

Hydraulic Power Manufacturing for Highly Scalable and Stable 2D Nanosheet Dispersions and Their Film Electrode Application

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As 2D-nanosheet dispersions greatly facilitate solution-based processes, the preparation of 2D nanosheets in various solvents offers considerable potential in many applications, from electronics to energy storage and conversion. However, significant improvements are required in production cost, scalability, yield, and processability to realize the full potential of 2D nanosheets. Herein, a fast, scalable, and versatile hydraulic power process for the large-scale production of 2D nanosheets (graphene, MoS₂, and boron nitride) dispersed in water is presented. A controlled, wavy Taylor-vortex flow allows for a high-shear mixing process with efficient mass transfer. The use of an ionic liquid dramatically improves the exfoliation of 2D materials, resulting in an extremely high yield (76.9%), a high concentration (20 mg mL⁻¹), and a high production rate (8.6 g h⁻¹). The computational fluid dynamics simulations reveal that the improved exfoliation performance originates from the high-shear mixing process, and the first-principles calculations rationalize this performance via the high adsorption energies of ionic liquids on 2D nanosheets. The highly stable 2D nanosheet dispersions efficiently facilitating the postprocesses of vacuum filtration and inkjet printing, resulting in highly conductive circuits and high-performance film electrodes for energy-storage applications, are also demonstrated.

2D nanosheets are widely used as films for circuits and electrodes in electronic and electrochemical devices.^[4–6] Various industrial manufacturing processes, including dip-coating, spray deposition, printing, roll-to-roll processing, and filtration, have been used in an attempt to produce large quantities of cost-effective and high-value film products, which are expected to address the challenges associated with energy consumption, environmental conservation, security, and the high-tech industry.^[5–9] Because these film-manufacturing techniques are continuous, large-scale, and solution-based, they require large quantities of feed materials in the form of 2D-nanosheet dispersions, suspensions, or inks.^[5–9] To reduce the unit cost of production, several studies have proposed a high-yield, high-throughput, and low-cost method for preparing 2D nanosheets.^[3,4,9,10] The concentration and stability of 2D nanosheets have proven to be critical factors in the thickness, uni-

formity, and quality of film products, which strongly influence device performance.^[4,8–10]

There have been extensive uses of both bottom-up and top-down approaches to produce 2D nanomaterials dispersed in a solution.^[11] Hydro/solvothermal synthesis^[12–14] and the molten-salt method^[15] represent bottom-up processes, whereas

1. Introduction

Ultrathin and layered 2D nanomaterials with unique properties and structures have become increasingly important in emerging applications involving catalysts, sensors, composites, electronics, and energy-storage/conversion systems.^[1–3] Most

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DOI: 10.1002/adfm.201802952

chemical oxidation (or intercalation) and exfoliation,^[11,16,17] liquid-phase exfoliation,^[5,18] sonication-assisted exfoliation,^[19,20] and fluid-dynamic exfoliation^[21,22] are well-known examples of top-down procedures. Compared to bottom-up methods, the direct exfoliation of bulk-layered compounds in liquid is more promising for the efficient, low-cost, and scalable production of 2D nanomaterials,^[9–11] and this method has expanded the scope of existing applications to include electronic and electrochemical devices.^[4–6,10] Among various exfoliation methods, the fluid dynamics approach based on multiple mechanical forces, such as, shear, extension, cavitation, collision, and pressure, is a promising scalable and efficient exfoliation method for the production of 2D nanosheets dispersed in a solution.^[5,9,11] Fluid mechanics has been utilized for the exfoliation of the layered organoclays into a polymer matrix through extruders to produce nanocomposites. Previous studies have reported that the fluid behavior, interfacial chemistry, and the use of appropriate surfactants or solvents all play a significant impact role on the exfoliation efficiency of 2D materials.^[23–29] Considering these key factors, various fluid-dynamic exfoliation methods, including vortex fluidics and pressure- and mixer-driven fluid dynamics have been developed to exfoliate 2D materials from layered silicates to other 2D crystals (i.e., graphene (Gr), MoS₂, and boron nitride (BN)). Recent researches focusing on industrially adoptable methods using rotor–stator mixers and ball mills have achieved high production rates of up to 2.5 g h^{−1} in laboratory-scale systems.^[30,31] However, these top-down, solution-based exfoliation methods^[18,31–33] for mono- or few-layer 2D nanosheets suffered from low yield (<15%) and low concentration (<5.8 mg mL^{−1}), as the exfoliating forces, such as sonicating, shearing, and ball milling, did not cover the entire reactor and were applied irregularly to the 2D materials due to inefficient mass transfer and mixing. Although exfoliation processes using suitable organic solvents or surface stabilizers provide higher yields and concentrations of 2D nanosheets,^[34–36] the prolonged processing they require can result in poor production rates.

In this article, we propose a new top-down approach using a high-throughput hydrodynamic exfoliation process to produce a highly stable colloidal suspension of 2D nanosheets (Gr, MoS₂, and BN) in water. An ionic liquid (IL)-assisted Taylor–Couette (TC) flow, with water as the working fluid, provides uniform and high shear rates, efficient mass transfer, and highly radial mixing along its entire length. This process enables rapid mass production of 2D nanosheets (≈8.6 g h^{−1}) with high yields (≈76.9%) and high concentrations (up to 17.2 mg mL^{−1}) that remain stable for more than a year. The 2D nanomaterial dispersions produced via the proposed method represent convenient and unique nanobuilding blocks for vacuum-filtered, energy-storing film electrodes and inkjet-printed electronic circuits.

2. Results and Discussion

2.1. Hydraulic Power Exfoliation of 2D Materials

Figure 1a shows an IL-assisted hydraulic power process for exfoliating and functionalizing (EF) 2D-nanosheet dispersions using commercially available bulk graphite, MoS₂, or

BN powders in a TC flow reactor. During this process, IL surfactants (5 wt%) were injected into a TC flow reactor as an exfoliating and stabilizing agent. We chose 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) as an IL due to its wide use as a surfactant, electrolyte, and binder in electronic and electrochemical applications.^[37] The devised fluidic reactor consists of rotating inner and stationary outer cylinders with a large-scale reactor volume (0.5 L) and a small annular size (0.68 cm) (Figure S1, Supporting Information). As fluidic behavior depends on rotational speed, a micro-sized, toroidal-shaped TC-vortex flow along the cylinder axis was generated via centrifugal and inertial forces at a critical rotational speed of 2000 rpm. As rotational speed has a profound influence on both exfoliation level and yield, the reactor rotational speed was optimized at 2000 rpm, resulting in effective shear rates (>10⁴ s^{−1}) and a stable Taylor-vortex flow (Figure 1a and Figure S2, Supporting Information). Periodic and uniform fluidic motion with intense radial mixing imparts a diverse set of fluid-dynamic forces, including shear, tension, cavitation, collision, and pressure, which allow for efficient exfoliation and high yields of 2D nanosheets. These forces differ intrinsically from the widely used, cavitation-dominated sonication process and are therefore more desirable in the exfoliation of 2D materials.

To investigate exfoliation performance using a hydrodynamic reactor, we used aqueous surfactant solutions comprised of sodium cholate (SC)/water, sodium dodecyl sulfate (SDS)/water, and an organic solvent of N-methyl-2-pyrrolidone (NMP). SC and SDS are general stabilizers used to produce colloidal suspensions of 2D nanomaterials,^[9,11] whereas NMP is a solvent commonly used for solution-based exfoliation.^[18,31] The fluid-dynamic exfoliation process using these solvents allowed us to produce large quantities of exfoliated Gr, MoS₂, and BN-nanosheet dispersions in just 1 h (Figure S3, Supporting Information). Furthermore, the yields (12.8–23.7%) and concentrations (0.13–0.24 mg mL^{−1}) are comparable or superior to previously reported values using solution-based exfoliation methods (Table S1, Supporting Information), which is attributed to the continuous, high-shear fluid mechanics of the entire TC reactor.

It is noteworthy that the addition of an IL dramatically improves the exfoliation of 2D materials, in terms of yield and concentration, compared to a fluid-dynamic exfoliation process using aqueous surfactant solutions and NMP. The exfoliation process was performed using an initial concentration range of 0.1–30 mg mL^{−1} of Gr, MoS₂, and BN. As the initial concentrations increased, so too did the final concentrations, whereas the yield decreased. The IL-assisted hydrodynamic exfoliation process resulted in a high yield: 76.9% for the EF-Gr sheets, 72.0% for the EF-MoS₂ sheets, and 71.2% for the EF-BN sheets (Figure 1b). When initial concentrations were increased to 200 mg mL^{−1}, the maximum concentrations of Gr, MoS₂, and BN in the EF nanosheets were 17.2, 13.3, and 11.8 mg mL^{−1}, respectively (Figure S4, Supporting Information). The maximum yield and concentration obtained even after a short exfoliation time (1 h) were much higher than those previously reported for solution-processed Gr, MoS₂, and BN (Figure 1c). Although a few studies produced higher concentrations using a lengthy exfoliation process, the production rates were significantly reduced. We applied a sonication pretreatment step^[38] prior to the hydrodynamic exfoliation process (Figure S5, Supporting Information).

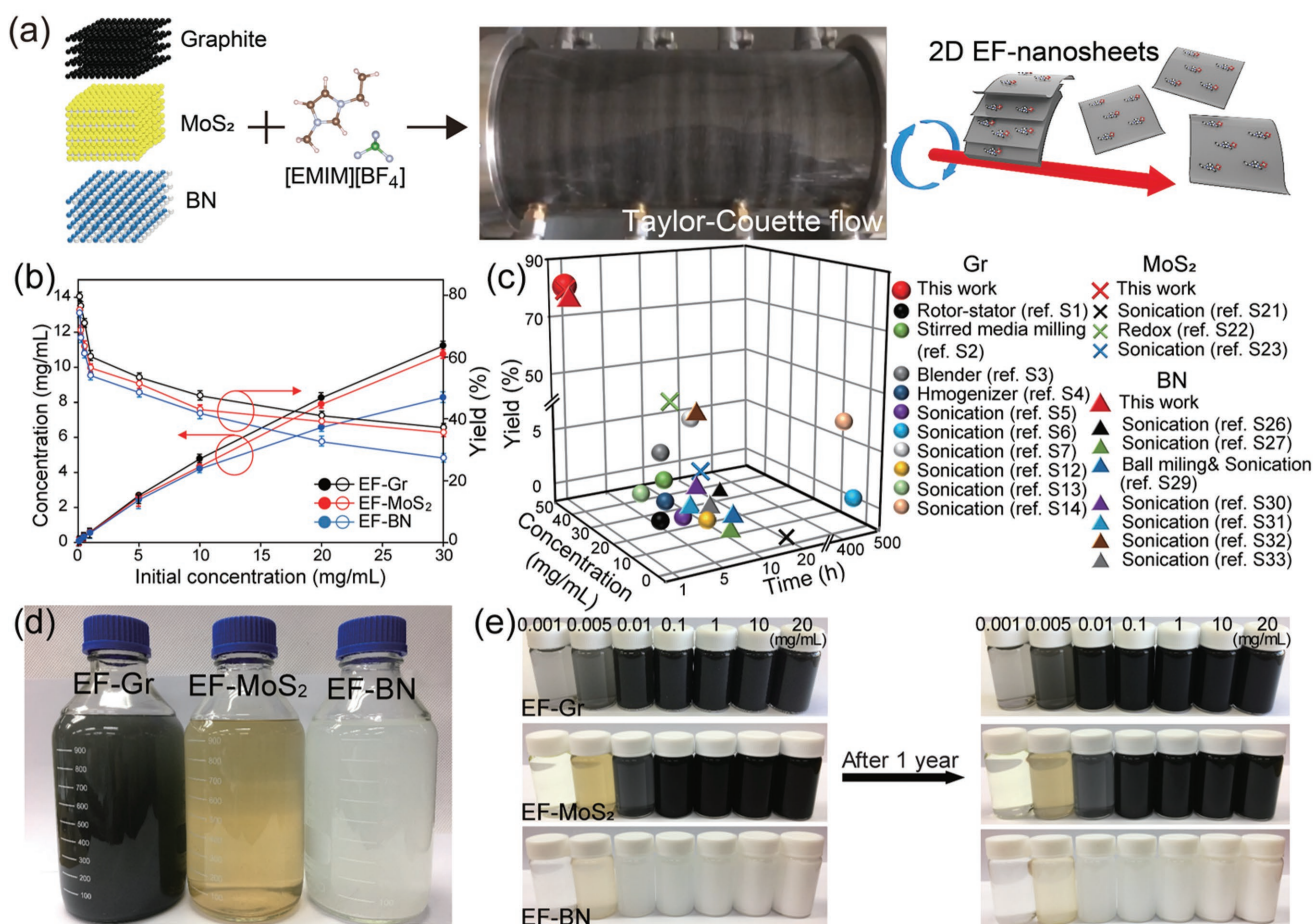


Figure 1. Production of EF nanosheets using hydraulic-power exfoliation: a) a photograph of a fluidic reactor operated at 2000 rpm and a schematic for the preparation of EF nanosheets using [EMIM][BF₄]; b) concentrations and yields of the EF-Gr, EF-MoS₂, and EF-BN sheets obtained at different initial concentrations of the materials (0.1–30 mg mL⁻¹); c) a 3D scatter plot showing concentration, yield, and processing time in the exfoliation of graphite, MoS₂, and BN reported in the literature; d) a photograph of the EF-Gr, EF-MoS₂, and EF-BN dispersions; e) a photograph of the EF-Gr, EF-MoS₂, and EF-BN dispersions at different concentrations (0.001–20 mg mL⁻¹) at the time of preparation and after one year.

This step led to an improvement in the exfoliation yields of the EF nanosheets, but the production rates were decreased owing to the prolonged pretreatment time (Figure S5, Supporting Information). Our fast and efficient hydrodynamic exfoliation process achieved extremely high production rates based on the concentrations and total volume of the products: 8.6 g h⁻¹ for the EF-Gr sheets, 6.6 g h⁻¹ for the EF-MoS₂ sheets, and 5.9 g h⁻¹ for the EF-BN sheets. The maximum production rates of the EF nanosheets are notably superior to those resulting from other solution-based methods (<2.5 g h⁻¹), such as shear, ball milling, redox, and sonication-assisted exfoliation (Table S1, Supporting Information). Our method also has potential for other layered crystals, and this process can be easily scaled up for mass production by increasing the reactor dimension and bulk loading the 2D materials.

2.2. Material Characterization of EF Nanosheets

The prepared EF nanosheets formed highly stable dispersions in water (Figure 1d). After collecting and freeze-drying

the 2D powder samples, they appeared to favor mono- or few-layer flakes over restacked structures, as evidenced by their significantly reduced and broadened X-ray diffraction (XRD) peaks in the *c*-direction (Figure S6, Supporting Information). Surprisingly, the EF-nanosheet powder was readily redispersed at concentrations as high as 20 mg mL⁻¹ in water, and they formed stable colloidal dispersions (Figure 1e). These dispersions remained stable for over one year without aggregation or precipitation. To support this finding, we measured the zeta values of the 2D-nanosheet dispersions, showing -39.7 mV for the EF-Gr sheets, -43.1 mV for the EF-MoS₂ sheets, and -65.4 mV for the EF-BN sheets. This long-term colloidal stability at high concentrations is attributed to the hydrophilic properties of the IL on the surfaces of the 2D nanosheets. During exfoliation, intermolecular interactions, such as π - π stacking and electrostatic interactions, may occur between the IL and the 2D nanosheets. The composition ratios of the EF nanosheets were determined via thermogravimetric analysis (TGA), showing 3.6 wt% of IL on EF-Gr, 4.5 wt% on EF-MoS₂, and 3.8 wt% on EF-BN (Figure S7, Supporting Information). In summary, IL-assisted

hydrodynamic exfoliation enables the high-throughput production of stable colloidal dispersions comprised of IL-functionalized 2D nanosheets.

The morphology and crystalline structure of the EF nanosheets were investigated via scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and Raman spectroscopy. The shear-dominant exfoliation with a short time of 1 h induced relatively large size. The shear-dominant exfoliation with a short time of 1 h induced relatively large size. Based on the SEM images, the average flake sizes were $60.56 \pm 16.42 \mu\text{m}$ for the EF-Gr, $582.7 \pm 162.1 \text{ nm}$ for the EF-MoS₂, and $38.52 \pm 13.15 \mu\text{m}$ for the EF-BN, using more than 200 sheets in each case (Figure 2a–f and Figure S8, Supporting Information). When we compare the average lateral size from the SEM and AFM images, we find similar values of $56.92 \pm 16.07 \mu\text{m}$ for the EF-Gr, $552.1 \pm 164.5 \text{ nm}$ for the EF-MoS₂, and $37.64 \pm 13.26 \mu\text{m}$ for the EF-BN (Figure S9a–f, Supporting Information). The relatively low size of EF-MoS₂ compared to EF-Gr and EF-BN is attributed to the different sizes of starting bulk materials of graphite (<200 μm), MoS₂ (<20 μm), and BN (<130 μm). The thickness distributions were statistically evaluated via AFM using >200 sheets in each case, and the results indicate few-layer structures: $1.6 \pm 1 \text{ nm}$ for the EF-Gr sheets, $1.8 \pm 1 \text{ nm}$ for the EF-MoS₂ sheets, and $1.6 \pm 1 \text{ nm}$ for the EF-BN sheets (Figure S9g–i, Supporting Information). Based on the thickness of the IL ($\approx 0.2 \text{ nm}$) absorbed onto

EF nanosheets, the thicknesses of a single layer for the EF nanosheets are $\approx 0.8 \text{ nm}$ for EF-Gr, 1.2 nm for EF-MoS₂, and 1.2 nm for EF-BN (Figure S9, Supporting Information). The single-layer thickness of EF nanosheets was similar to those of single-layer nanosheets obtained from other solution-based exfoliation methods (Table S2, Supporting Information). High-resolution TEM (HRTEM) images provided morphological and crystalline information (Figure 2g–i). Hexagonal structures were observed in the EF-Gr, EF-MoS₂, and EF-BN sheets, which strongly suggest that the original basal planes were not damaged during the IL-assisted hydrodynamic exfoliation process.

The crystalline structure and exfoliation levels in the EF-Gr, EF-MoS₂, and EF-BN sheets were measured via changes in the Raman peak intensities and frequencies (Figure 3).^[20,33,39,40] Raman scattering peaks were observed in the EF-Gr sheets (Figure 3a), which indicates that the D band (1345 cm^{-1}) associated with this defect is considerably less intense than the G band (1575 cm^{-1}), yielding an intensity ratio (I_D/I_G) of 0.17. This value suggests fewer structural defects, as it is much lower than the I_D/I_G values previously reported for graphene sheets using solution-based exfoliation methods (Table S1, Supporting Information).^[18,31,33] Compared to the 2D peaks of graphite, the EF-Gr exhibited more symmetrical and broad 2D peaks, which increased its full width at half maximum (FWHM) from 98 cm^{-1} (graphite) to 115.5 cm^{-1} . This indicates that the EF-Gr sheets are dominated by a mono- or few-layer structure.

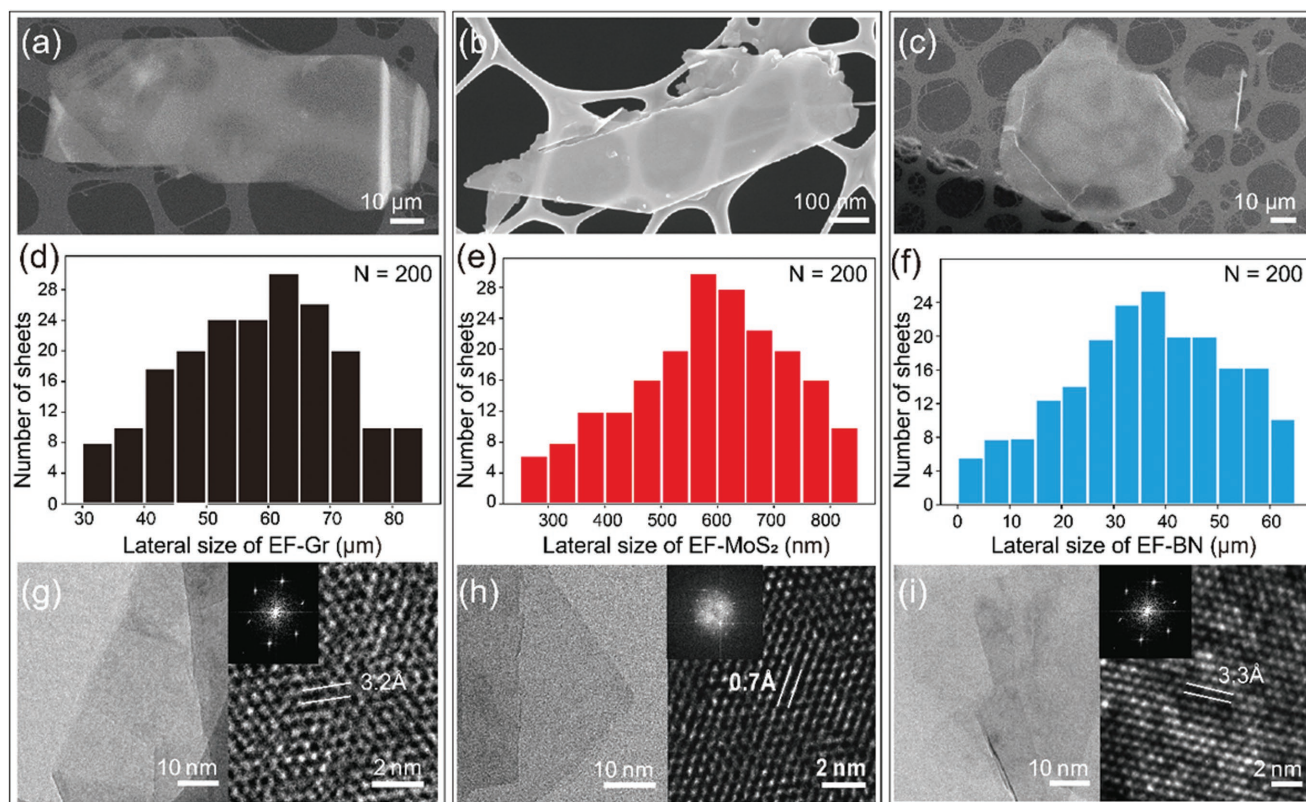


Figure 2. Morphological and structural characteristics of the EF nanosheets: SEM images of the a) EF-Gr, b) EF-MoS₂, and c) EF-BN sheets; histograms for the lateral size distributions of the d) EF-Gr, e) EF-MoS₂, and f) EF-BN sheets; HRTEM images of the g) EF-Gr, h) EF-MoS₂, and i) EF-BN sheets (inset: FFT images of the EF-Gr, EF-MoS₂, and EF-BN sheets).

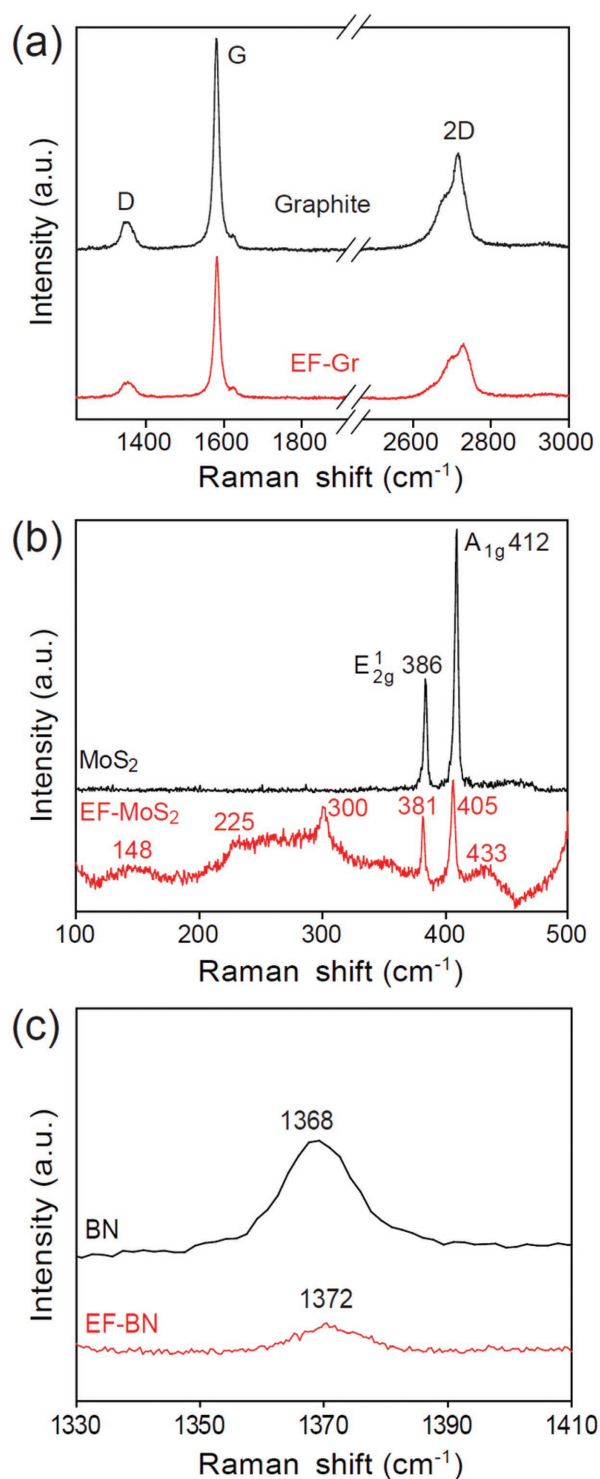


Figure 3. Raman spectra of a) graphite and the EF-Gr sheets, b) MoS₂ and the EF-MoS₂ sheets, and c) BN and the EF-BN sheets.

Compared to bulk MoS₂, the EF-MoS₂ displayed an increased FWHM at its E_{2g} and A_{1g} peaks, with decreased Raman-shift gaps (Figure 3b), indicating that the EF-MoS₂ sheets have a thickness of less than five layers each. Additional peaks at 148 cm⁻¹ (J₁), 225 cm⁻¹ (J₂), and 300 cm⁻¹ (J₃) were the same as

those found in 1T-phase MoS₂ prepared via the *n*-butyl-lithium intercalation method.^[6] These peaks are attributed to the formation of a distorted-1T structure, indicating the presence of distorted octahedral coordination in the EF-MoS₂ sheets. After exfoliating the bulk BN, the blueshift and widening of the peak in the G band of the Raman spectra (1372 cm⁻¹) represent an E_{2g} mode of vibration (Figure 3c), which provides clear evidence of a few-layer structure in the EF-BN sheets. These high-quality exfoliation states and crystalline structures were also observed in 2D nanosheets obtained from the NMP-based fluidic exfoliation process (Figures S10 and S11, Supporting Information). The difference between IL- and NMP-based exfoliation systems is that the use of IL induces the 1T phase of EF-MoS₂, while the 2H phase was observed with the use of the NMP system.

2.3. Freestanding and Flexible Energy Storage Films

The high colloidal stability and wide concentration ranges of the EF-nanosheet dispersions enabled the construction of macroscopic, freestanding, flexible films, which have an expanding range of applications in sensors, optoelectronics, functional films, and energy storage/conversion.^[6,10] These films were obtained via vacuum filtration using EF-nanosheet dispersions at a concentration of 2 mg mL⁻¹ (Figure 4a). Highly uniform, micrometer-thick films were produced by compressing the EF nanosheets into compact stacks (Figure 4b and Figure S12, Supporting Information). The flexible, freestanding EF-Gr films were used to make binder- and carbon-free electrodes for supercapacitors. Electrochemical performance was evaluated via cyclic voltammetry (CV) and galvanostatic charge/discharge using a three-electrode system and a 1 M aqueous electrolyte (Na₂SO₄). All the CV curves exhibited a rectangular shape at 10–500 mV s⁻¹, which indicates an ideal capacitive behavior (Figure 4c). At a current density of 0.5 A g⁻¹, the specific capacitance value of the EF-Gr film reached 325 F g⁻¹ (Figure 4d). When the current density was increased to 15 A g⁻¹, 94.3% of the initial capacity was retained, suggesting that the films have good rate capability. The EF-Gr films exhibited no capacitance losses, even after 5000 cycles under a current density of 2 A g⁻¹ (99.2% retention; Figure 4e). The enhanced electrochemical performance of the EF-Gr film is attributed to the hydrophilic and ionic-conductive functionalities of the IL on the surfaces of the EF-Gr sheets, as well as their high electrical conductivity. To investigate the effect of ILs on electrochemical performance, we tested the EF-Gr films obtained from sodium cholate (or NMP)-assisted fluidic exfoliation in the absence of an IL and found that the SC-Gr and NMP-based graphene (NMP-Gr) films exhibited much lower specific capacitances (137.5 and 214.0 F g⁻¹) and poorer rate capabilities (retention rates of 61.1 and 76.2% retention) than the EF-Gr films (Figure 4d). We also tested the supercapacitor performance of small-sized EF-Gr sheets with an average size of 678.6 ± 163.3 nm (Figure S13, Supporting Information). The specific capacitance of 331 F g⁻¹ found for the small-sized EF-Gr is similar to that of the large-sized EF-Gr (325 F g⁻¹), but the rate capability (89.3% retention) was decreased slightly compared to that of the large-sized EF-Gr (94.3% retention). The enhanced electrochemical performance of the EF-Gr film is attributed to

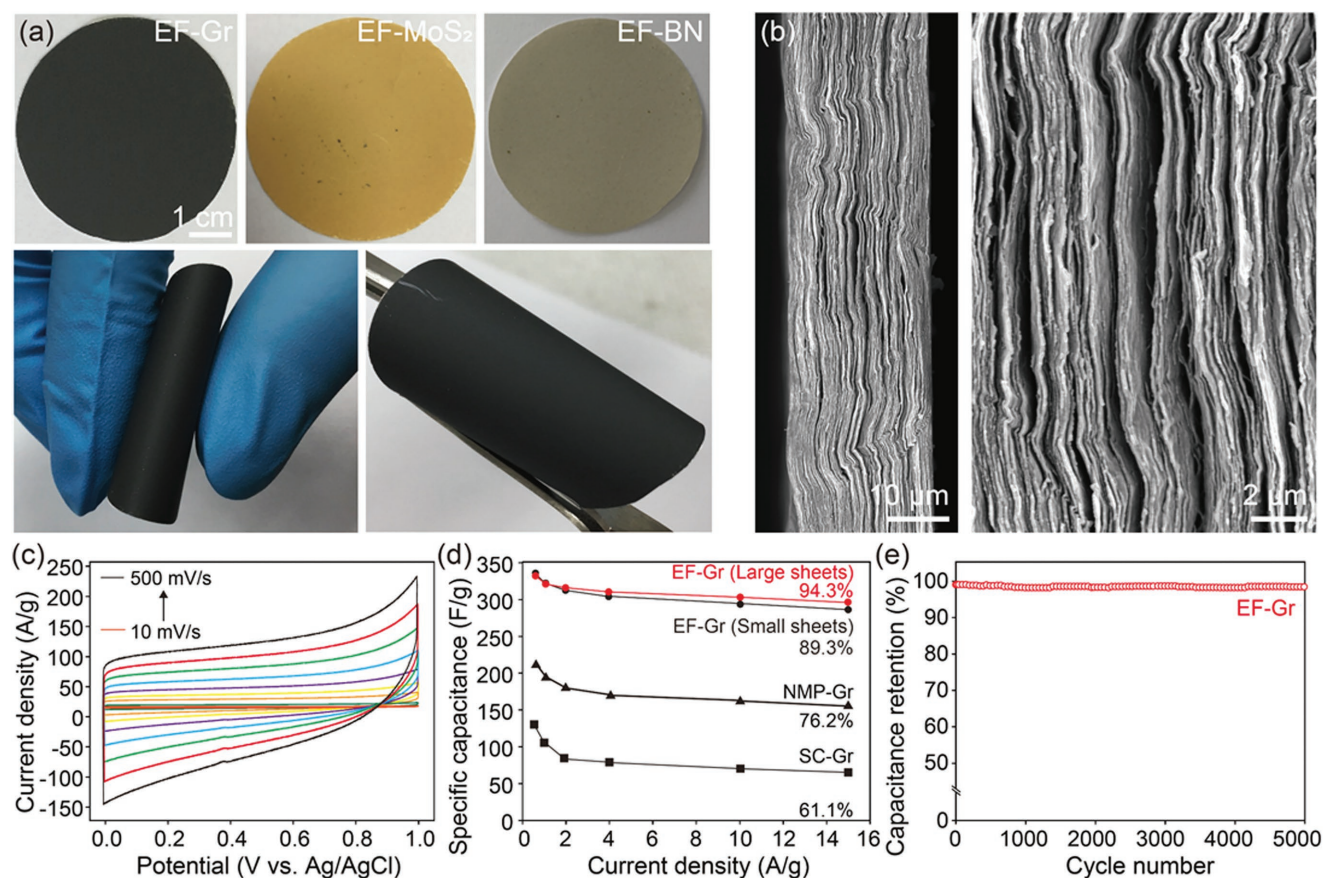


Figure 4. a) A photograph of the freestanding, flexible EF-Gr, EF-MoS₂, and EF-BN films; b) cross-sectional SEM images of the EF-Gr films at low and high magnification; c) CV curves for the EF-Gr films measured at different scan rates (10–500 mV s^{−1}) in a 1 M Na₂SO₄ electrolyte; d) specific capacitance values for the EF-Gr (large sheets), EF-Gr (small sheets), NMP-Gr, and SC-Gr films measured at different current densities (0.5–15 A g^{−1}); e) cycle performance of the EF-Gr film measured under a constant current density (2 A g^{−1}) over 5000 cycles.

the hydrophilic and ionic-conductive functionalities of the IL on the surfaces of the EF-Gr sheets and to the high electrical conductivity of the defect-free Gr sheets.

2.4. Inkjet-Printed EF-Nanosheet Circuits

Inkjet printing is an important technique used to fabricate many products via well-controlled ejections and depositions of small liquid-ink droplets onto various substrates, such as paper, plastics, textiles, and thin metallic and semiconducting films.^[8,13] To substantiate the colloidal stability of the 2D-EF-nanosheet dispersions as well as their use in inks, we performed inkjet printing using EF nanosheets dispersed in water. The inkjet-printing conditions were optimized using the inverse Ohnesorge number Z ,^[8] which is defined by the equation

$$Z = \sqrt{\rho \alpha} / \eta \quad (1)$$

where α is the nozzle diameter, γ is the surface tension, ρ is the density, and η is the ink viscosity. The flake size of the EF-nanosheet ink was controlled via ultrasonication and centrifugation. The concentration was controlled by redispersing the EF-nanosheet powders. The EF-Gr, EF-MoS₂, and

EF-BN inks were prepared at 4 mg mL^{−1} with an average flake size of 58 ± 0.35 , 58 ± 0.50 , and 35 ± 0.95 nm, respectively (Figure S13, Supporting Information). The Z value was calculated at ≈ 7 , which is within the standard range required for inkjet printing.^[8] Using an inkjet printer with the prepared inks, we were able to print letters (Figure 5a). Surface SEM images of the letters revealed uniform patterns of EF nanosheets, presumably caused by the effective dispersing and wetting capabilities of ILs (Figure 5b). Moreover, the inkjet-printed EF-Gr ink had an electrical conductivity of 9325 S m^{−1}, which is much higher than that of reduced graphene oxide (RGO) printed films (≈ 1000 S m^{−1}) described in previous studies.^[41–43] However, this electrical conductivity is slightly lower than that of NMP-Gr circuit obtained by inkjet printing of the NMP-Gr ink (Figure S14, Supporting Information) because the NMP-Gr surface is clearer than that of EF-Gr.^[41,44,45] This high electrical conductivity allowed us to print electrical circuits that were capable of powering a blue light-emitting diode (Figure 5c,d), which was attributed to the low amount of defects in the EF-Gr sheets and the ordered stacking induced by the IL (Figure 5e). The EF-Gr-based inkjet-printing process required neither thermal annealing nor chemical treatment—necessary components of GO- and RGO-based printing processes—to maximize electrical conductivity.

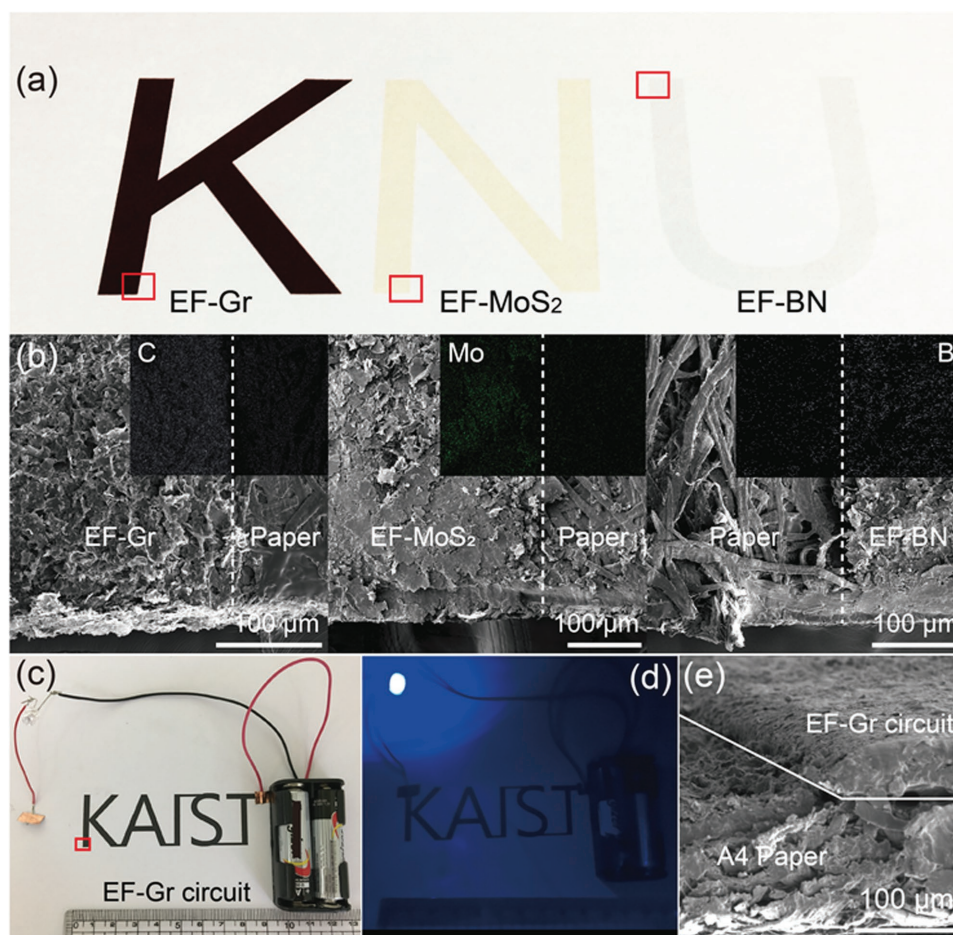


Figure 5. a) A photograph of inkjet-printed letters using the EF-Gr, EF-MoS₂, and EF-BN inks; b) surface SEM images of the regions enclosed by the red squares in (a) (inset: element mapping images of the C, Mo, and B signals); photographs of an inkjet-printed EF-Gr circuit on A4 paper under completely; c) open and d) closed states, which is able to power a blue light-emitting diode after connecting a battery (3.0 V); e) an SEM image of the region enclosed by the red square in (c), showing the ordered stacking of the EF-Gr sheets.

2.5. Computational Fluid Dynamics (CFD) and First-Principles Calculations

An understanding of how our IL-assisted hydrodynamic method enhances the exfoliation process is essential to academic and practical applications in materials science. Fluid-dynamic behavior and IL additives should be considered the key factors in achieving high exfoliation performance. To investigate the effect of fluid mechanics on the exfoliation process, we examined the process at different inner-cylinder rotational speeds in the range of 300–3000 rpm (Figure 6a). When the rotational speed increased from 300 to 2000 rpm, the EF-Gr, EF-MoS₂, and EF-BN yields increased by as much as 80%; however, at rotational speeds above 2000 rpm, the yields gradually decreased. CFD aids in the prediction of the TC flow state responsible for the greatest exfoliation yield, depending on the rotational speed of the inner cylinder. According to the ratio of the Reynolds number to the critical Reynolds number (Re/Re_C),^[46] the TC flow states can be divided into three regimes (Figure 6a,b): the Taylor-vortex flow (Region I, $1 < Re/Re_C < 1.16$), the wavy Taylor-vortex flow (Region II, $1.16 < Re/Re_C < 12.5$), and the turbulent Taylor-vortex flow (Region III, $12.5 < Re/Re_C < 23.6$).

In these regimes, the rotational Re number is defined by the following equation^[46]

$$Re = \frac{\omega r_i (r_i - r_o)}{\nu} \quad (2)$$

where ω is the inner cylinder angular velocity, r_i and r_o are the radius of the inner and outer cylinders, respectively, and ν is the kinematic viscosity of the fluid. The Re_C number is defined as the Re number at which the circular Couette flow transitions to the Taylor-vortex flow.^[46] The flow regimes were simulated using CFD at different rotational speeds of 300, 2000, and 3000 rpm, which revealed the radial and axial velocities in Regions I, II, and III (Figure 6c,d), respectively. At 300 rpm, a typical Taylor Couette flow was generated between a rotating inner and a stationary outer cylinder, where the flow was still laminar. The most well-developed and smallest micro-sized wavy Taylor vortices and the highest velocities were observed at 2000 rpm, producing uniform and strong tensile and shear-stress fields. It should be noted that these vortices were repeatedly combining and separating within 70 ms intervals, which is indicative of a quick and efficient mixing process (Figure S15,

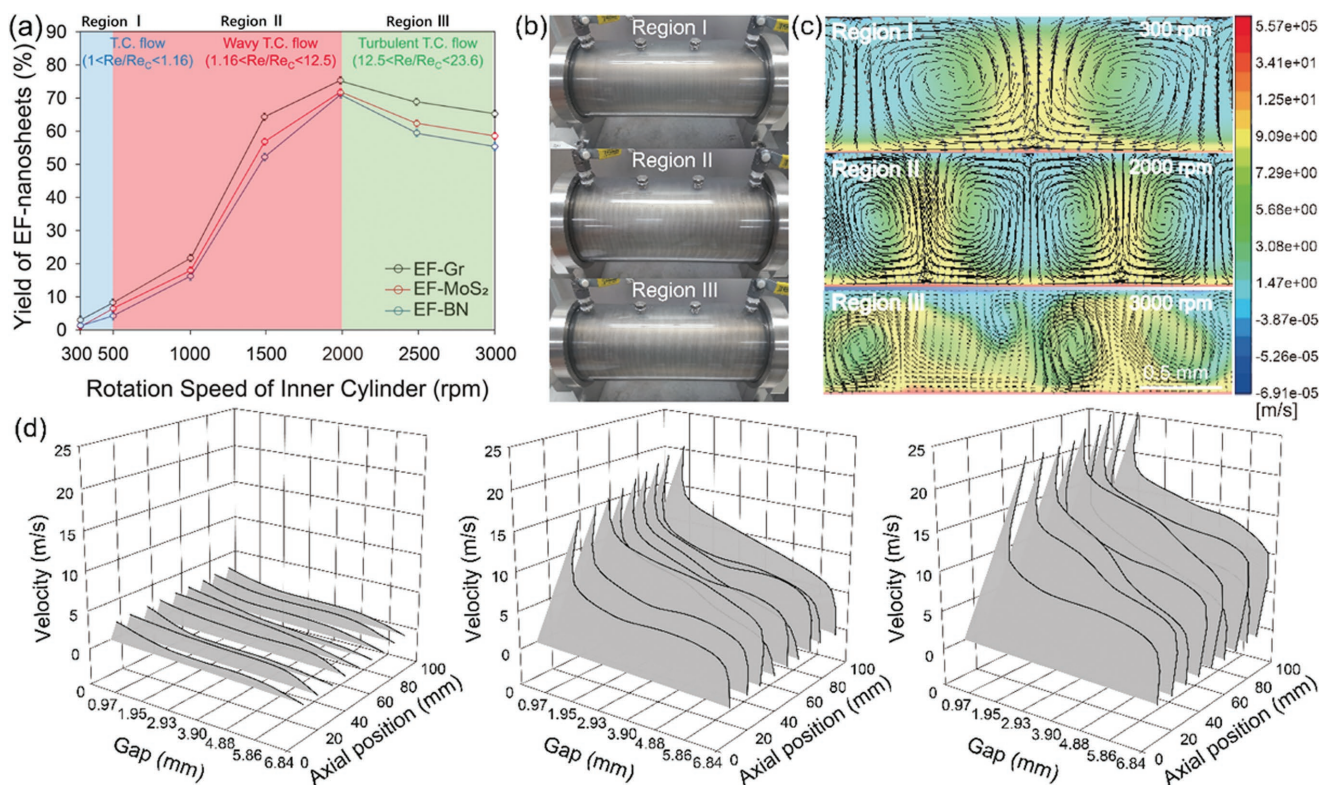


Figure 6. a) Yields of EF nanosheets produced at different rotation speeds (300–3000 rpm; feed concentration of 2D materials: 0.1 mg mL⁻¹); b) photographs of the flow regime in Regions I, II, and III of the rheoscopic fluid; c) radial velocity vectors at different rotation speeds (300, 2000, and 3000 rpm); d) axial velocity in the TC flow reactor at different rotation speeds (300, 2000, and 3000 rpm).

Supporting Information); however, this mixing process was not observed at 300 rpm. The CFD simulation at 3000 rpm revealed an aperiodic, turbulent Taylor-vortex flow, which may cause a weakened shear-stress field that is unfavorable for 2D material exfoliation. Therefore, the exfoliation process was optimized using a wavy Taylor-vortex flow with uniform, high shear stress and fast mass transfer, which contribute to the high yields and production rates of the EF nanosheets.

To explain the effects of the IL surfactants on the exfoliation process, both the structures of ILs and their interactions on exfoliated nanosheet surfaces should be considered. In this regard, we compared the yields and concentrations of the EF nanosheets with four different structures of ILs in a hydrodynamic exfoliation process: tetramethylammonium tetrafluoroborate ([TMA][BF₄]), [EMIM][BF₄], 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]), and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF₆]) (Figure 7a). The addition of hydrophilic [TMA][BF₄], [EMIM][BF₄], or [EMIM][EtSO₄] to water allowed us to achieve much higher yields and concentrations than the addition of NMP, which is widely used in solution-based exfoliation methods. To rationalize the experimental results, we performed first-principles calculations based on density functional theory (DFT). The adsorption structures and energies of the IL surfactants on the exfoliated, 2D surfaces of the Gr, MoS₂, and BN sheets are calculated and summarized in Figure 7b and Figure S16 (Supporting Information). Our DFT calculations reveal that the adsorption energies of [TMA][BF₄], [EMIM][BF₄], and [EMIM][EtSO₄] on the nanosheets are much

greater than that of NMP, which seems strongly related to the high exfoliation yields and concentrations caused by the incorporation of an IL. Figure 7c demonstrates the strong correlation between IL adsorption energies and exfoliation yields. The IL adsorption energies and exfoliation concentrations are also strongly correlated, as shown in Figure 7d.

Although [EMIM][PF₆] has a higher adsorption energy than [TMA][BF₄], [EMIM][BF₄], and [EMIM][EtSO₄], its yields and concentrations are much lower than those of other ILs. This is due to the low solubility of hydrophobic [EMIM][PF₆] in water, which is evidenced by the observed formation of aggregates at the bottom of the vial. When dissolving [EMIM][PF₆] in a miscible solvent, such as NMP, we observed dramatic increases in yields and concentrations, even higher than those of the other three ILs (Figure 7a). It is worth noting that the experimentally obtained yields and concentrations of the EF nanosheets are highly correlated with the calculated DFT adsorption energies between the exfoliated nanosheets and the organic compounds (Figure 7c,d). The use of [EMIM][BF₄] is most suitable in water-based exfoliation, resulting in an environmentally benign process.

Unlike pristine nanosheets, the IL-functionalized nanosheets formed stable dispersions without restacking. To understand this, the EF-Gr, EF-MoS₂, and EF-BN sheets were restored with and without [EMIM][BF₄] adsorbed on the nanosheets in the surrounding fluid. The structures and stacking energies of the EF nanosheets are shown in Figure 7e,f. The stacking energies of the [EMIM][BF₄]-adsorbed Gr, MoS₂,

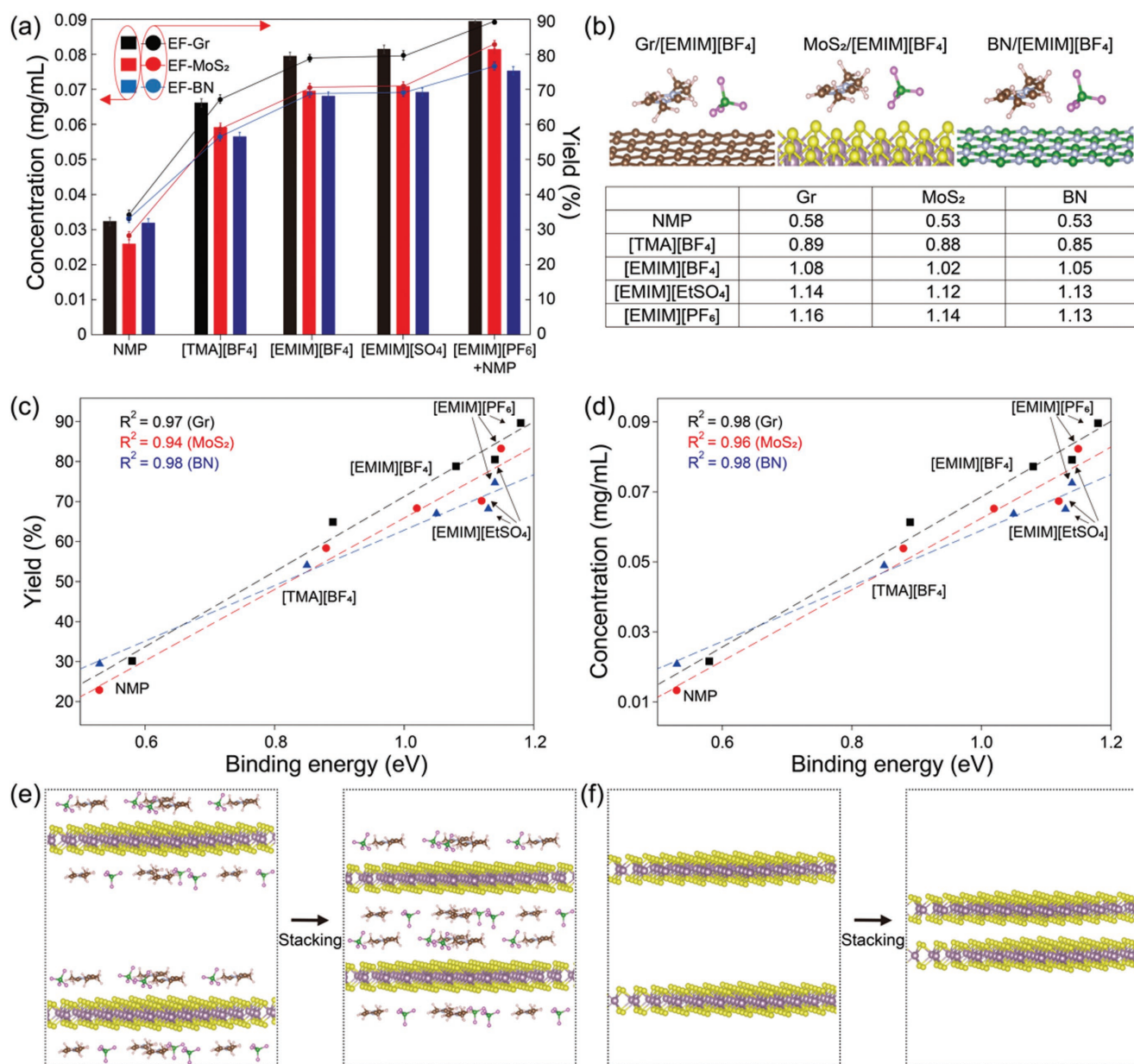


Figure 7. a) Concentrations and yields of the EF nanosheets using a variety of stabilizing reagents, including NMP, [TMA][BF₄], [EMIM][BF₄], [EMIM][EtSO₄], and [EMIM][PF₆]/NMP (feed concentration of 2D materials: 0.2 mg mL⁻¹); b) optimized [EMIM][BF₄] structures on the surfaces of the EF-Gr, EF-MoS₂, and EF-BN sheets, including the binding energies between the EF nanosheets and the stabilizing reagents; a graph of the correlations between the binding energies and c) yields or d) concentrations of the EF nanosheets with different stabilizing reagents; the stacking structures of the EF nanosheets e) with and f) without [EMIM][BF₄].

and BN sheets were reduced by 75% (36 meV fu⁻¹), 68% (52 meV fu⁻¹), and 69% (42 meV fu⁻¹), respectively, compared to the stacking energies of the pristine Gr (147 meV fu⁻¹), MoS₂ (163 meV fu⁻¹), and BN (136 meV fu⁻¹) sheets. This suggests that the restacking of IL-functionalized nanosheets is much more energetically unfavorable. The favorable adsorption of IL and the significantly reduced stacking energies of the exfoliated nanosheets prevent restacking, resulting in the stable dispersion of the 2D nanosheets. The exfoliated nanosheets prevent restacking, resulting in the stable dispersion of the 2D nanosheets.

The superior exfoliation performance and stable colloidal dispersion of EF nanosheets can be explained in terms of the following reasoning. The strong shear flow in a fluid dynamic system induces the displacement of the 2D sheets (i.e., graphene, MoS₂, and BN), thus overcoming the π - π stacking interactions between the 2D sheets. In addition, this shear flow allows IL surfactants to bind with 2D sheets by means of π - π and electrostatic interactions. As the ILs used in this work consist of large imidazolium cations and small anions, the imidazolium cations interact with the EF nanosheets and the anions of IL increase the negative surface charges of the

EF nanosheets, as demonstrated by zeta potential measurements (below -30 mV). The formation of negatively charged EF nanosheets electrostatically stabilized the colloidal dispersion in water against reaggregation by Coulomb repulsion, thus enhancing the exfoliation process. DFT calculations also support the stabilization of IL-functionalized EF nanosheets via the reduction of the stacking energy compared to bare EF nanosheets without IL.

3. Conclusions

We demonstrated that an IL-assisted hydraulic power process can efficiently exfoliate the 2D materials of graphite, MoS_2 , and BN in water at a large scale, thus forming highly stable colloidal suspensions. The introduction of an IL into this process resulted in substantial improvements to exfoliation yields (71.1–76.9%), concentrations (11.8–17.2 mg mL $^{-1}$), and production rates (5.9–8.6 g h $^{-1}$), which surpass those of previous, solution-based exfoliation methods. Our computational fluid dynamic simulations revealed that these outstanding exfoliation performances are caused by a wavy Taylor-vortex flow with uniform, high shear stress and fast mass transfer. Our first-principles calculations revealed a strong correlation between the high adsorption energies of ILs on 2D nanosheets and enhanced exfoliation performance, and disclosed significantly reduced stacking energies of exfoliated 2D nanosheets by $\approx 70\%$. The high quality of the exfoliated-nanosheet dispersions facilitated the postprocesses of vacuum filtration and inkjet printing, allowing for the production of flexible, energy-storing film electrodes and highly conductive circuits, respectively. The scalable, efficient, fluid-dynamic exfoliation method developed in this study offers significant opportunities for the exfoliation of various 2D materials, which can be used to optimize the cost-effective production of electronics, biosensors, and energy-storage/conversion systems.

4. Experimental Section

Materials and Chemicals: Graphite (<200 μm , ACS reagent) and MoS_2 (<20 μm , ACS reagent) were purchased from Sigma-Aldrich Corporation (USA). BN (<130 μm) was purchased from Alfa Aesar Corporation (USA). The ILs of [EMIM][BF $_4$] (99.0%), [TMA][BF $_4$] (99.9%), [EMIM][EtSO $_4$] (97.0%), and [EMIM][PF $_6$] (97.0%) were obtained from C-TRI Co., Ltd. (South Korea). SDS (ACS reagent), SC (ACS reagent), and NMP were purchased from Sigma-Aldrich Corporation (USA). All reagents were used without further purification.

Preparation of the EF Nanosheets: The exfoliation and functionalization of Gr, MoS_2 , and BN were performed in a Taylor–Couette reactor made of two concentric inner and outer cylinders of stainless steel, with a radius ratio of $\eta = R_i/R_o = 0.92$ and an aspect ratio of $\Gamma = L/d = 2.3$, where R_i is the inner cylinder's radius, R_o is the outer cylinder's radius, L is the cylinder length, and d is the outer cylinder's diameter. The Gr, MoS_2 , and BN powders were individually dispersed in a solution of deionized (DI) water/IL (5 wt%). Various initial concentrations of 0.1–200 mg mL $^{-1}$ were tested. The exfoliation time of 1 h was optimized by a preliminary experiment of exfoliation time versus final concentration of EF nanosheets (Figure S18, Supporting Information). The [EMIM][BF $_4$], [TMA][BF $_4$], [EMIM][EtSO $_4$], and [EMIM][PF $_6$] ILs were used as stabilizing and exfoliating agents. To enable comparisons with previous study findings, SDS, an SC surfactant (5 wt%), and an NMP solution

were also used. The feed solution was injected into the TC reactor and then processed for 1 h. After exfoliating and functionalizing the 2D materials, EF-nanosheet dispersions (0.5 L) were obtained and then centrifuged (420 g, 150 min) to obtain mono- or few-layer EF nanosheets while removing the unexfoliated 2D materials. Residual ILs and small-sized EF-nanosheets were removed via centrifuged 3200 g for 1 h. The as-obtained EF-nanosheets solution was purified thoroughly by dialysis for two weeks to remove remaining impurities. The EF-nanosheets were then filtered and washed with DI water several times. The powder samples were collected by freeze-drying the EF-nanosheet dispersions for 24 h, then weighed by an electronic scale (HS224S, Hansung Instrument Co., Ltd., South Korea) to measure exfoliation yield and concentration. In order to take account of the weight of the ionic liquid adsorbed on the EF-nanosheets, the weight percentage (Figure S7, Supporting Information) of the ionic liquid was subtracted from the measured weight of the powder and then calculated exfoliation yield and concentration. The redispersed EF-nanosheet solutions were created using mild sonication in DI water with various concentrations (0.1–20 mg mL $^{-1}$) of the EF-nanosheet powders.

Fabrication of the Freestanding EF-Nanosheet Films: The EF-Gr, EF- MoS_2 , and EF-BN films were prepared via vacuum filtration. The redispersed solutions (4 mg mL $^{-1}$) of the EF nanosheets were filtered using a 0.1 μm Anodisc filter membrane (Whatman, UK), and the freestanding films were then peeled off the membrane.

Fabrication of the Inkjet-Printed Circuits: The ink for inkjet printing was produced without any additives (i.e., binder and dispersion reagents) via simple, overnight sonication to reduce the dimensions of the EF nanosheets. The inkjet-printed circuits were designed using PowerPoint 2016 (Microsoft, USA), then printed using the inkjet printer (L220, Epson, Japan) on A4 paper using the EF-Gr, EF- MoS_2 , and EF-BN nanosheet inks. After printing, the inks were dried at room temperature for 24 h.

Characterization of Materials and Instruments: The SEM images were obtained via field-emission SEM (Magellan 400). The HRTEM images were acquired using a Titan Double Cs-corrected TEM (Titan-cubed G2 60-300) operating at 300 kV. The XRD data were obtained through a Rigaku SmartLAB D/teX Ultra 250 detector (9 kW), including a θ/θ goniometer equipped with a Cu K α ($\lambda = 1.5418$ Å) radiation generator. The Raman spectra were obtained using a LabRAM HR Evolution Raman spectrometer (HORIBA Jobin Yvon) with radiation provided by an air-cooled, frequency-doubled Nd:YAG laser (532 nm). The TGA was conducted using a TGA 92-18 analyzer (Setaram) with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The AFM measurements were taken with an AFM-Raman spectrometer (INNOVA-LABRAM HR800, Bruker Co., Ltd.).

Electrochemical Measurements: CV and galvanostatic charge/discharge were measured with a CHI 760D electrochemical workstation (CH Instruments) at room temperature. A conventional, three-electrode electrochemical cell, including a working electrode obtained from an EF-Gr film, a counter electrode obtained from a coiled platinum wire, and a reference electrode obtained from Ag/AgCl in 1 M of H $_2$ SO $_4$, was used in the experiment. EF-Gr films were used directly as working electrodes in the absence of additional binders and carbon additives. For electrical connection, the edges of the freestanding films were bonded with titanium foil using silver paste. The control sample of SC-Gr films was prepared and tested using the same sampling procedures and experimental conditions used for the EF-Gr films. The rate capabilities and cycle performances were evaluated via measurements of galvanostatic charge/discharge. The specific capacitance (C_f) of the EF-Gr and SC-Gr film electrodes were calculated from the galvanostatic charge/discharge curves, based on the following equation: $C_f = I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time after iR drop, m is the mass of the electrode, and ΔV is the voltage change during discharge.

CFD Simulations: CFD simulation, via the ANSYS Fluent 16.0 software package, was used to verify that the flow regimes depended on the rotational speeds of the inner cylinder. The dimensions of the simulated reactor were the same as those of the TC reactor in the exfoliation experiments. The geometry-conforming mesh was constructed with 20 million elements. The large eddy simulation (LES) model was applied, as it is considered a reliable tool for simulating transient

Table 1. Boundary conditions for the simulation of the fluidic reactor.

	Boundary condition
Inner cylinder	Moving wall, no slip
Outer cylinder	Stationary wall, no slip
Front and back walls	Wall, no slip

fluctuations.^[47] Neither a slip nor a moving wall condition was applied to any surfaces, including that of the inner cylinder rotating around the z-axis. The boundary conditions are summarized in **Table 1**. The shear rate was calculated using the equation $\dot{\gamma} = v/h$, where $\dot{\gamma}$ is the shear rate, v is the moving plate's velocity, and h is the distance between the two parallel plates.

First-Principles Calculations: The density functional theory-based calculations were performed using the Vienna Ab initio Simulation Package (VASP).^[48,49] The revised Perdew–Burke–Ernzerhof exchange–correlation functional was used,^[50,51] combined with the van der Waals density functional (vdW-DF)^[52,53] for nonlocal correlations, to ensure an accurate account of the dispersion interactions.^[54] The projector augmented wave (PAW) method was used to determine the electronic structures of the ion interactions. The Brillouin zones were sampled using a Γ -centered, $3 \times 3 \times 1$ k-point mesh, while the electronic states were smeared using the Methfessel–Paxton scheme with a broadening width of 0.1 eV. The electronic wave functions were expanded in a plane-wave basis set with a cutoff energy of 500 eV, and the atomic-relaxation process continued until the Hellmann–Feynman forces acting on the atoms were less than $0.02 \text{ eV } \text{\AA}^{-1}$. Periodic supercell geometries were constructed to model the Gr, MoS₂, and BN sheets using 5×5 , 4×4 , and 5×5 unit cells, respectively, and a vacuum layer of 15 Å was added onto each surface to eliminate the interlayer interactions. The adsorption energies of the ILs were defined as $E_{\text{ads}} = E(\text{IL/nanosheet}) - E(\text{IL}) - E(\text{nanosheet})$, where $E(\text{IL/nanosheet})$, $E(\text{IL})$, and $E(\text{nanosheet})$ represent the total energy of an IL-adsorbed nanosheet, ionic liquid, and pristine nanosheet, respectively. To describe the restacking of nanosheets, slab models of the pristine and IL-functionalized nanosheet layers with vacuum layers of 15 Å were used. In these models, the nanosheet slabs in which the ILs were adsorbed on both sides were used to represent the IL-functionalized nanosheet layers, and stacking these nanosheets from a sufficiently separated distance to stable interlayer spacing was considered. Stacking energy was defined as $E_{\text{stack}} = E_{\text{tot}}(d = \infty) - E_{\text{tot}}(d = d_{\text{stack}})$, where E_{tot} is the total energy per nanosheet and d_{stack} is the interlayer spacing after stacking.

Supporting Information

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

Acknowledgements

J.-M.J., and H.G.K., contributed equally to this work. This work was supported by the Engineering Research Center of the Excellence Program of the Korean Ministry of Science, ICT & Future Planning (MSIP)/National Research Foundation of Korea (NRF) (Grant Nos. NRF2014R1A5A1009799 and 2016R1A2B4013374). This research was also performed as the Technology Innovation Program (10070150) funded by the Ministry of Trade, Industry & Energy (MI, Korea) and a Project No. SI1809 (The Development of Sustainable Materials Technology for Eco-Automobile) supported by the Korea Research Institute of Chemical Technology (KRICT).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, computational fluid dynamics, density functional theory, hydrodynamic exfoliation, ionic liquids

Received: April 30, 2018

Revised: June 8, 2018

Published online: August 12, 2018

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