

Exploring Vibrational and Electronic Structure of Carbon Nitride Powders Using Monochromated Electron Energy-Loss Spectroscopy

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Graphitic carbon nitride (g-C₃N₄), a polymeric semiconductor with a 2.7 eV band gap, has garnered much interest due to its properties as a visible light photocatalytic material [2]. Many studies have explored the effect of doping and varied synthesis methods to increase light absorption but most characterization techniques are limited to the bulk [2]. Scanning transmission electron microscopy (STEM) can overcome this deficiency by providing structural and chemical information on the nanoscale through Z-contrast imaging and electron energy-loss spectroscopy (EELS). By placing a monochromated convergent electron beam just outside a specimen, high quality vibrational and valence EELS can also be performed [1]. This so-called ‘aloof beam’ EELS is of particular interest for studying the physical and electronic structure of photocatalytic nanomaterials, which may have sensitive surface motifs and/or surface electronic states associated with their defects and photocatalytic activity.

To begin investigating the local electronic and vibrational structure in this material, we have employed a Nion UltraSTEM-100 at 60 kV to perform monochromated aloof-beam low-loss EELS and transmission-beam core-loss EELS on a commercial g-C₃N₄ powder [5]. Liquid exfoliation was applied by sonicating a small amount of powder in ultrapure water for 40 minutes to obtain thin, sheet-like particles suitable for EELS analysis. Core-loss spectra both of the C-K and N-K edges were acquired in transmission mode with 0.2 eV/ch dispersion, 10 mrad beam convergence, and without monochromation. A monochromated, 0.05 eV/ch core-loss spectra of the C-K edge was also collected to determine the π^* peak width. Valence-loss spectra were acquired in aloof-beam mode with a 4 nm impact parameter, 10 mrad beam convergence, and 5 meV/ch dispersion. Vibrational spectra were acquired under the same conditions but with dispersion of 2 meV/ch.

Figure 1 shows high-angle annular dark field (HAADF) images taken of a g-C₃N₄ particle and confirms the sheet-like morphology. *Figure 2* shows core-loss spectra at different energy dispersions for a g-C₃N₄ particle. From *Figure 2(a)* the C/N-ratio was determined to be 0.80:1 through core-loss analysis in Gatan DigitalMicrograph software. The strikingly intense π^* -peak was measured to be 0.5 eV wide at half maximum from *Figure 2(b)*. The intensity of this feature indicates a high degree of unoccupied sp² states about the C atoms, which is consistent with the relative electronegativities of C and N and characteristic of its graphite-like structure. In *Figure 3*, the vibrational and valence-loss spectra for this material are displayed. *Figure 3(a)* shows a band gap of 2.7 eV, which was determined after background removal and linear extrapolation of the band gap edge signal. In the vibrational spectra, *Figure 3(b)*, the peaks at ~165 and 184 meV are likely associated with C-N and s-triazine ring modes, respectively, while the 46 meV wide peak centered at ~400 meV corresponds to N-H stretches [3-4].

The presentation will discuss the detailed interpretation of the images and spectra. Results will be presented on crystalline carbon nitride nanosheets and doped carbon nitrides. Our overall goal is to

elucidate changes in the electronic structure of this photocatalyst material arising from defects and dopants.

References:

- [1] Krivanek, O.J. *et al.* *Nature* **2014**, *514*, 209-212.
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 [5] The support from US Department of Energy (DE-SC0004954) and the use of AC-TEM at John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University is gratefully acknowledged.

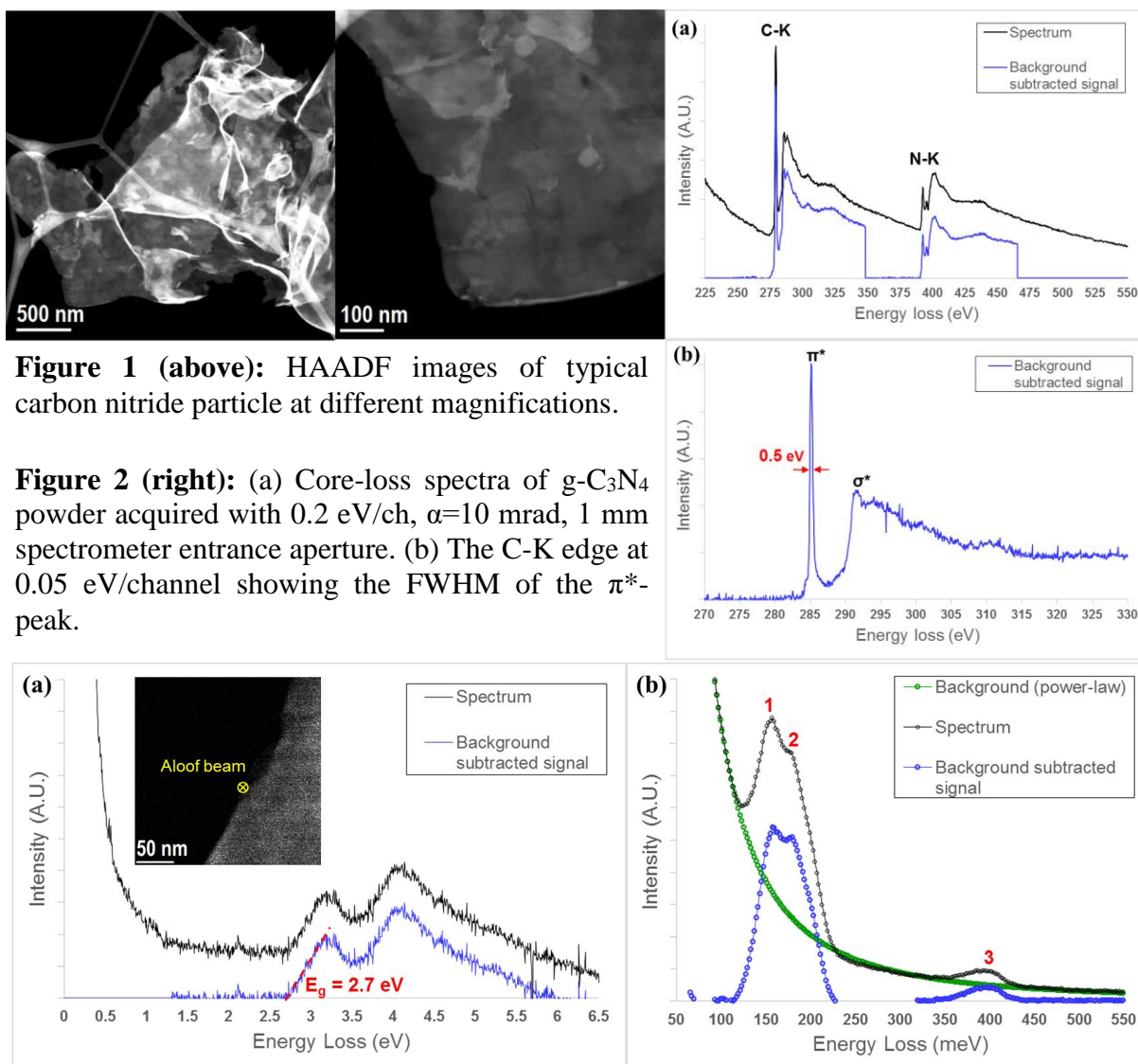


Figure 1 (above): HAADF images of typical carbon nitride particle at different magnifications.

Figure 2 (right): (a) Core-loss spectra of g-C₃N₄ powder acquired with 0.2 eV/ch, $\alpha=10$ mrad, 1 mm spectrometer entrance aperture. (b) The C-K edge at 0.05 eV/channel showing the FWHM of the π^* -peak.

Figure 3: Aloof-beam low-loss EELS of g-C₃N₄ powder showing (a) valence-loss spectra with 0.005 eV/ch and (b) vibrational spectra with 0.002 eV/channel. The peaks in (b) labeled 1-3 correspond to C-N, s-triazine, and N-H vibrational modes, respectively. Inset (top left) is HAADF image showing impact parameter of about 4 nm.