

Supporting Information: The structure of normal-alkanes adsorbed on hexagonal-Boron Nitride

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Details of bulk characterization of BN powders

Below we present a more detailed characterization of the h-BN powders used in this study. The results derived from scattering data have been used to inform our analysis of two-dimensional (2D) diffraction patterns from adsorbed n-alkanes.

Surface Area

The surface areas of the powders (as quoted by the supplier) are listed in Table S1. This has been verified by our own Argon volumetric adsorption isotherm measurements at $\sim 77\text{K}$, using the ‘point-B’ method¹.

Bulk powder diffraction of h-BN

We have measured the bulk powder diffraction pattern for each of our h-BN batches. The unit cell parameters were determined by a Pawley refinement and are listed in Table S1. The patterns were refined using TOPAS v.3.0 (Bruker AXS GmbH) in space group P63/mmc using the literature values² as inputs for the refinement. A pseudo-Voigt peak shape was used with a spherical harmonics correction³ applied to the lorentzian peak width to account for the anisotropic peak broadening observed for the different hkl reflections. Reasonable fits to the data were obtained with final R-factors (R_{wp}) of $\sim 11.2\%$ for all samples. The variation of the lattice parameters from the literature values is within the

range expected from the thermal expansion coefficients and from imperfections in the crystal structures that are a consequence of small particles^{2, 4}. The literature shows that the h-BN cell parameters display an anisotropic temperature dependence⁴ particularly for temperatures > 100K. Thus in the temperature range 10-298K, the a-parameter shows a variation of -0.05% (i.e. this cell parameter actually gets smaller) while the c-parameter increases by 0.82%. This behavior is qualitatively the same and of a similar magnitude to that seen for graphite. For our study the a-parameter is the important one as this corresponds to the basal-plane adsorption surface. This lattice contraction is small and is less than the estimated error in the fits to our 2D diffraction data.

As well as the presence of impurities, the imperfection of BN crystals is partly related to the particle size². The proportion of ‘turbostratic’ stacking faults (i.e. where layers are displaced from the regular *ABCA* arrangement) can be inferred from the deviation of the c-lattice parameter from the ideally perfect structure, and from the widths of various *hkl* Bragg peaks. Kurdyumov et al.² have determined an empirical equation for the dependence on the (002) d-spacing on the defect concentration, γ :

$$d_{002} = 3.3281 + 0.10272\gamma - 0.0905\gamma(1 - \gamma)$$

thus when $\gamma = 0$ (i.e. a perfect crystal) the (002) d-spacing = 3.3281 at 298K, and $c = 6.6562$. Since no crystal is perfect, the literature values tend to slightly deviate from this value depending on the details of the sample preparation etc. The average of most of the literature values reported⁴ is $c = 6.6576 \pm 0.003$ ($a = 2.5043 \pm 0.0004$). Based on this equation and allowing for thermal expansion, our samples (see Table S1) show a relatively high number of stacking faults, probably due to the small size of the crystallites.

As described in the main text, we can also use these diffraction patterns to determine the characteristic (or coherence) length for the crystallites in each powder. For completeness, these values are also listed for each batch in Table S1

Table S1 Characterization of BN powders. The surface area is from the suppliers analysis. The values for “perfect” crystals are taken from Kurdyumov et al.²

Powder grade & batch		Specific surface area $/\text{m}^2 \text{ g}^{-1}$	Cell parameters from Pawley refinement		Turbostratic defect conc., γ	Characteristic length, $L_{(110)} / \text{\AA}$
			a / \AA	c / \AA		
Perfect crystals at 298K		n/a	2.50428	6.6562	0	n/a
BN#3	HCPH	20.9	2.5078	6.6508	0.42	333
BN#4	HCP	11.57	2.5053	6.6726	0.53	385
BN#7	HCPH	15.56	2.5053	6.6327	0.30	343

Small-angle X-ray scattering

A Porod analysis of SAXS data (measured on I22 at Diamond) from our BN samples shows a significant deviation from the high angle limit of Q^{-4} variation. Instead we find that the exponent of the q-variation is between -3.3 and -3.8. Although there are many possible reasons for this, it is a good indication that the scattering particles are rough and inhomogeneous, which is consistent with the high proportion of stacking faults seen in the powder diffraction data. The analysis of small angle scattering data from powders can be very complex and other analyses including Debye and Guinier models can also be used⁵. In fact we can fit our data to a model with fractal dimensions but the validity of such an analysis is somewhat questionable, particularly as our data does not extend to very small angles. Since this is not the focus of this study we have therefore not analysed our SAXS data further. In general the SAXS scattering seen in the powder diffraction patterns after background subtraction does not extend to very low-Q and we believe that it is not appropriate to attempt to draw quantitative conclusions from an analysis of its form. Instead this feature is arbitrarily subtracted from the data in order to obtain a flat diffraction pattern.

References

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