

## **Aloof beam vibrational EELS: a tool for probing hydrogen/defect heterogeneity in graphitic carbon nitrides**

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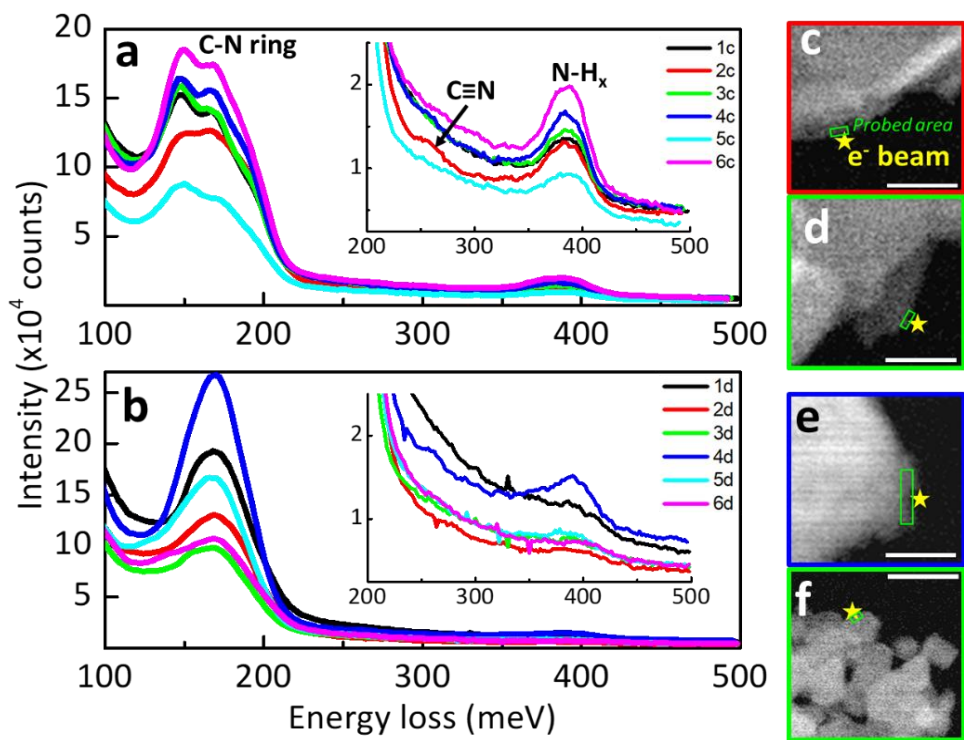
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Layered carbon nitrides have recently emerged as metal-free, visible-light absorbing semiconductors with growing interest as photocatalysts for hydrogen production.<sup>1</sup> While transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) are powerful tools to characterize nanoscale features in (photo)catalysts, their application to carbon nitrides is difficult due to radiation damage. Graphitic carbon nitride (g-CN<sub>x</sub>H<sub>y</sub>) compounds, based on layers of amine-bridged heptazine (C<sub>6</sub>N<sub>7</sub>) chains<sup>2</sup>, differentiated by their residual H-content, represent a class of material with ill-defined variation in structure. Molten-salt synthesis routes have yielded crystalline carbon nitrides based on triazine (C<sub>3</sub>N<sub>3</sub>) motifs with correspondingly less H-content.<sup>3</sup> 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<sub>x</sub>) content in both g-CN<sub>x</sub>H<sub>y</sub> and PTI/LiCl are correlated to photocatalytic hydrogen evolution rates. Chemical deposition approaches have yielded single-atom Pt co-catalysts with correspondingly higher photocatalytic activity.<sup>4</sup> 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.

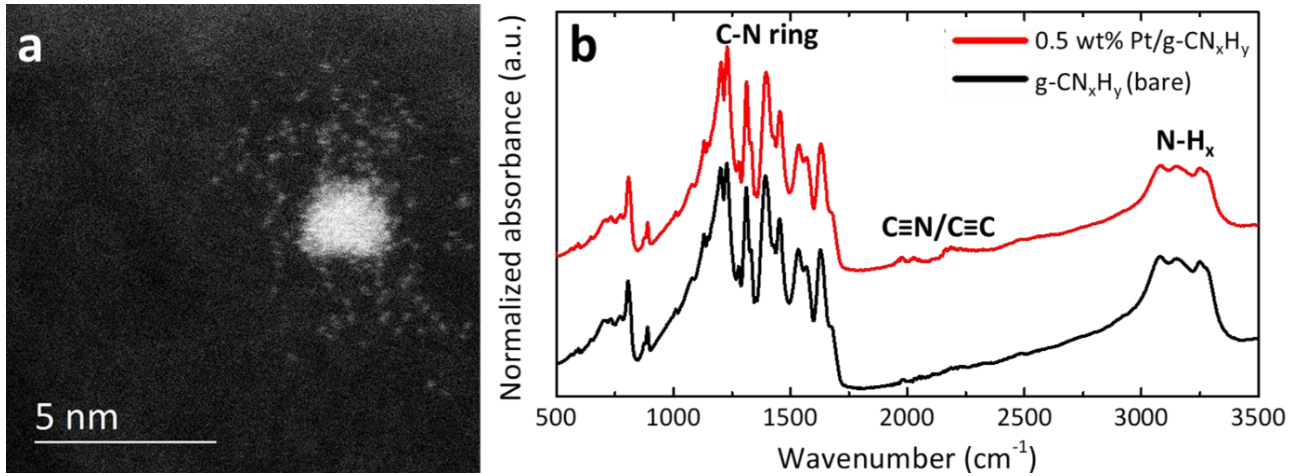
Here, we utilize vibrational EELS to locally probe bonding in g-CN<sub>x</sub>H<sub>y</sub> and PTI/LiCl, which are expected to contain a high and low degree of chemical heterogeneity, respectively. To mitigate radiation damage during vibrational EELS acquisition, an 'aloof-beam' configuration is employed, wherein the convergent electron beam is placed several nanometers outside the specimen. Figure 1(a)-(b) compares several vibrational EEL spectra from g-CN<sub>x</sub>H<sub>y</sub> and PTI/LiCl, respectively, from which the (N-H<sub>x</sub>)/(C-N ring) bonding ratios were calculated. In g-CN<sub>x</sub>H<sub>y</sub>, amine content is found to vary locally up to 27%.<sup>5</sup> Compared to the corresponding low dose STEM images, some of which are displayed in Figure 1(c)-(f), aloof-beam vibrational EELS provides useful information for analyzing heterogeneity in disordered materials such as g-CN<sub>x</sub>H<sub>y</sub>.

Pt-loaded g-CN<sub>x</sub>H<sub>y</sub> was obtained through a chemical deposition route in which NaBH<sub>4</sub> is used as a reducing agent for aqueous Pt<sup>4+</sup> ions to form single-atom dispersions, as shown in Figure 2(a).<sup>4</sup> Figure 2(b) compares the IR absorption spectra for bare and as-synthesized 0.5 wt% Pt/g-CN<sub>x</sub>H<sub>y</sub>, showing a significant increase in intensity between 1930-2400 cm<sup>-1</sup> which may be attributed to C≡N/C≡C species. While single atom dispersions can be obtained, the g-CN<sub>x</sub>H<sub>y</sub> 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.

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2. B. Lotsch et al. *Chem. Eur. J.* **2007**, *13*, 4969-80.
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**Figure 1:** Alost-beam vibrational EELS for (a) g-CN<sub>x</sub>H<sub>y</sub> and (b) PTI/LiCl. ADF-STEM images showing the e<sup>-</sup>-beam position (yellow star) and probed area (green rectangle) corresponding to spectrum (c) 2c, (d) 3c, (e) 4d, and (f) 3d; scale bars=50 nm.



**Figure 2:** (a) ADF-STEM image of 0.5 wt% Pt/g-CN<sub>x</sub>H<sub>y</sub> and (b) IR absorption spectra for bare and 0.5 wt% Pt/g-CN<sub>x</sub>H<sub>y</sub>.

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