Monochromated EELS and Optical Spectroscopy of Layered Carbon Nitrides

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Layered carbon nitride materials, including graphitic carbon nitride (g-CN_xH_y) and poly(triazine imide) with intercalated Li and Cl ions (PTI/LiCl), are emergent materials for energy-related applications including solar water splitting and "postsilicon" electronics [1, 2]. Synthesis of g-CN_xH_y and PTI/LiCl involves specific pyrolysis routes that achieve heptazine (C_6N_7) and triazine (C_3N_3) based structural motifs, respectively, with varying degrees of amine bridging-groups owing to incomplete condensation. Due to their polymeric nature, it is likely that a range of defects in addition to amine content contribute to their optoelectronic properties. A fundamental understanding between structure and defects' relationship to functionality will lead to rational engineering of these materials for efficient photocatalytic hydrogen production. Traditional optical characterization techniques, including infrared/visible/UV absorption and Raman scattering spectroscopy, are limited in the sense that they contain bulk-averaged signals. By employing monochromated electron energy-loss spectroscopy (EELS) with an aloof-beam geometry, vibrational modes and interband transitions can be probed on the nanoscale without damaging these beam-sensitive materials [3].

To determine the molecular species present with high spatial resolution, several vibrational EEL spectra (vibEELS) were acquired with a 2 meV/ch dispersion and approximate energy resolution (measured in the vacuum) of 16 meV. The bandgap energies were also measured in the valence-loss region using a dispersion of 5 meV/ch and corresponding energy resolution of ~25 meV. All EEL spectra were collected at 60-kV on a Nion UltraSTEM-100 using a convergence angle of 12 mrad. For g-CN_xH_y, a commercial powder ("Nicanite") was obtained from Carbodeon Ltd. and synthesis of PTI/LiCl powder was performed according to Schwinghammer et al [4]. Samples for EELS were prepared by immersing lacey-C grids in aqueous dispersions of the powders after ultrasonicating for 40 minutes. Bulk optical spectroscopic techniques including UV-Vis diffuse reflectance, FTIR absorption, and FT-Raman ($\lambda_{excitation}$=1064 nm) spectroscopy were also collected as a means for interpreting low-loss EEL spectra.

Several vibEEL spectra taken from outside the g-CN_xH_y and PTI/LiCl samples exhibit two major features centered at around 170 and 400 meV. *Figure 1(a)* displays these vibEELS "fingerprints" of heptazine- and triazine-based carbon nitrides; all were acquired with an impact parameter of ~4 nm. Variations in the vibEELS signal (spectra 2 and 4) are characterized by the presence of a very weak, additional peak at ~265 meV, which is believed to be due to small amounts of double/triple bonded carbon. From the FTIR absorption spectra, the vibEELS can be directly interpreted as containing excitations of C-N ring stretch/bending modes (140-200 meV) and N-H stretching modes (370-410 meV). An FT-Raman spectrum was also collected from the g-CN_xH_y powder. *Figure 1(b)* shows the raw FTIR and FT-Raman spectra from the g-CN_xH_y (heptazine-containing) sample. To simulate the effect of the EEL spectrometer energy resolution, the bulk optical spectra from g-CN_xH_y were convolved with a Gaussian of FWHM=16 meV. A comparison between the resulting spectra, all with the backgrounds subtracted, is found in *Figure 1(c)*. Using aloof-beam valence EELS as a probe (*Fig.2(a)*), the bandgap energies of three different layered carbon nitrides were found to be between 2.7-3.1 eV. The Kubelka-Munk diffuse reflectance spectra ($f(R)=(1-R)^2/2R$), commonly used for determining the UV-Vis
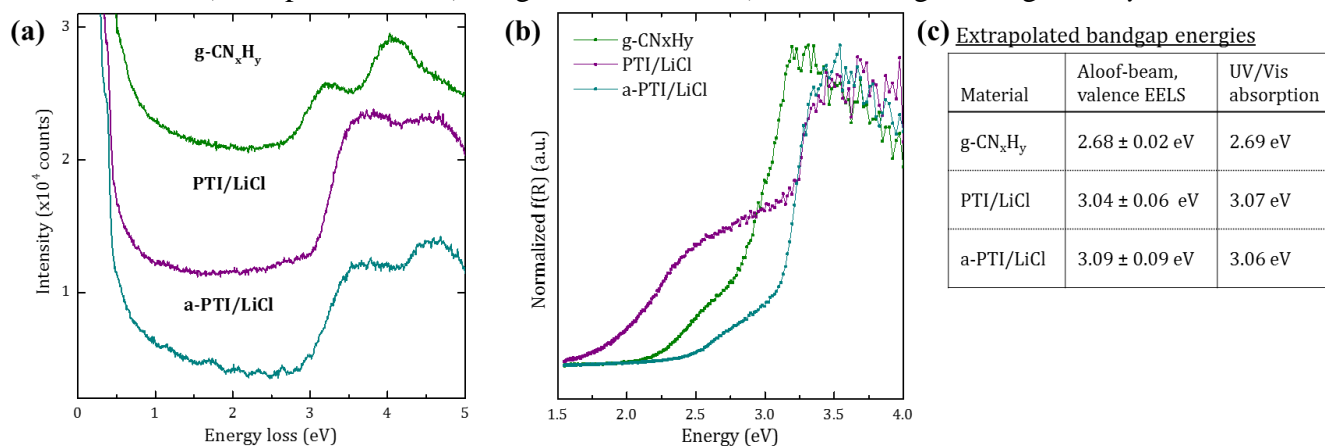
absorption of highly scattering powders, is quite different from EELS in that a 2.5-eV absorption feature is not observed in the later. *Figure 2(b)* shows the experimental UV-Vis absorption spectra from the three different carbon nitride powders that were also measured with valence EELS. A table displaying the similarity in bandgap energies derived from the valence EELS and UV-Vis absorption spectra are summarized in *Figure 2(c)*. A detailed interpretation of low-loss EELS, in the context of related bulk/optical spectroscopies, will be presented for the graphitic carbon nitride system with an overall goal of connecting the dots between nanoscale defects and functionality for photocatalytic water reduction.

References:
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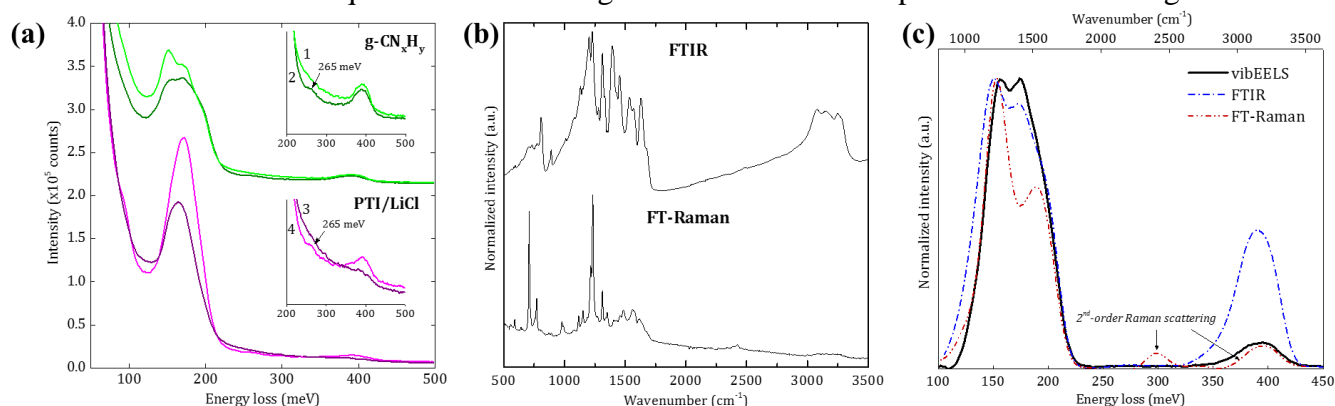
Figure 1. (a) Typical vibEELS from g-CN$_x$H$_y$ and PTI/LiCl. (b) Raw FTIR and FT-Raman spectra from g-CN$_x$H$_y$. (c) Processed FTIR and FT-Raman (background-subtracted, convolved with a Gaussian of FWHM=16 meV) compared to the (background-subtracted) vibEELS signal for g-CN$_x$H$_y$.

Material	Aloof-beam, valence EELS	UV/Vis absorption
g-CN$_x$H$_y$	2.68 ± 0.02 eV	2.69 eV
PTI/LiCl	3.04 ± 0.06 eV	3.07 eV
a-PTI/LiCl	3.09 ± 0.09 eV	3.06 eV

Figure 2. (a) Characteristic valence EELS spectra for g-CN$_x$H$_y$, PTI/LiCl, and amorphous PTI/LiCl (a-PTI/LiCl); spectra are shifted vertically for clarity. (b) Normalized UV-Vis absorbance, f(R), from the same materials. (c) Table summarizing the extrapolated bandgap energies from both spectroscopies.