

Spectroscopic size and thickness metrics for liquid-exfoliated h-BN

Aideen Griffin,¹ Andrew Harvey,¹ Brian Cunningham,² Declan Scullion,² Tian Tian,³ Chih-Jen Shih,³ Myrta Gruening,² John F Donegan,¹ Elton J. G. Santos,² Claudia Backes,⁴ Jonathan N. Coleman^{1*}

¹*School of Physics and CRANN & AMBER Research Centres, Trinity College Dublin, Dublin 2, Ireland*

²*School of Mathematics and Physics, Queen's University Belfast, Belfast, BT71NN, United Kingdom*

³*Institute for Chemical and Bioengineering, ETH Zürich, 8093 Zürich, Switzerland*

⁴*Chair of Applied Physical Chemistry, Ruprecht-Karls University Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany*

*colemaj@tcd.ie

Abstract: For many 2D materials, optical and Raman spectra are richly structured, and convey information on a range of parameters including nanosheet size and defect content. By contrast, the equivalent spectra for h-BN are relatively simple, with both the absorption and Raman spectra consisting of a single feature each, disclosing relatively little information. Here, the ability to size-select liquid-exfoliated h-BN nanosheets has allowed us to comprehensively study the dependence of h-BN optical spectra on nanosheet dimensions. We find the optical extinction coefficient spectrum to vary systematically with nanosheet lateral size due to the presence of light scattering. Conversely, once light scattering has been decoupled to give the optical absorbance spectra, we find the size dependence to be mostly removed save for a weak but well-defined variation in energy of peak absorbance with nanosheet thickness. This finding is corroborated by theoretical calculations. In addition, while we find the position of the sole h-BN Raman line to be invariant with nanosheet dimensions, the linewidth appears to vary weakly with nanosheet thickness. These size-dependent spectroscopic properties can be used as metrics to estimate nanosheet thickness from spectroscopic data.

Introduction

Hexagonal boron nitride (h-BN) is a layered material which is structurally analogous to graphite.¹ Its physical properties resemble graphite in a number of ways, for example in its high chemical stability, its large thermal conductivity and near superlative mechanical properties. However, it is electrically very different to graphite, displaying a large bandgap (5.5-6 eV) and negligible electrical conductivity.

Also like graphite,² h-BN can be produced in a 2-dimensional (2D) form by direct growth³ as well as by mechanical⁴ and liquid phase exfoliation.^{5, 6} The exfoliated material retains the properties of layered h-BN but in an ultra-thin, extremely flat morphology. This has resulted in 2D h-BN being deployed in a range of applications. For example, due to its high bandgap and extreme flatness, grown or mechanically exfoliated h-BN is widely used as a substrate or encapsulating material for electronic devices based on other 2D materials such as graphene or MoS₂.⁷⁻¹⁰ Alternatively, liquid-exfoliated h-BN nanosheets (which tend to be a few layers thick and 100s of nm in length) have been used in a range of applications from reinforcing⁶ or gas-barrier¹¹ fillers in polymer-based composites to thermally conductive inclusions¹² in oils to dielectric materials in electronic devices¹³⁻¹⁵ and electrochemical separators in electrolytically gated transistors.¹⁶

As with other 2D materials, the utility of h-BN in applications increases the importance of our ability to characterize it. As with all 2D materials, basic characterization to measure nanosheet size and thickness can be performed by transmission electron microscopy and atomic force microscopy. However, statistical analysis of individual nanosheet measurements using these techniques is time consuming and tedious. In contrast, optical spectroscopy generally probes the ensemble and provides averaged information. However, compared to other 2D nanomaterials optical spectroscopic characterization of h-BN has yielded much less information. For example, while MoS₂ and WS₂,^{17, 18} and to a lesser extent graphene,¹⁹ have information-rich optical absorption spectra which allow estimation of nanosheet size and thickness, the absorption spectrum of h-BN appears to be information-poor, displaying few features beyond a bandedge around 6 eV. Similarly, while the Raman spectra of MoS₂ and graphene yield information about nanosheet dimensions^{19, 20} and defect content,²¹ the h-BN Raman spectrum contains a single line,¹ the properties of which have not been concisely linked to any physical properties of the nanosheets. Although cathodoluminescence can give information about nanosheet thickness,²² these measurements are neither straightforward nor widely accessible.

Here we shown that the absorption and Raman spectra of liquid-exfoliated BN-nanosheets are not as bereft of information as has been previously thought. By performing optical characterization of fractions of size-selected, liquid-exfoliated nanosheets, we show that the extinction spectra are influenced by nanosheet lateral size while the nanosheet thickness can be extracted from either the absorption or Raman spectra.

Results and Discussion

Size selection of BN

Liquid phase exfoliation is a versatile nanosheet production method which exfoliates layered crystals down to few-layered nanosheets in appropriate stabilizing liquids.^{23, 24} It has been applied to a range of layered crystals including graphite, h-BN^{5, 6, 25-29} and MoS₂ and tends to yield polydisperse samples of nanosheets with broad lateral size (~100-1000 nm) and thickness (~1-20 layers) distributions.^{23, 30, 31} As a result, centrifugation-based size selection is necessary to enable any study where well-defined sizes are required. Such techniques range from density gradient ultracentrifugation,³⁰ which gives fine size control at low yield, to liquid cascade centrifugation (LCC),¹⁸ which gives coarser size control at considerably higher yield. Here we used LCC to size-select an as-prepared dispersion of BN nanosheets stabilized in an aqueous sodium cholate solution (see Methods for exfoliation protocol and cascade details), yielding fractions containing nanosheets of different lateral sizes and thicknesses.

In LCC, a dispersion is subjected to repeated centrifugation steps with successively increasing centrifugal accelerations (expressed as relative centrifugal field, *RCF*, in units of the earth's gravitational field, *g*). After each centrifugation step, supernatant and sediment are separated, the sediments are collected for analysis, while the supernatant is centrifuged at higher centrifugal acceleration.¹⁸ The sediments collected at low centrifugal acceleration contain large/thick nanosheets, while the fractions collected at higher centrifugal acceleration contain smaller and smaller nanosheets. This technique has a number of advantages; notably that collecting the product as a sediment allows redispersion into a range of liquid environments, simultaneously allowing solvent exchange and concentration increase. In addition, very little material is wasted with up to 95% of exfoliated product distributed among the fractions.¹⁸

We label samples using the lower and upper centrifugation rates used in the preparation of the fraction. For example, if the supernatant produced after centrifugation with *RCF*=5,000×*g*-force (5k-*g*) is then centrifuged at 10,000 *g* and the sediment collected after this step, we refer to the sample as 5-10 k-*g*.

Atomic Force Microscopy (AFM) was used to statistically analyze the nanosheet dimensions for each fraction with representative images displayed in Figure 1 A. In each dispersion, 200-350 nanosheets were measured, and their length (longest dimension), width (dimension perpendicular to length) and thickness recorded. The nanosheet length data were plotted as histograms with examples of the 0.4-1 k-*g* and 10-22 k-*g* fractions shown in Figure 1B. For each fraction, the nanosheet length follows a lognormal statistical distribution with smaller sizes obtained for increasing centrifugation speeds as expected. Additional histograms are given in the SI (Figure S1). The mean nanosheet length is plotted *versus* the central *g*-value (midpoint of high and low *g*-values used in the size selection) in figure 1C. Experimentally, we found roughly a power-law decay of $\langle L \rangle$ with central *g*-value with an exponent close to -0.5, similarly to other liquid-exfoliated 2D materials.¹⁸

Some care must be taken when analyzing the statistical nanosheet-height data. This is because the apparent AFM height of liquid-exfoliated nanosheets is typically larger than the theoretical thickness of the nanosheets due to adsorbed/intercalated water and surfactant. Similar to previous reports,^{17, 32, 33} we use step-height analysis to determine the apparent thickness of a single monolayer by measuring the height of the terraces of partially exfoliated nanosheets (Figure 1 D,E). Similar steps are then grouped and a plot of the mean step height versus step height group number (Figure 1, F) leads to an apparent monolayer height of 0.99±0.01 nm, similar to the step height of 0.9 nm previously found for graphene.³² Using this information we can determine the number of layers, *N*, of the nanosheets allowing the construction of histograms for each size-selected fraction. Typical histograms of the 0.4-1k *g* and 10-22k *g* (Figure 1 F) samples show an increase in monolayer and few-layer nanosheets and a narrowing of the distribution with increasing centrifugation speed. Histograms of all other sizes are shown in the SI (Figure S1). The arithmetic mean values of nanosheet layer number, $\langle N \rangle$, is plotted versus the central *g*-force in figure 1H and shows significant variation over the fractions from ~19 to 3.5. Experimentally, $\langle N \rangle$ followed a power-law with *g*-force, displaying an exponent of -0.4.

Atomic force microscopy (AFM) can be used to measure both nanosheet thickness and lateral dimensions; this means, for each nanosheet of a given thickness, the volume can be estimated as thickness×length×width (*N*×*L*×*W*). This allows for the calculation of the volume-fraction-weighted mean layer number, $\langle N \rangle_{vf} = \sum N^2 L W / \sum N L W$, where the summations are over all nanosheets. This is an alternative measure of nanosheet thickness which reflects the fact

that mass tends to be concentrated in thicker nanosheets (the difference between $\langle N \rangle$ and $\langle N \rangle_{vf}$ is akin to the difference between number-average-molecular-weight and weight-average-molecular-weight in polymer physics).³⁴ We find $\langle N \rangle_{vf}$ to be directly proportional to $\langle N \rangle$ with a ratio of ~ 1.5 (see SI, figure S2). As a result, both can be used to express the nanosheet thickness. We have added a plot of $\langle N \rangle_{vf}$ vs. central g -force in figure 1H.

This data implies that smaller/thinner nanosheets are separated from larger/thicker nanosheets when using a standard centrifugation cascade which means that $\langle N \rangle$ and $\langle L \rangle$ are intrinsically linked. However, from previous work on WS₂,¹⁸ we know that overnight centrifugation at low *RCF* (below the lower boundary of the initial trapping) can be used to prepare samples with a different relationship between length and thickness compared to the samples from a standard cascade. We find that this is indeed the case for the BN samples under study here (see methods and SI, figures S3-S4 and table S1). This is useful, as it allows to test whether observed systematic variations in the optical spectra are due to changes in lateral size or thickness. Throughout the manuscript, data from these samples is included in the plots and always collapses on the same curve as the data from the standard size selection.

Dependence of optical spectra on nanosheet dimensions

In the case of many 2D materials, including TMDs and graphene, it has been shown that optical extinction (and absorbance) spectra change systematically with nanosheet dimensions.^{17-19, 33, 35, 36} In this work we use UV Vis extinction and absorbance spectroscopy to investigate the effect of nanosheet size and thickness on the optical properties of liquid-exfoliated BN. Extinction spectra of the dispersions were measured in the standard transmission mode while absorbance spectra were acquired with the sample in the centre of an integrating sphere.^{17, 37} It should be noted that the extinction (Ext) is a combination of both the absorption (Abs) and scattering (Sca) where $Ext(\lambda) = Abs(\lambda) + Sca(\lambda)$.³⁸

Optical extinction spectra (extinction is related to the transmittance, T , via $T = 10^{-Ext}$, where $Ext = \epsilon Cl$, with ϵ the extinction coefficient, C the nanosheet concentration and l as the path length) were measured for the various samples produced. Spectra are shown in figure 2A and display a peak at ~ 6.1 eV (205 nm). Aside from this peak, the spectra are dominated by a broad scattering background,^{5, 17, 39} especially for the fractions containing larger nanosheets. Clearly the shape of this scattering background is highly dependent on nanosheet size. This is a significant problem as the extinction coefficient is usually considered to be an intrinsic property

which can be used to determine dispersion concentration. It is clear that concentration measurements are only possible if the size dependence of the extinction coefficient is determined.

The concentration of each dispersion was determined gravimetrically, i.e. by filtering a known volume of LPE BN and weighing the resultant white powder after washing with ~ 500 mL of water. This allowed us to convert Ext to extinction coefficient, with the data plotted at a fixed photon energy ($\epsilon_{3.1\text{eV}}$) *versus* the mean nanosheet length, $\langle L \rangle$, in figure 2B. We find a clear relationship between $\epsilon_{3.1\text{eV}}$ and $\langle L \rangle$ which empirically can be described by

$$\epsilon_{3.1\text{eV}} = 4 \times 10^{-4} \langle L \rangle^{2.55} \quad (1)$$

where $\langle L \rangle$ is in nm and $\epsilon_{3.1\text{eV}}$ is in $\text{Lg}^{-1}\text{m}^{-1}$. We note that this is actually a measure of the scattering coefficient in this, non-resonant, regime. Once $\langle L \rangle$ has been measured, for example by TEM or AFM, equation 1 can be used to find the extinction coefficient appropriate to the nanosheet length under study. Then, $\epsilon_{3.1\text{eV}}$ can be used to obtain the nanosheet concentration (using $C = Ext_{3.1\text{eV}} / l\epsilon_{3.1\text{eV}}$). Alternatively, if the extinction coefficient is measured, this information can be used to determine $\langle L \rangle$.

Of more basic interest than extinction is absorbance. As described recently, an integrating sphere can be used to separate the extinction spectra into their constituent absorbance and scattering components (Figure 3C).^{17, 19, 40} The scattering spectra (figure 2C inset) followed power-law decays in the non-resonant regime, as described for dispersions of MoS_2 nanosheets.¹⁷ More importantly, the absorbance spectra displayed a well-defined peak at 6.06-6.13 eV (205-202 nm) and an absorption edge at ~ 5.8 eV (~ 213 nm). In addition, the absorbance falls to zero at energies below 3.5 eV, consistent with a wide-bandgap semiconductor and confirming that the majority of the signal detected in the extinction spectra is due to scattering (SI Figure S5). However, we note that some small unexpected features were observed close to 4.2 eV. These will be discussed briefly below.

The main absorbance peak is attributed to free excitons associated with the band to band transition.⁴¹⁻⁴³ In BN grown by metal-organic chemical vapor deposition, these excitons were previously observed in photoluminescence measurements and are typically located at ~ 5.7 eV with impurity bound excitons also having been observed at ~ 5.5 eV, respectively.⁴¹⁻⁴³ In the absorbance spectra of LPE BN presented here, the excitonic peak is upshifted compared to these literature values, suggesting a Stokes-shift of up to 0.4 eV. However, the different

dielectric environment of the two sample types may also result in different exciton binding energies also contributing to this shift.

The data in figure 2C shows a small shift in the exciton energies over the range of the size-selected fractions. Because the exciton binding energy is sensitive to a combination of confinement effects and dielectric screening, we would expect the excitonic peak position to vary with nanosheet thickness. This is more clearly seen in a zoomed graph as plotted in figure 2D which clearly shows the peak to redshift as the nanosheet size increases. The peak position, E_{Abs} , is plotted versus $\langle N \rangle_{\text{vf}}$ in figure 3E and falls gradually from ~ 6.153 eV for a mean weighted thickness of 3.4 layers to ~ 6.118 eV for mean weighted thickness of 27 layers. This thickness dependence is corroborated by theoretical calculations as shown in the SI. Over the thickness range studied, the thickness-dependence of the peak position can be empirically fitted using an appropriate empirical function (dashed line). This can be rearranged to give an equation which allows us to determine $\langle N \rangle_{\text{vf}}$, once the peak absorbance is known:

$$\langle N \rangle_{\text{vf}} = 10^{43.5(6.152 - E_{\text{Abs}})} \quad (2)$$

where E_{Abs} is in eV.

Magnified views of the absorption curves, focusing on the region near 4 eV are shown in figure 2H. The spectra associated with larger nanosheets clearly show well-defined features in this regime. Weak features close to 4 eV are often observed in BN absorption spectra. These are typically assigned to donor-acceptor-pair transitions involving a nitrogen vacancy donor and a deep level acceptor such as carbon atoms occupying the nitrogen vacancy site.⁴³⁻⁴⁵ It is interesting to note that these impurity-related transitions decrease in intensity with decreasing layer number (Figure 2H inset). This is difficult to rationalize, as these impurities are attributed to substitutional defects in the BN lattice. Another possible explanation is that there is a zero-phonon transition at 4.15 eV with phonon replicas at higher energy.⁴⁶ Future studies using different BN starting materials are required to shine light on this phenomenon now that absorbance spectroscopy can be used as a readily available technique to not only investigate nanosheet length and thickness, but also the sample purity.

Dependence of Raman spectra on nanosheet dimensions

Raman spectroscopy has evolved as a powerful tool to characterize 2D materials, as the spectra typically contain information on nanosheet thickness, defect content, strain, doping, etc.^{21, 47} However, compared to graphene or other 2D materials, the Raman spectra of BN are relatively

poor in information. They are dominated by a single phonon mode, the so-called G band at around 1366 cm^{-1} (in addition to low frequency modes that are often not accessible⁴⁸).⁴⁹⁻⁵² A major issue with the Raman spectroscopy on BN is that the material is not resonantly excited, so the recorded signal is very weak. In addition, only minor peak shifts have been observed.⁵¹ For example, only the monolayer was reported to exhibit sample dependent blue-shifts compared to the bulk material with the magnitude of the shift also depending on strain.

To test whether we can nonetheless extract information, we subjected our size-selected LPE nanosheets to Raman spectroscopy after deposition on Si/SiO₂ wafers. The laser power was kept as low as possible to avoid heating effects, but high enough to reduce the noise in the spectra which introduces a larger error in fitting the data ($\sim 1.4\text{mW}$, see SI, figure S7). The normalized Raman spectra are shown in Figure 3A. In addition to the G-mode ($\sim 1366\text{ cm}^{-1}$), a secondary smaller and broad group of peaks are visible at higher Raman shift ($1400\text{-}1470\text{ cm}^{-1}$) which we attribute to the sodium cholate surfactant (see SI, figure S8). In addition to this mode, we expect a sodium cholate mode at $\sim 1365.2\text{ cm}^{-1}$, i.e. very close to the h-BN G-mode. To eliminate the effect of this SC mode, and to determine the width and position of the h-BN G-mode as accurately as possible, we therefore fit the main Raman peak to two Lorentzians, constraining one using the known position and width of the SC mode. An example of such a fit is shown for the 5-10 k-*g* sample (Figure 3B).

The resultant positions of the h-BN G-bands are plotted as a function of $\langle N \rangle$ in Figure 3C. As expected from literature, the peak position does not change systematically as function of nanosheet thickness and are centered around 1366 cm^{-1} as indicated by the dashed line. However, the G-mode does show variations in the peak width across the obtained fractions. We have analyzed the full width at half maximum ($\Gamma_{\text{G-band}}$) of the h-BN G-mode extracted from the Lorentzian fits and find a well-defined trend with linewidth increasing as central-*g* value increases.

Because the different fractions have varying values of both $\langle L \rangle$ and $\langle N \rangle$, it is important to isolate the source of the linewidth dependence. To do this, we note that the samples from the overnight centrifugation (see methods) display a different $\langle N \rangle$ - $\langle L \rangle$ relationship compared to the standard size-selected samples. This means the overall $\langle N \rangle$ - $\langle N \rangle$ relationship is not smooth and so any parameter which varies smoothly with $\langle N \rangle$ will not vary smoothly with $\langle L \rangle$. With this in mind, we find that a plot of $\Gamma_{\text{G-band}}$ versus $1/\langle L \rangle$ does not scale cleanly with $1/\langle L \rangle$ (SI, Figure S9), supporting the idea that the broadening is not related to nanosheet length.

However, as shown in figure 3D, we find a smooth, near-linear scaling of the G-mode width with $1/\langle N \rangle_{Vf}$ implying that the broadening is thickness dependent and so related to the nanosheet surfaces (i.e. the basal planes). A possible explanation of the broadening with nanosheet thickness would be related to solvatochromic effects, as a greater proportion of BN monolayers in the thinner nanosheets interact with the environment. To test whether the width of the G-mode is significantly influenced by the dielectric environment, a drop of *N*-cyclohexylpyrrolidone (CHP) was placed on the deposited BN nanosheets and Raman spectra acquired before and after the CHP treatment. As shown in the SI (figure S10), $\Gamma_{G\text{-band}}$ of this sample increases from $\sim 9 \text{ cm}^{-1}$ to $\sim 12 \text{ cm}^{-1}$ confirming that the nature of this broadening is solvatochromism at the outer monolayer-liquid/air interface. As such, one might also expect that the environment in which exfoliation was performed might have an effect on the linewidth obtained in subsequent Raman measurements, via the presence of residual surfactant or solvent. To test this, we transferred BN, initially exfoliated and size-selected in aqueous sodium cholate, to a range of liquid environments (aqueous sodium dodecyl benzene sulfonate, polyvinylalcohol, H_2O , isopropanol, CHP) prior to deposition on Si/SiO₂ for measurement. In each case, we do not find changes in the G-band width within the error of the fit (figure S11). This is also the case, when the sample is deposited on different substrates (aluminum and copper foil- figure S12). This suggests that the environment during exfoliation does not affect subsequent Raman measurements on deposited sheets and only the environment during the measurement is important. In addition, the nanosheet-air interface appears to be dominant. This suggests the Raman measurement to be quite robust to samples produced by different techniques.

Using the $\Gamma_{G\text{-band}}$ vs. $\langle N \rangle_{Vf}$ data, we can generate a very simple model to describe the thickness-dependence of $\Gamma_{G\text{-band}}$. We propose that the solvochromatic increase in linewidth compared to bulk scales with the fraction of monolayer surfaces within the nanosheet which are exposed to the environment. This implies a scaling of the form $\sim 2/(N+1)$ suggesting a width-thickness relationship of:

$$\Gamma_{G\text{-band}} = \Gamma_{G\text{-band}}^{\text{Bulk}} + \frac{2\Delta\Gamma_{M-B}}{\langle N \rangle_{Vf} + 1} \quad (3)$$

where $\Delta\Gamma_{M-B}$ is the width change going from bulk to monolayer. Applying this function to the data in figure 4D yields a very good fit and nicely captures small deviations from pure $1/\langle N \rangle_{Vf}$ -

type behavior. In this case, the data is consistent with $\Delta\Gamma_{\text{M-B}}=8.7 \text{ cm}^{-1}$, higher than the value of $3\text{-}4 \text{ cm}^{-1}$, implied by the data of Gorbachev for BN nanosheets on a SiO_2 wafer.⁵¹ In addition, the fit gives $\Gamma_{\text{G-band}}^{\text{Bulk}}=8.5 \text{ cm}^{-1}$. Considering that a FWHM of 8 cm^{-1} is found in high quality BN crystals,⁴⁸ this is very reasonable and suggests that basal plane defects (which would also broaden the BN G-mode⁵³) in our LPE BN samples produced from commercial powder are minor.

Rearranging the above equation yields a relationship which allows to estimate $\langle N \rangle$ once the G-band width has been measured:

$$\langle N \rangle_{\text{vf}} = \frac{2\Delta\Gamma_{\text{M-B}}}{(\Gamma_{\text{G-band}} - \Gamma_{\text{G-band}}^{\text{Bulk}})} - 1 = \frac{17.2}{(\Gamma_{\text{G-band}} - 8.5)} - 1 \quad (4)$$

where $\Gamma_{\text{G-band}}$ is in cm^{-1} . Because the reference experiments described in the SI show that the liquid environment prior to deposition has a negligible impact on the resultant liquid environment, we believe these metrics can be applied to a range of LPE samples (figure S11-12).

It is important to note that the numbers given in equation 4 are only strictly valid for measurements made at the same laser power as that used here (1.4 mW) due to slight power-dependent broadening of the G-band (see SI). However, this can easily be addressed, either by working at 1.4 mW or using the approximate power-dependent expression given in the SI (see figure S7).

Conclusion

By studying the dependence of extinction, absorption and Raman spectra on the dimensions of size-selected h-BN nanosheets, we have proposed metrics for estimating nanosheet thickness from optical spectra. The nanosheet thickness can be found from the position of the maximum in the absorbance spectrum due to thickness-dependent excitonic confinement. In addition, minor features in the absorbance spectra attributed to impurities can be used to assess the nanosheet quality. Alternatively, the nanosheet thickness can be extracted from the width of the Raman G-band due to the presence of solvatochromic effects. Since both metrics rely on changes in the dielectric environment with nanosheet thickness, we suggest that both thickness measurements could be applied to BN multilayers grown by methods such as CVD. This holds

in particular for the Raman metrics which show that the G-band width changes are very sensitive to the environment around the BN nanosheets. Like in our samples, the average dielectric constant will be a mixture of different contributions. In CVD-grown BN, these will be the BN-BN interface, the BN-air interface and the BN-substrate interface. Hence, we believe similar metrics for the scaling of the Raman BN Raman G-band width with thickness can be derived for CVD grown samples, although they may be quantitatively different from LPE samples.

Methods

Sample Preparation

BN dispersions were prepared by probe sonicating (VibraCell CVX, 750W) powder (Sigma Aldrich $\sim 1 \mu\text{m}$, 98%) at a concentration of 30 g L^{-1} dispersed in a 6 g L^{-1} aqueous solution of sodium cholate (Sigma Aldrich BioXtra, $\geq 99\%$) for 1 hr at 60% amplitude. The dispersion was then centrifuged in a Hettich Mikro 220R centrifuge equipped with a fixed-angle rotor 1016 at $2260 g$ for 2 hrs. The supernatant was removed and the sediment was redispersed in fresh surfactant solution ($\text{conc}=2 \text{ g L}^{-1}$) and subsequently sonicated for 6 hrs at 60% amplitude with a pulse of 6 on and 2 off. The resultant stock dispersion was centrifuged at $27 g$ for 2 h, sediment discarded and the supernatant subjected to size selection. For the size selection of nanosheets, we used a centrifugation cascade increasing the speed and moving the supernatant on to the next stage each time. The sediment after each centrifugation was collected and redispersed in fresh surfactant solution (SC concentration 0.1 g L^{-1}). The speeds used were $0.1k g$, $0.4k g$, $1k g$, $5k g$, $10k g$, $22k g$. For centrifugation $< 3k g$, a Hettich Mikro 220R centrifuge equipped with a fixed-angle rotor 1016 (50 mL vials filled with 20 mL each). For centrifugation $> 3k g$, a Beckman Coulter Avanti XP centrifuge was used with a JA25.15 rotor with 14 mL vials (Beckman Coulter), filled with 10 mL dispersion each. All centrifugation was performed for 2 h at 15°C . The data in Figure 1 uses the central g -force to express the consecutive centrifugation speeds. The central g force for a $0.4\text{-}1k g$ trapping (supernatant from $0.4k g$ then centrifuged at $1k g$ with the sediment collected) for example is $0.7k g$. In addition to these samples from the standard cascade, two additional samples were prepared with the goal to achieve a different quantitative relationship between lateral size and layer number. For this purpose, the samples $0.1\text{-}0.4k g$ and $0.4\text{-}1k g$ were centrifuged for 16 h overnight at $50 g$ (Hettich Mikro 220R centrifuge, fixed angle rotor 1195-A, 1.5 mL vials) The concentration of

BN in the fractions was determined by filtration and weighing (alumina membranes pore size 0.02 μm). Prior to weighing, the samples were washed with 600 mL of deionised water and dried in vacuum at 70°C.

Characterization

Optical extinction and absorbance measurements were carried out on a Agilent Cary 6000i spectrometer in quartz cuvettes with surfactant concentrations of 0.1 gL^{-1} to minimize the contribution from surfactant to the signal. The spectrometer was fitted with an integrating sphere (external DRA-1800) for absorbance measurements. In this case, the cuvettes were placed in the center of the sphere and the absorbance was measured with 10 cm^{-1} increments and a band widths of 2 nm. The optical density of the BN in the absorbance measurement was adjusted to 0.3-0.4 at the peak. The measurements of both extinction and absorbance spectra allows for the calculation of scattering spectra (Ext-Abs). In this case, the spectra were measured with 0.5 nm increments to give a higher resolution at lower energy. A Bruker Icon Dimension Atomic Force microscope in ScanAsyst mode with Bruker Oltespa-R3 cantilevers was used for AFM measurements. Each liquid dispersion (10 μL) was diluted with water until the sample was transparent (optical density in absorbance ~ 0.3 at the peak), drop cast onto a preheated (180 °C) Si/SiO₂ (300 nm oxide layer) wafer and individually deposited nanosheets analyzed. To correct the nanosheet length due to tip broadening, we used a previously established length correction.¹⁸ Raman spectroscopy was carried out on a Renishaw InVia-Reflex Confocal Raman Microscope with a 532 nm excitation laser in air under ambient conditions. The Raman emission was collected by a 50 $\times$, long working distance objective lens in streamline mode and dispersed by a 2400 l/mm grating with 10 % of the laser power (<1.4 mW). An automated internal calibration (quick calibration) was performed prior to the measurement to correct for the instrument response. Liquid dispersions were dropped (~ 20 μL) onto Si/SiO₂ wafers and left to dry in air before measuring. Minimum 5 spectra on different positions were recorded and averaged. In the streamline mode, where a larger sample area is sampled, we did not observe spot to spot variations except for absolute intensities. After averaging, the spectra were base-line corrected in the region of 1300-1420 cm^{-1} and fit to the appropriate number of Lorentzians. In the case of the samples in the SC environment, the data was fit to two Lorentzians with the SC contribution fixed at 1365.2 cm^{-1} with a width of 16.6 cm^{-1} .

Figures

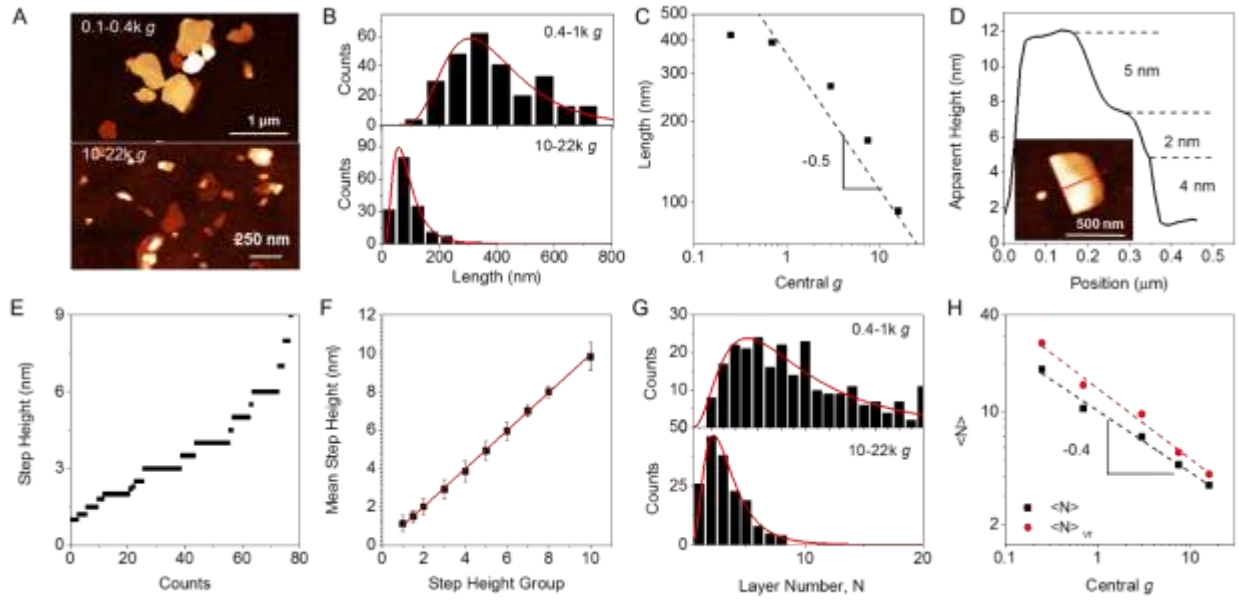


Figure 1: Microscopic characterization of size selected BN nanosheets. **(A)** Representative images of BN nanosheets from the 0.1-0.4k g and 10-22k g fractions. **(B)** Histograms of nanosheet lateral size for the fractions shown in A. **(C)** Mean nanosheet length as a function of central centrifugal force g . **(D)** Height profile along the line of the nanosheet in the inset showing clear, resolvable steps each consisting of multiple monolayers. **(E)** Step heights of >70 BN nanosheets in ascending order. The step height clustered in groups and is always found to be a multiple of ~ 1 nm, which is the apparent height of one monolayer. **(F)** The mean height for each group (the error is the sum of the mean step height error and the standard deviation in step height within a given group) is plotted in ascending order with the slope giving a mean monolayer step height of 0.99 ± 0.01 nm. **(G)** Histograms of layer number, N , for the fractions shown in A. **(H)** Mean layer number $\langle N \rangle$ and volume-fraction-weighted mean layer number $\langle N \rangle_{Vf}$ weighted, both plotted versus central centrifugal force g .

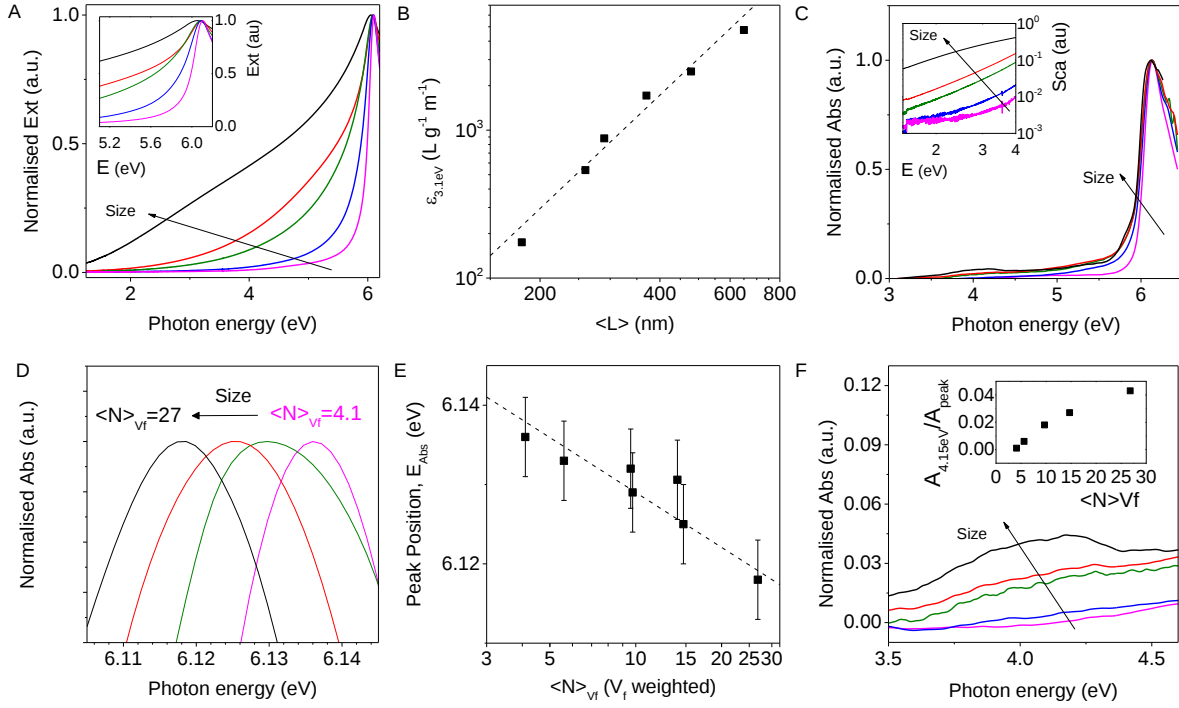


Figure 2: Extinction and absorbance spectroscopy of BN nanosheets. **(A)** Optical extinction spectra normalized to peak maxima showing dependence on nanosheet size. Inset: magnified view of peak region. **(B)** Extinction coefficient at 3.1 eV, $\epsilon_{3.1\text{eV}}$, plotted as a function of nanosheet mean length $\langle L \rangle$ as measured by AFM. **(C)** Normalised optical absorption spectra for different nanosheet sizes. Inset: Scattering spectra in non-resonant regime. **(D)** Zoomed image of (C) showing peak shifts. **(E)** Peak position of the absorbance spectra plotted versus the volume fraction weighted average layer number $\langle N \rangle_{\text{vf}}$ as measured by AFM. **(F)** Magnified view of absorption spectra in the energy range close to 4 eV. Inset: Absorbance at 4.15 eV normalized to peak absorbance plotted versus mean nanosheet thickness.

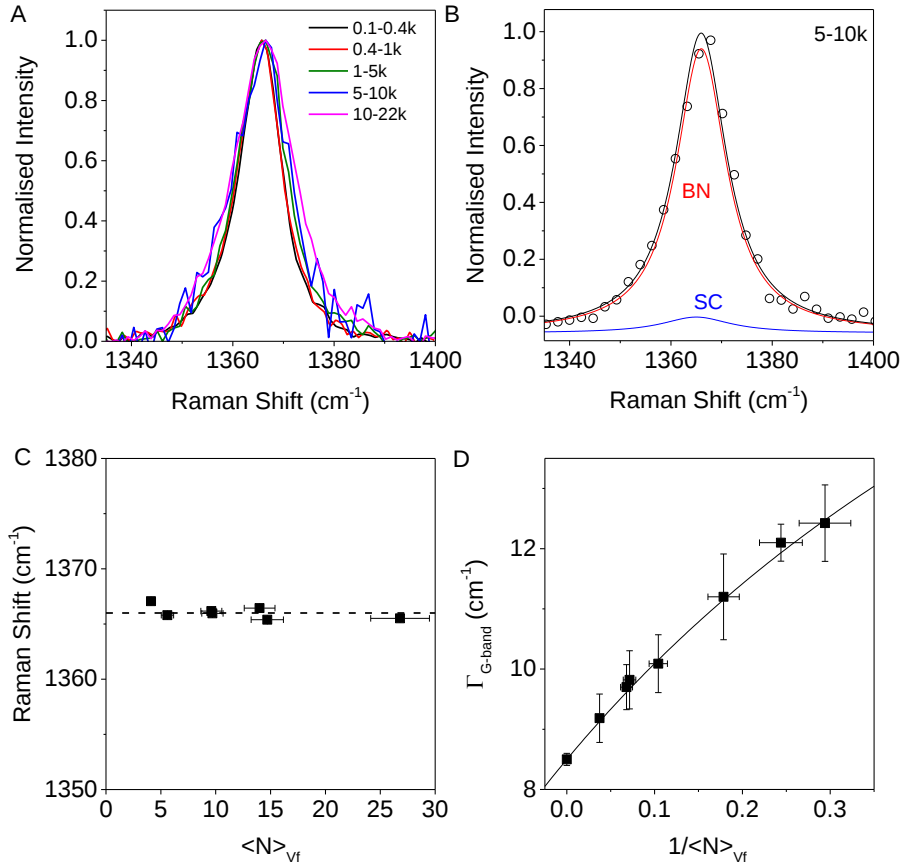
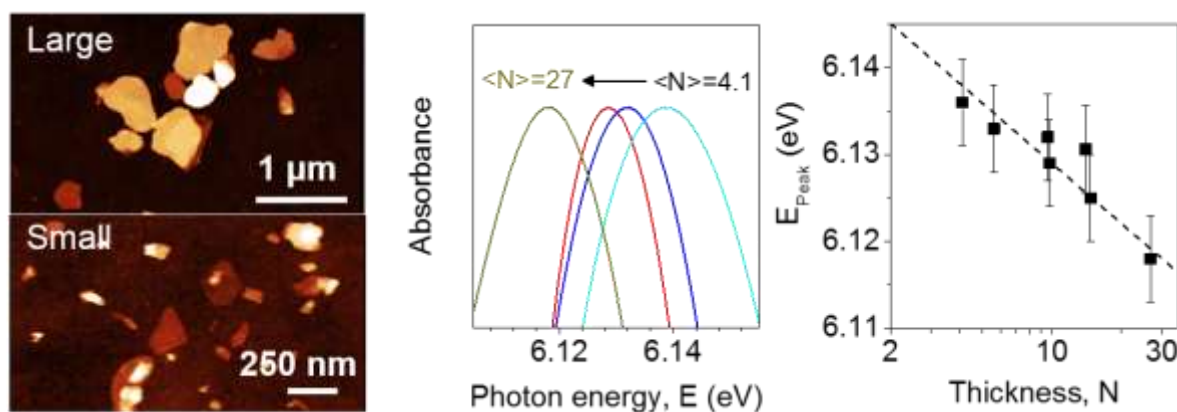


Figure 3: Raman spectroscopy of size-selected BN nanosheets. **(A)** Raman spectra of size-selected BN nanosheet dispersions normalized to the peak maxima at the G band frequency (~1366 cm⁻¹). **(B)** Fitted Raman spectrum of the fraction 5-10k g, normalized to the maximum intensity and fitted to two lines, one representing h-BN and the other representing sodium cholate. **(C)** Plot of the h-BN G-band position as function of mean layer number. The G-band is centered at 1367 cm⁻¹ (dashed line). **(D)** h-BN G-band peak width (full width and half maximum, FWHM, from fit) as function of the inverse nanosheet thickness. The dashed line is a fit to equation * consistent with broadening being due to solvatochromic effects.



ToC fig

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ASSOCIATED CONTENT

Supplemental Information

Complete AFM data, detailed spectroscopic analysis and theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Competing financial interests

The authors declare no competing financial interests.

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