2D Layered Nanomaterials



# High-Throughput Continuous Production of Shear-Exfoliated 2D Layered Materials using Compressible Flows

Reza Rizvi,\* Emily P. Nguyen, Matthew D. Kowal, Wai H. Mak, Sheikh Rasel, Md Akibul Islam, Ahmed Abdelaal, Anup S. Joshi, Shahab Zekriardehani, Maria R. Coleman, and Richard B. Kaner\*

2D nanomaterials are finding numerous applications in next-generation electronics, consumer goods, energy generation and storage, and healthcare. The rapid rise of utility and applications for 2D nanomaterials necessitates developing means for their mass production. This study details a new compressible flow exfoliation method for producing 2D nanomaterials using a multiphase flow of 2D layered materials suspended in a high-pressure gas undergoing expansion. The expanded gas-solid mixture is sprayed in a suitable solvent, where a significant portion (up to 10% yield) of the initial hexagonal boron nitride material is found to be exfoliated with a mean thickness of 4.2 nm. The exfoliation is attributed to the high shear rates ( $\dot{\gamma} > 10^5 \text{ s}^{-1}$ ) generated by supersonic flow of compressible gases inside narrow orifices and converging-diverging channels. This method has significant advantages over current 2D material exfoliation methods, such as chemical intercalation and exfoliation, as well as liquid phase shear exfoliation, with the most obvious benefit being the fast, continuous nature of the process. Other advantages include environmentally friendly processing, reduced occurrence of defects, and the versatility to be applied to any 2D layered material using any gaseous medium. Scaling this process to industrial production has a strong possibility of reducing the cost of creating 2D nanomaterials.

Prof. R. Rizvi, Dr. E. P. Nguyen, M. D. Kowal, W. H. Mak, Prof. R. B. Kaner Department of Chemistry and Biochemistry UCLA

607 Charles E. Young Drive East, Box 951569

Los Angeles, CA 90095, USA

E-mail: reza.rizvi@utoledo.edu; kaner@chem.ucla.edu Prof. R. Rizvi, Dr. S. Rasel, M. A. Islam, Dr. A. Abdelaal Department of Mechanical Industrial and Manufacturing Engineering University of Toledo

2801 W. Bancroft St, MS312, Toledo, OH 43606, USA

Dr. E. P. Nguyen School of Electrical and Computer Engineering RMIT University GPO Box 2476, Melbourne, VIC 3001, Australia

A. S. Joshi, Dr. S. Zekriardehani, Prof. M. R. Coleman Polymer Institute Department of Chemical Engineering University of Toledo 2801 W. Bancroft St., MS 401, Toledo, OH 43606, USA

2801 W. Bancroft St., MIS 401, Toledo, OH 43606, USA

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201800200.

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The field of 2D layered materials has gained significant interest over the last few decades due to unique properties that manifest when a bulk material is reduced to its 2D form. Layered materials that have been widely researched include graphene, transition metal dichalcogenides such as molybdenum disulfide (MoS<sub>2</sub>) and tungsten disulfide (WS2), and hexagonal boron nitride (BN). Their unique properties can include high mechanical strength,<sup>[1]</sup> high electrical and thermal conductivities,<sup>[2]</sup> high surface areas,<sup>[3]</sup> and exotic quantummechanical effects.<sup>[4]</sup> However, these properties are often dependent on the lattice structure and quality of the material, and the number of layers isolated.<sup>[5]</sup> As such, the past decade has seen tremendous research efforts on methods to synthesize and exfoliate high quality 2D materials, while optimizing yields and reducing costs and processing times.

The preparation of 2D materials can be categorized by either a bottom-up or a top-down approach.<sup>[6]</sup> The bottom-up

method, as the name suggests, constructs or "puts together" the 2D material from various chemical precursors or sources onto a substrate. Here common methods include chemical and physical vapor deposition. By contrast, the top-down approach focuses on separating or "exfoliating" a bulk 2D material into individual or few layers. This approach is usually favored in certain applications—such as nanocomposites, energy storage, printable electronic inks, etc.—over bottom-up methods because of the higher throughput and hence, scalability. This includes methods such as ion intercalation,<sup>[7]</sup> liquid phase exfoliation,<sup>[8]</sup> micromechanical cleavage<sup>[9]</sup> (i.e., the Scotch tape method), mechanical attrition (e.g., milling),<sup>[10]</sup> electrochemical exfoliation,<sup>[11]</sup> and the commonly used Hummer's method for oxidizing graphite,<sup>[12]</sup> which can then be used for the large scale production of reduced graphene oxide.

The liquid phase exfoliation techniques can be loosely classified into two categories based on the underlying deformation mechanism causing layer separation: 1) sonication, which causes cavitation and 2) shear-based liquid phase exfoliation. In the sonication methods,<sup>[13]</sup> an ultrasonic transducer is used to induce unstable cavitation bubbles in a liquid medium, which



upon their inevitable collapse emanate a shock (pressure) wave. The energy of this shockwave is sufficient to fragment nearby bulk 2D layered powders into smaller lengths as well as thicknesses along the weak, secondary bonded *c*-axis. The presence of surfactants and other stabilizers helps match the surface tensions<sup>[14]</sup> of the exfoliated particles to those of the liquid medium thereby stabilizing the colloidal suspension for any further end-use applications. By contrast, the recently introduced shear-based liquid phase exfoliation techniques rely on the viscous deformation of liquids to generate large velocity gradients (shear rates) that assist in layer separation. This was successfully demonstrated in a rotary mixing process by Paton et al.,<sup>[15]</sup> where a critical shear rate of 10<sup>4</sup> s<sup>-1</sup> was found necessary for layer separation. Such shear rates can be attained in certain rotary mixers where rotor-stator gaps are on the order of 100 µm. This was followed up with other studies<sup>[16]</sup> where high shear rates in common mixers and household blenders along with surfactants were used to exfoliate 2D layered materials, demonstrating the versatility of this simple technique. However, the scalability and the economic feasibility of these techniques are questionable as these time-based, batch treatments require large volumes of liquids and extensive size separation postprocessing to get 2D nanomaterial yields on the order of a few percent (1-5%). Recently, nonrotary, highspeed liquid flow through narrow channels has been shown to generate sufficient shear rates to cause exfoliation of graphite. Arao et al.<sup>[17]</sup> used a high-pressure homogenizer with a 10 µm laminar flow channel to generate high shear rates ( $\approx 10^6 \text{ s}^{-1}$ ) which were sufficient to exfoliate graphite (thickness = 4 nm) in the presence of surfactants. Karagiannidis et al.<sup>[18]</sup> demonstrated that extended time microfluidization under turbulent flow conditions with high shear rates ( $\approx 10^8 \text{ s}^{-1}$ ) results in a  $\approx 100\%$ yield (i.e., no need for size separation) of graphite nanoplatelets (thickness = 12 nm). The process required passing surfactant stabilized liquid suspensions of graphite through small orifices (100 µm) using high pressures (up to 200 MPa) for repeated cycles (up to 100 cycles). The process's advantages of impressive yields and no requirements for size separation are offset by the time-based cycling, the use of surface-property modifying surfactants, and a wide size distribution of the final product. A significant inconsistency in shear-based liquid exfoliation studies is the inability to rule out the possibility of cavitation occurring in areas of low pressure during high-speed turbulent flows. Instead, they have the tendency to ascribe the exfoliation to pure shear acting on the 2D materials resulting in adjacent layers sliding relative to one-another due to the self-lubricity property of 2D materials. Paton et al.<sup>[15]</sup> demonstrated the exfoliation of graphite in a rotating Couette arrangement (100 µm gap) where the only influencing factor seemed to be the cylinder rotational speed (shear rate). At first glance, the likelihood of unstable flow causing cavitation in this parallel plate arrangement with a low Reynolds number of 64-128 would appear slim, since the flow is assumed to be laminar. However, even by the authors own admission, this assumption may not be well grounded, since Couette flows are known to transition into secondary flows (mixed laminar-turbulent) well below their critical Reynolds numbers.<sup>[19]</sup> Arao et al.<sup>[17]</sup> acknowledge the presence of some cavitation in their experiments but rule it out within the 10 µm gap channel-where exfoliation is assumed

to occur-because of the assumption of laminar state of flow. Joseph<sup>[20]</sup> succinctly describes cavitation to be caused by an extensional fracture of a liquid at a particular principle normal stress, which is proportional to the applied shear rate. Additionally, Furukawa and Tanaka<sup>[21]</sup> have shown that beyond a certain critical shear rate, the density dependence of viscosity in most Newtonian fluids can lead to a violation of the incompressibility criterion and cause cavitation. It stands to reason, based on the work of Joseph and later by Furukawa and Tanaka, that onset of flow instability and cavitation cannot be ignored in shear-based liquid phase exfoliations of 2D materials, particularly at high shear rates (>10<sup>4</sup> s<sup>-1</sup>) and within confined geometries. This absence of dialogue on the contribution of cavitation, which is omnipresent in high-speed liquid turbulent flows, is a major gap in our knowledge of scalable top-down nanomanufacturing of 2D materials.

A collection of top-down techniques that are gaining considerable traction recently involve exfoliation using a supercritical fluid gaseous medium. The majority of gas-phase exfoliation studies thus far have used supercritical  $CO_2$  (sCO<sub>2</sub>) as the gaseous medium, although other substances such as water vapor and ethanol can also be used. The approach here is motivated by the logic that sCO<sub>2</sub> is a low-surface-tension fluid with a high, liquid like density, thus among liquid solvents it should be most apt for diffusing into the 2D layered materials. Perhaps one of the earliest demonstrations of the exfoliating ability of high-pressure sCO<sub>2</sub> was by Pu et al.<sup>[22]</sup> in 2009, where a timebased treatment of sCO2 was carried out on graphite before venting the products into a sodium dodecyl sulfate surfactant solution. Since then, there have been several studies into supercritical gas phase exfoliation of 2D layered materials, with two preferred methods emerging. The first approach is to combine various chemicals/surfactants with supercritical fluids to assist with the layer separation.<sup>[23]</sup> The second approach is to combine some type of mechanical agitation, either in the form of ultrasonication<sup>[24]</sup> or high-speed shear,<sup>[25]</sup> to assist in the breakup of the bulk 2D crystals. A recent review of supercritical fluid exfoliation of graphite<sup>[26]</sup> accurately captures the state of the emerging research landscape.

Apart from supercritical fluids, there have been very few investigations into the potential of other gaseous substances for exfoliating 2D layered materials. A patent by Jang et al.<sup>[27]</sup> describes a batch processing method where a pressure vessel containing 2D layered materials (graphite) is pressurized by various gases, such as hydrogen, helium, argon, carbon dioxide, and water vapor. It is expected that high pressures and high temperatures will improve the driving force for diffusion of gas molecules in between the layers of the 2D bulk crystals. Afterward, the pressure is rapidly released to cause the gas molecules in between the layers to expand and separate the layers. Unfortunately, the authors used data for electrochemically driven lithium-ion diffusion in graphite<sup>[28]</sup> and incorrectly applied it to support their hypothesis for gas molecule diffusion occurring within 2D material layers. It should be pointed out that the kinetic diameter of gases is more than 3 times the ionic radius of lithium.

It is important to realize that all gas phase processes to our knowledge require bulk processing with many<sup>[22,24,29]</sup> expecting that gas intercalation, being a diffusion problem, will require a







Figure 1. a) Process schematic of the compressible flow exfoliation setup including a description of the critical components and the initial and final structures of the BN powder. b) Still images of the collection vessel before, during, and after the CFE process for BN powder. c) Exfoliated suspensions of various 2D layered nanomaterials after centrifugation.

certain minimum time to reach completion. Furthermore, once gas diffusion is complete there is the perception that some time-based stimulus in the form of mechanical agitation/shear, ultrasound, or surfactant uptake is required to disturb the layered crystals. However, the initial premise of gas intercalation within 2D materials is highly improbable because of the large kinetic diameters of gases compared to the available interlayer spacing. For instance, the kinetic diameters of He and CO<sub>2</sub> are 2.6 and 3.3 Å, respectively,<sup>[30]</sup> whereas the interlayer spacing in graphite is only 3.35 Å.<sup>[31]</sup> A detailed study by Walker et al.<sup>[32]</sup> of graphite subject to atmospheres of multiple gases at various temperatures found no evidence of any changes to interlayer distances and gaseous penetration.

In a fitting merger of shear-based liquid phase exfoliation and supercritical gas treatment, here we demonstrate the continuous, high-throughput production of exfoliated 2D materials caused by shear due to high velocity flows of compressible gases. In our compressible flow exfoliation (CFE) process, 2D layered materials are rapidly jettisoned (Figure 1a,b) through a small orifice using high-pressure gases without the need for any time-based treatment, unlike other shear-based and gas processes. Shear-based exfoliation occurs due to the high velocities that expanding and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate ( $\dot{\gamma} \ge 10^5 \text{ s}^{-1}$ ) experienced by the 2D layered particles. We demonstrate the versatility of our method by applying this technique to exfoliate different 2D layered material (Figure 1c) as well as demonstrate that our method works, irrespective of the carrier fluid used. Our results indicate that shear is an inadvertent exfoliation mechanism in many reported supercritical fluid methods of producing graphene and other 2D layered nanomaterials.

Our method of CFE is capable of creating very fine colloidal suspensions of various 2D layered materials. Some samples of sprayed dispersions achieved after centrifugation are shown in Figure 1c for boron nitride, few-layer graphene (FLG), and molybdenum disulfide. All solutions were processed using CFE with helium at 14 MPa as the carrier gas flowing through a 0.1 mm gap annular orifice (1/4 turn open Swagelok valve), although other flow geometries, gases, and pressures conditions are possible as detailed below. To demonstrate the fast nature of our CFE process, similar suspensions were made using the popular liquid phase exfoliation (LPE) method by bath sonicating the same initial concentration for 3 h. The details for both the CFE and LPE processes are provided in the Experimental Section (Supporting Information). The CFE process was able to achieve high concentrations of colloidal 2D layered particles after the centrifugation process, as indicated by the extensive laser light scattering through the solution known as the Tyndall effect.<sup>[33]</sup> UV-Vis light scattering profiles for BN are shown in Figure 2a indicating that suspensions created through the CFE process are able to absorb significantly more light across a wide spectrum of wavelengths, when compared to the popular LPE method produced using bath sonication. It is important to note that the results of both techniques, CFE and LPE, are reported here without the use of surfactants or other surface energy modifying chemistries, which could result in higher concentrations but at the expense of deteriorating 2D material interface properties.<sup>[34]</sup> The results for the exfoliation of other layers compounds including graphite and molybdenum disulfide are shown in Figure S2 (Supporting Information).

Using literature standards for each of the three different 2D layered materials, we have compared the absorption at reference wavelengths and computed the concentrations of the suspensions through the Beer–Lambert law:  $A/l = \alpha C$ , which states that the light absorption, A, in a medium over a certain distance, l, is proportional to the concentration of the absorbing particles, C. The proportionality term is the extinction coefficient,  $\alpha$ , which is specific to a particular 2D layered material, solvent, and wavelength. The characteristics of our dispersions mimicked the reference conditions,<sup>[8,13]</sup> and hence,







**Figure 2.** The a) UV–Vis and b) Raman spectra for BN produced using continuous flow exfoliation (CFE) and the comparable liquid phase exfoliation technique. c) The AFM scan image of a BN flake isolated after CFE with insets showing the height profile of the flake and the thickness distribution of several flakes. d) The TEM images (scale bar: 800 nm) for various 2D materials produced by CFE along with their diffraction patterns (inset) at the marked spot—shown here are BN (left), graphite (middle), and MoS<sub>2</sub> (right).

the wavelength specific extinction coefficient available in the literature could be used for concentration analysis by UV–Vis. Furthermore, the exact concentrations were obtained using gravimetric measurements and are in good agreement with the concentrations found using UV–Vis light scattering (mean error  $\leq$  5%). Under the same conditions, our method of CFE achieved concentrations of 0.075, 0.028, and 0.026 mg mL<sup>-1</sup> for BN, graphite, and MoS<sub>2</sub>, respectively. These values are comparable to or much better than the control values obtained using liquid phase exfoliation of 0.004, 0.020, and 0.008 mg mL<sup>-1</sup> for BN, graphite, and MoS<sub>2</sub>, respectively.

The few-layer nature of the final product after CFE processing and centrifugal separation was evident through Raman spectroscopy analysis of drop-cast 2D layer flakes. Figure 2b illustrates the Raman emission intensity spectra obtained using a 633 nm laser excitation in the relevant bandwidths for BN, while Figure S3 (Supporting Information) includes the spectra of graphite and MoS<sub>2</sub>. Comparison of the spectral emissions for all three 2D layered materials suggests a significant reduction in the number of layers, when compared with reference information available in the literature. The bulk form of boron nitride exhibits a spectrum consisting of one prominent  $E_{2\sigma}$ phonon mode emission peak at 1366 cm<sup>-1.[35]</sup> The emission peak undergoes a gradual redshift to 1362-1364 cm<sup>-1</sup> as the number of layers is reduced to bilayer or few-layer. Finally, when monolayer BN is obtained, its emission peak is significantly blue-shifted to 1369 cm<sup>-1</sup>, which is quite distinct from its bulk emission spectrum. Examination of the acquired Raman spectrum (Figure 2b) for boron nitride processed using CFE indicates a significant redshift of the peak to 1362 cm<sup>-1</sup> suggesting a substantial presence of few-layer and bi-layer BN after processing. By contrast, the LPE processed control did not exhibit significant peak shifting indicating that the structure still consists of many stacked layers similar to bulk BN.

The Raman spectrum for bulk graphite (Figure S3b, Supporting Information), between the wavenumbers of 1500-3000 cm<sup>-1</sup> exhibits, two characteristic peaks; the G peak occurring at 1580 cm<sup>-1</sup>, which is the primary in-plane vibrational mode  $(E_{2\alpha})$ ,<sup>[36]</sup> and the 2D peak occurring at 2690 cm<sup>-1</sup>. Several differences exist between the Raman spectra of bulk graphite and single layer graphene,<sup>[36a]</sup> with the most noticeable being i) the increase in intensity (doubling) of the 2D peak when compared to the G peak, ii) the redshift of the 2D peak, iii) symmetric ordering of the 2D peak, and iv) the reduction of the full-width half maximum (FWHM) width of the 2D peak. Although all of these conditions are necessary to ascertain the presence of monolayer graphene, they may not all be present when analyzing few-layer graphene, or scans of a distribution of graphene with varying layer thicknesses.<sup>[8]</sup> A comparison of the Raman spectra for both CFE and LPE processed specimens against the spectrum for bulk graphite indicates two main differences; a significant redshift of  $\approx 8$  cm<sup>-1</sup>, and an increased symmetry of the 2D peak. It should be mentioned that a narrow symmetric peak is exclusive to monolayer graphene, however, the observation here of a wide symmetric peak (FWHM: 75 cm<sup>-1</sup>) indicates the likely occurrence of AB-stacking disorder (turbostratic graphene) due to restacking or folding of sheets.<sup>[37]</sup> Taken together, these two observations from the Raman spectra indicate, at the very least, a reduction in layer number thickness from bulk graphite powder after being processed by either continuous CFE process or the batch LPE process. The occurrence of a disorder-activated D peak at 1330 cm<sup>-1</sup> is indicative of defects, in particular those, which disrupt the sp<sup>2</sup> hybridization. Such defects can be interpreted to be either creation of

ADVANCED MATERIALS

new edges, vacancies, or substitutions (doping and functionalization), with the ratio between the peak intensities of the D to G peaks ( $I_D/I_G$ ) providing some limited indication of their population.<sup>[36a]</sup> It can be seen from Figure S3b (Supporting Information) that CFE processed graphite has the same D to G peak intensity ratios ( $I_D/I_G \approx 0.5$ ) while the LPE processed materials had a significantly higher peak ratio of 1.1 indicating a higher likelihood of sp<sup>2</sup> hybridization disruption due to LPE processing. Such defects could be present because of sonication at extended times, which can result in new edge formations from particle size reduction as well as point defect generation including oxidation.

The spectra for bulk MoS<sub>2</sub> before and after CFE and LPE processing are shown in Figure S3c (Supporting Information). Bulk MoS<sub>2</sub> exhibits two strong first order peaks,  $E_{2g}^1$  and  $A_{1g}$ , whose relative positions strongly correlate with the number of layers present.<sup>[38]</sup> The peak-to-peak wavenumber distance between the two first order peaks is  $\approx 26 \text{ cm}^{-1}$  for a 633 nm excitation source. Upon subsequent exfoliation to few-layer and to single-layer MoS<sub>2</sub>, the peak-to-peak distance gradually reduces to as little as 19 cm<sup>-1</sup>. The MoS<sub>2</sub> processed using CFE in this study has an  $E_{2g}^1$  and  $A_{1g}$  peak-to-peak distance of 22.8 cm<sup>-1</sup>, which according to a detailed description of MoS<sub>2</sub> Raman signatures by Li et al.<sup>[39]</sup> corresponds to a 3-4 layer thickness of the particles. The MoS<sub>2</sub> processed using the LPE technique also undergoes layer thickness reduction, albeit with weaker effect. as indicated by a peak-to-peak separation of 24.0 cm<sup>-1</sup>, which corresponds to a thickness of 4 or more layers.<sup>[39]</sup>

The structure of BN nanoparticles was characterized by atomic force microscopy (AFM) after CFE processing with a representative flake shown in Figure 2c. The flake exhibits a thickness of 2 nm and a width of 350 nm, giving an aspect ratio of 175. At an interlayer spacing of 0.32 nm,<sup>[40]</sup> a thickness of 2 nm corresponds to 6 layers of BN that were isolated. Further AFM characterization of additional BN particles reveals a distribution of particle thicknesses (Figure 2c, inset) and lengths (Figure S4, Supporting Information) when subject to the CFE process. Typically, higher driving pressures in CFE result in better flake quality. For instance, BN produced using He gas at 5.5 MPa (Figure S4a, Supporting Information) have an average flake thickness of 5.7 nm and length of 160 nm, giving an aspect ratio of 28, while at a pressure of 10 MPa (Figure S4b, Supporting Information) the flake thickness and length were 4.2 and 276 nm, corresponding to an aspect ratio of 66. Furthermore,  $\approx$ 27% of the flakes processed at 5.5 MPa had a thickness less than 3.2 nm (corresponding to 10 layers or less) with this proportion increasing to 43% at a higher pressure of 10 MPa.

The structures of CFE processed BN, FLG, and MoS<sub>2</sub>, as imaged by transmission electron microscopy (TEM), are shown in Figure 2d. The size of these particles typically ranges from 100 to 800 nm indicating a reduction of particle size compared to the starting particle sizes of 13  $\mu$ m for BN and 1  $\mu$ m for graphite and MoS<sub>2</sub>. These particles are sufficiently thin after exfoliation, as indicated by their electron-transparency. Furthermore, some flakes appear to be single crystals, while others appear polycrystalline on the basis of their electron diffraction patterns (Figure 2d, insets). The polycrystallinity is indicative of basal plane rearrangement (turbostraticity), further evidence for which is found in the Moiré patterns occasionally observed during TEM of BN (Figure S5, Supporting Information). Similar Moiré imaging projections have been observed during restacking of planes when drying from suspension,<sup>[41]</sup> or from the mechanical folding and shifting of individual planes during shear processing.<sup>[42]</sup> Further TEM images of CFE processed 2D nanomaterials are provided in Figure S6 (Supporting Information) along with their LPE counterparts. Clear differences in the shape and surface topology characteristics between the two processes are evident such as straighter edges in CFE processed BN (Figure S6a, Supporting Information), compared to LPE processed BN (Figure S6d, Supporting Information), which consists of more rounded out edges. Furthermore, CFE processed 2D layered materials contain fewer residual small particle debris compared to the LPE processed particles, which we attribute to the harsher conditions experienced during ultrasonication for extended times in LPE processing. Ultrasonication for extended times (hours, days) has been known to cause structural damage, in particular particle size reduction, of many nanomaterials including carbon nanotubes and 2D layered materials such as graphene,<sup>[43]</sup> BN,<sup>[44]</sup> and MoS<sub>2</sub>.<sup>[45]</sup> Residual small particle debris with sizes less than 50 nm are quite prominent in the particles processed using LPE, whereas their CFE equivalents are nearly void of such small-scale residuals. Furthermore, despite some restacking and visual aggregation, the CFE processed suspensions are for the most part still stable after 6 months of storage (Figure S6g, Supporting Information).

The material characterization results presented thus far indicate that CFE is equal to or better than the comparable topdown technique of LPE in terms of 2D nanomaterial concentrations, layer thickness, and structural defects. In regards to processing, the advantages of CFE over LPE include the rapid, high-throughput and continuous nature of the process as well as the use of environmentally friendly gasses instead of handling potentially hazardous solvents in LPE. In contrast to the time-based treatment in ultrasound and shear based LPE processes, the CFE process works with a rapid, single pass of the 2D layered materials through a fine nozzle/orifice. Recently, a microfluidization technique<sup>[18]</sup> that forces surfactant suspended graphite in an incompressible liquid through a fine orifice at high pressures was shown to be effective at creating 2D nanosheets of graphite. The process required an intensifier pump and multiple passes through the orifice in order to achieve a 100% yield. Although no postprocess centrifugation was required, the technique is still time dependent and required the use of surfactants, which can be detrimental to the interfacial properties of 2D materials. Similar to several existing top-down processes, both CFE and microfluidization rely on imparting shear forces on the particles to cause layer separation. However, to our knowledge CFE is the only process that utilizes the stored potential energy in high pressure compressed gases to achieve supersonic velocities that generate the shear required for layer separation, while simultaneously utilizing the gas phase for suspending the exfoliated particles during the brief process.

A series of controlled experiments (**Figure 3**) were performed to quantify the effect of various process parameters such as the upstream gas pressure, starting BN amount, process time, gas type, and flow geometry. Initial experiments were carried out using a Swagelok needle valve partially opened at a 1/4 turn to







**Figure 3.** a–d) Plots showing the effects of initial BN concentration (a), upstream gas pressure (b), flow geometry (tube diameter) (c), and carrier gas type (d) on the final BN concentration and yield in CFE. All error bars represent the standard deviation (n = 3).

create an annular gap of  $\approx 0.1$  mm along with a converging portion just before the gap and a diverging portion right after the gap (Figure S7, Supporting Information). Other valve settings were experimented with as well, with larger openings giving lower process yields due to insufficient shear, while smaller openings resulted in the valve being clogged and the complete restriction of flow. Experiments with flow through constant area stainless steel channels (30 cm length) with varying inner diameters (1.3, 2.1, 3.1, 3.8, and 4.6 mm) were also performed to clarify the role of shear during CFE processing. The effect of the amount of starting bulk 2D material on the final 2D nanomaterial concentration obtained is shown in Figure 3a. The initial concentration is defined as the ratio of BN powder fed into the gas flow to the volume of liquid solvent that it sprays into after the CFE process is complete. The final concentrations are based on gravimetric measurements after centrifuging and careful drying. Regardless of the flow geometry (valve or tube), an increase in the initial concentration results in a concomitant rise in the final concentration with only 2 s of process run time. However, this effect is limited at higher BN loading amounts, particularly for the valve, where the flow is restricted because of clogging from the highly packed BN powder. The ratio between the final and initial concentrations in Figure 3a can be interpreted as the yield of the process, which for CFE is between 5 and 10%. This yield is comparable, if not better than most liquid phase processes that do not rely on surfactants or surface functionalization<sup>[13]</sup> (a comparison is provided in Table S1, Supporting Information). As can be seen from Table S1 (Supporting Information), the CFE method, detailed here, is able to exfoliate in a matter of seconds (2 s), as opposed to several minutes or hours required in other comparable processes. Furthermore, if this process is run continuously then the yield can be driven up further through material recovery and recycling.

The effect of the stagnant upstream pressure on the final concentration is detailed in Figure 3b. Expansion of the compressed

gas, at this stagnant upstream pressure, through a fine orifice is responsible for the high velocities required to shear the suspended 2D layered materials. Figure 3b shows this effect both for the needle valve, which has a varying geometrical configuration, and for straight tubes, which have a constant cross-section. Concentrations of 0.04 mg mL<sup>-1</sup> can be obtained at pressures as low as 1.4 MPa (200 psi)-which is within the operating pressures of many consumer-grade air compressors. When the BN powder feedstock is forced through the valve, increasing the pressure resulted in higher final concentrations of the BN nanomaterial, indicating gradually improved yields in the process. A maximum concentration of 0.2 mg mL<sup>-1</sup> is achieved at the maximum pressure (11 MPa) tested. Continuous operations at such high pressures, however, would bring into consideration safety and economic concerns that would have to be addressed in any future industrial implementation of the CFE process. By contrast, when forced through a straight tube, the final concentration initially increases and then plateaus at 0.11 mg mL<sup>-1</sup> for pressures of 5.5 MPa or more. This plateau behavior of final concentration versus pressure at high pressures was observed for all straight tube configurations, albeit at varying final concentrations.

The effect of varying inner diameters on the final concentration for the straight tube flow configuration at 5.5 MPa is shown in Figure 3c. As the tube diameter is increased, there is a rapid increase in the final concentration peaking at 0.11 mg mL<sup>-1</sup> at a diameter of 2.1 mm followed by a gradual decrease. Smaller tube diameters of 0.5 and 0.1 mm were also tested, but they significantly impeded the flow at the applied pressures. The final series of experiments investigated the effect of various gases used in CFE with the results summarized in Figure 3d. Helium, nitrogen, and carbon dioxide at a common pressure of 5.5 MPa through both valve and straight tube configurations were tested. The final concentrations using helium flowing through the valve were significantly better (0.15 mg mL<sup>-1</sup>) than nitrogen (0.03 mg mL<sup>-1</sup>) and carbon dioxide (0.03 mg mL<sup>-1</sup>). A similar



Figure 4. CFD simulation results showing: a) a surface plot of velocity variations, b) a surface plot of shear rate variations near the throat, and c) a line scan profile of the shear rates at the minimum cross-section (red line in Figure 4b). The simulation conditions are for BN particles in helium gas at an upstream pressure of 5.5 MPa and a gap of 0.1 mm.

trend was observed for the straight tube configuration. Other carrier gases such as argon, a heavier monatomic gas, and compressed air, a gaseous mixture, had similar results as nitrogen and were significantly lower than those obtained using helium.

It is well known that within certain pressure differentials, compressible fluids passing through a converging–diverging channel achieve supersonic velocities governed by a differential relation based on the conservation of mass and momentum<sup>[46]</sup>

$$\frac{\mathrm{d}V}{V} \Big[ M^2 - 1 \Big] = \frac{\mathrm{d}A}{A} \tag{1}$$

where dV/V is the fluids relative change in instantaneous velocity (V), dA/A is the relative change in the flow channel's instantaneous area, and M is the fluid's Mach number, defined as its velocity V relative to the velocity of the speed of sound,  $V_{\rm s}$ . Specifically, the average flow velocity in the narrowest portion (the "throat") of the channel (dA/A = 0) is equal to the speed of sound in that fluid. Depending on the design of the channel exit (diverging portion), it can achieve even higher velocities (supersonic) after leaving the throat. This increase in velocity is concomitant with a rapid pressure drop (flow expansion) in the diverging portion of the CD nozzle. Using this simple picture of supersonic compressible flows and the assistance of computational fluid dynamics (CFD), we can examine in detail the geometry specific nature of the flow through a partially open needle valve and elucidate the mechanisms responsible for the observed exfoliation of 2D nanomaterials. CFD

simulations were performed in COMSOL Multiphysics v5.3 (High Mach Number-Fluid Physics Model) with the 2D geometry modeled (Figure S7, Supporting Information) using CAD software as per the supplier's dimension of the needle valve. Typical results of flow simulations are shown in Figure 4, which describes the case of helium gas at 5.5 MPa flowing through the partially open needle valve (0.1 mm gap). The velocity surface plots (Figure 4a) demonstrate that the valve acts as an adjustable converging-diverging nozzle capable of achieving supersonic flows within the pressure range of interest. The surface plots indicate significant regions after the throat of the nozzle where the velocities exceed 1600 m s<sup>-1</sup>, corresponding to Mach 1.6 (the speed of sound in helium at room temperature is  $\approx 1000 \text{ m s}^{-1}$ ). Other regions of high Mach flow are also present in the valve; however, the primary region of interest is the throat portion where rapid changes in velocities occur within small flow cross-sections. These changes in velocities, V, can be understood through its spatial gradient, the shear rate,  $\dot{\gamma}$ , defined as  $\dot{\gamma} = \partial V / \partial x$ , which for the simulated flow is plotted in Figure 4b. This surface plot indicates that shear rates in excess of 10<sup>5</sup> s<sup>-1</sup> are easily achieved for rapidly accelerating flows through a fine CD-nozzle. A line scan profile (Figure 4c) along the throat portion of the nozzle (red line in Figure 4b) indicates that the shear rate starts out highest near the wall at  $4 \times 10^5$  s<sup>-1</sup>, before rapidly decreasing to  $1 \times 10^5$  s<sup>-1</sup> and then gradually rising again to  $3 \times 10^5$  s<sup>-1</sup>. This skewed profile of the shear rate along the throat is attributed to the asymmetric channel profile. Regardless, it can be seen that the entire flow,

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including suspended BN and other 2D layered particles, is subject to shear rates in excess of 10<sup>5</sup> s<sup>-1</sup>. This key observation is a link between the exfoliation results using compressible gases in CFE to the shear dominated exfoliation mechanisms utilized in other liquid-based top-down 2D nanomaterial production processes.<sup>[15-18]</sup> The instantaneous changes in momentum acting on the suspended 2D particles in a multiphase gas flow subject to such shear rates would significantly alter the kinetic energy of the particles, some of which would be dissipated as work done toward overcoming the secondary *c*-axis bonds of the 2D layered materials. The layer shear mechanism involved in CFE is equivalent to that observed in liquid phase exfoliation by highspeed shearing.<sup>[15]</sup> In this comparable method, effective exfoliation of 2D nanomaterials occurs provided that the shear-rates are higher than a critical value of  $10^4$  s<sup>-1</sup> and that the material is subjected to that shear-rate (i.e., cycled) for a sufficient amount of time. In the present CFE process, the 2D layered materials are easily subject to shear rates higher than 10<sup>5</sup> s<sup>-1</sup> and make only one pass through the nozzle with a very small residence time thus making it a continuous, high-throughput operation.

Other conditions, representative of the valve experiments in Figure 3b, but at various pressures, were simulated in CFD (Figures S8 and S9, Supporting Information) to provide insights into the shear rates developed in supersonic flows through fine orifices. It can be seen that the shear rate distribution in the valve evolves as the pressure is increased from 1.4 to 2.8 and 5.5 MPa while remaining more or less steady at 14 MPa. At low pressures, areas of high shear ( $\dot{\gamma} > 10^4 \text{ s}^{-1}$ ) exist only near the wall in the diverging portion of the CD nozzle inside the valve. As the upstream pressure driving the flow is doubled to 2.8 MPa, shear rates of 10<sup>5</sup> s<sup>-1</sup> or greater are experienced throughout the CD nozzle. Further doubling of the pressure to 5.5 MPa (Figure S9c, Supporting Information) causes the regions of high shear ( $\dot{\gamma} > 10^5 \text{ s}^{-1}$ ) to further enlarge. Raising the pressure beyond 5.5 MPa did not significantly change the distribution and magnitude of the high shear zones inside the valve. The evolution of the shear zones as predicted by the simulations can be directly correlated with the experimentally observed dependence of the final concentration on the upstream pressure (Figure 3b). The final concentration more than triples from 0.04 to 0.15 mg mL<sup>-1</sup> as the pressure is increased from 1.4 MPa to 5.5 MPa, after which it slowly increases to 0.2 mg mL<sup>-1</sup> at 11 MPa.

It is important to point out that supersonic flows and changing area profiles may not be a necessary requirement in CFE. Rather, the shear rate, which is related to the overall flow velocity and the flow channel width, is of considerable importance. The advantage of using gases for shearing 2D layered materials is their inherent compressibility, which can be utilized to accelerate to and decelerate from high velocities across short distances, thereby imparting a high shear rate on any suspended solids including 2D materials. Perhaps the most straightforward demonstration of this effect is the straight tube experimental results of Figure 3b,c. The flow profiles in these experiments are within the consideration of Fanno flow, which describes the adiabatic expansion of a compressible gas inside a constant area duct with a known friction factor.<sup>[46]</sup> For considerably long ducts, gas expansion during flow causes maxima in the mass flow rate and a state of choked flow exists where the flow velocity reaches the speed of sound (Mach 1). Once choked flow is achieved, no further increase in the upstream pressure will cause faster velocities. This understanding of Fanno flow correlates well with the achieved final concentrations in Figure 3b for straight tubes, which become invariant with pressures of 5.5 MPa and higher. Despite the doubling of pressure, velocities faster than the speed of sound are unattainable in these straight tubes and hence the maximum shear rate and shear rate distribution experienced by the multiphase flow remains unchanged.

Aside from velocity, the shear rate experienced by the flow is dependent on channel width considerations. Assuming friction effects at the wall (no-slip condition), the shear rate should be highest at the walls and lower at the center of the flow. Complicating this simple explanation is the consideration of turbulent flows, as in the case here, where analytical expressions of velocity and shear rate profiles are nonexistent. The Reynolds number, characterizing the laminar-turbulent flow classification based on the fluid's velocity, V, channel diameter, D and the fluid's kinematic viscosity, v is given by the relation: Re = VD / v.<sup>[46]</sup> For the case of helium at Mach 1 through a 2.1 mm channel, the Reynolds number is 18 000, which is well above the turbulentlaminar flow boundary (Re = 2300). Thus, in addition to wall friction, a further contribution to the high shear rates experienced in turbulent flows comes from the sudden, erratic changes in the local velocity profile arising from the stochastic generation of eddies. These changes in velocity over a short span would give rise to the high shear rates experienced in the centerline of the flow profile (e.g., Figure 4c). In the straight tube experiments, the channel width has an effect in imparting shear on the 2D layered materials, and hence, on the final concentration achieved. It is evident from Figure 3c that reducing the tube diameter from a starting value of 4.6 mm tends to improve the final concentration, and hence, the overall yield of the CFE process. This effect can be explained in terms of shear rate where a reducing tube diameter at the same velocity will impart greater shear rates on the flow because of an increased fraction of the wall (zone of high shear rate) relative to the overall flow cross-section. Almost halving the tube diameter from 4.6 to 2.1 mm has the effect of increasing the concentration to 0.11 mg mL<sup>-1</sup>-an improvement by a factor of 5.4 times. However, further reduction of the tube diameter to 1.3 mm has the unintended effect of severely decreasing the concentration to 0.045 mg mL<sup>-1</sup>. At this diameter, the flow did not achieve the choked condition as per Fanno flow and it was audibly apparent that the exit flow velocities were considerably less than Mach 1. Friction effects tend to dominate at smaller tube diameters resulting in considerably lower flow velocities and hence shear rates. For instance, changing the tube diameter from 2.1 to 1.3 mm for helium flowing at Mach 1 increases the friction factor from 0.028 to 0.035, as per the Moody-Colebrook relationship.<sup>[46]</sup> In addition to wall friction, the reduced diameter lowers the Reynolds number from 18 000 to 11 000, thus reducing the turbulent nature of the flow and the effectiveness of eddies to generate high shear rates.

Perhaps the most convincing demonstration of the compressible gas dynamic principles at work in the CFE process is by varying the carrier gas. This was experimentally observed and is summarized in Figure 3d, which shows that the final concentration obtained by helium is almost 5 times better than those using nitrogen or carbon dioxide in both straight tube and valve



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(CD nozzle) configurations. At 293 K, the speed of sound in helium is roughly 1000 m s<sup>-1</sup>, while nitrogen and carbon dioxide are considerably lower at 350 and 270 m s<sup>-1</sup>, respectively. Provided choked flow (Mach 1) is achieved for these gases, helium being the lighter and faster gas imparts sufficiently higher shear rates than the other heavier gases. Hydrogen gas would serve as an even better medium for exfoliating 2D layered materials, since it is a lighter gas than helium, having a higher speed of sound (1270 m s<sup>-1</sup>), as well as being more abundant and cost-effective. However, safety considerations prevented us from evaluating high-pressure hydrogen in CFE processing of 2D layered materials.

To demonstrate the utility of our ultrafast compressible flow exfoliation method, we considered improving the barrier properties of poly(ethylene terephthalate) (PET) by reinforcing it with the exfoliated 2D layered nanomaterials. PET is commonly used for food and beverage packaging where the simultaneous requirements of high optical transparency and limiting oxygen transport have proven to be a technical challenge. Numerous inorganic compounds such as mineral particles,<sup>[47]</sup> nanoclays,<sup>[48]</sup> and 2D nanomaterials<sup>[49]</sup> have been investigated as a potential reinforcing phase to improve the oxygen barrier properties. However, most studies show significant improvements only at high inorganic volume content where the optical transparency as well as mechanical strength and ductility of PET become compromised. Other approaches such as using layer-by-layer fabrication<sup>[50]</sup> have proven to be useful for improving barrier properties at low inorganic volume content while maintaining decent optical transmissivity. However, these techniques are still far from being demonstrated for mass-production and so the scalability of such a layer-by-layer approach, especially for low-value consumer packaging applications, is questionable.

In the present application, concentrated suspensions of CFE-BN and bulk-BN powder were added to a powdered PET resin by evaporating the isopropanol in the presence of the resin followed by mixing in the melt phase at 265 °C (details in the Experimental Section) and extruding into continuous films. The melting temperature  $(T_m)$  and enthalpy of melting  $(\Delta H_m)$  of PET, as measured by a second differential scanning calorimetry (DSC) heat trace, was found to remain unchanged at 246 °C and 40 J  $g^{-1}$ , respectively, regardless of the type and amount of BN added (Table S2, Supporting Information). The addition of BN to PET did increase the apparent glass transition temperature of PET by ≈1.5–2 °C with no significant differences observed for the type of BN (CFE or bulk) or the amount (0.017 or 0.15 vol%). The PET composites show a crystallization peak during cooling that resulted in the disappearance of cold crystallization during the second heating trace (Figure S10, Supporting Information). While cooling from the melt (10 °C min<sup>-1</sup>), the crystallization peak for PET was at 198 °C, which increased to 207 °C for PET containing 0.017 and 0.15 vol% of CFE-BN. In comparison, the crystallization peak for bulk BN was at 203 and 206 °C for 0.017 and 0.15 vol%, respectively, indicating slower crystallization kinetics of the bulk BN particles compared to the exfoliated BN, which can be attributed to the heterogeneous nucleation effect of nanomaterials.<sup>[49,51]</sup> The final PET films were optically transparent (94% transmittance) and remained transparent (>90%) when 0.017 and 0.15 vol% of CFE-BN or bulk-BN powder were added (Figure 5a). The transmitted light when subject to



**Figure 5.** PET–BN nanocomposites prepared using CFE exfoliated and bulk boron nitrides at 0.017 and 0.15 vol% of boron nitride and their: a) visual light transmittance, b) tensile Young's modulus, and c) oxygen permeation rate (OPR) at 0.15 vol% BN. d) A tilted view of a freeze-fractured cross-section of PET–CFE-BN 0.15 vol% showing the protruded boron nitride particles (scale bar:  $10 \,\mu$ m). All errors represent the standard deviation (*n* = 3).





wide-angle scattering (>2.5° from normal) is defined as optical haze, and this was found to be smaller for the exfoliated 2D nanomaterials than the bulk BN nanomaterials (Table S3, Supporting Information).

At a low volume content of 0.017 vol% BN, there was no noticeable difference in the tensile Young's modulus of the PET films (888 MPa) for either the nanoparticles or the bulk particles (Figure 5b). Addition of 0.15 vol% CFE-BN resulted in an improvement in the modulus of PET by 21% to  $1072 \pm 15$  MPa. By contrast, the same amount of bulk-BN to PET resulted in only a 12% improvement in the modulus (993  $\pm$  55 MPa). No significant variations in PET's tensile strength and strain at failure were observed (Table S4, Supporting Information) for the type of BN (CFE or bulk) or the amount (0.017 or 0.15 vol%), which is likely due to the low amounts that were added. Prior to the oxygen permeation measurements, the PET and PET-BN films were biaxially stretched down to a 20 µm thickness at a low stretch speed and temperature (Supporting Information), where concerns surrounding strain induced crystallization can be neglected.<sup>[52]</sup> Similar to the mechanical properties, a low volume content (0.017 vol%) of either the CFE-BN or bulk-BN did not result in any change to PET's steady-state oxygen permeation rate (OPR), which was  $0.27 \pm 0.01$  cm<sup>3</sup> cm m<sup>-2</sup> d atm. Adding 0.15 vol% of the compressible flow exfoliated BN resulted in the OPR dropping by 26% to  $0.20 \pm 0.01$  cm<sup>3</sup> cm m<sup>-2</sup> d atm. Interestingly, the same amount of bulk-BN to PET caused the OPR to increase to  $0.37 \pm 0.08$  cm<sup>3</sup> cm m<sup>-2</sup> d atm, which would be detrimental to any barrier packaging applications. It is suspected that larger layered aggregates in the PET-bulk-BN films could have delaminated during the stretching phase to open up new low resistance pathways for permeation. An SEM image (Figure 5d) shows thin sheets of CFE-BN protruding out of a freeze-fractured surface of 0.15 vol% PET-BN nanocomposites, viewed at a tilt, indicating some dispersion of the BN nanoparticles. The significantly improved mechanical and barrier properties of the CFE-BN nanocomposites are attributed to the exfoliation of the layered BN particles into thin sheets, which can be easily dispersed and result in a more efficient load transfer across the polymer-particle interface as well as creating a more tortuous pathway for permeation.

Here we have introduced a new method-CFE-for exfoliating 2D layered materials by compressible fluids flowing through fine nozzles in a continuous manner. The underlying principle is based on accelerating multiphase flows of 2D layered materials suspended in a compressible media to supersonic velocities whereby sufficient shear rates ( $\dot{\gamma} > 10^5 \text{ s}^{-1}$ ) are generated to cause layer reduction and exfoliation. Using helium gas and boron nitride particles, the CFE process was able to create suspensions of 2D nanomaterials in isopropanol that have an average thickness of 4.2 nm, and an average length of 276 nm (aspect ratio  $\approx$  65). The CFE process is capable of exfoliating other 2D nanomaterials such as few-layer graphene and molybdenum disulfide, using a multitude of gases such as helium, nitrogen, or carbon dioxide. Apart from the high concentrations (0.2 mg mL<sup>-1</sup>) and yields (10%) achieved in a short duration, the advantages of CFE include the ability to isolate the exfoliation and suspension stabilization processes from each other, environmentally friendly processing and reduced occurrence of defects that might otherwise arise in comparable

liquid phase, time-based treatments. Nanocomposites produced using CFE processed boron nitride had significantly improved mechanical and barrier properties when used in the plastic PET compared to neat PET and bulk-BN counterparts, all the while preserving the optical properties. Using a continuous flow of compressible gasses for high-throughput 2D nanomaterials production could represent a paradigm shift in their economic feasibility for mass manufacturing.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

2D materials, boron nitride, compressible flow, exfoliation, graphene

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- [1] C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385.
- [2] a) A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* 2008, *8*, 902; b) K. I. Bolotin, K. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H. Stormer, *Solid State Commun.* 2008, 146, 351.
- [3] a) S. Stankovich, D. A. Dikin, G. H. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, *442*, 282; b) Y. Xu, Z. Lin, X. Zhong, X. Huang, N. O. Weiss, Y. Huang, X. Duan, *Nat. Commun.* **2014**, *5*, 4554.
- [4] a) Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, F. Wang, *Nature* 2009, 459, 820;
  b) B. Trauzettel, D. V. Bulaev, D. Loss, G. Burkard, *Nat. Phys.* 2007, 3, 192; c) C. L. Kane, E. J. Mele, *Phys. Rev. Lett.* 2005, 95, 226801.
- [5] a) K. Nagashio, T. Nishimura, K. Kita, A. Toriumi, *Appl. Phys. Express* 2009, 2, 025003; b) H. Li, J. Wu, Z. Yin, H. Zhang, *Acc. Chem. Res.* 2014, 47, 1067.
- [6] a) J. M. Tour, Chem. Mater. 2013, 26, 163; b) X. Huang, Z. Zeng,
   H. Zhang, Chem. Soc. Rev. 2013, 42, 1934.

#### **ADVANCED** SCIENCE NEWS

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- [7] L. M. Viculis, J. J. Mack, R. B. Kaner, Science 2003, 299, 1361.
- [8] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, *Nat. Nanotechnol.* 2008, 3, 563.
- [9] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 2004, *306*, 666.
- [10] W. Zhao, M. Fang, F. Wu, H. Wu, L. Wang, G. Chen, J. Mater. Chem. 2010, 20, 5817.
- [11] A. Abdelkader, A. Cooper, R. Dryfe, I. Kinloch, *Nanoscale* **2015**, *7*, 6944.
- [12] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* 2007, 45, 1558.
- [13] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, *Science* 2011, *331*, 568.
- [14] M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, ACS Nano 2010, 4, 3155.
- [15] K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, *Nat. Mater.* **2014**, *13*, 624.
- [16] a) E. Varrla, C. Backes, K. R. Paton, A. Harvey, Z. Gholamvand,
  J. McCauley, J. N. Coleman, *Chem. Mater.* 2015, *27*, 1129;
  b) E. Varrla, K. R. Paton, C. Backes, A. Harvey, R. J. Smith,
  J. McCauley, J. N. Coleman, *Nanoscale* 2014, *6*, 11810; c) S. Majee,
  M. Song, S.-L. Zhang, Z.-B. Zhang, *Carbon* 2016, *102*, 51; d) M. Yi,
  Z. Shen, *Carbon* 2014, *78*, 622.
- [17] Y. Arao, Y. Mizuno, K. Araki, M. Kubouchi, Carbon 2016, 102, 330.
- [18] P. G. Karagiannidis, S. A. Hodge, L. Lombardi, F. Tomarchio, N. Decorde, S. Milana, I. Goykhman, Y. Su, S. V. Mesite, D. N. Johnstone, R. K. Leary, P. A. Midgley, N. M. Pugno, F. Torrisi, A. C. Ferrari, ACS Nano 2017, 11, 2742.
- [19] a) D. Coles, J. Fluid Mech. 1965, 21, 385; b) J. P. Gollub,
   H. L. Swinney, Phys. Rev. Lett. 1975, 35, 927.
- [20] D. D. Joseph, J. Fluid Mech. 1998, 366, 367.
- [21] A. Furukawa, H. Tanaka, Nature 2006, 443, 434.
- [22] N.-W. Pu, C.-A. Wang, Y. Sung, Y.-M. Liu, M.-D. Ger, Mater. Lett. 2009, 63, 1987.
- [23] S. Xu, Q. Xu, N. Wang, Z. Chen, Q. Tian, H. Yang, K. Wang, Chem. Mater. 2015, 27, 3262.
- [24] Y. Gao, W. Shi, W. Wang, Y. Wang, Y. Zhao, Z. Lei, R. Miao, Ind. Eng. Chem. Res. 2014, 53, 2839.
- [25] L. Li, J. Xu, G. Li, X. Jia, Y. Li, F. Yang, L. Zhang, C. Xu, J. Gao, Y. Liu, *Chem. Eng. J.* **2016**, *284*, 78.
- [26] H. Gao, G. Hu, RSC Adv. 2016, 6, 10132.
- [27] B. Z. Jang, A. Zhamu, J. Guo, USPTO Patent US7785492B1, 2010.
- [28] M. Levi, D. Aurbach, J. Phys. Chem. B 1997, 101, 4641.
- [29] a) W. Wang, Y. Wang, Y. Gao, Y. Zhao, J. Supercrit. Fluids 2014, 85, 95; b) H. S. Sim, T. A. Kim, K. H. Lee, M. Park, Mater. Lett. 2012, 89, 343.
- [30] N. Mehio, S. Dai, D.-E. Jiang, J. Phys. Chem. A 2014, 118, 1150.

- [31] G. Bacon, Acta Crystallogr. 1951, 4, 558.
- [32] P. Walker, H. McKinstry, C. Wright, Ind. Eng. Chem. 1953, 45, 1711.
- [33] D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, Nat. Nanotechnol. 2008, 3, 101.
- [34] M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. McGovern, J. Am. Chem. Soc. 2009, 131, 3611.
- [35] R. V. Gorbachev, I. Riaz, R. R. Nair, R. Jalil, L. Britnell, B. D. Belle, E. W. Hill, K. S. Novoselov, K. Watanabe, T. Taniguchi, *Small* 2011, 7, 465.
- [36] a) A. C. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov, S. Roth, *Phys. Rev. Lett.* 2006, *97*, 187401; b) A. C. Ferrari, D. M. Basko, *Nat. Nanotechnol.* 2013, *8*, 235.
- [37] Y. Hao, Y. Wang, L. Wang, Z. Ni, Z. Wang, R. Wang, C. K. Koo, Z. Shen, J. T. Thong, Small 2010, 6, 195.
- [38] a) C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, ACS Nano 2010, 4, 2695; b) E. P. Nguyen, B. J. Carey, T. Daeneke, J. Z. Ou, K. Latham, S. Zhuiykov, K. Kalantar-zadeh, Chem. Mater. 2014, 27, 53.
- [39] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, D. Baillargeat, Adv. Funct. Mater. 2012, 22, 1385.
- [40] Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, Nano Lett. 2010, 10, 4134.
- [41] Y. Liao, W. Cao, J. W. Connell, Z. Chen, Y. Lin, Sci. Rep. 2016, 6, 26084.
- [42] W.-Q. Han, L. Wu, Y. Zhu, K. Watanabe, T. Taniguchi, Appl. Phys. Lett. 2008, 93, 223103.
- [43] a) M. Quintana, M. Grzelczak, K. Spyrou, B. Kooi, S. Bals, G. Van Tendeloo, P. Rudolf, M. Prato, *Chem. Commun.* 2012, 48, 12159; b) U. Khan, A. O'Neill, M. Lotya, S. De, J. N. Coleman, *Small* 2010, 6, 864.
- [44] K. Kouroupis-Agalou, A. Liscio, E. Treossi, L. Ortolani, V. Morandi, N. M. Pugno, V. Palermo, *Nanoscale* 2014, 6, 5926.
- [45] L. Muscuso, S. Cravanzola, F. Cesano, D. Scarano, A. Zecchina, J. Phys. Chem. C 2015, 119, 3791.
- [46] B. R. Munson, D. F. Young, T. H. Okiishi, Fundam. Fluid Mechanics, John Wiley and Sons, Hoboken, NJ, USA 1990.
- [47] I. U. Unalan, G. Cerri, E. Marcuzzo, C. A. Cozzolino, S. Farris, RSC Adv. 2014, 4, 29393.
- [48] a) M. Frounchi, A. Dourbash, *Macromol. Mater. Eng.* 2009, 294, 68; b) K. H. Wang, M. H. Choi, C. M. Koo, Y. S. Choi, I. J. Chung, *Polymer* 2001, 42, 9819.
- [49] S. Xie, O. M. Istrate, P. May, S. Barwich, A. P. Bell, U. Khan, J. N. Coleman, *Nanoscale* **2015**, *7*, 4443.
- [50] M. A. Priolo, D. Gamboa, K. M. Holder, J. C. Grunlan, Nano Lett. 2010, 10, 4970.
- [51] C. I. Calcagno, C. M. Mariani, S. Teixeira, R. Mauler, *Polymer* 2007, 48, 966.
- [52] S. Zekriardehani, S. Jabarin, D. Gidley, M. Coleman, *Macromolecules* 2017, 50, 2845.

