

Utilizing Aloof-beam Vibrational EELS for the Detection of Hydrogen and Defect Heterogeneity in Carbon Nitrides

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Layered carbon nitrides have recently emerged as metal-free, visible-light absorbing semiconductors with growing interest as photocatalysts for hydrogen production [1]. While transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) are powerful tools to characterize nanoscale features in (photo)catalysts, their application to layered carbon nitrides is difficult due to radiation damage. Graphitic carbon nitride (g-CN_xH_y) compounds, based on layers of amine-bridged heptazine (C₆N₇) chains [2], differentiated by their residual H-content, represent a wide-ranging class of material with ill-defined variation in structure. Molten salt synthesis routes have yielded crystalline, layered carbon nitrides based on triazine (C₃N₃) motifs with correspondingly less H-content [3]. These are referred to as poly(triazine imide) with intercalated halide ions (such as Li and Cl), or PTI/LiCl. Amine (*i.e.* N-H_x) content in both g-CN_xH_y and PTI/LiCl are correlated to changes in photocatalytic hydrogen evolution under visible-light, suggesting these defects can regulate optical absorption or charge transfer kinetics depending on how the host structure is modified. To enhance photocatalytic performance, carbon nitrides are often functionalized with Pt which act as hydrogen evolution co-catalysts. More recently, chemical deposition approaches have yielded single-atom co-catalysts with correspondingly higher photocatalytic performance [4]. While infrared (IR) spectroscopy enables comparison of H-content between carbon nitrides, it lacks the spatial resolution needed for unambiguously correlating defects with catalytically relevant sites.

Here, we utilize vibrational EELS to locally probe bonding in g-CN_xH_y and PTI/LiCl, which are expected to contain a high and low degree of chemical heterogeneity, respectively. Figures 1(a)-(b) compares low dose rate TEM images of g-CN_xH_y and PTI/LiCl. While PTI/LiCl possesses hexagonal in-plane symmetry as evidenced in the corresponding FT (inset, Figure 1(b)), g-CN_xH_y demonstrates limited long-range order. To mitigate radiation damage during vibrational EELS acquisition, an ‘aloof-beam’ configuration is employed, wherein the convergent electron beam is placed several nanometers outside the specimen. Figure 1(c)-(d) compares several vibrational EEL spectra from g-CN_xH_y and PTI/LiCl, respectively, from which the (N-H_x)/(C-N ring) bonding ratios were calculated. In g-CN_xH_y, amine content is found to vary locally up to 27%. Upon probing small volumes through vibrational EELS, C≡N defects in g-CN_xH_y are also revealed. Compared to the corresponding low dose STEM images, some of which are displayed in Figure 1(e)-(h), aloof-beam vibrational EELS provides useful information for analyzing heterogeneity in polymeric, disordered materials such as g-CN_xH_y.

Pt-loaded g-CN_xH_y was obtained through a chemical deposition route in which NaBH₄ is used as a reducing agent for aqueous Pt⁴⁺ ions to form single-atom dispersions, as shown in Figure 2(a) [4]. Figure 2(b) compares the IR absorption spectra for bare and as-synthesized 0.5 wt% Pt/g-CN_xH_y, showing a significant increase in intensity between 1930-2400 cm⁻¹ which may be attributed to C≡N/C≡C species. While single atom dispersions can be obtained, the g-CN_xH_y support appears to be altered which may in turn affect photocatalytic performance. Similarly, an aloof-beam approach may be exploited to identify the spatial distribution of such defects resulting from this method of single-atom Pt loading.

References:

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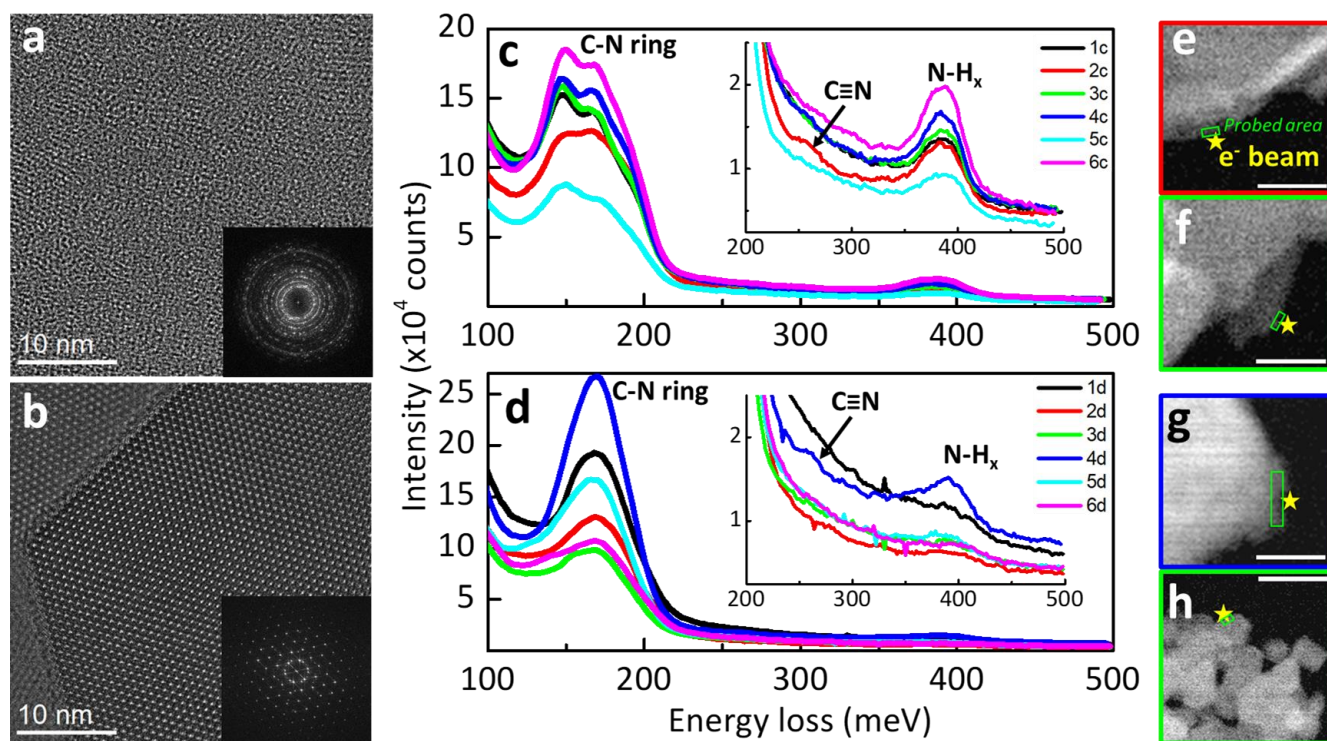


Figure 1. Low dose rate ($<20 \text{ e}^-/\text{\AA}^2/\text{s}$) TEM images of (a) $\text{g-CN}_x\text{H}_y$ and (b) PTI/LiCl , both viewed approximately perpendicular to the basal planes. Several aloof-beam vibrational EELS spectra for (c) $\text{g-CN}_x\text{H}_y$ and (d) PTI/LiCl . ADF-STEM images showing the e^- -beam position (yellow star) and probed area (green rectangle) corresponding to spectrum (e) 2c, (f) 3c, (g) 4d, and (h) 3d; scale bars=50 nm.

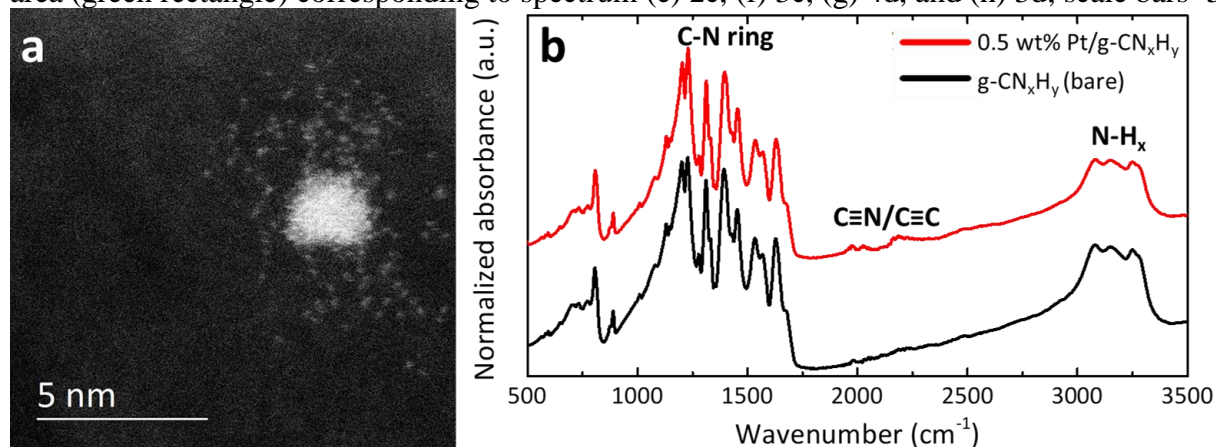


Figure 2. (a) An ADF-STEM image of the Pt-loaded (0.5 wt% Pt) $\text{g-CN}_x\text{H}_y$, confirming single-atom dispersions, and (b) IR absorption spectra for bare and Pt-loaded $\text{g-CN}_x\text{H}_y$.