whereas the previous hinged on the formation of a distinct B-C feature, a significantly more binary application.

As integrated here, analysis involves the identification and quantification of various characteristic structures. The $C=N-C$ structure, inherent to the constituent triazine and

heptazine rings, would be expected to persist throughout the synthesis. More telling, then, is the concentration of the other species.

The reaction pathway generally proceeds via successive condensation of neighboring molecules via the elimination of the peripheral amine groups (Fig 6.10): the concentration of the peripheral $C-NH_2$ groups would be expected to decrease, replaced by $(C)_2-NH$ linkers and ultimately the graphite-like $(C)_3-N$. These are fairly subtle differences, but ones that XPS may be capable of distinguishing.

Fig 6.10. Evolution of the concentrations of the various N bonding configurations for the melamine to g-CN reaction pathway described in Fig 6.4. Initially, melamine is comprised of equal quantities of N incorporated into the aromatic ring (*i.*) and in the terminal amines (*ii.*). The latter of which serves as the primary functional unit during the successive condensations, with perhaps the most fundamental being the linking of two neighboring groups (*iii.*), and eventually three (*v.*). A crucial marker is the formation of heptazine, a planar structure comprised of 3 triazine rings with a N at the center (*iv.*). It is important to note that *iv.* is illustrated here as aromatic, but that is simply to denote its position in the molecule and differentiate it from *v.*, as both are singly-bonded to 3 C's.

Fig 6.11 shows the full spectra of both melamine and its pyrolyzed product, GCN-1001; the former is confirmed to consist only of the expected C and N, while the latter

demonstrates that no unexpected elements were introduced during the synthesis. The small amount of O observed in the melamine signal (~ 2 atom%), likely attributable to adsorbed surface contaminants, was reduced upon pyrolysis. The composition of GCN-1001 closely matches what would be expected for polymeric melon (Table 6.1); however, as evidenced in the disparity between the observed and expected concentrations of raw melamine, the pure composition is generally a secondary output relative to the wealth of data attainable via deconvolution.

Fig 6.11. *Top*: Full XPS spectra of melamine and GCN-1001 shows no new elements were introduced during the pyrolysis procedure. *Bottom*: High-resolution scans of the C1s and N1s regions used for deconvolution analysis, each scaled to comparable intensities.

Table 6.1. Elemental concentrations for measured spectra and representative structures (excluding H)

Structure	C (at. %)	N (at. %)	O (at. %)	N/C
Melamine (meas.)	39.5	57.6	2.9	1.46
<i>d. Melamine (theor.)</i>	33.3	66.6	<i>n/a</i>	2.00
GCN-1001 (meas.)	39.6	59.3	1.1	1.50
<i>f. Melon (theor.)</i>	40.0	60.0	<i>n/a</i>	1.50
<i>h. g-CN (theor.)</i>	42.9	57.1	<i>n/a</i>	1.33

Deconvolution is contingent on proper assignment of the constituent peaks. Because the ease of fitting a data set increases with the number of constituent features (“with a high enough order polynomial, you can fit an elephant”[96]), it becomes increasingly imperative that they are each attributed with the correct energy and width when applying a large number of peaks in order to generate accurate and meaningful quantifications.

The spectra for the C1s of both samples are largely identical, featuring a single, well-defined peak which can be safely assigned to the $N=C-N$ of the triazine ring. This feature is essentially invariant between the two, an expected result given that C isn’t primarily involved in any condensation reactions. However, the peak for the reacted material is shifted ~ 0.4 eV towards higher binding energy. This likely represents the transition of the carbon’s localized environment from a single-ringed triazine to the more extended heptazine system. The persistence of the single, smaller peak at ~ 283 eV, assigned to adventitious and/or contaminant hydrocarbons, mitigates the aforementioned shift arising due to experimental artifact.

The N1s region for both melamine and GCN-1001 are dominated by a large peak at 397 eV. The spectra for melamine is otherwise featureless, save for a wide peak at high energy corresponding to $\pi-\pi^*$ excitations, characteristic of aromatic systems, whereas the spectra for GCN-1001 exhibits significant broadening on the high energy side of the main

peak. These counts represent the condensation products that form during pyrolysis, and would thus be expected to contain the requisite characteristic features.

Fig 6.12. *Left*: Deconvolution of the N1s feature of melamine. The spectra can be well defined according to the stoichiometry, with the single feature comprised of equal parts of the C=N-C unit of the triazine ring and the peripheral C-NH₂ amine groups. The secondary feature at high energy (visible in both systems) is consistent with $\pi-\pi^*$ excitations from aromatic compounds. *Right*: Introducing additional features in quantities consistent with polymeric melon is a distinctly poor fit to the data.

The simple, well-defined stoichiometry of melamine offers a promising starting point, especially given that it is a quality-controlled commercial standard. The main feature was fitted using the two constituent features: the pyrrolic C=N-C of the ring and the peripheral C-NH₂ functional group. The latter is typically taken to occupy a binding energy 0.5-1.5 eV greater than the former[97]–[100]. The peak was thus deconvoluted to this specification, under the restraint that they occupy equal areas to reflect the matching contributions from each (Fig 6.12, left).

These parameters were then applied to the GCN-1001 feature, along with peaks corresponding to the other anticipated features. Of the possible N bonding environments, the N at the center of the heptazine ring ((C)₃-N) is expected to possess the greatest binding energy, ~3-4 eV greater than the main ring N[98]–[103]. The linker (C)₂-NH unit (often referred to as “N in a graphitic environment”) is generally represented as having a slightly lower energy than the center N[97], [98], [104]. Scaling the concentrations of the

remaining structures according to the predicted chemistry for polymeric melon resulted in a notably poorer fit to the data than what was observed for melamine. In addition to the expected features failing to account for a significant percentage of their respective plot regions, there exists an otherwise unaccounted for concentration of counts at ~401 eV. This could potentially be attributed to various oxide groups[103], [105]–[107], although the reduced oxygen concentration in the pyrolyzed sample relative to its precursor likely prohibits this assignment.

These results seem to indicate some degree of variation from the ideal stoichiometry. The best fit to the data (Fig 6.13) generates results far from consistent with any previously discussed structures, with the unknown features comprising ~8%.

Fig 6.13. A best fit to the data yields stoichiometrically-inconsistent quantities. The representative structures also don't account for a significant number of higher-energy counts; these are tentatively assigned to a single peak representative of a number of possible oxide structures.

Supporting this, it can be shown that the maximum possible concentration of the C=N-C feature, relative to the otherwise unoccupied area under the curve (excluding the counts attributed to the π - π^* shakeup feature) is essentially 50% (Fig 6.14). This is

problematic because, as indicated by Fig 6.10, the concentration of this structure should be demonstrating a clear increase from 50% for all subsequent structures past melamine in the reaction pathway. Given the ambiguity of these results, XPS is shown to be inadequate to independently characterize the g-CN system.

Fig 6.14. Maximizing the contribution of the C=N-C feature demonstrates a ceiling of ~50% with respect to the additional counts introduced in the synthesis. As demonstrated from Fig XX, all subsequent structures post-melamine contain a greater quantity, potentially indicating non-idealized chemistry.

EELS

The resolution and localization native to TEM-based techniques make them especially attractive tools in materials characterization. Samples are required to be electron transparent (~100 nm thickness), which is prohibitive in regards to activated carbons due to the extensive preparation necessary coupled with the amorphous nature of the material. Thus, despite the wealth of information potentially attainable, the ALL-CRAFT team has largely typically eschewed exploring such analysis.

This is a direct result of the subtractive process used to produce activated carbons, wherein the output is comprised of the largely-intact skeleton of the bulk parent material.

Graphitic carbon nitrides, on the other hand, do not suffer the same drawbacks as their manufacture process is additive: thermal treatment condenses precursor molecules into a system consisting of discrete planar elements. Thus, these materials are much more readily implementable for TEM analysis; while SEM indicated g-CN samples to feature similar grain sizes as activated carbons, simple sonication in ethanol is sufficient to exfoliate them to electron-transparent aliquots.

EFTEM allows for the generation of elemental maps through filtering for the emission energies characteristic for those particular elements. As expected, the MU-developed carbon nitride demonstrates a uniform distribution of both carbon and nitrogen throughout (Fig 6.15). This is evidence that the reaction is at least proceeding as the stoichiometry predicted and subsequently not generating large aggregates of decomposition byproducts. Past this initial confirmation, there isn't much else to learn from EFTEM in this application.

Fig 6.15. (*left to right*) Unfiltered EFTEM image (essentially bright-field mode) of a well-oriented particle, and carbon, nitrogen, and composite maps of the assigned mixed colors in RGB. The system is confirmed to be quite uniform as expected, resulting in the relatively homogeneous mix of the two maps. The object in the lower left of the carbon map is the edge of the carbon grid that the sample is suspended over.

EELS, on the other hand, is a technique theoretically capable of yielding more readily quantifiable chemical information. EELS is highly dependent on the thickness of the sample, as excessive thicknesses introduce multiple-scattering artifacts, so regions under study must be screened prior to data collection. As a rule, quality TEM (and

EELS/EFTEM/etc) requires sample thicknesses less than around one mean free path (<~200 nm at 300 kV for carbon based materials). This is a measurement that can be and is performed in-situ.

Once a sample is determined to be sufficiently thin, regions can be selected to perform EELS, whereupon elemental analysis can be determined from the generated spectrum. Unlike many techniques, EELS is especially sensitive to low-Z elements. In addition to composition, the signal is generated via the beam's interaction with both inner shell (for high-Z) and valence (for low-Z) electrons; this, in turn, then carries information regarding the sample's unique binding environment. However the resolution of the spectrometer at MU's EMC is limited to 1 eV, and is subsequently incapable of analysis more refined than basic composition.

Fig 6.16. (left) A thickness map from EFTEM confirming the region was suitable for EELS and EFTEM. All regions colored green and blue were lower than one mean free path, while the bright regions at the top are of greater thickness and excluded. (right) EEL spectrum with clear defined k-edges for both nitrogen and carbon. Future work includes calibrations of convergence and collection angles and background allowing for quantitative chemical analysis to determine the exact chemical ratios.

XRD

Both of the previously-discussed techniques were based on analysis and classification of the local chemistry, and only proved capable of returning relatively ambiguous results regarding the nature of MU-produced carbon nitride. As these samples

are significantly more crystalline than nanoporous carbon, a number of other methods, which generate unique properties depending on a material's physical structure and ordering, are made available. Of these, XRD is immediately attractive. Powder diffractometers are generally very accessible instruments and return extensive structural information without significant obstacles in data collection or analysis, making them indispensable materials characterization tools.

Powder XRD was thus performed on GCN-1001 as a means to directly determine its main structural characteristics (Fig 6.17). The profile is dominated by a sharp peak at 27° ; this corresponds to a distance of $3.27\text{\AA}$, in good agreement with the inter-planar spacing of graphitic carbon nitrides reported in the literature[89], [108]. The reduced spacing compared to that of crystalline graphite (generally accepted as $3.35\text{\AA}$ [109], [110]) reflects a stronger van der Waals attraction between opposing C_3N_4 sheets. The small feature at 57° has been shown to form at higher temperatures where the inter-planar peak becomes most defined[108], and can thus be attributed to the corresponding higher-order reflection. Finally, the profile contains a wide feature at low angle, with a maxima at $\sim 12.7^\circ$ ($d = 6.96\text{\AA}$). This is assigned to in-plane features, as it is similar to the expected value for the heptazine-to-heptazine distance as measured from the centers of neighboring groups ($7.30\text{\AA}$ [111]). The decreased distance may reflect in-plane buckling, and coupled with the dramatic broadness relative to the dominant stacking feature, could be indicative of significant disorder in the plane.

Fig 6.17. Powder XRD profile of GCN-1001, with preliminary assignments of the dominant structural features.

To characterize GCN-1001, models from representative systems were collected from the literature; the requisite data included the crystal system, lattice parameters, allowed reflections, and relative intensities. The reported reflections were plotted against the experimental data, with the intensities scaled to match the dominant interplanar spacing feature. The goodness of fit was judged qualitatively by how well the associated lines accounted for the observed features in GCN-1001's spectra. Lastly, each model was optimized for the data by via slight manipulation of the lattice parameters.

First, the data is fit to the heptazine-based graphitic carbon nitride structure (Fig. 6.18,[112]). The model features a hexagonal unit cell with a 112 atom basis: 64 N and 48 C. The planes are aggregated using an AB stacking motif, with the heptazine unit of one plane positioned opposite the voids of the adjacent planes.

The data is capable of fitting to the model with only minor modifications to the lattice parameters. As expected from earlier, the peak at $\sim 13^\circ$ correlates with the predicted

{100} feature of the model; this corresponds to a heptazine-heptazine distance of 7.1 Å, in good agreement with the literature[111]. However, the model predicts significant contributions from the {102} and {210} reflections at 30° and 33°, respectively, that are absent in the data. Further, most of the other expected low-angle features are not accounted for, indicating this model doesn't comprehensively characterize the system, if it's even applicable at all.

Fig 6.18. Powder XRD profile of GCN-1001 fitted according to the model of heptazine-based g-CN (inset). Allowed reflections and relative intensities collected from[112].

Table 6.2. Lattice constants and calculated crystalline density for fitted graphitic heptazine.

	a (Å)	c (Å)	V _{cell} (Å ³)	M _{cell} (g/mol)	ρ _{crys} (g/cm ³)
Model[112]	8.434	6.772	1252	1472.98	1.95
Fitted GCN-1001	8.20	6.52	1139		2.15

Next, the model is compared to a carbon nitride structure comprised of a triazine basis (Fig. 6.19,[113]). The model features a hexagonal unit cell with a smaller, 42 atom basis: 24 N and 18 C. As with the heptazine-based system, the planes are also aggregated using an AB stacking motif, similarly with the triazine units opposite the adjacent voids.

Fitting to this model yielded similar success as the previous. Little modification is required to align the major features, but is entirely incapable of describing the low-angle behavior of the spectra. On top of this, the predicted significant contribution from the {021} reflection does not appear in the data. A small peak at $\sim 21^\circ$ agrees well with the {100} peak of the model; this feature corresponds well to the expected distance between two linked triazine units ($4.7 \text{ \AA}$, [114]).

Fig 6.19. Powder XRD profile of GCN-1001 fitted according to the model of triazine-based g-CN (inset). Allowed reflections and relative intensities collected from [113].

Table 6.3. Lattice constants and calculated crystalline density for fitted graphitic triazine.

	a (Å)	c (Å)	V _{cell} (Å ³)	M _{cell} (g/mol)	ρ _{crys} (g/cm ³)
Model[113]	4.742	6.7205	392.6	566.373	2.34
Fitted GCN-1001	4.81	6.52	391.9		2.34

The models of the two known possible structures of g-CN both failed to provide a satisfactory fit to the data. The spectra contained features consistent with the primary repeating elements (linked heptazine-to-heptazine and triazine-to-triazine), but the bulk of the low-angle peaks remained unidentified, while several predicted lines were not present.

Cumulatively, this may point to evidence of incomplete condensation, as aforementioned linked units comprise the earliest-formed structures throughout the synthesis route (Fig 6.4), and would subsequently be expected to lack the higher-order uniformity of the full crystalline planes.

To this end, a polymeric system, composed of independent chains of linked heptazine units arranged so as to form discrete basal planes, is applied to the system (Fig 6.20,[115]). It is believed that this was the structure produced (and subsequently christened ‘melon’) by Justus Liebig, the pioneer of modern nitrogen chemistry, as early as 1834[116], [117]. While theorized to potentially eventually condense into contiguous C_3N_4 sheets, there’s evidence it may instead undergo decomposition prior to any further condensation[116].

This particular model features a 72 atom basis: 36 N, 24 C, and 12 H. Here, the planes are comprised of alternating, ‘interlocking’ chains, and are designated using an AA stacking motif. Upon fitting, this model is immediately more promising than the prior. Aside from the interplanar spacing at 27° , the expected peaks appear largely in the $10\text{-}20^\circ$ region, with the strongest reflection, $\{210\}$, aligning well with the peak at 13° (Fig 6.20, left).

Further, this model is designated as triclinic, with freedom given to γ (the angle between the in-plane vectors $\hat{a}$ and $\hat{b}$) to deviate from 90° . Physically, this corresponds to reorienting the chains relative to one another, a shearing that would be otherwise restricted in a contiguous crystalline basal plane. Such a transformation also results in breaking the symmetry of reflections in the h - k plane, reducing the intensity of such features by splitting previously superimposed peaks. For example, with $\gamma = 90^\circ$ (Fig 6.20, left), the peak at 13°

is assigned to the combined $\{210\}$ reflections that, while aligning well, yields a peak far too strong in intensity than observed with the data; using $\gamma = 87^\circ$ (Fig 6.20, right) separates this into discrete $\{210\}$ and $\{2\bar{1}0\}$ features. In addition to reducing the expected intensity, this helps account for the observed broadness.

Fig 6.20. Powder XRD profile of GCN-1001 fitted according to the model of polymeric carbon nitride (insets), with $\gamma = 90^\circ$ (left) and $\gamma = 87^\circ$ (right). Allowed reflections and relative intensities collected from [115].

Table 6.4. Lattice constants and calculated crystalline density for fitted polymeric heptazine.

	a (Å)	b (Å)	c (Å)	γ ($^\circ$)	V_{cell} (Å ³)	M_{cell} (g/mol)	ρ_{crys} (g/cm ³)
Model[115]	16.2	12.1	3.27	86-90	~640		2.09
Fitted GCN-1001	17.1	12.2	3.26	90	682.2	804.612	1.96
Fitted GCN-1001	17.1	12.2	3.26	87	681.3		1.96

While the polymeric melon model appears to suitably describe much of the experimental spectra, many features remain undefined, suggesting the presence of one or multiple additional phases. Notably, the peaks at $\sim 21^\circ$ and $\sim 26^\circ$ were fit exceptionally well by the triazine-based g-CN model (Fig 6.19). Because of the drastically different reaction pathway required to form the two systems (i.e. the latter resists the formation of the fundamental heptazine unit, which is clearly represented in the data), it's unlikely that GCN-1001 is a composite of the two. So, analogous structures are considered.

Melamine is a natural candidate, given that serves as the precursor of the synthesis and is comprised of a single triazine ring. Profiles for melamine, as well as its linked adduct melam, are given by [118]. Experimental spectra collected from the melamine used to produce GCN-1001 are shown to be consistent with the model (Fig 6.21), confirming their suitability.

Fig 6.21. Experimental powder XRD profile of precursor melamine (black) compared to the model (yellow) given by [118].

The compound fit of GCN-1001, comprised of melamine, melam, and polymeric melon, is given below in Fig 6.22. The suitability of these assignments indicates the final product is likely a heterogeneous mixture of structures subject to varying levels of condensation. As such, other intermediate products, such as melem and other heptazine-based adducts, are likely present but not accounted for here.

Fig 6.22. Assuming a structure primarily composed of polymeric carbon nitride (blue), with various uncondensed intermediate products, represented by melamine (yellow) and melam (orange)[118], yields a robust fit to the data.

HRTEM

Powder XRD yields data representative of the bulk: while the measurements generated can be assumed to be taken as essentially universal, any nonuniformity in the system can make refined interpretation challenging. HRTEM, on the other hand, is another technique capable of characterizing crystal structure, but does so far more locally. This allows for analysis to be performed on individual, user-selected crystals.

An HRTEM image of GCN-1003 is shown below in Fig 6.23. The extensive crystallinity of the system is immediately apparent through the appearance of numerous visible fringes; these lines represent Bragg diffraction from a continuous lattice and are correlated to a particular d-spacing within the crystal[119]. These can be measured directly, or alternatively, simultaneously quantified for the entire imaged region via FFT

analysis[120], a functionality built-in as standard in many advanced image processing software packages such as DigitalMicrograph and ImageJ.

The FFT of this region reveals the presence of many discrete repeating elements, indicative of a considerable degree of crystallinity. However, there is also a non-insignificant degree of disorder present as well. For one, many of the characteristic fringes are radially smeared, pointing towards variance in orientation. In addition, the distribution of fringes lacks the periodicity expected from a single-crystal system.

Fig 6.23. (CW from top left) (a) HR-TEM image of GCN-1003; the enhanced inset exemplifies the extensive visible crystallinity throughout the entire region. (b) FFT of (a) confirms this crystallinity (albeit fairly disordered) through the appearance of several well-defined repeating elements. (c) Inverse-FFT of the points indicated in (b) seems to suggest the extent of discrete crystals is limited to $\geq \sim 50\text{nm}$. (d) Overlay of (a) and (c).

The FFT procedure is reversible, and thus performing an inverse FFT on a generated FFT yields the parent image. This can be leveraged to explore specific components. As each point in the FFT represents a particular fringe in the parent image (in both spacing and orientation), creating a mask around a point and performing an inverse FFT results in an image that isolates the corresponding real-space structures. In a uniform system, this ‘fringe map’ would be expected to be fairly ubiquitous, with most differences largely attributable to variations in thickness; GCN-1003 noticeably lacks this continuity. Instead, many of the most prominent points in the FFT are associated with much more discrete areas, suggesting individual crystal formation to have an apparent ceiling of ~50 nm (Fig 6.23).

FFT’s may be generated from selected regions within an image as well, enabling more localized characterization of these structures. In doing so, one particular structure is consistently observed across a wider area (Fig 6.24). Filtering the FFT using the cumulation of the constituent fringes demonstrates this unique structure to exist on a considerably larger scale than what was observed in Fig 6.23. In addition to being fairly pervasive, these result in especially clearly-defined FFT patterns. As such, this particular pattern is a promising candidate for quantitative analysis.

Fig 6.24. (*left*) FFTs generated from selected regions reveal a persistent structure populating significant fraction of the imaged region. (*right*) Applying a mask based on these fringes (inset) to the FFT of the full image, and performing an inverse FFT allows for generation of the real space analog to these fringes; the resulting map confirms that this particular structure is especially widespread.

As with powder diffraction, the output signal is directly dependent on the analyzed crystal's lattice structure. The large volume interaction native to powder diffraction incorporates diffraction patterns from all observable (allowed) incident directions, yielding a “spherically-averaged” signal that's representative of the structure and readily database-comparable. In contrast, HRTEM instead generates a pattern that is explicitly dependent on the orientation of the analyzed crystal relative to the incident beam (known as the *zone axis*). Specifically, the visible points in the FFT represent crystalline reflections that are perpendicular to the particular zone axis. A single crystal can yield numerous unique patterns depending on its orientation, and thus, analysis generally operates in the domain of confirming a structure rather than freely identifying it. Even given this constraint, this processing often requires significant effort.

A number of software packages exist to analyze crystalline systems (CrystalMaker, CRISP, VESTA, etc); however, these require the structures to have been previously well-characterized and databased. As none were readily available for the particular carbon

nitride systems under investigation, a tool was developed in Mathematica to facilitate this analysis based on the measurements from the observed lattice points (Table 6.5). A comprehensive description of the utility's methodology and implementation can be found in Appendix 4.

Table 6.5. Measurements of the 3 dominant fringes in the FFT from Fig 6.24.

d_1 [nm ⁻¹]	d_2 [nm ⁻¹]	d_3 [nm ⁻¹]	$\phi_{1 \rightarrow 2}$ [°]	$\phi_{2 \rightarrow 3}$ [°]
6.63	4.51	5.73	53.4	43.5

Applying these values to the primary fringes in the data set using either graphitic carbon nitride model failed to yield reasonable assignments. The polymeric model, on the other hand, produced a viable set of possible reflections: $\{2\bar{1}0\}$, $\{310\}$, and $\{120\}$, and an associated zone axis of $[001]$. This is powerful as it independently implies that the dominant observed orientation is along the interplanar axis, a natural result for a planar material. Extending this to additional observable fringes also returned potential reflections ($\{2\bar{2}0\}$ and $\{130\}$), although these were noticeably poorer fits to the data.

As with the previous XRD fitting, a reconciliation might be found through minor modification of the model. Typical crystalline systems aren't capable of such manipulation, and thus such an issue would instead normally result in discarding the model. However, as the model used here is polymeric rather than crystalline, a degree of adjustment to the lattice parameters isn't unreasonable.

A plot of the cumulative relative differences in d-spacings and inter-reflection angles for the 5 previously assigned reflections (Fig 6.25, left), indicates local minima for a and b lattice parameters approximately 10% from the each's theoretical values (Table 6.6). Implementation of these new parameters yields a distinctly improved fit to the experimental data compared to the original (Fig 6.25, right). This puts HRTEM in

agreement with XRD: the carbon nitride materials produced by MU are more readily characterized as stacked polymeric chains rather than graphene-like sheets, lacking the planar order inherent to the latter.

Fig 6.25. Density plot (*left*) of the a and b lattice parameters in relation to the cumulative error in fitting the assigned reflections to the observed FFT (*right*). The purple dots show the fit using values based on the model given by [115], while the red dots represent a modified model generated by minimizing the cumulative error.

Table 6.6. Lattice parameters of polymeric carbon nitride as given in the literature compared to the results of HRTEM analysis

Model	a [Å]	b [Å]	c [Å]
Original [115]	16.2	12.1	3.27
Modified	14.9	13.5	3.27

Note: c was left unmodified as it was assumed any variance in the structure would more likely propagate through the polymeric plane (relative positioning of chains, etc) rather than in their stacked spacing; the source of the model accounts for this via alterations of γ (the angle between a and b), instead. Further, the assignment of a [001] zone axis renders all observed points independent of c .

CHAPTER 7 – Graphitic Carbon Nitride Exfoliation and Hydrogen Storage Performance

7.1 Sample synthesis and performance

The pyrolysis of melamine, as described previously in Chapter 6.2, was found to be a reliable method to produce graphitic carbon nitrides. The process routinely yielded consistent samples on the gram scale with promise of eventually scaling to industrial quantities. The process was reproducible, with disparate samples demonstrated to be structurally consistent (Fig 7.1).

Fig 7.1. XRD profiles (*left*) and N_2 pore size distribution (*right*) of three identically-manufactured samples: GCN-1039 (produced in chemistry) and GCN-1042 (produced in physics) are shown to be similar structurally to the original GCN-1001.

GCN-1039 is a large-scale reproduction of the original sample, GCN-1001; the XRD profile is largely the same, albeit with a minor peak broadening of the dominant interplanar spacing feature as well as a uniform increase in counts in the 15-25° range (corresponding to major planar features), both of which may indicate a slight increase in sample heterogeneity. GCN-1042 is the first of several samples produced by the team in physics and its XRD profile is virtually identical to that of GCN-1039. N₂ porosimetry demonstrates all samples to be similarly mesoporous: each feature dominant pore populations at ~35 Å and ~150 Å, with the bulk of the pore space contributed from pores greater than 100 Å.

The persistent structure of MU-produced graphitic carbon nitrides subsequently translates to consistent H₂ storage performance. Unfortunately, this performance is quite poor, with excess adsorption that is orders of magnitude below that of a typical activated carbon (Fig 7.2, left). This can be primarily attributed to the prohibitively low surface area available to the gas, with each determined to contain only 12-14 m²/g. This is reinforced by each sample demonstrating similar areal excess adsorption (Fig 7.2, right)

Fig 7.2. Comparison of gravimetric (*left*) and areal (*right*) excess adsorption for a representative activated carbon (3K-0079) and a number of graphitic carbon nitrides. The dashed lines in the areal excess plot represent a B-spline interpolation, included for clarity.

The areal excess plot, which is simply the excess adsorption normalized to the specific surface area, represents a rough gauge of a material's binding energy. By accounting for the total sites available, any remaining behavior is attributable to the strength of the solid-gas interaction potential. Thus, by having comparable areal excess adsorption to activated carbons, the surfaces of graphitic carbon nitrides can be inferred to be similarly adsorbent.

This is supported through calculations of isosteric heat in the low-pressure Henry's Law regime. Values determined for GCN-1001 and GCN-1039 are found to be slightly elevated than that of activated carbon, albeit well within variance (Table 7.1). GCN-1001 in particular comes in at 8.0 kJ/mol, but is likely subject to significant error: the 5 distinct 77K measurements demonstrate poor agreement, while the lone "good" 87K measurement displays an appreciable amount of non-linearity. GCN-1039, on the other hand, has four measurements at each temperature that are in good agreement (Fig 7.3).

Table 7.1. Comparison of surface and pore space parameters (determined via N₂ sorption) and H₂ storage parameters of a representative activated carbon (3K-0079) and a number of graphitic carbon nitrides.

Sample	Σ [m ² /g]	TPV [cm ³ /g]	ϕ	G _{ex} (35bar) [g/kg]	ΔH [kJ/mol]
3K-0079	2700	1.83	0.785	57	7.1 ± 0.18
GCN-1001	14	0.15	0.222	0.30	8.0 ± 1.5
GCN-1010	12	0.13	0.192	0.24	--
GCN-1039	14	0.16	0.236	0.43	7.5 ± 1.1

Fig 7.3. Low-pressure regimes of the gravimetric excess adsorption used to calculate the isosteric heats for GCN-1001 (*left*) and GCN-1039 (*right*).

In addition to lower surface areas, g-CN samples also suffer from dramatically diminished nanoporosity. Activated carbons, in addition to their characteristically excellent specific surface areas, also feature large specific pore volumes. Crucially, the bulk of this pore volume is contributed from nanopores; as demonstrated with 3K-0079, about 90% of the pore volume can be attributed to pores smaller than 50 Å (Fig 7.4). In comparison, GCN-1039 has negligible porosity in this domain, with half of the total pore volume attributed to pores greater than 200 Å. Because the overlapping Van der Waals potentials of closely adjacent sheets is responsible for generating the highest density storage, the apparent scarcity of such structures indicates g-CN materials are far from optimized as-is.

Fig 7.4. Comparison of the cumulative pore volumes (*left*) and pore size distributions (*right*), relative to their respective total pore volumes, of 3K-0079 and GCN-1039.

He pycnometry of GCN-1001 determines the skeletal density to be 1.9 g/cm^3 , slightly lower from the 2.0 g/cm^3 consistently found for activated carbons (Fig 7.5). Due to the especially sensitive and time-intensive nature of He pycnometry measurements, it is not implemented as routine characterization of materials. As such, this value will be taken as representative for all subsequent g-CN materials until further measurements become warranted (e.g. in the case of an exceptional or otherwise anomalous performance).

Fig 7.5. Comparison of the skeletal densities, determined via He pycnometry, of a representative activated carbon (*left*) and graphitic carbon nitrogen (*right*) [37].

With the expectation that increased surface area and nanoporosity will translate directly and immediately to improved H₂ storage, various minor modifications to the synthesis protocol were implemented (Table 7.2, Fig 7.6). First, samples GCN-1042 and -1044 were subjected to an acetonitrile wash to extract residual melamine, melam, and melem suggested to be present via the XRD analysis from Fig 6.22[121], [122]. This purification failed to generate any meaningful additional surface area, with results limited to < 1 m²/g (essentially within the error of the measurement).

Next, GCN-1047 was produced using cyanamide, another reported precursor[123], rather than melamine. This is effectively initiating the condensation from a more fundamental position (i.e. starting at *a* instead of *c* in Fig 6.4), although theoretically the reaction should still proceed through melamine. This too did not produce further surface area, with measurements actually indicating somewhat reduced values.

Fig 7.6. N₂ porosimetry measurements of MU-produced carbon nitrides. Each were found to host surface areas within 6-15 m²/g (left) regardless of various minor modifications to the synthesis (as described in Table 7.2). Pore size distributions were roughly consistent for each as well (right), with the exception of the samples produced from cyanamide, which most significantly demonstrated reduced contribution in sub-50 nm pores.

Table 7.2. Surface and pore space parameters (determined via N₂ sorption) of graphitic carbon nitrides.

Sample	Σ [m ² /g]	TPV [cm ³ /g]	ϕ	Synthesis Notes
3K-0079	2700	1.83	0.785	Activated Carbon
GCN-1001	12	0.15	0.222	Melamine pyrolyzed at 550°C for 5 hrs
GCN-1002	7.8	0.08	0.137	<i>Same as GCN-1001</i>
GCN-1010	12	0.13	0.192	<i>Same as GCN-1001</i>
GCN-1011	6.7	0.08	0.137	<i>Same as GCN-1001</i>
GCN-1039	14	0.16	0.236	<i>Same as GCN-1001</i>
GCN-1042	6.4	0.08	0.138	<i>Same as GCN-1001</i>
GCN-1052	6.8	0.08	0.134	GCN-1042 washed with acetonitrile at 60°C for 1 hr
GCN-1044	6.8	0.09	0.151	<i>Same as GCN-1001</i>
GCN-1055	7.1	0.09	0.151	GCN-1044 washed with acetonitrile at 60°C for 1 hr
GCN-1047	5.7	0.08	0.137	Cyanamide pyrolyzed at 550°C for 5 hrs
GCN-1062	5.8	0.11	0.176	Cyanamide pyrolyzed at 550°C for 5 hrs, temperature ramped manually

Lastly, an alternative temperature ramping profile was adopted for GCN-1062. As default during the synthesis, the temperature was increased stepwise 50°C every 30 minutes until being held at 550°C. This assignment was somewhat arbitrary, and disregards particular reaction kinetics; as correlated via the ammonia production observed through a bubbler, the reaction rate varied greatly across the range of temperatures. In an effort to improve homogeneity, temperature was increased manually to maintain a roughly consistent rate of ammonia expelled from the reaction vessel (i.e. maintaining a consistent quantity of ammonia in the reaction environment). The effective profile is shown below in Fig 7.7. Ultimately, this yielded no appreciable differences from the standard heating profile (of GCN-1047).

Fig 7.7. Temperature ramping profiles used for the synthesis of typical g-CN_s (blue) and GCN-1062 (orange). Dotted lines indicate the approximate temperatures for various notable reaction milestones[85], [124].

The final temperature offers another potential variable to explore, especially given that spectroscopic analysis seemed to indicate the final product was comprised of polymeric melon chains rather than a continuous g-CN network, and higher temperatures have previously driven successive condensations. It stands to reason then that increasing the reaction temperature further may serve to catalyze further consolidation.

However, while the g-CN network forms at 525°C[85], it is reported that the larger scale g-CN structures become unstable around 600°C, with complete decomposition occurring at 700°C[124]. Further, the literature indicates these polymeric chains may actually be an alternate product with respect to fully-formed g-CN sheets, rather than an intermediate structure[117], [125]. Given that these chains seem to demonstrate analogous graphite-like behavior as evidenced by XRD (likely through aggregations of chains approximating basal plane structures), significant modifications to the pyrolysis temperature is not explored.

7.2 Physical Exfoliation: Sonication

XRD analysis of g-CN samples reveals a highly graphitic-like planar structure (Fig 6.17), but the low porosity ($\phi \geq 0.23$) indicates the constituent surfaces are largely inaccessible to gas. Assuming a uniform solid, the size of an individual particle is related to its surface area by:

$$\Sigma [m^2/g] = \frac{6000}{\rho [g/cm^3] * W[nm]} \quad (7.1)$$

where W represents the diameter of a hypothetical sphere (or equivalently, the side length of a hypothetical cube). A sample with $\Sigma = 7 \text{ m}^2/\text{g}$ can therefore be approximated as being comprised of discrete particles that are 450 nm wide or, given that individual planes are separated by 3.35 Å, ~1350 stacked sheets. If a majority of the interior volume of these aggregates is truly inaccessible to gas, this represents a tremendous amount of surface area potentially available.

As such, sonication was quickly considered as a means of exfoliating g-CN samples to generate additional surface area. Sonication is a process whereby acoustic energy, having been transformed to mechanical upon impingement on some enveloping medium (i.e. bath or suspension), is applied to a material, causing disruptions at the molecular level. Its effectiveness and ease of use have made it integral for various applications, including sample homogenization, synthesis of nanomaterials/nanoemulsions, liquid degassing, and most relevantly, “to break up aggregations micron-sized colloidal particles”[126].

In regards to the latter, 16 hours of sonication in water has been shown to improve the photoluminescence yield of C_3N_4 (produced via a similar polymerization of melamine) by 20% through the separation of bulk g-CN into 25 nm thin films[127]. GCN-1001 was

subjected to the same exfoliation treatment (producing sample GCN-1003), which resulted in a marked improvement to the pore space. The porosity saw a dramatic rise, from 0.22 to 0.48; this was contributed to by an increase in pore volume from pores of all size (Fig 7.8). Further, the surface area almost tripled, increasing to nearly 40 m²/g.

Fig 7.8. Pore size distribution (*left*) and cumulative pore volume (*right*) of g-CN before (*black*) and after (*red*) bath sonication. The closed and open circles represent the supernatant and the sediment products, respectively, after centrifugation.

In addition to sonication, GCN-1003 was also subjected to centrifugation, which was made readily accessible due to the sample necessarily sitting in solution. During centrifugation, the rotation separates the suspension, with the largest suspended particles pulled towards the bottom. In most applications, this precipitate constitutes the valuable portion of the sample, e.g. purified cellular media. In this case, however, it represents particles that have been less successfully exfoliated, with the supernatant containing the most promising particles. Comparing the sediment (GCN-1004) to the material isolated from the supernatant confirms that centrifugation is a critical component in the exfoliation process, with the pore size distribution and porosity largely identical to the unexfoliated precursor (Fig 7.8), and only negligible improvements to specific surface area (13 m²/g).

While these results are encouraging, the surface areas achieved are still far too low for the materials to be considered as competitive storage media. Given the efficacy of the previous sonication, increasing the power and/or time is an attractive proposition; however, as implemented, the procedure was already placing considerable stress on the hardware. This hurdle is overcome by replacing the bath sonicator with a probe sonicator, which is capable of delivering significantly greater intensity due to the reduced volume of the vibrational source.

Fig 7.9. Experimental setup used for exfoliation of g-CN via probe sonication. *Left*: Variable power probe sonicator (model Qsonica Q55). *Middle*: g-CN in solution post-centrifugation. *Right*: Apparatus assembled in-house to perform freeze-drying.

The exfoliation configuration is shown in Fig 7.9. A Qsonica Q55, fitted with a 3.2 mm tip, was used for sonication. To help ensure thorough exfoliation, solvent volume was limited to 20 mL; at a ratio of 10 mg GCN/1 mL solvent, this corresponds to a maximum of 200 mg of g-CN exfoliated per cycle. Generally, multiple batches were produced in series and combined to yield sufficient quantities of samples for analysis. Sonication was performed at the maximum 55 W with the sample vial sitting in an ice bath to limit solvent evaporation. To prevent the instrument from overheating, sonication was performed using a 30 minute on/15 minute off cycle. After sonication, the sample was centrifuged at $5\times g$ for 5 minutes and the supernatant collected. Finally, the sample was freeze dried using a

house-made apparatus that included a dry ice (and acetone) bath with an intermediate liquid nitrogen cold trap to collect the extracted solvent.

The effect of the sonication can be immediately qualitatively observed directly: manual agitation of the precursor results in the bulk of the powder quickly settling out, while the sonicated sample remains distinctly homogenized for several hours (Fig 7.10). This gives rough evidence of a reduced constituent particle size, and subsequently successful exfoliation.

Fig 7.10. GCN-1039 with (*left*) and without (*right*, GCN-1041) sonication treatment, 3 hrs post-agitation.

Some effects of probe sonication on the structure of g-CN can be discerned more quantitatively via XRD. The profile of the exfoliated sample is largely similar to the untreated precursor, most notably in the persistence of the feature dominant corresponding to the interplanar spacing, indicating the crystalline structure is generally maintained (Fig 7.11, left). The most distinct difference is a sharpening of the peak at $\sim 13^\circ$, assigned to the major in-plane features.

The authors of the polymeric model adopted for MU-produced GCN's (Fig 6.20) noted the reverse of this phenomenon (i.e. broadening of this feature) to be correlated with an increasing pyrolysis temperature[115]. This was attributed to improvement in the overall crystallinity of the system: as further ammonia release is induced at higher processing temperatures, the distance between individual melon chains is reduced, driving

the system towards true graphitization. This results in a shearing of the triclinic unit cell's basal plane, which is subsequently accompanied by a loss of certain symmetries. In this case, the (210) and the ($2\bar{1}0$) reflections, which occur at 13.2° , are no longer superimposed and this feature is reduced (Fig 7.11, right).

Fig 7.11. The XRD profile of g-CN exfoliated via probe sonication (*left*) indicates a structure that is largely similar to its untreated precursor, save for a sharpening of the peak at 13° . The authors of the polymeric model implemented in Fig 6.20 attribute such behavior to a relaxation of in-plane shearing (*right*, [115]), supportive of successful exfoliation.

Thus, the appearance of a well-defined peak at that angle can be interpreted to correspond to a “relaxation” of this shearing as exfoliation counteracts the condensation induced by pyrolysis. Such a result is promising as it implies that sonication is effective at generating disruptions and dislocations at the microscale, but is not so destructive as to entirely degrade the matrix.

The exfoliation can be observed directly via STEM. GCN-1039 was prepared for imaging by dispersing particulates in isopropanol with 15 minutes of bath sonication. Despite this process necessarily selecting for the smaller particles within the sample (an aliquot of the supernatant suspension was deposited on the grid), the majority of observed

particles were quite large, generally greater than 1 μm in diameter (Fig 7.12). Further, despite imaging at 200 kV, they were generally entirely electron opaque, indicating an substantial thickness and density.

Fig 7.12. STEM imaging of unexfoliated GCN-1039 shows constituent grains to be large and dense.

To contrast this, images were collected of a commercial exfoliated graphene (xGnP-m5), controlled to consist of individual platelets with diameter of 5 μm and thicknesses of 6-8 nm[128]. This sample was prepared under identical conditions as GCN-1039 (specifically in regards to the mass to solvent ratio), yet featured an appreciably higher quantity of particles collected on the grid (Fig 7.13, left); this likely reflects the reduced size of individual particles allowing them to be more readily suspended in solution and ultimately deposited on the grid. Despite this, the differences in the bulk material are readily apparent: particles demonstrate distinct sheet-like behavior (note the rolled up platelet in Fig 7.13, right) and are clearly electron transparent, with the texture of the supporting grid prominently visible through the material (Fig 7.13, center).

Fig 7.13. STEM imaging of a commercial exfoliated graphite (xGnP-m5,[128]), collected as a reference, demonstrates the appearance expected for well-exfoliated sheets.

This difference may be quantified via EELS analysis. EELS data takes the form of a histogram representing the energy loss per electron due to interaction within the sample; typically this is used for elemental analysis via peaks that appear at energies characteristic for the element and bonding environment. A prominent component of the spectrum is the zero loss peak which represents electrons that are either non-interacting or elastically scattered. Thus, the ratio of zero loss intensity to total incident flux is naturally a function of sample thickness, explicitly expressed as:

$$t/\lambda = -\ln (I_0/I_{tot}) \quad (7.2)$$

This value is routinely generated as quality control when evaluating EELS measurements, as fine structure analysis requires minimizing the plural scattering effects within the sample (ideally to less than 1 mean free path (mfp)).[129], [130].

Determination of the absolute thickness requires calculation of the electron mean free path within the system (λ)[131]:

$$1/\lambda = \frac{11\rho^{0.3}}{200F * E_0} \ln \left(\frac{\alpha^2 + \beta^2 + 2\theta_E^2 + \delta^2}{\alpha^2 + \beta^2 + 2\theta_c^2 + \delta^2} * \frac{\theta_c^2}{\theta_E^2} \right) \quad (7.3)$$

This value requires precise inputs for sample density and probe calibrations which would likely contribute to a not insignificant level of error; in addition, the g-CN samples were found to be appreciably beam sensitive, further complicating such a measurement. However, generating rigorous quantifications of particulate thickness is ultimately not as meaningful as demonstrating a clear improvement over the raw material. Thus, comparative measurements of t/λ are sufficient, especially in conjunction with values determined for the commercial graphite as reference. Representative values are shown below in Fig 7.14.

Fig 7.14. Examples of EELS spectra and relative thicknesses (expressed in units of electron mean free paths) for GCN-1039 (*top*) and commercial graphite xGnP-m5 (*bottom*). The thickness of the unexfoliated g-CN results in significant inelastic scattering within the bulk, especially compared to the individual graphite platelets, where the zero loss peak dominates.

EELS measurements of the two samples yields striking differences, as expected. The particles of GCN-1039 were uniformly well above 1 mfp (typically 2.5-5 mfp), with many so thick that they were entirely electron opaque, rendering measurement impossible.

xGnP-m5, on the other hand, featured much more moderate values, with well-resolved sheets generally 0.25-0.5 mfp.

The results for GCN-1113 are shown below (Fig 7.15). GCN-1113 is the intermediate product of GCN-1039 and GCN-1141: post-sonication and centrifugation treatment in isopropanol, but prior to the freeze drying that led to the final product.

Fig 7.15. STEM imaging (*top*) and EELS thickness measurements (*bottom*) of GCN-1113, the intermediate product between GCN-1039 and GCN-1141 (post-probe sonication and pre-freeze drying).

The effects of exfoliation are immediately apparent. The largest particles observed were an order of magnitude smaller than those from the unexfoliated precursor, with the vast majority reduced to well below 1 μm . The extent of the exfoliation is reflected in EELS thickness measurements as well, as particles returned values typically >1 mfp. Interestingly, STEM imaging revealed the many rod-like structures that appear

significantly more crystalline than a majority of the more amorphous neighboring particles (Fig 7.15, top right), potentially serving as evidence of multiple phases.

N₂ sorption measurements for probe sonicated samples are summarized in the following figures and table. Pore volumes increased significantly, but in contrast to bath sonicated samples (which generated additional porosity from pores of all sizes, Fig 7.9), probe sonicated samples saw the bulk of the improvement in pores < 50 Å (Fig 7.16). However, the bath sonicated samples still saw a greater enhancement in overall porosity, with both methods exhibiting similar improvements to surface area (Table 7.3, Fig 7.17).

Fig 7.16. Pore size distributions and cumulative pore volumes (*inset*) of samples exfoliated via probe sonication (*red*) relative to the parent samples (*black*).

Table 7.3. Samples exfoliated via sonication and their respective N₂ porosimetry measurements (where available).

Sample	Precursor	Solvent	Sonic.	Time (hr)	Σ (m ² /g)	$\Sigma/\Sigma_{\text{prec}}$	ϕ	ϕ/ϕ_{prec}
-1003	-1001	Water	Bath	16	38	2.7	0.48	2.17
-1008	-1001	Water	Bath	16	32	2.3	0.47	2.14
-1018	-1014	Water	Bath	16	24	n/a	0.35	n/a
-1127	-1039	Water	Probe	2	21	1.5	0.32	1.41
-1141	-1039	Isoprop.	Probe	1	28	2.0	0.38	1.67
-1146	-1042	Isoprop.	Probe	2	18	2.8	0.20	1.43
-1147	-1045	Isoprop.	Probe	4	16	n/a	0.30	n/a

Fig 7.17. The surface areas of samples exfoliated via bath (*light red*) and probe (*dark red*) sonication all show significant, relative to their precursors.

7.3 Physical Exfoliation: Ball Milling

Sonication, both bath and probe, proved promising: samples consistently exhibited a 2-3x improvement in specific surface area and porosity. Unfortunately, the absolute metrics ($\Sigma < 40 \text{ m}^2/\text{g}$) are still far too prohibitively low for these materials to be considered competitive storage candidates. Thus, other exfoliation techniques are explored, either as an alternative or supplemental treatment.

Ball milling, whereby morphology change and homogenization is induced within a sample through tumbling in the presence of a hard, durable milling agent (e.g. steel spheres), offers a number of attractive experimental advantages. For one, it doesn't inherently require suspension within a liquid medium, thus removing a significant source of chemical contamination as well as the drying procedure. (However, centrifugation as a secondary treatment would still likely generate similar benefits.) Further, as a technique it is considerably more scalable than sonication: there's almost no upper limit to the size, as

tumblers with capacities of thousands of pounds are very common in mining, and many configurations are suited for more or less continuous operation.

Ball milling has been demonstrated to be effective in generating significant surface area in g-CN materials: GCN, having been synthesized from pyrolysis of melamine and subjected to 500 rpm ball milling, saw an increase from 10 m²/g to 97 m²/g [132]. This was accomplished through a reduction of the bulk g-CN into nanoplatelets 2-6 nm wide and 0.35-0.7 nm thick (i.e. single/double layer).

As described in the literature and subsequently reproduced, exfoliation was carried out using a planetary mill (Fig 7.18). This particular configuration features two degrees of rotation, with the rotating grinding jars affixed to a platform that spins in the opposite direction, and subsequently results in more effective grinding via the additional Coriolis forces generated.

Fig 7.18. Fritsch Pulverisette 7 planetary mill used to exfoliate GCN.

Milling was performed by loading the 45 mL grinding jars with the sample and 25×5 mm stainless steel balls. As only one of the grinding stations was used, a counterweight was loaded in the second. Grinding was initially performed at the maximum 800 rpm, with

additional samples prepared at 400 rpm. Milling was paused at 4 hour intervals to measure the temperature of the jars and ensure unwanted heat wasn't being generated.

After ball milling, samples became noticeably darker, a phenomenon not mirrored in sonicated samples (Fig 7.19). Initially, this was attributed to potential steel contamination from the milling process. SEM-EDS analysis, however, showed samples to be uniformly devoid of metallic contributions, returning only the expected C and N (plus minor O). Therefore, the color change can be reasonably attributed to a modification of the electronic structure and thus reflective of an effective exfoliation.

Fig 7.19. (top left) Photograph of g-CN samples that have been untreated, sonicated, and ball-milled (from L-R: GCN-1039, GCN-1141, and GCN-1143). While the sonicated sample is very similar in appearance to the untreated precursor, the ball milled sample was visibly darker. BSE imaging (top right) exhibits very little contrast, making discrete metallic contamination unlikely. This is confirmed by EDS mapping (bottom right), with analysis of the spectral data showing no counts above background for elements expected from stainless steel (Fe, Ni, and Cr).

XRD analysis reveals ball milling to induce a much more profound modification to the crystal structure, with both the main features at 13° , and more dramatically at 27° , becoming significantly more broadened. This indicates a loss of long range order from both in- and intra-planar components, consistent with the formation of well-exfoliated platelets. These results mirror those reported in [132] (Fig 7.20, right).

Fig 7.20. The XRD profile of GCN-1143, exfoliated via 800 rpm ball milling for 16 hours, exhibits a severe degradation of the crystal structure compared to the parent material (*left*). This mirrors behavior of ball milled g-CNs reported in [132] (*right*).

N_2 sorption measurements for ball milled samples are summarized in the following figures and table. Unlike with the sonicated samples, those that had been ball milled exhibited a near-uniform decrease in pore volume. At 800 rpm, samples milled for 4, 16, and 32 hours had identical pore size distributions; GCN-1148, which was ball milled at 400 rpm, exhibited a similar but much less severe reduction (Fig 7.21). Further, as opposed to the anticipated ~ 10 -fold surface area growth, BET measurements actually indicate surface area in 800 rpm ball milled samples to be halved relative to their parent materials (Fig 7.22). 400 rpm ball milling had no apparent effect on surface area.

Fig 7.21. Pore size distributions and cumulative pore volumes (*inset*) of samples exfoliated via ball milling (*blue*) relative to the parent samples (*black*). The results of ball milling at 800 rpm are shown on the left, and 400 rpm on the right.

Table 7.4. Samples exfoliated via ball milling and their respective N₂ porosimetry measurements (where available).

Sample	Precursor	RPM	Time (hr)	Σ (m ² /g)	$\Sigma/\Sigma_{\text{prec}}$	ϕ	ϕ/ϕ_{prec}
1142	1039	800	4	6.3	0.46	0.11	0.49
1143	1039	800	16	7.2	0.52	0.13	0.56
1145	1039	800	32	7.6	0.55	0.12	0.52
1148	1044	400	16	7.1	1.0	0.11	0.69
1149	1044	400	4	n/a	n/a	n/a	n/a

Fig 7.22. The surface areas of samples exfoliated via 800 RPM (*dark blue*) are uniformly roughly half of the parent material, regardless of milling time; 400 RPM ball milling (*light blue*) had essentially no effect on the surface area.

7.4 Nanoparticle templating

g-CN materials have thus far demonstrated a strong preference for the formation of large aggregates that are demonstrably impenetrable to sorbate gasses. Physical exfoliation, conceivably a readily available means of improving the media, has been mostly ineffectual at increasing the accessibility of the pore space. As such, we look to ways to prevent these structures from coalescing during the immediate synthesis.

Hard templating offers one such route (Fig 7.23). Hard and soft templating methods have been integral in the development of nanomaterials, wherein a readily crystallizable material acts as a scaffold, influencing the growth of another; once this material has been successfully patterned, the template material is removed, typically via chemical etching. This step in particular poses a distinctly nontrivial challenge, often requiring harsh acids (and subsequently the associated specialty equipment, PPE, training, etc) as well as extended production time. Given the difficulties involved, and especially considering one of the driving motivations towards exploring g-CN is the supposedly fairly rudimentary synthesis, the results would need to demonstrate sufficiently exceptional improvement to warrant implementation.

Fig 7.23. Schematic representation of the hard templating and etching process implemented to produce high surface area g-CNs. Figure reprinted from[133].

Various modifications would be eventually implemented, but the general synthesis protocol follows that described by Goettmann[134]. First, 1 g of cyanamide is melted, and 4 g of colloidal silica (*Ludox HS-40*, 40 wt% SiO₂ in H₂O[135]) is added dropwise under magnetic stirring. The solution is heated, via the flow deposition apparatus described in Sec 4.2, under Ar flow to 550°C using a 4.5°C/min ramp rate and held at temperature for 4 hours. Etching is then carried out through the exposure to 60 mL of 4M ammonium bifluoride (NH₄HF₂) for 48 hours (reaction given below, eq 7.4). Finally, the sample was washed in water and ethanol, and dried under vacuum at 70°C.

Various modifications would eventually be implemented in response to observations made during synthesis. Initial sample production was accompanied by a significant quantity of condensation outside of the heating zone; upon etching, no sample remained, suggesting the aforementioned condensation likely contained the solubilized cyanamide. Thus, to prevent this, efforts were undertaken to reduce the water content prior to pyrolysis: samples were allowed to sit in air for 8 hours to allow for passive evaporation,

with later samples also incorporating 15 minutes of heating at 110°C prior, and even further dehydration accomplished via overnight heating at 60°C[136]. All methods were successful in generating meaningful yield post-etching. However, these samples featured a color gradient that deepened downstream (Fig 7.24b), indicating the Ar flow to be influencing the reaction kinetics; reducing the flow rate from 0.3 SCFH (corresponding to ~1.5 cell volumes per minute) lessened this effect, ideally signifying a more homogeneous sample.

Fig 7.24. Comparison of SiO₂-templated g-CN products; in all samples, Ar travelled from left to right. *a.* Pyrolysis initialized with the water from the colloidal silica solution included (GCN-1064). *b.* Water driven off prior to pyrolysis (GCN-1067). *c.* Environmental Ar flow rate reduced (GCN-1072). *d.* Non-templated g-CN for reference (GCN-1042).

Finally, during outgassing at 150°C in preparation for N₂ porosimetry analysis, GCN-1067 underwent significant decomposition, resulting in a white solid depositing along the walls of the sample cell. This was attributed to C_xN_y intermediate products (most likely cyanamide) present within the templated sample. For sample purification, as well as to prevent elutriation through the instrumentation, a sample washing protocol was

introduced consisting of 3 separate washes with 100 mL acetone[136] (selected due to its good solubility with the anticipated C_xN_y products at room temperature).

As a control, GCN-1200 was created by pyrolyzing colloidal silica by itself. Resulting particles were large, with the long dimensions routinely well exceeding 1 mm, as well as highly angular and smooth, indicating a high degree of crystallinity. As expected, elemental analysis showed contributions solely from Si and O.

Fig 7.25. SEM-EDS of pyrolyzed silica (GCN-1200). Particles are large, smooth, and elementally consistent.

Templating g-CNs onto silica results in grains that are considerably smaller than bare silica ($< 500 \mu\text{m}$). The influence of the g-CN is apparent through visual inspection (Fig 7.26): the grains of GCN-1200 are transparent and glassy, while those of GCN-1067 feature a coarser surface as well as varying yellow hues, ostensibly correlated to the gradient observed across the sample bulk (Fig 7.24b).

Fig 7.26. Optical images of pyrolyzed colloidal silica (GCN-1200, *top*) and g-CN templated onto colloidal silica (GCN-1067, *bottom*).

The templating is readily evident through BSE imaging, which distinguishes the two materials through inherent elemental contrast, with the light and dark phases corresponding to the silica and GCN, respectively. This assignment is supported by EDS elemental mapping, also confirming that g-CN is additive onto the SiO_2 scaffold. The visible g-CN demonstrates a pronounced gradient amongst the particles, indicating an apparent dramatic heterogeneity in concentration throughout the sample.

Fig 7.27. SEM-EDS of g-CN templated onto silica (GCN-1067). Particles are smaller than silica alone, which display a varying quantity of g-CN across the surface. Note: in the BSE image (*bottom middle*) where EDS hyperspectral mapping was performed (*bottom right*), the g-CN phase appears bright due to charge accumulation; at lower magnifications (*bottom left*), this effect is not prevalent and the g-CN contrast is represented appropriately.

However, two such neighboring grains are observed to feature a similar hue under optical microscopy, with the “bare” particle perhaps even slightly deeper (Fig 7.28). This disparity can be most likely attributed to the interaction volumes associated with each technique. The electrons fundamental to SEM imaging are subject to intense scattering upon incidence with the sample and thus can only return information from the immediate surface (~ 100 nm for BSE[137]). Photons, which rely on different interaction mechanisms, are capable of transmission on the macroscale (generally in well-oriented crystal systems) as evidenced in the native transparency of GCN-1200 (Fig 7.26). Therefore, if it can be inferred from the optical images that the two particles possess comparable quantities of g-CN while plainly demonstrating differing amounts on the exterior surface from SEM, then

it is reasonable to presume considerable templating sites are accessible (and successfully utilized) within the bulk of the scaffolding material.

Fig 7.28. BSE imaging (*left*) demonstrating one particle that is entirely coated in templated g-CN while an adjacent particle is almost completely devoid. Optical imaging of the same region (*right*) implies them to contain comparable quantities of GCN.

Further, the g-CN visible on the exterior of grains was found to be notably beam sensitive: beam raster on localized areas over a short amount of time (~minutes) induced decomposition of the g-CN within those regions (Fig 7.29). This likely indicates the g-CN forms as discrete thin films, the desired result of templated growth. As the cumulative volume of these surface films wouldn't be expected to be sufficient to account for the full g-CN yield post-etching, and there were no observable instances of discrete aggregations of bulk g-CN, this further supports significant g-CN formation within the bulk of the scaffold.

Fig 7.29. g-CN templated onto the surface of Si granules is extremely beam sensitive, demonstrating degradation from the SEM beam exposure.

Etching yielded appreciable quantities of GCN; however, SEM revealed the result was large (~100-500 μm) aggregates not unlike what was observed for g-CNs produced via simple pyrolysis. BSE imaging indicated a single dominant phase marked with sporadic discrete higher density particulates, which EDS identified as g-CN and residual SiO_2 , respectively. In addition, trace remnants of F from the ammonium bifluoride etching agent can be observed.

Fig 7.30. SEM-EDS of templated g-CN post-etching (GCN-1156).

XRD measurements of etched samples confirm the structural parallels to non-templated g-CN_s (Fig 7.31). The profile is similarly bimodal, with peaks indicating consistent features. The peak corresponding to the interplanar spacing of the etched sample carries a slight shift ($\sim +0.28^\circ$) indicating a higher stacking density of sheets, but this ultimately equates to a negligible difference in real space ($\sim -0.03 \text{ \AA}$).

Fig 7.31. Comparing the XRD profile of g-CN produced by templating/etching of cyanamide with colloidal Si reveals a similar, albeit slightly less distinctly crystalline structure as pure pyrolyzed cyanamide.

N₂ sorption measurements for SiO₂-templated samples are summarized in the following figures and table. First, the colloidal silica (GCN-1200) demonstrates not-insignificant pore space on its own, supporting its promise as a good scaffold material. Further, the BET surface area is found to be 97 m²/g. Given that the theoretical surface area (eq 7.1) of 12 nm SiO₂ particles is 215 m²/g, there's likely a degree of aggregation (albeit minor: 97 m²/g corresponds to a particle twice the reported width of the silica).

g-CN templated onto silica generated a comparable specific pore volume; however, it also saw a ~50% increase in volume from pores <10 nm. This was associated with a similar increase in surface area. Washed samples seemed to yield 20-25% greater surface area compared to unwashed. It's unknown if this is an inherent improvement associated with the washing (e.g. removing low surface area C_xN_y intermediates) or sample variance.

Upon etching, this pore structure largely collapsed, with total pore volume diminishing to as low as 10% of its pre-etched values. The resulting material bore results strikingly similar to g-CN_s produced via simple pyrolysis (specifically those synthesized from cyanamide, GCN-1047 and GCN-1062). All surface areas fall within 3-6 m²/g, and the associated pore size distributions feature essentially identical bimodal distributions, with dominant populations at 35 and 150 Å, and all. The strongest distinction between the two lies with the total pore volume. While the templated and etched g-CN_s contained pore volumes that were 2-5x smaller than the pyrolyzed samples, this was shown to be largely attributable to meso/macropores as ~90% of the pore volume was generated by pores >100Å; in contrast, about half of the pore space in templated samples was due to pores <150Å. Altogether, this contributes to the characterization of a material that demonstrates a remarkably strong propensity for aggregation, and a subsequent resilience to exfoliation.

Fig 7.32. Pore size distribution (*left*) and cumulative pore volume (*right*) of colloidal silica (*black*) and g-CN templated onto silica, before (*dark green*) and after (*light green*) chemical etching.

Fig 7.33. Pore size distribution (*left*) and cumulative pore volume relative to total pore volume (*right*) of g-CNs produced from simple pyrolysis of cyanamide (*gray*) and after templating/etching with colloidal silica (*light green*).

Table 7.5. Lot numbers (where assigned), unique synthesis parameters, and N₂ porosimetry measurements (where collected) for g-CN samples templated with silica and etched.

Templ. Wash Etched	Dry.	Ar flow	Etch	Σ	TPV	ϕ
Lot Num: GCN-####		[SCFH]	[days]	[m ² /g]	[cm ³ /g]	
1064	-	-	n/a	0.3	-	- / - / -
1066	-	1155	<i>a</i>	0.3	5	- / - /4.6 - / - /0.05 - / - /0.09
1067	-	1156	<i>a+b</i>	0.3	2	120/- /3.2 0.28/- /0.02 0.35/- /0.04
1068	-	1157	<i>b</i>	0.3	2	- / - / - - / - / - - / - / -
1069	-	-	<i>b</i>	0.3	-	- / - / - - / - / - - / - / -
1070	-	-	<i>b</i>	0.3	-	- / - / - - / - / - - / - / -
1071	-	1158	<i>a</i>	0.3	2	- / - /4.9 - / - /0.04 - / - /0.07
1072	1076	-	<i>a+b</i>	<0.1	-	- /146/- - /0.31/- - /0.37/-
1073	-	-	<i>b</i>	<0.1	-	- / - / - - / - / - - / - / -
1074	-	n/a [†]	n/a	0.3	2	- / - / - - / - / - - / - / -
1075	-	-	<i>b</i>	0.3	-	- / - / - - / - / - - / - / -
1202	1204	1208	<i>c</i>	0.3	2	- /150/2.9 - /0.36/0.02 - /0.35/0.04
1200	-	-	n/a	0.3	-	97/- / - - 0.29/- / - - 0.28/- / -
Ramped Pyrolysis						
Lot Num: GCN-####		(n/a)		Σ	TPV	ϕ
				[m ² /g]	[cm ³ /g]	
GCN-1047				5.7	0.08	0.137
GCN-1062				5.8	0.11	0.173

a: Allowed to evaporate at room temperature for 8 hr

b: Boiled at 110°C for 15 min + stirring

c: Placed in a furnace at 60°C for 8 hr

[†]: No sample remaining after etching

Fig 7.34. The surface areas of g-CNs templated on colloidal silica are slightly greater than just the silica; upon chemical etching, the vast majority of this surface area is lost, yielding values similar to g-CNs produced via simple pyrolysis.

CHAPTER 8 – Summary and Future Work

Climate change is rapidly becoming the paramount concern of our times. Addressing our dependence on fossil fuel consumption is imperative to limiting the emission of greenhouse gasses which, left unchecked, will result in catastrophic and irreversible harm done to the environment. Great strides have been made to shift towards greener energy sources such as solar, wind, nuclear, etc; however, the inherent lack of a fixed infrastructure has limited their efficacy in the transportation sector, especially at the consumer level.

To this end, H_2 (and to a lesser extent, CNG) is an attractive alternative. In addition to producing significantly less greenhouse gasses, their implementation as a vehicle fuel source requires relatively minor modification to existing combustion-based design. However, for such technologies to see widespread adoption by the public, they would need to provide at the very least a comparable consumer experience. Current CNG vehicles require the inclusion of large, bulky tanks in order to match the range of a typical gasoline-powered system, while H_2 is without a viable storage solution for use in personal vehicles.

Thus, there exists considerable interest in technologies to improve onboard fuel storage capacities. The development of adsorbents is one such area, wherein gasses are confined within the internal void spaces of a solid. The specific composition of these

materials is specifically coordinated to be attractive to that particular gas molecule. This phenomenon (physisorption) allows for storage of a greater volume of fuel at a dramatically reduced pressure from what is required in traditional compressed systems; these lower pressures then allow for greater flexibility in the form factor of storage tanks.

Activated carbons have been long lauded for their adsorptive properties. The activation process, which can be carried out via numerous processes, generates extensive surface areas and nanoporous volumes. The ALL-CRAFT team demonstrated remarkable tunability and consistency of the resulting pore space through control of the implemented synthesis parameters[44]. Further, activated carbons can be produced from a wide array of organic precursors, notably those that would otherwise be considered waste products: peach pits, olive stones, etc; in particular, the ALL-CRAFT team utilized corncob.

Despite their promise, activated carbons have proven inadequate to meet H₂ energy density goals outlined by the DOE. Their characteristic surface areas, while impressive, are ultimately finite (2965 m²/g for a single graphene sheet[33]). Given its relative proximity to the current ceiling for BET surface area (7839 m²/g for MOF DUT-60[138]), enhancements to the chemical environment offers a more accessible avenue towards improved storage capability.

The incorporation of boron into the graphitic lattice is predicted to significantly augment the binding energy of H₂ onto carbon. Indeed, characterization of B-doped activated carbons demonstrates such gains; however, these samples also invariably exhibit reduced surface areas. This reduction in adsorption sites often more than offset any additional H₂ uptake afforded by the surface functionalization.

Coupled with the majority of measurable B (typically >80%) residing in environments *other* than substituted into the graphene lattice, this is indicative of poor dispersion of the boron dopant throughout the pore network during the initial deposition step, leading to surface agglomerations that fail to enhance adsorptive binding energy and clogs pores. To address this, a custom apparatus was developed to facilitate thorough deposition of boron through incorporating inert gas flow. Samples doped using this method were demonstrated to contain boron throughout the entirety of individual grains. However, while the portion of B substituted into the matrix trended upward, the highest quantity recorded was still only 40%, leaving considerable quantities of undesirable B groups.

Future samples may benefit from further treatment to remove these species. For instance, boron reacts vigorously with the halogen group to form boron trihalides (BX_3); exposing the doped material to one of these may react with, and drive off, any adsorbed B-containing molecules. Of the halogens, Br is especially promising. In addition to being the only of them to be liquid at room temperature, greatly simplifying the reaction, its product (BBr_3) vaporizes at 91°C , allowing it to be driven off with fairly low temperature outgassing. Care should be taken to limit the temperature though as bromine has been documented to attack the B-C bonds of boron carbide at 800°C [139].

Graphitic carbon nitrides (g-CNs) were explored as another potential sorption material. Similar to doped carbons, carbon nitrides are planar materials where alternating partial charges give rise to strong binding energy at the surface. Further, the molecular configuration features regular in-plane voids, allowing for greater surface areas than what's possible for activated carbons. Crucially, these materials can be produced by a simple 1-step reaction, from a number of inexpensive synthetic precursors.

Unfortunately, such promise has yet to be realized as all produced samples consistently featured prohibitively low surface areas ($<20\text{m}^2/\text{g}$) due to sheets aggregating in gas-impenetrable solids. Various methods were attempted to improve upon this. Physical exfoliation via sonication only generated only marginal additional surface area and pore space. Ball milling demonstrated evidence of structural exfoliation, but was ultimately found to cause a decrease in the pore volume. Templating g-CN onto colloidal silica yielded encouraging initial results, with surface areas measuring an order of magnitude greater than the non-templated counterparts (and 50% greater than the colloidal silica alone). However, upon etching the silica, the surface area was reduced to non-templated levels (and even less in some cases), indicating immediate reaggregation to bulk crystals.

Clearly, given the difficulty encountered in exfoliating these g-CN materials, more sophisticated mechanisms must be explored. As the aggregation is likely driven by electrostatic forces, implementation of ionic liquids as solvents may encourage more thorough and permanent exfoliation[140]. Also, crystallographic analysis revealed MU-produced g-CN materials to be likely comprised of ordered polymeric chains; a more rigorous investigation of the initial synthesis parameters (not unlike that undertaken to determine the optimal KOH concentration and activation temperature in the development of activated carbons) may pinpoint those that would more reliably generate the desired 2D graphene-like sheets.

APPENDIX 1 – Experimental Procedures

Nitrogen Porosimetry

Porosimetry is an especially vital technique in the characterization of porous materials, wherein a non-interacting gas is allowed to permeate the internal volume of a material across a range of pressures. Due to its accessibility, N₂ is commonly used, although He, Ar, and Hg are commonly used as well; in particular, the small molecular size of He ensures maximum permeation through all accessible void space, and is thus employed when measuring a material's skeletal density (*He pycnometry*).

A number of different fundamental properties can be determined depending on the specific conditions applied. For one, the formation of a single, complete monolayer is naturally associated with N₂ molecules occupying all available adsorption sites, and thus subsequentially the total available surface area (Σ). For primarily microporous materials, this occurs well below the saturation pressure of the adsorbate ($P_0 = 1.0067$ bar at 77.3K), with surface areas accepted to be attainable via the application of Brunauer-Emmett-Teller (BET) theory in the pressure range $0.1 < P/P_0 < 0.3$ [141].

On the other end, as the pressure of the adsorbate approaches the saturation pressure P_0 , it can be assumed that the pore space has been completely filled; therefore, N_2 measurements are collected at $P/P_0=0.995$ to yield the total accessible pore volume (*TPV*). Applying this to eq. 2.5 yields the material-independent porosity.

Further, the rate at which pores fill depends on their width, with larger pores filling first. The behavior across a full isotherm is thus indicative of the constituent pore populations present (Fig A1.1); this includes possible hystereses arising from asymmetric adsorption and desorption. Various models exist that provide a pathway to fine analysis of such behavior. Quenched Solid Density Functional Theory (*QSDFT*) is one such that has proven particularly robust for carbonaceous materials with significant surface roughness, making it suitable for nanoporous activated carbons[142]. Applying *QSDFT* to N_2 adsorption/desorption measurements produces a more discretized quantification of the internal void space, via a distribution across specific pore sizes.

Fig A1.1. IUPAC classification of the major physisorption isotherm shapes characteristic for different pore filling behavior[143]. Of particular note is isotherm IV(a), which is denoted to be representative of sorption in slit-shaped mesopores and describes the bulk of MU-produced activated carbons.

77K N₂ isotherms were primarily collected in-house using the Quantachrome Autosorb 1-C. All analysis was performed using Quantachrome's processing suite, including the provided QSDFT kernel for PSD measurements.

Experimentally, sample to be analyzed is loaded into the cell, outgassed, and weighed. The quantity analyzed is non-trivial: having too little surface area ($> 10 \text{ m}^2/\text{g}$) dramatically increases the error, while too large of a surface area ($< 25 \text{ m}^2/\text{g}$) increases equilibration time. Given that the total analysis time is limited by the evaporation of the liquid nitrogen cooling bath, this can be easily prohibitive. Thus, sample mass was generally limited to ~25-35 mg, although greater quantities were included if the surface area was expected to be significantly lower than $1000 \text{ m}^2/\text{g}$.

Electron Microscopy

The umbrella of electron microscopy covers a wide array of analyses, both qualitative and quantitative, made accessible via a focused beam of electrons impinging upon a sample. Signals are derived from both principal and ancillary phenomena, and can yield valuable information pertaining to a sample's morphology and/or composition. A brief description of these are given here:

Incident electrons can either transmitted through, scattered by, or absorbed into the sample. In thin samples, the bulk of the signal will be transmitted, yielding a "bright field" image that reflects the localized density and/or thickness within the imaged region. As the sample thickness increases, increased scattering reduces (and eventually eliminates) transmission. Higher density regions will naturally scatter more strongly, so collecting such signal produces a "dark field" image analogous to that from transmitted electrons.

Fig A1.2. Ag nanoparticles deposited into cellulose, as simultaneously imaged in SEM via (*l-r*) transmitted, backscattered, and secondary electrons. Transmitted and backscattered electrons both yield contrast representative of density (i.e. elemental) distribution; in thin samples, where absorption is minimal, their combined collected signals account for essentially the entirety of the incoming beam. Secondary electrons are ejected from the surface of the sample, and thus reflect a sample's topography.

The interaction of the high intensity beam with the sample surface is responsible for many ionization events for each incident electron. If this ionization occurs sufficiently near the surface of the sample, the freed electrons can escape. Collecting these electrons, generally through a biased detector such as the Everhart-Thornley, forms a secondary electron image that represents local topography.

The aforementioned ionizations result in inner-shell vacancies within the atoms of the sample, which are quickly filled from the outer shells. Such transitions release excess energy via the emission of photons, the energy of each is equivalent to the difference in energy between the those specific shells. Given that these are well tabulated for all elements and transitions, these photons are referred to as characteristic X-rays and can be collected to identify the specific chemistry present.

Transmitted electrons are traditionally collected using a CCD camera, with qualitative information of localized densities apparent from the net intensities detected. However, each electron also carries information regarding its interaction with the sample. Passing the transmitted through an EEL spectrometer distinguishes the energy loss

experienced by individual electrons from inelastic scattering. Similar to EDS, the resulting signal can be used to classify the chemistry of the sample, but to a much finer degree as it is sensitive to the specific bonding environment rather than simply a particular orbital.

SEM-EDS Imaging and Analysis

SEM imaging was primarily performed using the FEI Quanta 600FEG environmental SEM and the FEI Scios DualBeam FIBSEM, both housed at MU's Electron Microscopy Core. Powdered samples were mounted to Al stubs using double-sided carbon adhesive. Conditions varied depending on the particular application, but generally utilized low voltages (2 or 5 kV) and low beam currents. The low voltage produced the greatest surface sensitivity and morphology, while the low beam currents ensured optimal resolution. Low-vacuum mode was implemented as needed for samples demonstrating charge-buildup

EDS was performed using a Bruker Quantax 200 silicon drift detector. For qualitative purposes (elemental mapping, etc), higher voltages (~20 kV) and currents were implemented. The higher voltages ensured signals from all elements of interest would be generated, while higher currents improved X-ray production. For quantitative purposes (calculation of elemental composition, etc), the voltage was reduced to a value corresponding to an overvoltage of ~2-2.5x (typically 8 or 10 kV) to minimize errors. Data reduction was performed using Bruker's Esprit software suite.

STEM/HR-TEM/EELS Imaging and Analysis

TEM was performed using the FEI Tecnai F30, equipped with a Quantum Gatan Imaging Filter for EELS, housed at MU's Electron Microscopy Core. Samples were

prepared by suspending an aliquot in isopropanol via bath sonication, and pipetting onto a holey carbon grid.

HR-TEM images were collected at 300 kV, and FFT analysis performed using Gatan's Digital Micrograph suite. More refined analysis followed a custom protocol described in Appendix 4.

Bulk g-CN crystals were observed to be sensitive under the beam, and so images and EELS spectra were collected using STEM mode and a reduced voltage of 200 kV to limit induced damage. EELS spectra were collected and analyzed using Gatan's Digital Micrograph suite.

Focused Ion Beam Milling

FIB-SEM cross-sectioning was performed using the FEI Scios DualBeam FIBSEM, housed at MU's Electron Microscopy Core, equipped with a Ga⁺ ion source. All work was performed using an ion energy of 30 kV. First, a 2 µm thick protective strip of Pt was deposited across the top surface of the grain. Rough milling to produce a cross-section was performed at 30 nA, while successive polishings were performed at 7, 2, and 0.5 nA.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements, as the name implies, are based on the photoelectric effect: monochromated X-rays are incident upon the sample where they are absorbed by constituent electrons. These excited electrons are freed and collected by a detector that measures its energy. Given that the electrons themselves are measured directly, this affords

a higher degree of resolution than other techniques, and is thus capable of differentiating several simultaneous chemical states upon spectral deconvolution.

XPS was performed using the Kratos Axis 165 spectrometer in the Advanced Materials Characterization Laboratory (AMCL) at University of Missouri Science and Technology (MST). Full spectra were collected using a monochromatic Al beam at 150W, from 0 to 1100eV, step size 0.5eV, and 0.5s dwell time. Single peaks were fit to each element present to determine rough atomic composition. For fine peak deconvolution, high resolution scans were collected for the elements of interest using a refined step size of 0.1eV. Spectral analysis and deconvolution was performed using CasaXPS.

Volumetric Hydrogen Sorption

Volumetric measurements, as performed on the Hiden HTP-1 and Quantachrome Autosorb 1-C, are predicated on tracking the movement of gas molecules. To begin, the sample to be analyzed is loaded into the appropriate sample cell (which has been thoroughly volume- and mass-calibrated) and sealed. Upon outgassing, the system is weighed to determine the sample mass.

To measure uptake, first a dedicated dosing volume, which is separated from the reactor vessel containing the sample, is pressurized. Once equilibrated, the two volumes are exposed to one another, allowing gas flow from the dosing volume into the reaction vessel; upon equilibrium once more, the volumes are separated again. As pressure and temperature are recorded at each step, the number of gas molecules transferred into the reaction volume is can be determined. With the total pore volume having been determined prior from N₂ porosimetry, the pressure drop expected from simple expansion (in the

absence of adsorption) can be calculated; additional pressure loss is thus directly attributed to adsorbed molecules.

A tremendous benefit volumetric measurements have over gravimetric measurements is that successive measurements can be performed in series, allowing for the collection of full isotherms. Further, digital sensors and pneumatics provide the capability for the process to be automated, resulting in increased efficiency and reliability.

X-ray diffraction (XRD)

X-ray diffraction measurements were performed using the Siemens D500 powder diffractometer (housed in Deepak Singh's laboratory space in Physics). XRD offers direct analysis of a material's crystal lattice: a monochromated X-ray is swept across a sample at various angles of incidence and the intensity of the reflected radiation recorded. Crystalline materials will exhibit increased intensity at certain angles; these correspond to constructive interference generated by reflected radiation from neighboring planes that satisfy Bragg's Law[144], and can be compared to databased spectra to characterize a material's crystalline phase.

The diffractometer utilized standard Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$); voltage and current were set to 40 kV and 30 mA, respectively. A goniometric stage facilitated automated scattering angle vs. intensity collection. Data was collected in the range $10^\circ < 2\theta < 100^\circ$, with a step size of 0.04° and a rate of 2 sec/step. The sample was mounted to a plastic holder that possessed a single, wide diffraction feature at $2\theta < 15^\circ$, which was later subtracted from the experimental data.

The representative structures under investigation (proposed constituent bases of graphitic carbon nitride) are fairly understudied, and were subsequently not found in the available crystallographic databases. Thus, spectral modelling consisted of collecting the position and relative intensities of allowed reflections from experimental data found in the literature, and normalizing them to the experimental data.

Prompt Gamma Neutron Activation Analysis

The boron content of doped nanoporous carbons were determined via prompt-gamma neutron activation analysis (PGNAA) performed at the University of Missouri Research Reactor (MURR). Precise measurements of the concentrations are vital, both as efficacy feedback for the various doping mechanisms as well as setting the framework for the greater exploration of the surface modification's effect on hydrogen uptake. However, boron's low mass and similarity to the surrounding carbon matrix prohibit precise measurements by most analytical methods; to this end, neutron scattering based techniques are especially attractive due to boron's notably elevated scattering cross-section[145]. This sensitivity allows for detection as low as 10 ppb[146].

Samples are loaded into small plastic vials and massed prior to submission. The analysis involves directly irradiating the samples through the reactor beamport, 'activating' them via excitation from the incident neutrons. As the sample nuclei return to ground they emit characteristic gamma rays which are collected and compared to element-specific calibration curves, returning the mass; the weight percent boron is then calculated using the initial mass measurement.

Fourier Transform Infrared Spectroscopy

Microscopic FTIR was carried out to characterize the boron-carbon bonding environment. Doped powders were prepared by grinding with crystalline KBr in a 1:3000 mass ratio. 90 mg of the mixture was loaded into the die assembly and pressed with a manual hand press; if the resulting pellet remained opaque, it was discarded and a new pellet formed.

Measurements were performed on a Nicolet Galaxy 5020 FTIR spectrometer equipped with an infrared microscope to isolate the desired signal. Spectra were collected in the range $4000\text{-}600\text{ cm}^{-1}$, using a resolution of 1 cm^{-1} , and averaged of 32 scans[74].

APPENDIX 2 – Rapid Methane Screening Instrument

A2.1 Manometric measurements

There exists two primary methods to quantify gaseous uptake of a material: gravimetry and manometry (see Section 2.3). Of the two, the gravimetric technique offers greater simplicity in measurement and analysis. There are several drawbacks, however; notably, the intrinsic dependence on the mass ratio of sorbent to sorbate precludes measurement of H₂. Further, it is a more labor- (and subsequently time-) intensive method, and is thus generally more suited for collection of a single data point of interest (e.g. 35 bar, etc) rather than a full isotherm. This significantly limits the analytical capacity of the resulting data, as interpolation and extrapolation of isothermal data can facilitate calculation of many sorbate metrics of particular interest (binding energy, saturation pressure, etc).

Manometric (volumetric) measurements present remedies towards both deficiencies. Instead of relying on mass measurements, data is collected barometrically, and is thus suited for low as well as high density gasses. In addition, integration of digital pressure readouts and pneumatic valves allows for instrument design that is essentially entirely automated. ALL-CRAFT's Autosorb 1-C and Hiden HTP1-V are two such

commercially-available instruments. These instruments also allow for isothermal data collection across a wide range of temperatures; the considerations this would impose on a gravimetric instrument all but prohibit this option.

Fig A2.1. Comparison of isothermal data collected for sample 5K-0280 via the gravimetric (left) and the Hiden (volumetric, right) instruments. Each data point from the gravimetric instrument required individual effort to collect, and thus reflected a minimum of several man-hours. In contrast, data from automated instruments like the Hiden require no manual input once started, and yields significantly more data in a comparable amount of time.

Collection time is still considerable, even with equilibration time optimized via continuous monitoring of system parameters. Thus, a full “suite” of measurements for a single sample (i.e. H₂ measurements at 77/87/273/303 K on the Hiden) can be expected to occupy up to several days of instrument time, making instrument availability a precious commodity.

To this end, a system was designed to enable rapid screening of samples, with the goal of preventing poor performing samples from occupying this resource. This instrument was designed with simplicity in mind, as every joint and fitting may eventually be the source of a future leak. Further, components were selected to tolerate measurements up to 70 bar.

A2.2 Design and operating procedure

As is characteristic of manometric measurements, the system is built around the concept of discrete but connected dosing and cell volumes. The dosing volume is defined as the region bound by the ball valves at the inlet, outlet, and within the cell assembly, and contains an integrated digital pressure gauge. The cell assembly connects to the dosing volume via a VCO fitting, and features a VCR filter gasket to prevent carbon elutriation through the system. The desired gas is attached through the inlet with a pressure regulator that defines the dosing pressure.

The system has undergone a number of modifications since it was first established[83]; in addition to consolidating a few joints to reduce potential sources of leak, perhaps the most notable was replacing the existing tubing with those featuring thicker walls. Not only does this provide for increased pressurization, it also served to reduce the dosing volume. The prior configuration featured a dosing volume that was significantly greater than the sample volume – not ideal as this corresponds to a more minimal gas transfer, and subsequently increased error. The prior configuration corrected for this by the inclusion of displacement rods in the dosing volume. Alternatively, a dosing volume significantly smaller than the cell volume may require an undesirable number of dosings to achieve the requisite uptake pressure. As such, the goal for this redesign was for both volumes to be approximately equivalent, which was eventually realized.

Fig A2.2. Photo of the Rapid Methane/Hydrogen Screening Instrument (left), and associated schematic diagram (right). The cell assembly volume is highlighted in gray.

Integral to any uptake measurement, gravimetric or manometric, is a precise sample mass. This is performed by first collecting the mass of the empty cell, and subtracting this from the mass of the cell with carbon. Prior to the mass measurement (and the isotherm collection), the sample is outgassed; first, for 30 minutes in ambient, followed by ~2.5 hours at 400 °C to remove any adsorbed atmospheric gasses.

The cell, kept under vacuum via the integrated valve, is attached to the full system via the VCO fitting. With the cell valve closed, the dosing volume is pressurized by opening the inlet valve. If needed, the pressure is adjusted via the tank's regulator. After closing the inlet valve, the system is allowed to stabilize and the pressure and temperature recorded. The cell assembly valve is opened, exposing the sample to the pressurized dosing volume. Upon equilibration, the next pressure and temperature are recorded; the equilibration time increases for larger samples masses or exceptionally strong adsorbers. Finally, the cell valve is closed, and the pressure and temperature recorded once more. This process is repeated for additional data points as required.

The interval between data points depends on the pressure differential between the dosing and current cell values. Automated systems account for this by using a dynamic

dosing pressure, resulting in data that is fairly evenly spaced (Fig A2.1). The rapid screening instrument, on the other hand, makes no effort to provide a similar outcome, rather using a dosing pressure that is just above the particular pressure of interest (e.g. 35 bar). This generates a few data points at lower pressure, with an increased concentration near the desired pressure, facilitating the eventual interpolation in this region.

Fig A2.3. (Left) Consecutive CH₄ uptake measurements of MWV-0261 demonstrates the repeatability of measurements from the rapid screening instrument. Using a dosing pressure of 40 bar ensures a greater density of data points near 35 bar, facilitating quality interpolation at this pressure. (Right) Data from the rapid screening instrument is shown to be continuous and reliable up to 70 bar.

A2.3 Data processing

The driving concept of manometry is the tracking of gas molecules upon expansion. This requires that the dosing and cell volumes are well-established prior to measurement (see Section A2.4). Excess adsorption, the directly measurable quantity, is given by:

$$m_{\text{excess}} = m_{\text{cell,total}} - m_{\text{cell,free}} \quad (\text{A2.1})$$

where $m_{\text{cell,total}}$ is the total quantity of gas that expands into the cell volume, and $m_{\text{cell,free}}$ is the expected quantity in the absence of adsorption; the former is given by the difference in gas molecules in the dosing volume prior to and following the opening of the cell valve:

$$m_{cell,total} = (\rho^0 - \rho') * V_d \quad (A2.2)$$

while the latter represents the volume available for the gas to expand into:

$$m_{cell,total} = \rho' * (V_c - V_s) \quad (A2.3)$$

ρ^0 and ρ' are the pressures before and after opening the cell valve, and V_d , V_c , V_s are the dosing, cell, and sample volumes. Combined:

$$m_{excess} = \rho^0 * V_d - \rho' * (V_d + V_c - V_s) \quad (A2.4)$$

For successive measurements, the quantity of gas already in the cell from prior data points needs to be accounted for. Thus, the excess for data point j is given by:

$$m_{excess} = \sum_i^{j-1} [(\rho_i^0 - \rho''_i)V_d] + (\rho_j^0 V_d - \rho'_i(V_d + V_c - V_s)) \quad (A2.5)$$

Here, ρ'' is the pressure after reclosing the cell valve; it only differs from ρ' by the exclusion of the valve's volume and thus shouldn't be expected to vary greatly. These calculations are coded into the dedicated template file; entering the recorded pressures and temperatures performs the requisite calculations.

Fig A2.4. Screenshot of the RMS data processing template file.

A2.4 Volume calibration

Manometric measurements rely on precisely determined values for the dosing and cell volumes. Any change to these volumes, such as after repairing a system leak (Section A2.5), necessitates a recalibration.

At a minimum, two measurements are required to solve for the two unknown volumes (V_d and V_c). A simple volume expansion with an evacuated cell provides one of these measurements:

$$\rho^0 * V_d = \rho' * (V_d + V_c) \quad (\text{A2.6})$$

For the second, a displacer of a known volume V_{disp} is loaded into the cell:

$$\rho^0 * V_d = \rho' * (V_d + V_c - V_{disp}) \quad (\text{A2.7})$$

While two dosings serve as the minimum required, the importance of the measurement compels duplication for the sake of statistics. Also, there are 3 spacers

available, which may be combined as desired for the sake of duplication as well as for quality control of the spacers themselves. This allows for up to 8 spacer permutations; if each are measured once, this generates 56 unique pairs for analysis. However, the ideal scenario sees 2-3 dosings per permutation to so that individual outlier measurements may be identified and excluded.

An excel template was developed to aid this analysis. The calculations use the following form of eq A2.7, which reduces the two input measurements to a single ratio:

$$(1 - \rho^0/\rho') * V_d + V_c = V_{disp} \quad (A2.8)$$

After importing each calibration measurement, the volumes are initially automatically calculated as the average of each eligible pair of measurements (measurements with identical displacer conformations are excluded).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1																				
2																				
3																				
4																				
5																				
6																				
7																				
8																				
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Fig A2.5 Screenshot of the *Input* tab of the volume calibration processing file. Each dosing is allocated its own column, with the user-required information for each highlighted in blue.

The file also facilitates analyses of the calibration data itself. The statistics tab compares the input ratio for each configuration, allowing for individual measurements to be excluded from further consideration. A separate tab gives the calculated volume results for each pair of measurements to provide further quality control.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1																				
2																				
3																				
4																				
5																				
6																				
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Fig A2.6. Screenshot of the *Statistics* and *Calculations* tabs of the volume calibration processing file. In the *Statistics* tab, multiple measurements for a common spacer configuration may be compared to identify outliers; in this example, measurement #11 exhibits a significantly greater percent error

A2.5 Leak test procedure

Leaks in a manometric system are directly contrarian to the technique's core principles, and so it is imperative that these are addressed immediately upon identification; generally, these will present as a system that fails to equilibrate within a reasonable timeframe, outside of temperature-induced effects. The o-ring and gasket of the cell assembly are both the most common and readily accessible sources to check. Past this, testing becomes significantly more intricate.

Compression fittings are designed to create a seal from a very specific degree of tightening, with overtightening often constituting an underappreciated portion of leaks. Thus, it's essential to identify the particular faulty connection, rather than relying on tightening all possible joints. A number of particular checks can be performed to help narrow down the suspect sources; these will involve inducing a specific pressure gradient between discrete volumes. For each, it is important that no sample is included, to mitigate and adsorptive or desorptive effects. Also, if possible, using H₂ or He will aid the process, as their small molecular size makes them especially susceptible to leaks, enhancing any observed leaks.

1. Internal: across the inlet valve. This is perhaps the most straightforward source, as it is the only one that could propagate as an observed increase in pressure. Attach the empty cell, increase the source pressure via the regulator, close the inlet valve, and vent the system via the exhaust. Close all valves, and observe the pressure; any accumulated pressure will necessarily indicate a leak across the inlet valve.
  2. Internal: across the sample valve. Outgas the empty cell, and attach it to the system. Open the source valve, and allow it to remain open, while keeping the sample valve closed. After an amount of time (the longer the better), close the source valve, and vent the system via the exhaust. With all other valves closed, open the sample valve. If the valve is working properly, the gauge should register very little change, and potentially a small pressure drop. If there is a cross-valve leak however, gas will have infiltrated the evacuated cell, and the gauge will register an increase in pressure.
  3. External: via sample or dosing volumes. From personal experience, cross-valve leaks constitute a higher percentage of leak sources than what random chance would suggest. This isn't terribly surprising, given the dramatic difference in the frequency with which they are manipulated.
- With these eliminated, however, leaves only the possibility of an external leak, i.e. one that vents gas to the environment. These are significantly less straightforward to troubleshoot as the ability to track molecular movement for later comparison is eliminated. However, it is possible to determine if the leaking joint is located in the dosing or cell volumes. After connecting the

sample cell, and with the cell valve closed, pressurize the dosing volume; a decreasing pressure indicates the leak exists somewhere in the dosing volume.

If the pressure stays steady and only begins leaking after the cell valve is open, the leak is located on the cell volume.

The latter requires less work to troubleshoot due to the reduced number of joints, as well as the ability to move the cell off-instrument for closer inspection. For leaks in the dosing volume, commercial products exist which may identify the problematic connections: liquid leak detector (Swagelok's Snoop) and flexible films (Detectape) can be applied to suspect joints to visually indicate gas expulsion.

If none of the above are able to remedy the leak, it must be identified by individually removing components piecewise until it is resolved; the removed component can be replaced with end endcap. Before removing a fitting, the position of the nut should be marked on the tube to prevent overtightening during reassembly.

APPENDIX 3 – Ono-Kondo Model of Adsorption

A3.1 Modeling Adsorption

Several mathematical models exist to describe adsorption phenomenon; three of the most common are the Langmuir, Freundlich, and Redlich-Peterson models[147]. The Langmuir model[63] is formulated via site-specific analysis, based on the interaction between individual adsorbate molecules and the adsorbent surface:

$$\frac{m_{ads}}{m_s} = \frac{ab\rho}{1 + b\rho} \quad (A3.1)$$

The Freundlich equation[148] represents an empirical approximation of solute concentration:

$$\frac{m_{ads}}{m_s} = a\rho^{1/b} \quad (A3.2)$$

However, it has been shown to be a poor descriptor for porous media in non-standard (e.g. high pressure or low temperature) conditions[70].

The Redlich-Peterson model[149] was proposed as a hybrid that overcomes the individual concentration limits of the previous two models:

$$\frac{m_{ads}}{m_s} = \frac{ab\rho}{1 + b\rho^c} \quad (A3.3)$$

Analytically, this form prohibits expressing the density in terms of the uptake; this makes it incompatible for data interpolation, and subsequently, calculation of isosteric heats.

Fig A3.1. Comparison of Langmuir, Freundlich, and Redlich-Peterson fits to a 77K absolute adsorption isotherm for sample 3K-0285 (top) and associated residual plots (bottom).

A3.2 Monolayer Ono-Kondo model

The Ono-Kondo model is subsequently shown to be considerably more adept at characterizing porous media, under a wide spectrum of conditions[150]. Rather than characterizing single-particle interactions, it instead considers a more macroscopic view of the system, with its conceptual backbone based on investigating fluid gradients in the presence of an interacting surface. Additionally, rather than formulated via absolute adsorption, it instead describes Gibbs (‘excess’) adsorption; this is significant as it is the value most readily measured directly, whereas determination of absolute adsorption requires assumptions of the film geometry, which isn’t clearly understood[21].

$$\frac{m_{exc}}{m_s} = 2a \frac{\left(1 - \frac{\rho}{b}\right) \left(1 - e^{\frac{c}{T}}\right)}{\left(1 + \left(\frac{b}{\rho} - 1\right) e^{\frac{c}{T}}\right)} \quad (\text{A3.1})$$

The Ono-Kondo model carries the further advantage of having been constructed using physically significant parameters: b is the *adsorbed film saturation density* (i.e. the condition in which the density of the adsorbed film matches that of the bulk), c is the binding energy of the gas-solid interaction, T is the temperature of the isotherm, and a is a simple scaling factor. This formulation natively utilizes a binding energy that is in units of negative Kelvin; it can be expressed in units of positive kJ/mol as:

$$\frac{m_{exc}}{m_s} = 2a \frac{\left(1 - \frac{\rho}{b}\right) \left(e^{\frac{c}{RT}} - 1\right)}{\left(e^{\frac{c}{RT}} + \frac{b}{\rho} - 1\right)} \quad (\text{A3.2})$$

Table A3.1. Description of terms contained in the Ono-Kondo model.

Term	Units	Description
ρ	g/L	Gas density (independent variable)
a	g/kg	Scaling factor
b	g/L	Adsorbed film saturation density (ρ_{sat})
c	kJ/mol	Binding energy of the gas-solid interaction (E_b)
T	K	Isotherm temperature (fixed)
R	kJ/K·mol	Gas constant

Fig A3.2 Demonstration of each term's effect on the shape of the model. (*Top left*) The scaling term a increases the overall height of the model; it has no direct physical significance. (*Top right*) b reflects the model's intersection with the x -axis; this represents the saturation density within the pore space, which typically takes the value of 100 g/L for carbonaceous materials[21]. c (*Bottom left*) and T (*Bottom right*) are coupled within the model via $e^{c/T}$, and thus share an inverse relation. Decreasing c yields a flatter curve; given that this reflects the material's binding energy, it would be expected that a less strongly-binding system would yield reduced excess adsorption. T represents the temperature of the isotherm and is a constant.

A3.3 Fitting Initialization

A successful fit often hinges on the quality of the parameter initialization. Elmar Dohnke demonstrated a cryogenic saturated film density of approximately 100 g/L for a

number of different carbon-based adsorbent materials[21]; subsequently, this will serve as a suitable initial value for b .

a and c are parameters that are strongly correlated with the isotherm's maxima.

Thus, using

$$\frac{d}{d\rho} \left(\frac{m_{exc}}{m_s} \right) = 0 \quad (A3.3)$$

returns a peak position and value of:

$$\left\{ \rho_{pk}, \left(\frac{m_{exc}}{m_s} \right)_{pk} \right\} = \left\{ \frac{b}{\left(e^{\frac{c}{2RT}} - 1 \right)}, \frac{2a}{1 + \frac{2\rho_{pk}}{b}} \right\} \quad (A3.4)$$

By using a data point that approximates the peak of the curve, a and c can be initialized with

$$a = 0.5 \left(\frac{m_{exc}}{m_s} \right)_{pk} \left(1 + \frac{2\rho_{pk}}{b} \right) \quad (A3.5)$$

$$c = 2RT \ln \left(\frac{b}{\rho_{pk}} + 1 \right) \quad (A3.6)$$

Table A3.2. Initialized values for 3K-0285, along with the ultimate fits

Parameter	Units	Initialized Values	Fitted Values
a	g/kg	32.2	35.6
b	g/L	100.00	100.0
c	kJ/mol	2.86	2.50
T	K	77	77
ρ_{pk}	g/L	12	12.43
$G_{ex,pk}$	g/kg	52	53.50

Fig A3.2. Ono-Kondo model fitted to the 77K gravimetric excess adsorption isotherm for sample 3K-0285. Fitting parameters used are given in Table A3.2.

APPENDIX 4 – g-CN Crystal Structure Determination from HRTEM-FFT Analysis

A4.1 HR-TEM and FFT introduction

HR-TEM is a powerful tool capable of direct analysis of crystalline systems wherein well-oriented crystals generate visible fringes via Bragg diffraction. These fringes, correlated to particular d-spacings within the crystal[119], can be measured directly from collected images or alternatively, simultaneously quantified for the entire imaged region via FFT analysis[120]. This is a functionality built-in as standard in many advanced image processing software packages such as DigitalMicrograph and ImageJ.

As each distinct point in the generated FFT is correlated to a particular repeating element (representing a particular structural feature), it helps to account for noise associated with individual fringes by essentially averaging over the entire imaged range, making it a generally more reliable dataset for analysis and quantification.

As demonstrated in Fig 6.23(first HRTEM image), gCN-1003, a carbon nitride produced from the pyrolysis of melamine, exhibited extensive (albeit fairly disordered) crystallinity throughout,. However, a particular pattern emerged throughout most of the region (Fig A4.1), potentially demonstrating a dominant phase/structure suitable for analysis.

Fig A4.1. (*left*) FFTs generated from selected regions reveal a persistent structure populating significant fraction of the imaged region. (*right*) Applying a mask based on these fringes (inset) to the FFT of the full image, and performing an inverse FFT allows for generation of the real space analog to these fringes; the resulting map confirms that this particular structure is especially widespread.

Analysis typically consists primarily of comparing measured d-spacings to tabulated structures using dedicated software packages. The d-spacing is calculated from generated FFT's via:

$$d(\text{\AA}) = 20/x_{pt-pt}(nm^{-1}) \quad (\text{A4.1})$$

where x_{pt-pt} is the center-to-center distance between the symmetric points of a fringe. Once potential candidates are identified for each and confirmed to be coplanar (i.e. simultaneously viewable from a common perpendicular 'zone-axis'), a simulated FFT can be generated to ensure a match.

However, this naturally relies on the structure having been previously characterized and databased. Graphitic carbon nitride materials are only somewhat recently receiving more focused attention in the materials community, and as such associated structural entries are not readily available. Comparison with other C-N materials was unsurprisingly fruitless. Thus, further analysis requires a more manual approach.

A4.2 Description of algorithm and initial results

To characterize this system, a utility was developed in Mathematica to correlate well-resolved points from an FFT with reflections for a given crystal system, along with the associated zone axis. For 3 discrete points, there exist 5 unique measurements with which to compare to the theoretical system: in addition to the individual d-spacings, the angle between fringes is characteristic of the angle between the associated lattice planes (Fig A4.2).

Fig A4.2. Measured d-spacings and inter-planar angles for the 3 most prominent fringes observed in the FFT from Fig A4.1.

In the utility, the formulae are generalized for a triclinic system (all parameters are unconstrained); however, for this investigation, orthorhombic symmetry ($\alpha = \beta = \gamma = 90^\circ$) was employed, resulting in the following effective simplifications:

$$d_i = \left(\left(\frac{h_i}{a} \right)^2 + \left(\frac{k_i}{b} \right)^2 + \left(\frac{l_i}{c} \right)^2 \right)^{-1/2} \quad (\text{A4.2})$$

$$\cos(\phi_{ij}) = \left(\frac{h_i h_j}{a^2} + \frac{k_i k_j}{b^2} + \frac{l_i l_j}{c^2} \right) * d_i * d_j \quad (\text{A4.3})$$

Possible reflections are identified by sequentially testing a list of candidates against rules based on these values and the lattice parameters of the tested crystal system. The algorithm developed is outlined below:

1. First, a list of all possible basic reflections (positive values only) is generated based on a given maximum index (e.g. a maximum of 3 would generate a list of candidates $\{1,0,0\}, \{0,1,0\} \dots \{3,3,2\}, \{3,3,3\}$). Using an initial higher value increases the likelihood of the identifying the correct set of reflections, but also necessarily more computationally intensive.
2. A list of candidate reflections is generated for each point by comparing the theoretical d-spacings to the measured values, within a user-selected tolerance.
3. These lists are expanded by including all possible negative permutations of each reflection (e.g. $\{0,1,2\}$ expands to $\{0,1,2\}, \{0,-1,2\}, \{0,1,-2\}, \{0,-1,-2\}$).
4. 2 new lists are generated by comparing the angle between candidate reflections 1-2 and 2-3 to the measured values, within a user-selected tolerance.
5. These are merged into a single list by collecting candidates from the subsets that contain a common second reflection.
6. This list is reduced by ensuring that angle between the first and third reflections matches the sum of 1-2 and 2-3.
7. Finally, the list is further reduced by ensuring the three reflections are coplanar ($1 \times 2 = 2 \times 3$).
8. The output table reports the zone axis and percent difference for each measurements, and sorts by the cumulative percent difference.

Fig A4.3. Flow chart of the employed algorithm. Each box represents a separate list (or set of lists) of candidate reflections from which to test against the given operation. The width of each box very roughly approximates the relative number of candidates in each.

The inclusion of all possible permutations generates results that are essentially identical due to symmetry. For completeness, all are included in the output results, and grouped together. A screenshot of the utility and results table (after applying the values from Fig A4.2) is shown below (Fig A4.4),

Measured d-Spacings

$d_1[\text{\AA}] = 6.63$
 $d_2[\text{\AA}] = 4.51$
 $d_3[\text{\AA}] = 5.73$

☐ 5%
☐ 10%
☒ 20%

Measured Refl. Angles

$\phi_{1-2}[^\circ] = 53.4$
 $\phi_{2-3}[^\circ] = 43.5$

☐ 5%
☐ 10%
☒ 20%

Lattice Parameters

$a[\text{\AA}] = 16.2$
 $\alpha[^\circ] = 90$
 $b[\text{\AA}] = 12.1$
 $\beta[^\circ] = 90$
 $c[\text{\AA}] = 3.27$
 $\gamma[^\circ] = 90$

Maximum Indices

8

Calculate Possible Reflections

Zone Axis	v_1	$d_1[\text{nm}]$	v_2	$d_2[\text{nm}]$	v_3	$d_3[\text{nm}]$	θ_{1-2}	θ_{2-3}	CumDiff
{0, 0, -5}	{-2, -1, 0}	6.731 (1.5%)	{-3, 1, 0}	4.931 (9.3%)	{-1, 2, 0}	5.668 (-1.1%)	57.8 (8.2%)	45.5 (4.6%)	24.7%
{0, 0, -5}	{2, 1, 0}	6.731 (1.5%)	{3, -1, 0}	4.931 (9.3%)	{1, -2, 0}	5.668 (-1.1%)	57.8 (8.2%)	45.5 (4.6%)	24.7%
{0, 0, 5}	{-2, 1, 0}	6.731 (1.5%)	{-3, -1, 0}	4.931 (9.3%)	{-1, -2, 0}	5.668 (-1.1%)	57.8 (8.2%)	45.5 (4.6%)	24.7%
{0, 0, 5}	{2, -1, 0}	6.731 (1.5%)	{3, 1, 0}	4.931 (9.3%)	{1, 2, 0}	5.668 (-1.1%)	57.8 (8.2%)	45.5 (4.6%)	24.7%
{0, 0, -6}	{0, -2, 0}	6.05 (-8.7%)	{-3, -2, 0}	4.029 (-10.7%)	{-3, 0, 0}	5.4 (-5.8%)	48.2 (-9.7%)	41.8 (-3.9%)	38.8%
{0, 0, -6}	{0, 2, 0}	6.05 (-8.7%)	{3, 2, 0}	4.029 (-10.7%)	{3, 0, 0}	5.4 (-5.8%)	48.2 (-9.7%)	41.8 (-3.9%)	38.8%
{0, 0, 6}	{0, -2, 0}	6.05 (-8.7%)	{3, -2, 0}	4.029 (-10.7%)	{3, 0, 0}	5.4 (-5.8%)	48.2 (-9.7%)	41.8 (-3.9%)	38.8%
{0, 0, 6}	{0, 2, 0}	6.05 (-8.7%)	{-3, 2, 0}	4.029 (-10.7%)	{-3, 0, 0}	5.4 (-5.8%)	48.2 (-9.7%)	41.8 (-3.9%)	38.8%
{0, 0, -6}	{-2, 1, 0}	6.731 (1.5%)	{0, 3, 0}	4.033 (-10.6%)	{2, 2, 0}	4.847 (-15.4%)	56.2 (5.2%)	36.8 (-15.4%)	48.1%
{0, 0, -6}	{2, -1, 0}	6.731 (1.5%)	{0, -3, 0}	4.033 (-10.6%)	{-2, -2, 0}	4.847 (-15.4%)	56.2 (5.2%)	36.8 (-15.4%)	48.1%
{0, 0, 6}	{-2, -1, 0}	6.731 (1.5%)	{0, -3, 0}	4.033 (-10.6%)	{2, -2, 0}	4.847 (-15.4%)	56.2 (5.2%)	36.8 (-15.4%)	48.1%
{0, 0, 6}	{2, 1, 0}	6.731 (1.5%)	{0, 3, 0}	4.033 (-10.6%)	{-2, 2, 0}	4.847 (-15.4%)	56.2 (5.2%)	36.8 (-15.4%)	48.1%
{0, 0, -7}	{-1, -2, 0}	5.668 (-14.5%)	{-4, -1, 0}	3.841 (-14.8%)	{-3, 1, 0}	4.931 (-13.9%)	51. (-4.5%)	42.6 (-2.1%)	49.8%
{0, 0, -7}	{1, 2, 0}	5.668 (-14.5%)	{4, 1, 0}	3.841 (-14.8%)	{3, -1, 0}	4.931 (-13.9%)	51. (-4.5%)	42.6 (-2.1%)	49.8%
{0, 0, 7}	{-1, 2, 0}	5.668 (-14.5%)	{-4, 1, 0}	3.841 (-14.8%)	{-3, -1, 0}	4.931 (-13.9%)	51. (-4.5%)	42.6 (-2.1%)	49.8%
{0, 0, 7}	{1, -2, 0}	5.668 (-14.5%)	{4, -1, 0}	3.841 (-14.8%)	{3, 1, 0}	4.931 (-13.9%)	51. (-4.5%)	42.6 (-2.1%)	49.8%
{0, 0, -7}	{-1, 2, 0}	5.668 (-14.5%)	{2, 3, 0}	3.61 (-20.%)	{3, 1, 0}	4.931 (-13.9%)	46.9 (-12.2%)	39.5 (-9.2%)	69.8%
{0, 0, -7}	{1, -2, 0}	5.668 (-14.5%)	{-2, -3, 0}	3.61 (-20.%)	{-3, -1, 0}	4.931 (-13.9%)	46.9 (-12.2%)	39.5 (-9.2%)	69.8%
{0, 0, 7}	{-1, -2, 0}	5.668 (-14.5%)	{2, -3, 0}	3.61 (-20.%)	{3, -1, 0}	4.931 (-13.9%)	46.9 (-12.2%)	39.5 (-9.2%)	69.8%
{0, 0, 7}	{1, 2, 0}	5.668 (-14.5%)	{-2, 3, 0}	3.61 (-20.%)	{-3, 1, 0}	4.931 (-13.9%)	46.9 (-12.2%)	39.5 (-9.2%)	69.8%

Fig A4.4. Screenshot of the utility developed to analyze experimental HRTEM data. Measurements from generated FFTs, as well as the lattice parameters of the structure under investigation are input into the top panel; the program then generates a list of potential reflections (as well as the associated zone axis), sorted via the cumulative percent difference of the calculated vs measured values. Because of symmetry, multiple permutations exist for each solution; each are reported and grouped together.

The number of potential candidates for each step are listed below as an example of the scale involved in the algorithm. This model wasn't initially a good fit for the data and thus the number of potential candidate reflections remained fairly low throughout, but testing with characterized systems from the literature often generated preliminary candidate lists in the thousands, spurring the impetus for reduction and minimization where possible. As this was developed primarily to solve a single system, this brute force method sacrificed elegance for thoroughness and ease of computation.

Table A4.1. Size of the candidate lists across each step of the algorithm, as computed in the processing of the structure observed in gCN-1003.

Step #	Brief Description	# Cand.
1	Basic reflections based on max. index (n=6)	83
2	Candidates that match d-spacing	{4,9,6}
3	Positive/negative permutations	{12,30,20}
4	Subsets that match inter-refl angle	{40,52}
5	Pairing subsets with common refl 2	72
6	Angle between 1-3 matches sum of 1-2 & 2-3	36
7	All reflections are coplanar	20

Analysis of the most prominent features of the FFT results in a reasonable assignments: the points refer to the $\{2\bar{1}0\}$, $\{310\}$, and $\{120\}$ reflections, along the $[00\bar{1}]$ zone axis (Fig A4.5, left). This is powerful as it independently implies that the dominant observed orientation is along the interplanar axis, a natural result for a planar material. However, while extending this to additional observable fringes also returned potential reflections ($\{2\bar{2}0\}$ and $\{130\}$), these were considerably poorer fits to the data.

Fig A4.5. *Left*: The fitting protocol, applied to the 3 most prominent FFT points and using the initial lattice parameters of polymeric carbon nitride from the literature[115], yields reasonable assignments. *Right*: When applied to more peripheral features, the fits are significantly less robust.

Table A4.2. Measured d-spacings and inter-planar angles of two sets of points used for analysis (Fig A4.5)

d-spc (pt#1)	d-spc (pt#2)	d-spc (pt#3)	ϕ_{1-2}	ϕ_{2-3}
{2,1,0}: 6.63 Å	{3,-1,0}: 4.51 Å	{1,-2,0}: 6.63 Å	53.4°	43.5°
{2,2,0}: 5.01 Å	{3,-1,0}: 4.51 Å	{1,-3,0}: 4.34 Å	67.0°	53.9°

A4.3 Optimization of input model

As with the previous XRD fitting, a reconciliation might be found through minor modification of the model. Typical crystalline systems aren't capable of such manipulation, and thus such an issue would instead normally result in discarding the model. However, as the model used here is actually polymeric rather than crystalline, a degree of adjustment to the lattice parameters isn't unreasonable.

The source of the model[115] accounts for such incongruencies via alteration of γ , the angle between the in-plane vectors a and b . In accordance with the methodology employed in fitting the XRD data, variations in the parameters a and b themselves will instead be investigated; as with the XRD fitting, the goal isn't to generate an absolute model, but rather to simply identify a reasonable candidate for classification. c is unchanged as modifications to the planar structure wouldn't be expected to affect the inter-planar spacing (a moot point though since the fringes are populated along the $\{0,0,1\}$ zone axis, the observed fringes are all independent of c regardless).

The model was best fit through minimization of cumulative relative differences ($|\text{meas.} - \text{calc.}|/\text{meas.}$) for the d-spacing of the 5 observed and identified fringes, as well as the angle between each and the $\{3,-1,0\}$ fringe. The values for each of these 9 values, as well as the associated relative difference, are given below in Table A4.3.

Table A4.3. The reflections and values used to optimize the fit of the fringes to the FFT; the measured values are compared with those calculated using the original model's parameters before and after adjusting to minimize the total relative difference (reported in parentheses).

#1:{2,-2,0}	#2:{2,-1,0}	#3:{3,1,0}	#4:{1,2,0}	#5:{1,3,0}
Value	Measurement	Original Model	Adjusted Model	
d ₁	5.08 Å	4.85 Å (0.046)	5.00 Å	(0.016)
d ₂	6.81 Å	6.73 Å (0.012)	6.53 Å	(0.041)
d ₃	4.62 Å	4.93 Å (0.067)	4.67 Å	(0.010)
d ₄	5.61 Å	5.67 Å (0.010)	6.14 Å	(0.094)
d ₅	4.30 Å	3.91 Å (0.090)	4.30 Å	(0.000)
φ ₁₋₃	68.4°	77.3° (0.130)	66.9°	(0.003)
φ ₂₋₃	57.6°	57.8° (0.004)	46.4°	(0.145)
φ ₃₋₄	43.7°	45.5° (0.041)	42.1°	(0.040)
φ ₃₋₅	51.9°	52.0° (0.001)	50.5°	(0.021)
Sum		(0.401)	(0.370)	

A local minima in the cumulative errors is found for lattice parameters that differ from the original model's by only ~10% (Table A4.4). This is demonstrated visually in the plot shown in Fig A4.6 (left); this plot is represented on a log scale to help highlight the localized minima, while the linear representation in Fig A4.7 shows the range of values that offer fairly similar improvement. The fringe positions using the original and modified values are compared in Fig A4.5 (right) via the purple and red dots, respectively.

Table A4.4. Lattice parameters of polymeric carbon nitride as given in the literature compared to the results of HRTEM analysis

Model	a [Å]	b [Å]	c [Å]
Original[115]	16.2	12.1	3.27
Modified	14.9	13.5	3.27

Fig A4.6. Density plot (*left*) of the a and b lattice parameters in relation to the cumulative difference in fitting the assigned reflections to the observed FFT (*right*). The purple dots show the fit using values based on the model given by [115], while the red dots represent a modified model generated by minimizing the cumulative error. The density plot represents the cumulative error using a log scale to highlight the location of the local minima; the same plot using a linear scale is shown in Fig A4.7.

Fig A4.7. Linear-scale version of the plot from Fig A4.6 demonstrates the wide range of acceptable values, as well as the fairly minor change in relative difference incurred throughout these values; this helps demonstrate the suitability of the model in classification of GCN-1003.

APPENDIX 5 – g-CN Sample Description and Synthesis Parameters

Table A5.1. Synthesis details of unexfoliated GCN sample production.

Sample	Precursor	Produced:	Description
GCN-1001	Melamine	Chemistry	Melamine treated at 550C for 5 hours under argon flow
GCN-1002	Melamine	Chemistry	Melamine treated at 550C for 5 hours under argon flow
GCN-1010	Melamine	Chemistry	Repeat Synthesis of GCN-1001
GCN-1011	Melamine	Chemistry	Repeat Synthesis of GCN-1001
GCN-1014	Melamine	Chemistry	Bulk GCN Material
GCN-1039	Melamine	Chemistry	New large batch of GCN
GCN-1051	GCN-1039	Physics	Washed 473 mg GCN-1039 with acetonitrile over 1 h at 60 C
GCN-1042	Melamine	Physics	Melamine treated at 550C for 5 hours under argon flow
GCN-1052	GCN-1042	Physics	Washed 480 mg GCN-1042 with acetonitrile over 1 h at 60 C
GCN-1043	Melamine	Physics	Melamine treated at 550C for 5 hours under argon flow
GCN-1044	Melamine	Physics	Melamine treated at 550C for 5 hours under argon flow
GCN-1055	GCN-1044	Physics	Washed 330 mg GCN-1044 with acetonitrile over 1 h at 60 C
GCN-1045	Melamine	Physics	Melamine treated at 550C for 5 hours under argon flow
GCN-1046	Melamine	Physics	Melamine treated at 525C for 5 hours under argon flow
GCN-1047	Cyanamide	Physics	Cyanamide treated at 550C for 4 hours under argon flow (first test)
GCN-1050	GCN-1047	Physics	Material carried out at 310C during synthesis of GCN-1047
GCN-1058	GCN-1047	Physics	Washed 477 mg GCN-1047 with acetonitrile over 1h at 60 C
GCN-1060	Cyanamide	Physics	Cyanamide (1g) treated at 550C for 4 hours under argon flow
GCN-1061	Cyanamide	Physics	Cyanamide (1g) treated at 550C for 4 hours under argon flow (manual profile)
GCN-1062	Cyanamide	Physics	Cyanamide (1g) treated at 550C for 4 hours under argon flow (5 K/min ramp)

Table A5.2. Sonication parameters used to exfoliate GCN.

Sample	Precursor	Solvent	m(GCN):V(Sol)	Time	Profile	Power	Notes
XF/GCN-1100	GCN-1039	Ethanol	11.3mg:20mL	0.5 hr	15 on/15 off	55W	
XF/GCN-1101	GCN-1039	Ethanol	17mg:23.7mL	0 hr	n/a	55W	Non-sonicated reference
XF/GCN-1102	GCN-1039	Ethanol	200mg:20mL	1 hr	30 on/30 off	55W	Mass production: 6x200mg=1.2g
XF/GCN-1103	GCN-1039	Ethanol	400mg:20mL	1 hr	30 on/30 off	55W	Mass production: 3x400mg=1.2g
XF/GCN-1106	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	
XF/GCN-1122	XF/GCN-1106	Water	115mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1104 after washing (Impure water)
XF/GCN-1107	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	
XF/GCN-1123	XF/GCN-1107	Water	175mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1106 after washing (Impure water)
XF/GCN-1108	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	Bottle was deformed by heat and holder in the 40 min son. phase
XF/GCN-1124	XF/GCN-1108	Water	180mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1107 after washing (Impure water)
XF/GCN-1104	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	Mass production: 6x200mg=1.2g
XF/GCN-1126	XF/GCN-1104	Water	124mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1109 after washing (Impure water)
XF/GCN-1105	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	Mass production: 3x400mg=1.2g
XF/GCN-1127	XF/GCN-1105	Water	328mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1105 after washing (Impure water)
XF/GCN-1109	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	
XF/GCN-1125	XF/GCN-1109	Water	159mg:20mL	1 hr	30 on/15 off	55W	Resonication XF/GCN-1108 after washing (Impure water)
XF/GCN-1110	GCN-1039	Water	200mg:20mL	1 hr	30 on/30 off	55W	Stable in solution more than 12 h
XF/GCN-1111	GCN-1039	Isoprop.	200mg:20mL	1 hr	30 on/15 off	55W	
XF/GCN-1112	GCN-1039	Isoprop.	200mg:20mL	1 hr	30 on/15 off	55W	
XF/GCN-1113	GCN-1039	Isoprop.	200mg:20mL	1 hr	30 on/15 off	55W	
XF/GCN-1114	GCN-1039	Isoprop.	200mg:20mL	1 hr	30 on/15 off	55W	
XF/GCN-1115	GCN-1039	Isoprop.	200mg:20mL	1 hr	30 on/15 off	55W	
XF/GCN-1128	GCN-1039	Water	200mg:20mL	1 hr	30 on/15 off	55W	Add'1 10 mg/ml sample to add the lost GCN in washing process
XF/GCN-1146	GCN-1042	Isoprop.	1000mg:100mL	2 hr	30 on/15 off	55W	Sonicated in 5 batches with ice bath
XF/GCN-1147	GCN-1045	Isoprop.	1000mg:100mL	4 hr	30 on/15 off	55W	Sonicated in 5 batches with ice bath

Table A5.3. Comparison of surface and pore space parameters (determined via N₂ sorption) and H₂ storage parameters of a representative activated carbon (3K-0079) and a number of graphitic carbon nitrides.

Sample (XE/GCN-#)	Prec. (GCN-#)	Suspension 10mg(GCN):1mL(≠)	Sonic. cond.'s		Centrifugation		Sonication/Centrifugation Constituent Samples	Notes
			Time	Power	Time	RCF Bath		
1116	1039	Isopropanol	0.5hr	55W	5min	5g 20°C	#1111+#1112	1st part of decantation after centrif.
1117	1039	Isopropanol	0 hr	55W	5min	5g 20°C	#1111+#1112	2nd part of decantation after centrif.
1118	1039	Isopropanol	1 hr	55W	5min	5g 20°C	#1113+#1114+#1115	1st part of decantation after centrif.
1119	1039	Isopropanol	1 hr	55W	5min	5g 20°C	#1113+#1114+#1115	2nd part of decantation after centrif.
1120	1039	Isopropanol	1 hr	55W	5min	5g 20°C	#1111+#1112	3rd part of decantation after centrif.
1121	1039	Isopropanol	1 hr	55W	5min	5g 20°C	#1113+#1114+#1115	3rd part of decantation after centrif.
1129	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 1st 1st part
1130	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 1st 2nd part
1131	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 2nd 1st part
1132	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 2nd 2nd part
1133	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 1st 3rd part
1134	1039	Water	1 hr	55W	5min	5g 17°C	#1122+#1123+#1124	2 Centrifugation tubes 2nd 3rd part
1135	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 1st 1st part
1136	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 1st 2nd part
1137	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 2nd 1st part
1138	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 2nd 2nd part
1139	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 1st 3rd part
1140	1039	Water	1 hr	55W	5min	5g 17°C	#1125+#1126+#1128	2 Centrifugation tubes 2nd 3rd part
1141	1039	Isopropanol	1 hr	55W	5min	5g 17°C	#1116+#1117+#1118+#1119	Freeze Dried with 80% Isopropanol + 20% Peters Lab Water
1144	1039	Water	1 hr	55W	5min	5g 17°C	#1129+#1132+#1135+#1138	Freeze Dried 100% Water
1150	1042	Isopropanol	1 hr	55W	5min	5g 17°C	#1146	Dried at room temperature

Table A5.4. Ball milling parameters used to exfoliate GCN.

Sample	Precursor	Time	Heat Profile	RPM	Balls
XF/GCN-1142	GCN-1039	4 hr	(1hr ON/20min OFF) x4	800	25*(5mm)
XF/GCN-1143	GCN-1039	16 hr	(4hr ON/20min OFF) x4	800	25*(5mm)
XF/GCN-1145	GCN-1039	32 hr	(4hr ON/20min OFF) x8	800	25*(5mm)
XF/GCN-1148	GCN-1044	16 hr	(4hr ON/20min OFF) x4	400	25*(5mm)
XF/GCN-1149	GCN-1045	4 hr	4hr ON	400	25*(5mm)

Table A5.5. Synthesis parameters used to produce GCNs via SiO₂ templating.

Templated (GCN-#)	Washed (GCN-#)	Etched (ET/GCN-#)	mCN :mSi	Pretreatment	Ramp	Temp	Wash	Etch	Notes
1064	-	-	1g:4g	n/a	4.5°C/min	550°C	-	-	
1066	-	1155	1g:4g	Open to atm at RT for 8hr	4.5°C/min	550°C	-	4M ABF (5 days)	
1067	-	1156	1g:4g	Boiled at 110°C for 15min, open to atm at RT for 8hr	4.5°C/min	550°C	-	4M ABF (2 days) at 100°C	
1068	-	1157	1g:4g	Boiled at 110°C for 15min	4.5°C/min	550°C	-	4M ABF (2 days)	
1069	-	-	1g:4g	Boiled at 110°C for 15min	4.5°C/min	550°C	-	-	
1070	-	-	1g:4g	Boiled at 110°C for 15min	4.5°C/min	550°C	-	-	
1071	-	1158	1g:4g	Open to atm at RT for 8hr	4.5°C/min	550°C	-	4M ABF (2 days)	
1072	1076	-	1g:4g	Boiled at 110°C for 15min, open to atm at RT for 8hr	4.5°C/min	550°C	100mL acetone x3	-	
1073	-	-	1g:4g	Boiled at 110°C for 15min	4.5°C/min	550°C	-	-	
1074	-	n/a [†]	1g:4g	n/a	4.5°C/min	550°C	-	4M ABF (2 days)	[†] No sample remains after etch
1075	-	-	1g:4g	Held at RT for 1hr, boiled at 110°C for 15min	4.5°C/min	550°C	-	-	
1200	-	-	0g:4g	n/a	4.5°C/min	550°C	-	-	SiO ₂ -only ref.
1202	1204	1205	1g:4g	Held at 60°C in furnace for 8 hr, ground before pyrolysis	4.5°C/min	550°C	100mL acetone x3	4M ABF (2 days)	
-	-	1206	1g:4g	Held at 60°C in furnace for 8 hr, ground before pyrolysis	4.5°C/min	550°C	100mL acetone x3	4M ABF (2 days)	
-	-	1207	1g:4g	Held at 60°C in furnace for 8 hr, ground before pyrolysis	4.5°C/min	550°C	100mL acetone x3	4M ABF (2 days)	
-	-	1208	1g:4g	n/a	-	-	-	-	Combine 1205+1206+1207

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