

## Spectroscopic Investigations of the Structure of Graphitic Carbon Nitrides for H<sub>2</sub> Storage

D. Stalla<sup>1</sup>, T. Lam<sup>2</sup>, M. Lee<sup>3</sup>, P. Pfeifer<sup>1</sup>

<sup>1</sup>Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, MO, USA

<sup>2</sup>Electron Microscopy Core, University of Missouri-Columbia, Columbia, MO, USA

<sup>3</sup>Department of Chemistry, University of Missouri-Columbia, Columbia, MO, USA

Until recently, gas storage relied on heavy, bulky compressed cylinders that limit space and fuel efficiency, rendering it an unattractive option for consumers. Adsorbent systems, on the other hand, attempt to ameliorate this by storing gas at significantly lower pressures, allowing for the implementation of more conformable tanks. A paramount challenge in the physisorption community is to develop a high surface area material featuring sufficient functionalizations to generate stronger binding energies with sorbent gasses for room-temperature storage.

Graphitic carbon nitrides (sheets of C<sub>3</sub>N<sub>4</sub>, *gCN*) are as such considered a possible candidate. Alternating N and C atoms lead to negative and positive partial charges, expected to result in strong dipole interactions, and therefore high binding energies, with adsorbed H<sub>2</sub> molecules. In addition, the valence structure in individual sheets of *g-CN*, hosts regular patterns of in-plane voids, which contribute to high surface area by way of surface area across voids. The promise is that successful exfoliation of *gCN*, resulting in high edge-to-in-plane surface ratios, materials with surface areas 4000-6000 m<sup>2</sup>/g and elevated binding energies can be manufactured. Knowledge of the specific structures comprising our samples will be crucial in order to further identify the physical and chemical interactions undertaken during formation. Ultimately, a better understanding of the reaction mechanisms will allow for the manufacture of samples more fully optimized for hydrogen storage.

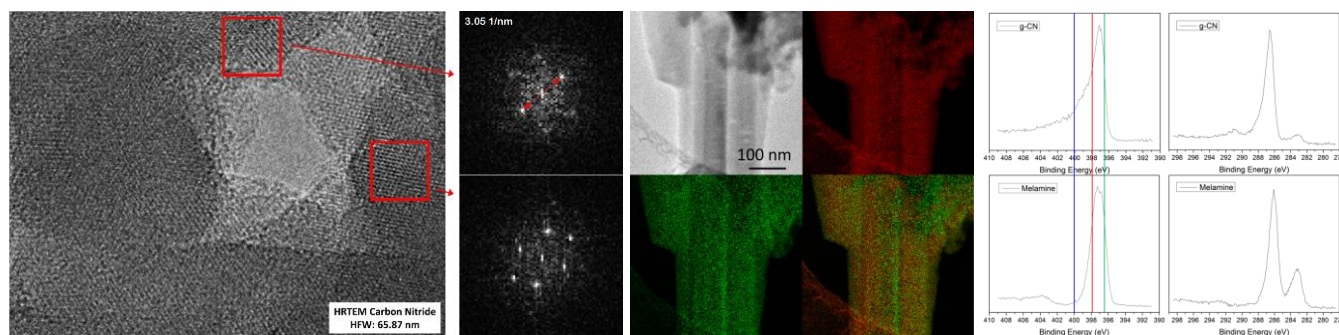
HR-TEM measurements collected on MU-manufactured *gCN* show extensive sheet-like structures with significant crystalline diffraction patterns throughout. Measuring these diffraction patterns yields a repeating distance of 3.28 Å, which agrees with the literature values for the interplanar spacing of *gCN*. EF-TEM mapping performed on sufficiently thin sections demonstrates a uniform distribution of C and N throughout the sample, as expected; this serves as evidence that the reaction is proceeding as stoichiometrically predicted. In order to directly measure the constituent structure, an XRD spectrum was collected and compared to allowed reflections compiled from the literature [1,2] for various models. While none individually comprehensively described the spectrum, adopting a two phase approach (comprised of a 55%/45% mixture of polymeric heptazine chains and graphitic triazine units, respectively) adequately accounts for all features present. To supplant this, high resolution XPS measurements were collected as well. This proved to not be a straightforward analysis, as the literature is divided as to whether to assign the aromatic sp<sup>2</sup>-bonded N signal at higher or lower energy than that of the generated sp<sup>3</sup>-bonded 'linker' N signal; however, as MU-manufactured *g-CN* is synthesized from a well-defined precursor, comparing the two spectra allows for peak assignments independent of those reported in the literature.

Initial H<sub>2</sub> uptake measurements have been minimal compared to more-established carbonaceous sorbents. Its poor performance can be attributed to a dramatically low surface area, 13 m<sup>2</sup>/g vs the theorized maximum exfoliated 4000-6000 m<sup>2</sup>/g. Normalizing excess adsorption to surface area gives a rough estimate of the materials binding energy, and in this regard, MU *gCN* shows a marked improvement over

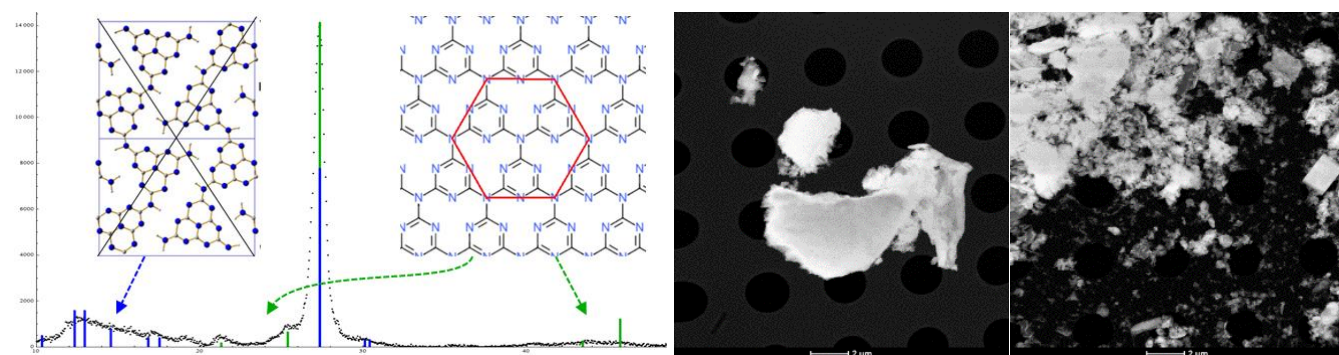
functionalized and non-functionalized carbon based materials. STEM images reveal the graphitic planes to be aggregating into large crystals, rather than retaining their high-surface-area sheet-like form. Therefore, exfoliation techniques (such as bath sonication, ball milling, and centrifugation) have been carried out in order to improve on the surface area, and ultimately, the H<sub>2</sub> uptake. STEM on the physically exfoliated product subsequently shows significant fragmentation of the aggregations, both qualitatively and through EELS measurements of  $t/\lambda$ .

## References

- [1] G. Algara-Siller *et al*, *Ang. Comm.* **53** (2014), p. 7450-7455.  
 [2] T. Tyborski *et al*, *J. Phys.: Condens. Matter*, **25** (2013), p. 395402.



**Figure 1.** (left) HR-TEM confirms high crystallinity of g-CN samples. Quantification of live FFT generates a repeating distance of 3.28Å, consistent with the accepted interplanar spacing from the literature. (center) EFTEM mapping (CW: BF, C, N, C/N composite) confirms a uniform distribution of carbon and nitrogen. (right) XPS indicates the formation of a new N environment (leftmost asymmetry in top left spectrum compared to bottom left), confirming the presence of a new sp<sup>3</sup> bonded ‘linker’ N in the synthesized g-CN.



**Figure 2.** (left) XRD spectrum is resolved via the adoption of a two-phase system (using allowed reflections collected from the literature) comprised of polymeric chains of heptazine units [2] and a graphitic structure based on triazine units [3]. Peak assignments are corroborated by the agreement between crystalline densities calculated from the composite structure and skeletal densities measured from He pycnometry. (right) STEM images of g-CN before and after sonication (performed to increase surface area) shows significant exfoliation of previously aggregated clusters; quantitative analysis shows average particle thickness (via  $t/\lambda$ ) is reduced by ~10x.