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Revealing the Structure of Graphitic Carbon Nitride through Low-Dose TEM using a Direct Electron Detector

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Graphitic carbon nitrides (commonly referred to as g-CN_xH_y or g-C_3N_4) have recently garnered interest due to their visible-light activity for photocatalytic water reduction [1]. Similar to graphite, g-CN_xH_y has a hexagonally symmetric in-plane structure but with periodic replacement of C-atoms with N-atoms resulting in bandgap formation and regular voids within the layers. Due to the synthesis strategy, residual hydrogen becomes trapped in the structure thus preventing long range planar order [2]. Because g-CN_xH_y is extremely beam sensitive, conventional high dose imaging with transmission electron microscopy (TEM) renders the material amorphous [3]. However, by combining low electron doses with direct electron detectors, the structure of g-CN_xH_y can be imaged using high-resolution TEM.

All TEM images were collected on an image-corrected FEI Titan electron microscope operating at 300 kV. To enhance the bright contrast of atoms/motifs, a negative spherical aberration coefficient of -20 μm was employed. All images were acquired on a Gatan K2 IS detector operated in counting mode. As such, the Titan monochromator focus was adjusted to achieve a dose between ~4-7 e/pixel/s on the detector array. A commercial g-CN_xH_y powder was obtained from Carbodeon Ltd. and used as-received. Preparation of a TEM specimen involved ultrasonicating an aqueous suspension of the crushed powder for 12 hours followed by submerging a lacey-C/Cu grid in the solution and allowing it to air dry. To interpret the TEM images, an x-ray diffraction (XRD) pattern was collected on the bulk powder.

Two representative images of g-CN_xH_y, including the pseudo-(001) zone axis and a side view of the graphitic layers, are shown in *Figure 1(a)-(b)*. To achieve a good signal-to-noise ratio in the plan-view image, a 10-second total exposure was broken into 100 frames and alignment of the stack was performed using a bandpass filter in GMS-3 software. From the FFT of the plan-view image (*Fig.1(c)*), the crystallinity of this material becomes apparent with the most prominent spatial frequency corresponding to the in-plane repeat distance separating heptazine motifs at ~6.7 Å. Diffuse intensity and broken rings in the FFT suggest the layer stacking may be randomly oriented. *Fig.1(a)* also appears to consists of multiple sheets and buckled regions, thus reducing the ability to distinguish the 2D-motif. The corresponding FFT of the side-view image (*Fig.1(e)*) reveals the "graphitic" separation distance of 3.2 Å. *Figure 1(d)* contains the XRD pattern for this material and the proposed structure model of a fully-condensed g-C_3N_4 single sheet, both of which were used to index the FFT's and qualitatively interpret the image contrast, respectively. Fourier analysis was performed on the boxed region in the plan-view image, *Fig.2(a)*, to quantitatively interpret some of the image contrast. *Figure 2(b)* contains the FFT of the region of interest showing six well-defined central spots corresponding to an average spacing of 6.4 Å. After isolating these (100)-like spots using a mask tool (*Fig.2(c)*), an inverse-FFT (IFFT) was performed to yield an image containing contrast from only the bridged-heptazine units (*Fig.2(d)*). The region of interest together with the IFFT (*Fig.2(e)*) clearly illustrate that the bright and dark regions are indeed due to the alternating heptazine/void in-plane structure of condensed g-C_3N_4, on the nanometer length scale. Real-space averaging techniques will be combined with higher resolution imaging to explore the extent of planar and stacking disorder in g-CN_xH_y materials [4].

References:
[1] X. Wang *et al.* Nat. Mater. **8**, (2009), p. 76.
[2] B.V. Lotsch *et al.* Chem. Eur. J. **13**, (2007), p. 4969.
[3] D.M. Haiber *et al.* Microsc. Microanal. **22** (Suppl **3**), (2016), p. 986.
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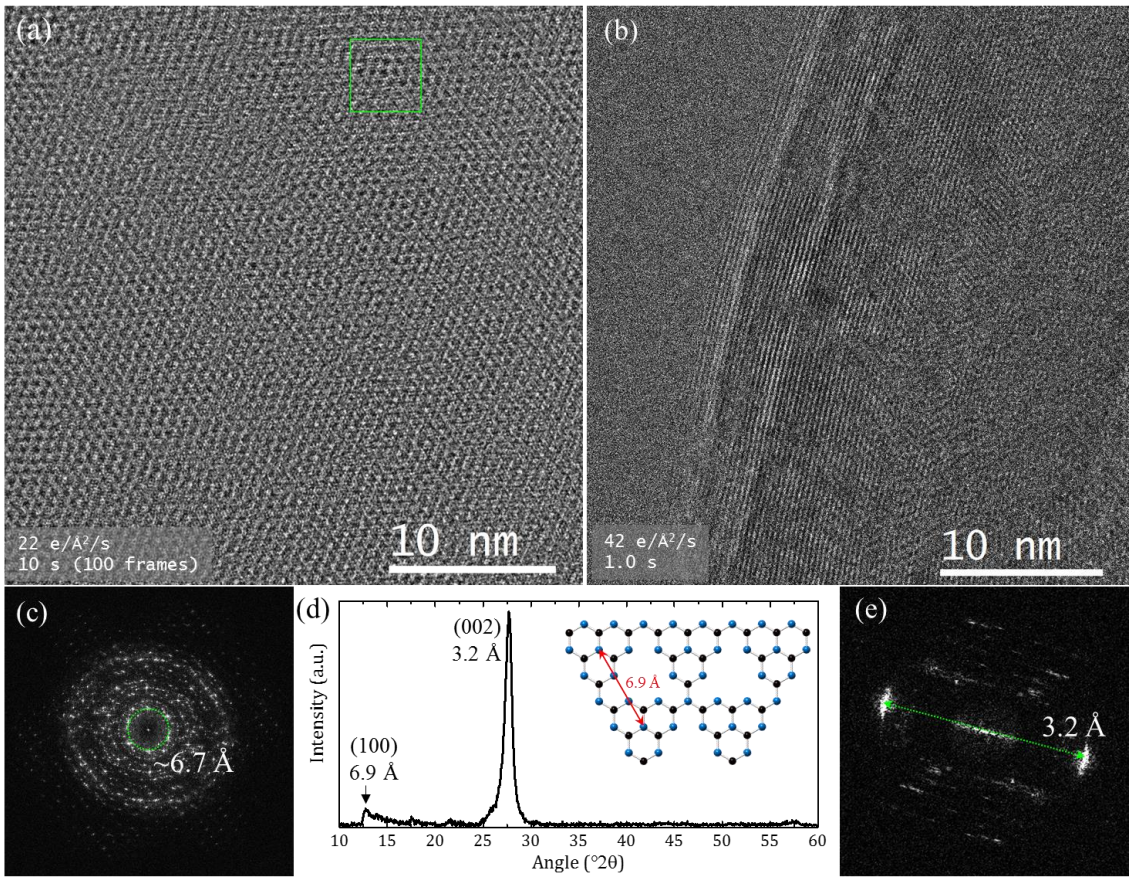

Figure 1. Low-dose TEM images of g-CN_xH_y in (a) plan-view and (b) side-view. Corresponding FFT's are shown for (c) plan-view and the (e) side-view with characteristic d-spacing values labeled. (d) Background-subtracted XRD spectrum for g-CN_xH_y; inset: 2D single-sheet structure model of fully-condensed g-C_3N_4 (C-atoms=black; N-atoms=blue) with the (100) spacing indicated.

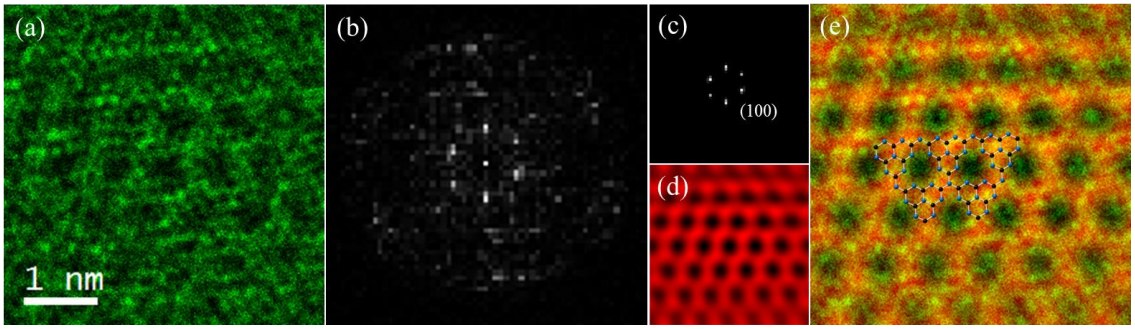

Figure 2. (a) Region of interest from *Fig.1(a)* with (b) corresponding FFT. (c) FFT after applying a mask to isolate the (100) spots and its corresponding (d) IFFT image. (e) Composite image of the region of interest (green) and the IFFT (red); an overlay of the 2D structure model is also displayed.

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