Production of High-Concentration Graphene Dispersions in Low-Boiling-Point Organic Solvents by Liquid-Phase Noncovalent Exfoliation of Graphite with a Hyperbranched Polyethylene and Formation of Graphene/Ethylene Copolymer Composites

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Supporting Information

ABSTRACT: We report in this paper the successful production of stable high-concentration graphene dispersions in low-boiling-point, low-polarity conventional organic solvents (chloroform and THF) by liquid-phase noncovalent exfoliation of graphite assisted with a hyperbranched polyethylene (HBPE) as the stabilizer. In the exfoliation process, HBPE adsorbs onto the surface of exfoliated graphene flakes, providing steric stabilization against their restacking.



A systematic investigation on the effects of exfoliation conditions, including the solvent and the amounts of graphite and HBPE, has been conducted. Graphene dispersions with the concentration up to 0.18 mg/mL in chloroform and 0.045 mg/mL in THF have been obtained. It is also demonstrated that the dispersions can be further concentrated by solvent evaporation to give highly concentrated stable dispersions at 3.4 mg/mL. Through their characterizations with transmission electron microscopy, atomic force microscopy, and Raman spectroscopy, the majority of the graphene products is found to be high-quality, defect-free, few-layer graphene flakes with the layer number between 2 and 4 and the lateral dimension in the range of 0.2–0.5 μ m. The dispersions can be fabricated into flexible conductive free-standing graphene films and be used to prepare graphene/ethylene copolymer composites through solution blending, which show significant enhancements in both thermal and mechanical properties.

1. INTRODUCTION

Since its first isolation in 2004 by micromechanical cleavage of graphite,¹ graphene has received intense attention from various research fields.²⁻⁸ Its unique atomically thin two-dimensional lattice structure constructed with sp²-bonded carbons and extraordinary properties (such as electrical, mechanical, thermal, and optical properties) have endowed its numerous emerging applications in a broad range of fields, such as electronics and photonics,⁹⁻¹¹ energy conversion and stor-age,¹²⁻¹⁵ polymer nanocomposites,¹⁶⁻²⁰ and catalysis.^{21,22} For most graphene-based applications, large-scale, stable, highconcentration dispersions of high-quality graphene in specific solvents are often desired. Thus far, a great number of methods have been developed for the production of graphene dispersions in various aqueous or organic solvents from pristine graphite, graphene oxide, expanded graphite, and graphite intercalated compounds, respectively.²³⁻²⁶ In particular, the most commonly used methods employ graphene oxide (GO) as the starting material that is produced by oxidation of graphite and involve the exfoliation and reduction of GO either thermally or chemically.^{27–30} These methods render chemically converted graphene (CCG), which is usually stable in aqueous

or organic solvents in the presence of stabilizers. Large-scale dispersions of CCG at high concentrations can be obtained in these methods, promoting their dominant use in the preparation of graphene/polymer composites^{16–20} and many other applications. However, compared to pristine graphene that is free of defects, the obtained CCG usually shows significantly reduced electrical properties owing to the considerable disruption in the π -orbital structure even after reduction.^{23–30} Besides, the adopted processes often involve harsh, nonenvironmentally friendly chemistry.

As a result, an alternative method has been explored for producing the dispersions of defect-free graphene by liquidphase exfoliation of pristine graphite in some particular organic solvents such as *N*-methylpyrrolidone (NMP),^{24,31-35} dimethylformamide (DMF),³⁶ and *o*-dichlorobenzene (ODCB).^{35,37} These solvents have the surface energy matching well with that of graphene, and graphite can thus be directly exfoliated into graphene sheets in them simply by means of sonication.

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Meanwhile, some other specialty solvents, including ionic liquids^{38–40} and fluorinated aromatic solvents⁴¹ that can have interactions with the π -electrons on the graphene, have also been reported to successfully render graphene dispersions by sonication. This liquid-phase exfoliation method has the advantage of giving stable dispersions of graphene without defects owing to the absence of oxidation.²⁴ However, the particular solvents required are often expensive and/or have a high boiling point, rendering difficulty in further processing. It is thus highly desired to exfoliate graphite in conventional solvents having a much lower boiling point, like water, tetrahydrofuran (THF), chloroform, etc. However, it has been found that these conventional solvents are often the poor ones for graphite exfoliation due to their unmatched surface energy.^{42–44}

To circumvent the above disadvantage, liquid-phase exfoliation of graphite in various conventional low-boilingpoint solvents with the presence of stabilizers has been explored. The stabilizers include surfactants, $^{45-50}$ functionalized aromatic molecules, $^{51-62}$ and polymers. $^{63-68}$ While sonication serves to exfoliate graphite by overcoming the van der Waals interactions, the stabilizers adsorb onto the exfoliated graphene sheets through noncovalent interactions (such as hydrophobic interactions $^{45-50,63-68}$ and $\pi-\pi$ stacking interaction $^{51-62}$) to prevent their restacking and render their stable dispersion. The low-boiling-point solvent used in this strategy is somehow mainly restricted to water in the majority of the reports, with only few highly polar organic solvents (ethanol^{61,64,67} and methanol^{61,67}) used. The resulting aqueous dispersions have enabled the preparation of the graphene composites with several water-soluble polymers.^{60,62,67} High-concentration graphene dispersions in nonpolar or weakly polar low-boilingpoint organic solvents (such as THF and chloroform), however, have rarely been achieved, while such dispersions are highly attractive for the preparation of polymer composites since a large number of commodity polymers are soluble in these solvents. Coleman et al.⁶⁸ have recently shown that graphite can be exfoliated in THF or cyclohexanol with a range of conventional polymers, such as polybutadiene, polystyrene, poly(vinyl chloride), poly(vinyl acetate), poly(methyl methacrylate), cellulose acetate, etc., as stabilizers. Though effective, graphene concentration in the dispersions obtained therein, however, is often too low (e.g., in the range of 0.006-0.022 mg/mL in THF) to meet requirements in large-scale applications. Through a modeling study, Coleman et al. have predicted that maximal graphene concentration can be reached when the polymer and solvent have similar solubility parameters as the graphene sheets.⁶⁸ The search for a suitable polymer/solvent combination is thus important to render highquality graphene dispersions at high concentrations in conventional low-polarity, low-boiling-point organic solvents.

In this paper, we demonstrate the successful liquid-phase exfoliation of graphite in THF and chloroform with a hyperbranched polyethylene (HBPE) as the noncovalent polymer stabilizer, which renders directly high-concentration (up to 0.045 mg/mL in THF and 0.18 mg/mL in chloroform) dispersions of few-layer graphene flakes. The dispersions can be further concentrated to reach the graphene concentration as high as 3.4 mg/mL while remaining stable. HBPE is a novel polyethylene grade synthesized through the unique ethylene chain walking polymerization technique and without containing any specific functionality.^{69,70} We have recently discovered that it can efficiently functionalize and solubilize multiwalled carbon

nanotubes at surprisingly high concentrations in THF and chloroform (with solubility up to ca. 1.2 mg/mL in chloroform and 0.9 mg/mL in THF).⁷¹ This is achieved through the noncovalent nonspecific CH- π interactions between HBPE and the nanotube surface. While conventional linear polymers of ethylene and other olefins are commonly ineffective for the nanotube dispersion, the success with HBPE is attributed to its unique hyperbranched chain architecture, which unprecedentedly renders strong CH- π interactions for the efficient functionalization and dispersion of the nanotubes.⁷¹ The resulting carbon nanotubes functionalized with HBPE have been further demonstrated to show excellent dispersion in ethylene copolymer composites to render significantly enhanced properties.^{72,73} This stimulated our investigation herein, which describes its use in the noncovalent liquid-phase exfoliation of graphite. A systematic study on the effects of exfoliation parameters on the graphene concentration has been carried out, accompanied with the detailed characterization of the resulting graphene flakes. Meanwhile, the applications of the obtained graphene dispersions in the preparation of thick graphene films and graphene/ethylene copolymer composites are also demonstrated.

2. EXPERIMENTAL SECTION

Materials. Natural graphite was purchased from Aldrich (product number 332461). It was sieved through a 500 μ m mesh sieve to remove large particles before use. The HBPE was synthesized via ethylene chain walking polymerization with a Pd-diimine catalyst, [(ArN=C(Me)-(Me)C=NAr) Pd- $(CH_3)(N \equiv CMe)$]⁺SbF₆⁻ (Ar = 2,6-(*i*Pr)₂C₆H₃), at 35 °C and ethylene pressure of 1 atm (see our earlier papers^{74,75} on the details of the polymerization). As per polymer characterization with triple-detection gel permeation chromatography (GPC), the HBPE has an absolute weight-average molecular weight (M_w) of 100 kg/mol, a polydispersity index (PDI) of 1.23, and a weight-average intrinsic viscosity $([\eta]_w)$ of 11.8 mL/g in THF at 33 °C. The elastomeric ethylene-norbornene copolymer (ENC) used as the matrix polymer for graphene composites was synthesized via "living" copolymerization of ethylene and norbornene with the Pd-diimine catalyst at 15 °C, an ethylene pressure of 1 atm, and a norbornene feed concentration of 0.35 M in chloroform for a polymerization time of 4 h, by following our recently reported procedure.⁷⁶ With an overall norbornene content of 8.2 mol % (as per ^{13}C NMR spectroscopy), this polymer should be featured with a gradient composition profile as per our earlier study,⁷⁶ with one end featured with alternating ethylene-norbornene units and the other end being pure hyperbranched ethylene segments. From triple-detection GPC, the polymer is narrow distributed with an absolute $M_{\rm w}$ of 46 kg/mol and a PDI of 1.14. Thermal characterization with differential scanning calorimetry (DSC) indicates that it has two glass transitions centered at -65 and 101 °C, respectively, as well as a weak melting endotherm centered at -31 °C with a melting enthalpy of 5 J/g. The two glass transitions are attributed to the hyperbranched polyethylene segments and alternating ethylene-norbornene segments, respectively, with the latter one at 101 °C being very weak due to the low content. Solvents, including THF (>99.0%), chloroform (>99.0%), heptane (>99.0%), and toluene (>99.9%), were obtained from Fisher Scientific and were used as received.

General Procedure for Liquid-Phase Graphite Exfoliation with HBPE in Different Solvents and Characterizations. Graphite exfoliation assisted with HBPE in different solvents (THF and chloroform) was undertaken by using the following sonication-centrifugation process. A mixture of graphite and HBPE at prescribed amounts in the solvent (generally, 10 mL, except in large-scale exfoliation experiments involving the use of 200 mg of graphite and 400 mg of HBPE in 100 mL of solvent) was sonicated at room temperature in a bath sonicator (Branson 3510 with a measured ultrasonic power of 70 W) for 48 h. During the sonication process, the temperature of the sonication bath was maintained constant by a continuous flow of water. The resulting mixture was subsequently centrifuged at 4000 rpm for 45 min and was then left undisturbed overnight. The supernatant graphene dispersion was then collected. Various characterization techniques were employed to characterize the graphene dispersions/products.

To determine graphene concentration (C_{G} , mg/mL) in the dispersion, UV-vis spectroscopic analysis was performed on an Ultraspec 2100 Pro UV-vis spectrophotometer with a 1 cm cell. After proper dilution if necessary, the graphene dispersion was scanned from 190 to 900 nm at a resolution of 2 nm. The absorbance at 660 nm (A_{660}) was used to calculate $C_{\rm G}$. All reported concentrations are the average of at least three measurements. The specific extinction coefficient of graphene at 660 nm was determined to be 42.3 mL/mg/cm in THF and 45.4 mL/mg/cm in chloroform. To determine the extinction coefficient, two graphene dispersions (ca. 80 mL for each) were prepared by following the above sonication-centrifugation procedure with the composition of 200 mg graphite/400 mg HBPE/100 mL solvent. The $C_{\rm G}$ values of both dispersions were determined directly by pipetting a precise volume of dispersion into a thermogravimetric analysis (TGA) sample pan. It was dried by solvent evaporation and was subsequently heated to 800 °C at 20 °C/min in N₂ atmosphere on a TA Instruments Q50 thermogravimetric analyzer to determine precisely the graphene mass by removing the polymer, with which the $C_{\rm G}$ value of the dispersion was calculated. The average C_G values on the basis of at least five repeat measurements were 0.0777 \pm 0.0045 mg/mL in THF and $0.0519 \pm 0.0019 \text{ mg/mL}$ in chloroform. The dispersions were subsequently diluted to ten known concentrations and measured for the absorbance to determine the extinction coefficients.

To prepare graphene samples for characterizations with transmission electron microscopy (TEM) and atomic force microscopy (AFM), a graphene dispersion in chloroform (50 mL with $C_G = 0.050 \text{ mg/mL}$) was vacuum-filtered onto a porous alumina membrane (Whatman Anodisc 47, pore size 20 nm) and was rinsed with 50 mL of chloroform to remove free HBPE. The resulting graphene solids were then redispersed in chloroform (50 mL) under sonication. TEM samples were prepared by depositing a few drops of the dispersion onto holey carbon grids (400 mesh). TEM images and selected area electron diffraction were captured on a Philips EM400 transmission electron microscope operated at 100 keV. AFM samples were prepared by placing a freshly cleaved mica piece in the dispersion overnight for sample deposition and then taken out and dried for the measurements. Contact mode images were captured on a Bruker multimode atomic force microscope with a silicon tip on a nitride lever (SNL-10) having a force constant of 0.12 N/m.

Raman spectra of the graphene products (excitation at 514 nm) were recorded on a Reinshaw Invia Laser Raman spectrometer. Graphene films were prepared by vacuum

filtering graphene dispersions (30 mL with $C_{\rm G}$ = 0.051 mg/mL) in chloroform onto porous alumina membranes, followed with rinsing with 30 mL of chloroform and drying at room temperature. The films on the alumina membranes were then directly used for Raman characterization.

The mass content of the adsorbed polymer in the graphene solids obtained by filtration and washing was determined through TGA measurements on the TA Instruments Q50 thermogravimetric analyzer. The measurements were conducted under N_2 atmosphere with a continuous flow of 60 mL/min and a balance flow of 40 mL/min. A sample (ca. 5 mg) was first heated to 100 °C and held at this temperature for 10 min and then heated to 800 °C at 20 °C/min. Polymer mass content was calculated from the mass loss (polymer) and residual mass (graphene) at 550 °C. Fourier-transform infrared (FTIR) spectra of the graphene solids were obtained on a Nicolet 6700 FTIR spectrometer. The samples were prepared as pellets with spectroscopic-grade KBr.

X-ray diffraction (XRD) measurements were carried out on the graphene/HBPE mixtures containing free HBPE. The graphene dispersions (about 20 mL with $C_{\rm G}$ = 0.051 mg/mL in chloroform or 0.025 mg/mL in THF) were spray coated on glass sample plates, followed with solvent evaporation under flowing air at room temperature. For the graphite/HBPE mixture, the XRD sample was prepared by casting a mixture of graphite (50 mg) and HBPE (200 mg) in THF (50 mL), followed with drying. Wide-angle XRD patterns were recorded on an X'Pert Pro diffractometer with Co radiation (wavelength 1.79 Å) at room temperature.

Preparation of Graphene Film and Characterizations. A graphene dispersion (150 mL with $C_{\rm G} = 0.157$ mg/mL) in chloroform was vacuum filtered onto an alumina membrane and subsequently washed with 100 mL of chloroform, giving a graphene film deposited on the membrane. After being soaked in a NaOH aqueous solution (0.05 M) for about 5 min, the film was peeled off from the membrane and was thoroughly washed with deionized water, followed with drying in a vacuum oven at 60 °C overnight. SEM images of the free-standing graphene film were taken on a JEOL JSM-7401F field-emission scanning electron microscope. Electrical conductivity of the film was measured using a Keithley 2400 source meter with a four-probe method.

Preparation and Characterizations of Graphene/ENC **Composites.** A combined, large-volume graphene dispersion (1920 mL at average $C_G = 0.07 \text{ mg/mL}$) in chloroform was obtained by using the sonication-centrifugation procedure at the composition of 200 mg graphite/400 mg HBPE/100 mL solvent. The solvent in the dispersion was removed by evaporation, and the resulting graphene-HBPE mixture was redispersed in THF under sonication. The dispersion was subject to ultracentrifugation at 30 000 rpm for 30 min. The precipitate was redispersed in 80 mL of THF under sonication and underwent an additional three cycles of ultracentrifugation-redispersion for the removal of free HBPE. The final precipitate was dispersed in 40 mL of chloroform under sonication, rendering a stable dispersion with $C_{\rm G}$ = 3.4 mg/mL. From TGA measurement, the graphene precipitate after drying has a HBPE content of 39.4 wt %.

Graphene/ENC composites at different graphene contents (1.0-5.3 wt %) were prepared using the ENC as the matrix polymer via solution blending. A desired volume of high-concentration graphene dispersion obtained above was added into a solution of ENC (1.0 g) in chloroform (30 mL) under

stirring, followed with sonication at room temperature for 8 h. Methanol (80 mL) was then added into the dispersion to precipitate out the graphene/ENC composite, which was further washed with acetone (40 mL) and then dried under vacuum at 50 °C for 48 h. The graphene content in the composites was confirmed with TGA. DSC characterization of the composites was carried out on a TA Instruments Q100 differential scanning calorimeter in the standard DSC mode under a N2 atmosphere. The samples were first heated from room temperature to 150 °C at 10 °C/min and then cooled to -90 °C at 5 °C/min, and the data were collected on a subsequent heating ramp from -90 to 150 °C at 10 °C/min. XRD analysis was also carried out on the composites, which were coated onto glass sample plates. Dynamic mechanical analysis (DMA) of the composites was carried out on a TA Instruments DMA Q800 at room temperature in the tensile oscillation mode. Sample bars with the dimension of 20 mm $(length) \times 5 mm (width) \times 1 mm (thickness)$ were prepared by compression molding in a Carver Press at ca. 200 °C. For the conductivity measurements, sample disks (10 mm in diameter and 1 mm in thickenss) were also prepared by compression molding. The measurements were carried out on an Autolab PGSTAT100 in the potentiostat mode by applying a DC voltage of 10 V across the sample thickness.

3. RESULTS AND DISCUSSION

Preparation of Graphene Dispersions with HBPE. Four conventional organic solvents, chloroform, THF, n-heptane, and toluene, are used for liquid-phase exfoliation of graphite in the presence of HBPE. These are generally poor solvents ineffective for graphite exfoliation in the absence of stabilizers. HBPE is soluble in all of them at room temperature with increasing solubility following the above order. In the exfoliation process, the graphite dispersions in the various solvents containing HBPE are sonicated for 48 h at room temperature, followed with mild centrifugation at 4000 rpm to remove macroscopic aggregates. Figure 1(a) shows the images of the dispersions obtained in the four different solvents at the sonication composition of 20 mg graphite/40 mg HBPE/10 mL solvent. Dark stable graphene dispersions are obtained in both chloroform and THF, while the resulting dispersions in heptane and toluene are nearly colorless. This indicates the successful graphite exfoliation with HBPE in the former solvents but not in the latter ones. This is in agreement with our previous study on the solubilization of multiwalled carbon nanotubes with HBPE, where nanotube dispersion at high concentrations can be achieved effectively in chloroform and THF but not in either heptane or toluene.⁷¹ Following this, our subsequent systematic study is carried out with chloroform and THF as the solvent. The effects of the sonication conditions, including graphite feed concentration (i.e., the starting concentration of graphite used for sonication, $C_{G,F}$) and mass ratio of HBPE to graphite, on the graphene concentration (C_G) in the resulting dispersions have been investigated, along with the detailed characterization of the graphene products.

The $C_{\rm G}$ value of the dispersions is quantified from their UV– vis absorbance at 660 nm by following the Lambert–Beer Law. Generally, the UV–vis spectra of the dispersions are flat and featureless except below 350 nm (see the inset in Figure 1(b) as an example). As per our earlier study,⁷¹ HBPE shows no absorbance in the entire UV–vis wavelength range at the concentrations used herein. The absorbance of the dispersions should thus result completely from the dispersed graphene.



Figure 1. (a) Photos of graphene dispersions obtained with HBPE in different solvents at a sonication condition of 40 mg HBPE/20 mg graphite/10 mL solvent/48 h. (b) UV–vis absorbance at 660 nm (A_{660}) as functions of graphene concentration ($C_{\rm G}$) for graphene exfoliated with HBPE in THF and chloroform, respectively. Inset: representative absorption spectrum for a graphene dispersion at $C_{\rm G}$ = 0.005 mg/mL and HBPE concentration of 0.4 mg/mL in chloroform.

This enables the direct quantification of $C_{\rm G}$ from the absorbance. The UV-vis extinction coefficient of graphene in both chloroform and THF was determined by measuring the absorbance at 660 nm for ten reference dispersions of different but known graphene concentrations in each solvent (see Figure 1(b) for the dependence of absorbance on concentration in both solvents). The reference dispersions in each solvent were prepared at different dilutions from a graphene dispersion whose C_G was precisely determined (0.0777 mg/mL in THF and 0.0519 mg/mL in chloroform, see Experimental Section). From Figure 1(b), a linear dependence of the absorbance on concentration is found in both solvents, giving the extinction coefficient of 42.3 and 45.4 mL/mg/cm in THF and chloroform, respectively. Since the coefficients in both solvents have not been previously reported in the literature, a direct comparison with literature data is not possible. Nevertheless, the coefficients determined herein are very close to the value of 36.2 mL/mg/cm (at 660 nm) determined by Coleman et al. for pristine graphene in NMP,^{32,68} with the small differences resulting possibly from the use of different solvents.

Figure 2(a) shows the effect of $C_{G,F}$ on the C_G value of the resulting graphene dispersions at the fixed HBPE feed concentration ($C_{HBPE,F}$) of 4 mg/mL in both solvents (10 mL). Increasing $C_{G,F}$ from 1 to 10 mg/mL leads to the increased C_G in both solvents. The C_G values achieved in THF are in the range of 0.016–0.045 mg/mL while those in chloroform are relatively higher, in the range of 0.025–0.18 mg/mL. These ranges of C_G values are similar to or even better than those achieved by surfactant- or polymer-assisted exfoliation in water at similar conditions. With surfactant



Figure 2. (a) Graphene concentration (C_G) as a function of graphite feed concentration $(C_{G,F})$ in dispersions obtained with HBPE at 4 mg/ mL in THF and chloroform, respectively. (b) Proportion of exfoliated graphene $(C_G/C_{G,F})$ at different $C_{G,F}$ in dispersions shown in (a). (c) C_G as a function of mass ratio of HBPE to graphite in THF and chloroform, respectively, at $C_{G,F} = 2$ mg/mL.

stabilizers, Coleman et al. achieved the concentration of 0.002-0.05 mg/mL with the use of sodium dodecylbenzene sulfonate (at a sonication time of 30 min)⁴⁵ and high concentration of 0.14-0.3 mg/mL with the use of sodium cholate but subject to long sonication (200–430 h).⁴⁹ With polymer stabilizers, Bourlinos et al. obtained aqueous graphene dispersion at 0.15-0.20 mg/mL with polyvinylpyrrolidone,⁶³ and Hersam et al. achieved the concentration of 0.07 mg/mL with block copolymers.⁶⁵ The highest concentration of 0.18 mg/mL achieved herein in chloroform is also significant compared to the concentration value of ca. 0.25 mg/mL obtained by liquid-phase exfoliation in NMP as the best known solvent without a stabilizer at a sonication time of ca. $48 \text{ h}.^{32}$

Figure 2(b) shows the percentage proportion of the exfoliated graphene relative to the fed graphite $(C_G/C_{G,F})$ as a function of $C_{G,F}$. Generally, it is in the range of 2-3% in chloroform or 0.2-2% in THF, with a general decreasing trend following the increase of $C_{G,F}$ from 1 to 10 mg/mL. These ranges of proportion are also similar to those achieved in surfactant-assisted exfoliation at similar conditions.⁴⁵ In both solvents, the highest proportion (2.7% in chloroform and 2.1% in THF) is achieved at $C_{G,F} = 2 \text{ mg/mL}$. We subsequently investigated the effect of the mass ratio HBPE/graphite on $C_{\rm G}$ in the exfoliated dispersion at $C_{G,F} = 2 \text{ mg/mL}$. Figure 2(c) shows the dependence of C_G on the mass ratio of HBPE/ graphite, which varies from 0 to 10. In both solvents, an increase in $C_{\rm G}$ is noted with the increase of the mass ratio from 0 to 1, which should be attributed to the increased coverage of HBPE on the graphene surface by adsorption. Further increase of the mass ratio from 1 to 10, however, shows only marginal changes in C_G . The highest C_G values are 45.1 and 64.9 mg/mL in THF and chloroform, respectively, achieved at the HBPE/ graphite mass ratio of 1. Again, the $C_{\rm G}$ values achieved in chloroform in these experiments are always higher than the counter ones in THF, confirming the solvent effect. Given the established trends, the mass ratio of HBPE/graphite was kept at 2 in all the subsequent experiments to minimize the use of HBPE while at maintained exfoliation efficiency. All the dispersions obtained herein are found to be stable without observable precipitates after standing for two weeks or longer. In particular, those obtained at relatively high HBPE/graphite mass ratios (\geq 1) were found stable with negligible precipitates even after 1 year. Those obtained at lower ratios (<1) showed some precipitates after long standing; however, the precipitates can be redispersed back after short sonication. The above results thus confirm the high effectiveness of HBPE in rendering high-concentration graphene dispersions in chloroform and THF.

Characterization of Graphene Flakes and Evidences of Exfoliation. To further confirm the presence of exfoliated graphene sheets and elucidate their nature in the dispersions, we conducted detailed characterization of the graphene products with the use of TEM, AFM, Raman spectroscopy, and XRD. To facilitate these characterizations, large-scale graphene dispersions were obtained from a standard sonication condition: $C_{G,F} = 2 \text{ mg/mL}$ and HBPE/graphite mass ratio of 2 in 100 mL of chloroform/THF. Most characterizations reported herein were performed on the graphene dispersions obtained in chloroform given the higher graphene concentration achievable in it. In the characterizations requiring the use of graphene products without containing free HBPE (TEM, AFM, and Raman), the graphene dispersions were filtered onto a 20 nm alumina membrane, thoroughly washed, and redispersed back into the same amount of pure solvent. On the basis of TGA measurement (see Figure S1 in Supporting Information), the graphene solids obtained from the dispersions in chloroform and THF after filtration and wash have a typical weight loss of ca. 28% and 46%, respectively, at 550 °C. Given the filtration and wash procedure applied, the graphene solids should only contain a negligible amount of free HBPE. The TGA weight loss should correspond predominantly to the weight fraction of HBPE adsorbed on the graphene surface.

Figure 3(a) shows a representative low-magnification TEM image of the graphene flakes without free HBPE on a holey carbon grid. A large number of graphene flakes are observed with lateral dimensions in the range of 0.2–0.5 μ m. These lateral sizes are relatively smaller compared to the sizes (ca. 1 μ m) reported in the literature^{32,45} for liquid-phase exfoliated graphene. This possibly results from different sonication conditions, such as the sonication power and time, as well as the different pristine graphite. The majority of the flakes was found electronically transparent, unlike pristine graphite or thicker multilayer graphene that usually exists as larger and dark flakes in the TEM image owing to the stacking of a great number of graphene layers. This indicates that the graphene products obtained herein are mostly thin few-layer flakes. Figures 3(b)-(d) show the high-resolution TEM images of some representative flakes. In Figure 3(b), two pieces of fewlayered graphene flakes partially overlapped. Some small dark spots at a size of about 3 nm were also noted in both Figures 3(c) and (d), which possibly result from unknown impurities. The flake in Figure 3(d) appears to be a bilayer graphene on the basis of its electron diffraction pattern, where its {2110} diffraction spots are more intense relative to the {1100} spots.³¹

AFM analysis further supports the TEM results. Figure 4(a) shows a large-scan-area contact-mode image of the graphene flakes deposited on a mica substrate. Consistent with the TEM results, the majority of the flakes has lateral sizes in the range of ca. 0.2–0.5 μ m. Some larger flakes having lateral dimensions



Figure 3. (a) Low-magnification TEM image of graphene flakes deposited on a holely carbon film; the flakes were obtained with HBPE in chloroform, and free HBPE was removed by filtration. (b-d) High-resolution TEM images of representative graphene flakes in (a). Inset in (d) is an electron diffraction pattern of the graphene flake shown in (d).

above 1 μ m are also observed, possibly resulting from flake reaggregation during the sample preparation step. Figures 4(b) and (d) present the higher-magnification AFM images for two individual flakes. From their corresponding height profiles in Figures 4(c) and (e), they show a nonuniform surface, suggesting the presence of adsorbed HBPE on the flake. In both flakes, their height is around 2.2 nm. Since a single-layer graphene sheet has an AFM thickness of ca. 1 nm, the flakes should be single-layer or bilayer graphene with some adsorbed HBPE on the surface.

Figure 5(a) shows the Raman spectrum of a graphene film without containing free HBPE, along with that of the pristine graphite as a reference sample. For the purpose of comparison,

the two spectra have been normalized with respect to the Gband at 1582 cm⁻¹. In addition to the G-band, a D-band at 1350 cm⁻¹ and a 2D-band at around 2700 cm⁻¹ typical of graphitic materials are observed in both spectra. While the Dband is indicative of the presence of defects, the shift/ broadening of the 2D-band is often used to distinguish singlelayer and few-layer graphene with the layer number $<5.^{77,78}$ The intensity ratio of \hat{D} - and G-bands (I_D/I_G) is found to be 0.25 and 0.15 in the graphene film and pristine graphite, respectively. The ratio of 0.25 is small relative to typical values (0.35-0.7) reported in the literature for some high-quality graphene flakes obtained by liquid-phase exfoliation.^{32,33,47,49} It thus confirms that the graphene products obtained herein have high quality, and the D-band should arise predominantly from the defects at the flake edges given their relatively smaller flake size. From Figure 5(b), a distinct difference in the shape of the 2D-band is noted between the two spectra. The 2D-band in graphite consists of two components of different intensity with the peak maximum position at 2728 and 2615 cm⁻¹, respectively.77,78 The 2D-band in the graphene film is a single but broadened peak with the peak maximum position moved to ca. 2701 cm^{-1} . This is characteristic of few-layer graphene with a layer number between 2 and 4 since multilayer graphene with a layer number >5 should have the same 2D-band as graphite.77,78 Along with the TEM and AFM results, the Raman results provide the direct evidence supporting the successful exfoliation of the graphite into mainly high-quality, few-layer graphene flakes with low defects. Meanwhile, the graphene products may also contain a very small amount of single-layer graphene, which should have a single sharp 2D-band at ca. 2680 cm^{-1.77,78} Due to the peak overlapping, its content cannot be determined.

The above characterizations with TEM, AFM, and Raman spectroscopy were also performed on the graphene products obtained in THF, with similar results obtained. To avoid being repetitive, those results are not included. In addition to the above characterizations, we further performed XRD characterization on the graphene–HBPE mixtures obtained directly by evaporating the solvent from the dispersions without the removal of free HBPE. Figure 6 shows the XRD spectra of two mixtures obtained from the dispersions in chloroform and THF, respectively, along with the spectrum of a graphite–



Figure 4. (a) Wide-field AFM image (height mode) of graphene flakes deposited on a mica surface; these flakes were obtained with HBPE in chloroform, and free HBPE was removed by filtration. (b) AFM image (height mode) for a graphene flake. (c) Height profile for the flake shown in (b). (d) AFM image (height mode) for another graphene flake. (e) Height profile for the flake shown in (d).



Figure 5. Raman spectra (excitation at 514 nm) for a graphene film deposited on an alumina membrane and the pristine graphite. The graphene film was obtained by filtering a graphene dispersion in chloroform onto an alumina membrane followed with washing and drying.



Figure 6. Wide-angle XRD patterns for the graphite–HBPE (20/80, w/w) mixture (a) and two graphene–HBPE mixtures (1/99, w/w) obtained from dispersions in THF (b) and chloroform (c), respectively. The patterns were first normalized relative to the intensity of the HBPE amorphous halo at $2\theta = 21.5^{\circ}$, and then the patterns for the two graphene mixtures were scaled up by a factor of 25 to ensure all samples have the same graphene/graphite content.

HBPE mixture at 20% of graphite. The two graphene mixtures have a very similar graphene content of about 1 wt %, as calculated from their C_{G} values and the feed concentration of HBPE. The latter graphite mixture was prepared by solution mixing of graphite and HBPE followed by solvent evaporation. The three spectra were first normalized relative to the intensity of the HBPE amorphous halo centered at $2\theta = 21.5^{\circ}$ (*d*-spacing = 0.48 nm),^{71,79} and the two spectra of the graphene mixtures were then scaled up by 25 times to simulate the same graphene/graphite content for comparison. As shown in Figure 6, the graphite mixture shows a sharp intense diffraction peak at $2\theta = 30.9^{\circ}$ (d-spacing = 0.33 nm), which corresponds to the (002) diffraction characteristic of the graphitic structure.⁸⁰ In the spectra of the two graphene mixtures, only the amorphous halo of HBPE is present with the absence of the two graphite diffraction peaks. This also testifies the successful exfoliation of graphite and the sole presence of graphene few-layer flakes in the products.

Mechanism of Graphene Stabilization and Solvent Effect. The presence of HBPE at a significant amount (as per TGA results in Figure S1 in the Supporting Information) in the graphene products despite extensive washing indicates its adsorption on the surface of graphene flakes. The adsorbed HBPE is believed to play the role in sterically stabilizing the exfoliated graphene flakes against their restacking by reducing their van der Waals interactions (see Scheme 1). In our

Scheme 1. Noncovalent Liquid-Phase Exfoliation of Graphite in THF or Chloroform with HBPE as the Stabilizer



previous work on HBPE-assisted solubilization of carbon nanotubes,⁷¹ the adsorbed HBPE on the surface of carbon nanotubes has been directly evidenced with TEM. The adsorption is proposed to occur via noncovalent nonspecific CH- π interactions between HBPE and the nanotube surface given the absence of any specific functionality. 71,81 CH $-\pi$ interactions are generally weak hydrogen bonds.⁸² Resembling dendrimers, HBPE has a globular highly compact dendritic architecture with high-density branch ends on its surface.^{69,70} Its high-density branch structure is reasoned to give rise to significant attractive CH- π interactions between HBPE and the nanotube surface, enabling its adsorption and subsequent solubility of the nanotubes at high concentrations.⁷¹ Given the similar surface chemical structures of graphene flakes and carbon nanotubes, the adsorption of HBPE on the graphene flakes is also reasoned to result from CH- π interactions.

Figure 7 shows the FT-IR spectra of the graphene products without free HBPE obtained from dispersions in THF and chloroform, respectively, along with those of pure HBPE and pristine graphite for comparison. Two sets of signals, the C–H stretching vibration signals at 2850 and 2930 cm⁻¹ and the C– H bending signals at 1380 and 1460 cm⁻¹, are present in the spectrum of HBPE. Both sets of signals are also present in the two graphene products, confirming spectroscopically the presence of adsorbed HBPE. For the C–H stretching vibration signals, no appreciable difference is noted between the pure HBPE and the graphene products. However, there is a distinct difference in C–H bending signals between the samples. In contrast to the sharp C–H bending signals in pure HBPE at 1460 and 1380 cm⁻¹, the bending signals in the graphene products are in a much broader range of 1610–1290 cm⁻¹ and



Figure 7. FT-IR spectra for graphene samples (without free HBPE) prepared from dispersions in THF and chloroform, respectively. The spectra for HBPE and pristine graphite are also included for comparison.

are less well-defined, with the strongest signal shifted to 1580 cm⁻¹. This change in C–H bending signals is the evidence supporting the occurrence of $CH-\pi$ interactions between HBPE and graphene flakes.⁸² A similar change was also noted in the case of HBPE adsorbed on carbon nanotubes.⁷¹ Given their spherical dendritic chain architecture, the adsorption of HBPE should be partial, with some sites on one side of its spherical surface anchored onto the graphene surface and the

other side protruding into the solvent to provide steric stabilization (see Scheme 1 on the adsorbed HBPE). The occurrence of partial polymer adsorption is required to achieve graphene stabilization. 68

We now discuss the solvent effect on the concentration of graphene dispersion. From the $C_{\rm G}$ data shown above, the solvent has a dramatic effect on the exfoliation process. While stable dispersions with high C_G values are obtained in THF and chloroform, the exfoliation is unsuccessful in both heptane and toluene. The same phenomenon was also noted in the solubilization of carbon nanotubes with HBPE.⁷¹ This suggests that the solvent affects polymer adsorption on the exfoliated graphene, as pointed out by Coleman et al. in their study on the liquid-phase graphite exfoliation with conventional polymers as the stabilizer in various organic solvents.⁶⁸ For a given surface, there is a competition for adsorption between polymer and solvent.^{68,83,84} For successful partial adsorption of the polymer to occur, the two competing interactions, i.e., the polymergraphene interaction leading to adsorption and the polymersolvent interactions resulting in desorption, should be similar.⁶⁸ The complete inefficiency of exfoliation in heptane and toluene indicates the absence of sufficient polymer adsorption on the graphene surface for steric stabilization. This should result from the stronger polymer-solvent interaction compared to the polymer-graphene interaction in the two solvents. The higher solubility of HBPE in heptane and toluene than in THF and chloroform is one evidence supporting the stronger polymersolvent interaction in the two former solvents.⁷

Coleman et al.⁶⁸ have modeled polymer adsorption and derived the following simple expression in terms of the Hildebrand solubility parameters to quantify the effects of the polymer stabilizer and solvent on the concentration of the exfoliated nanosheets:



Figure 8. Graphene film: (a) a photo of the film; (b) and (c) SEM images of the film surface at different magnification; (d) a cross-sectional SEM image for the fractured edge of the film. The film was obtained by filtering 150 mL of graphene dispersion in chloroform onto an alumina membrane followed with washing and drying.

$$C_G \propto \exp\left[-\left(\frac{(\delta_S - \delta_P)(\delta_G - \delta_S)}{kT}\right)^2\right]$$
 (1)

where k is Boltzmann constant; T is the temperature; and δ_{s_i} $\delta_{\rm P}$, and $\delta_{\rm C}$ are the solubility parameter of the solvent, polymer, and graphene, respectively. With this expression, they have predicted that the nanosheet concentration can be maximized if $\delta_{\rm S} \approx \delta_{\rm P} \approx \delta_{\rm G}$, which is supported by experimental evidence. We also attempt to employ eq 1 to semiquantitatively examine the solvent effect on the C_G value. To do so, we take the solubility parameter of regular polyethylene, 16.1 MPa^{1/2,85} for HBPE. The other solubility parameters are taken as $\delta_{\rm G} = 21.25$ MPa^{1/2},⁶⁸ $\delta_{\rm S} = 18.5$ MPa^{1/2} for THF, 18.7 MPa^{1/2} for chloroform, 18.3 MPa^{1/2} for toluene, and 15.3 MPa^{1/2} for *n*heptane.⁸⁵ With these parameters, the term, $[(\delta_{\rm S} - \delta_{\rm P})(\delta_{\rm G} - \delta_{\rm P})(\delta$ $(\delta_{\rm S})^2$, is 43.5, 44.0, 42.1, and 22.7 MPa² in THF, chloroform, toluene, and heptane, respectively. According to eq 1, the $C_{\rm G}$ value in the four solvents should thus increase in the order: chloroform < THF < toluene < heptane. This differs drastically from the trend found herein. Possibly, eq 1 is oversimplified due to the assumptions employed in the derivation⁶⁸ and does not fit this particular system.

From the TGA results shown in Figure S1 (Supporting Information), the adsorbed amount of HBPE on graphene sheets in THF is significantly more than that in chloroform. However, the $C_{\rm G}$ values obtained in chloroform are consistently higher than the counter ones in THF as shown in Figure 2. This difference should result from the relatively higher power of chloroform in solvating the graphene sheets due to its closer Hildebrand solubility parameter (18.7 MPa^{1/2}) toward that of graphene (21.25 MPa^{1/2}).^{42,43} From Figure 2c, a significant $C_{\rm G}$ value of 0.017 mg/mL is achieved in pure chloroform without HBPE, while the corresponding value in THF is much smaller, 0.001 mg/mL. As per our previous study⁷² on the adsorption of HBPE on carbon nanotubes, the adsorbed HBPE covers only about 25% of the nanotube surface. This should also be the case here, with the adsorbed HBPE covering only a small portion of the graphene surface and the rest of the majority of the surface exposed to the solvent. The use of a solvent of higher power in solvating graphene will thus further help stabilize the graphene sheets and lead to a higher C_{G_i} in addition to the contribution from the adsorbed HBPE.

Preparation and Characterizations of Graphene Film. As an example on the application of the graphene dispersions obtained herein with the use of HBPE, a free-standing thick graphene film was prepared by vacuum filtering a graphene dispersion in chloroform (150 mL at $C_{\rm G}$ of 0.157 mg/mL) onto a porous alumina membrane. The film was washed thoroughly with pure chloroform to remove free polymer and was dried. As shown in Figure 8(a), the film is bendable without breaking and has a smooth metallic shiney surface with a weight of 25.9 mg and a diameter of 38 mm. On the basis of weight loss at 550 °C in TGA measurement, the adsorbed HBPE has a mass percentage of 27 wt % in the film. The morphology of the film was characterized with SEM. Figures 8(b) and (c) show the SEM images of the film surface at different magnifications. Figure 8(d) shows a cross-sectional image of the fractured edge of the film. From the images, the film is well packed without significant porosity. From Figures 8(b) and (c), the surface of the film is relatively smooth though some graphene flakes can be seen. The fractured cross-section in Figure 8(d) appears to be smooth and homogeneous without the layered structures

typically observed in films of graphene or graphene oxide.^{23–26,32,86–88} This suggests strong interactions between the polymer and graphene flakes.⁶⁴ From Figure 8(d), the film has an average thickness of ca. 18 μ m. The density of the film is estimated to be about 1260 kg/m³ from its mass and volume by assuming the absence of porosity in the film. It is comparable to the values of 1200–1350 kg/m³ reported for films (with 40–45% porosity) prepared from graphene dispersions obtained in NMP³² and the values of 1000–1440 kg/m³ for films prepared from dispersions obtained in water with a surfactant stabilizer.⁴⁹ However, it is significantly lower compared to the density of ca. 2200 kg/m³ for graphite,^{89,90} due to the presence of adsorbed HBPE and the possible porosity in the film.

Though containing the adsorbed HBPE at a significant content, the film is electrically conductive. The electrical conductivity of the film was measured to be 214.0 S/m (corresponding resistivity = $4.70 \times 10^{-3} \Omega$ m) with the fourprobe measurement technique. This value is lower compared to those reported in the literature for various graphene films prepared from dispersions obtained without the use of stabilizers, such as those obtained from graphene dispersions in NMP $(6500-18\ 000\ \text{S/m})^{31,32}$ and those obtained from reduced GO $(7000-10\ 000\ \text{S/m})^{88,91,92}$ The lower conductivity of the film obtained herein should be attributed to the adsorbed HBPE present at a high content. A low conductivity of 35 S/m was reported by Coleman et al.⁴⁵ for graphene films prepared from aqueous dispersions obtained with the use of a surfactant stabilizer. The low conductivity therein results from the presence of residual surfactant at ca. 36 wt % in the film. On the basis of the conductivity data, the quality of the graphene film obtained herein and its constituting flakes is comparable to or even better than that of the films prepared from dispersions stabilized with the surfactant. Meanwhile, the film obtained herein is flexible and freestanding. Its dimensions can be controlled/adjusted by changing processing parameters, such as the volume of graphene dispersion used for preparation, graphene concentration, etc. Future work will be carried out to functionalize the films by introducing specific functionalities into HBPE.

Preparation and Characterizations of Graphene/ENC **Composites.** Graphene/polymer composites have been extensively investigated.^{16–20} However, there have been only very few studies^{67,93,94} reporting the use of high-quality pristine graphene obtained from liquid-phase exfoliation for the composite construction due to the overwhelming difficulty in obtaining high-concentration graphene dispersions. In the majority of the reports, reduced graphene oxide was used instead as the nanofiller. In the limited cases involving pristine graphene, highly polar polymers (such as polyurethane,⁹³ polyvinylpyrrolidone,⁶⁷ and poly(vinyl chloride)⁹⁴) were employed as the polymer matrix since the graphene dispersions were obtained in polar solvents (e.g., DMF). The preparation of composites comprised of nonpolar polymers such as ethylene copolymers and pristine graphene has not yet been reported owing to the difficulty in achieving high-concentration graphene dispersion in low-polarity organic solvents. Tackling this challenge, we further demonstrate the application of the high-concentration graphene dispersions obtained herein in the preparation of graphene/ethylene copolymer composites through solution blending in chloroform.

A low-polydispersity ethylene-norbornene copolymer (ENC), synthesized through Pd-diimine-catalyzed "living" copolymerization of ethylene and norbornene,⁷⁶ was designed

and employed as the polymer matrix. This ethylene copolymer has a unique gradient composition according to our earlier study,⁷⁶ with one end featured with ethylene-norbornene alternating units, the other end being pure hyperbranched polyethylene segments, and in between being hyperbranched polyethylene sequences with sporadically interspersed isolated norbornene units. Designed at a low overall norbornene molar content of 8.2%, it behaves like an elastomer and is soluble in chloroform or THF at room temperature, which facilitates the convenient preparation of the composites through solution blending. Meanwhile, its possession of hyperbranched polyethylene sequences should also render its good compatibility with the graphene flakes having surface-adsorbed HBPE, which is beneficial to uniform dispersion of the graphene flakes within the polymer matrix.

For the preparation of the composites, a highly concentrated graphene dispersion (40 mL) with $C_G = 3.4$ mg/mL in chloroform was obtained by concentrating a large-volume dispersion (ca. 1920 mL) and removing the free HBPE by centrifugation. From TGA weight loss data at 550 °C, a graphene solid obtained from the dispersion upon drying has a polymer content of 39.4 wt %, which should correspond primarily to the adsorbed HBPE. Six graphene/ENC composites at different graphene mass content (1.0, 1.8, 2.5, 3.2, 4.0, 5.3 wt %, respectively, as per TGA residual mass at 550 °C) were compounded. The corresponding volumetric content of graphene in the composites is 0.27, 0.40, 0.48, 0.54, 0.60, and 0.67 vol %, respectively, by assuming the density of graphene and ENC being 2200 and 800 kg/m³, respectively. Systematic characterizations of the thermal, dispersion, electrical, and mechanical properties of the composites were undertaken.

Figure S2(a) in the Supporting Information shows TGA curves of the composites and the neat ENC in N_2 . Figure S2(b) (Supporting Information) displays the curves in the narrower region of 430-530 °C for a better comparison. Upon the addition of graphene, a significant improvement in the thermal stability of the composites is noted even at the lowest graphene content of 1.0 wt %. With the increase of the graphene content, the curves show a small but consistent shift toward the highertemperature direction as shown in Figure S2(b) (Supporting Information). Figure S2(c) plots the degradation temperature at 5% weight loss $(T_{5\%})$ as a function of graphene content. $T_{5\%}$ increases significantly from 417 °C for neat ENC to 446 and 463 °C for the composites of 1.0 and 5.3 wt % of graphene, respectively. The presence of graphene flakes having high aspect ratios clearly slows down the thermal decomposition of the polymer by restricting polymer chain mobility.^{16,38}

Figure S2(d) (Supporting Information) compares the DSC thermograms of the composites. The neat ENC has two clear transitions attributable to the hyperbranched polyethylene segments with low/zero norbornene content, a glass transition (T_g) centered at -66 °C, and a weak melting endotherm (T_m) centered at -31 °C. In addition, it has a second but very weak T_g at ca. 101 °C attributable to the chain segments having considerable norbornene content. These transitions are preserved with negligible changes in the composites of the graphene content of 1.0-3.2 wt %. In the other two composites of higher graphene content (4.0 and 5.3 wt %), the lower T_g is still observed with no appreciable change. The melting endotherm, however, becomes ill defined, with very weak nearly featureless signals in the broad temperature range from -50 to 50 °C. This confirms that the graphene fillers have

restricting effects on the chain relaxation processes of the polymer.

XRD characterization of the composites was undertaken to examine the dispersion state of the graphene flakes. Figure S3 in the Supporting Information compares the XRD patterns of the composites having a graphene content of 3.2 and 5.3 wt % with those of neat ENC and a graphite/ENC composite with 5 wt % pristine graphite. In the figure, the patterns of the three composites have been normalized to the same graphene/ graphite content. An amorphous halo at $2\theta = 20.8^{\circ}$ resulting from the polymer is present in all the samples. The graphite/ ENC composite shows a sharp intense peak at 30.9° for the graphitic structures. In the patterns of the two graphene composites, a small peak at 30.9° is also observed but is very weak and relatively broad compared to that in the graphite/ ENC composite. It indicates the presence of a very small amount of restacked graphene sheets formed during the preparation of high-concentration graphene dispersion and/or the solution blending of the composites. Restacking of the graphene sheets has often been seen in the graphene/polymer composites.¹⁶ In other composites with a lower graphene content, this peak is much weaker, showing the reduced restacking at the lowered graphene content. These XRD results thus confirm the good dispersion of the graphene flakes in the composites despite the presence of a very low level of restacking.

To determine the electrical properties of the composites, disk-shaped samples (10 mm diameter and 1 mm thickness) were prepared by compression molding and were subject to a DC voltage of 10 V across the thickness. Those having the graphene content in 1.0-3.2 wt % behaved essentially as an electrical insulator, with no measurable electrical current at the sensitivity of 1×10^{-12} A. Increasing graphene content to 4.0 and 5.3 wt % leads to a current of 2.2×10^{-11} and 2.4×10^{-8} A, respectively, which corresponds to a conductivity of 2.8×10^{-11} and 3.1×10^{-8} S/m, respectively. The drastic increase in the conductivity in the latter two composites suggests that the electrical percolation threshold of the composites is around 5.3 wt % or 0.67 vol % of graphene. This value falls in the typical percolation threshold range of 0.1-0.8 vol % reported for various graphene/polymer composites.¹⁶⁻²⁰

DMA characterizations of selected composites were carried out in the tensile oscillation mode to investigate the effect of graphene incorporation on their dynamic mechanical properties. Figure S4 in the Supporting Information plots the storage modulus curves (E' vs frequency) of the various composites at 23 °C. Increasing the graphene content from 0 to 4.0 wt % leads to a continuous upshift of the curves. At the frequency of 10 Hz, the modulus increases from 73 MPa for neat ENC to 129 MPa for the composite with 4.0 wt % or 0.60 vol % of graphene, corresponding to an increase of 77%. A similar trend of increase is also noted with the loss modulus (E'') curves, with tan $\delta = 0.1$ (i.e., E''/E') found for all samples across the whole frequency range investigated. These DMA results thus confirm the significant reinforcing effects of the incorporated graphene flakes on the mechanical properties of the composites. Due to limited sample amounts at this stage of study, static tensile measurements on these composites were not conducted.

4. CONCLUSIONS

Liquid-phase noncovalent exfoliation of graphite has been successfully demonstrated in both THF and chloroform in the

presence of a HBPE as the stabilizer. High-concentration graphene dispersions have been yielded, with the C_{G} value in the range of 0.016-0.045 mg/mL in THF or 0.025-0.18 mg/ mL in chloroform depending on the feed concentrations of both graphite and HBPE. The solvent plays an important role in the exfoliation, with higher $C_{\rm G}$ values in chloroform than in THF and with heptane and toluene being completely ineffective. The success of this method is reasoned to result from the adsorption of HBPE on the surface of the exfoliated graphene flakes, which renders steric stabilization against their restacking. The successful exfoliation has been confirmed by the characterizations of the graphene flakes with TEM, AFM, Raman, and XRD techniques. The majority of the graphene flakes has been found to have a layer number between 2 and 4 with low defects and has the lateral dimension in the range of 0.2–0.5 μ m. A free-standing graphene film having an average thickness of ca. 18 μ m has been subsequently prepared from a dispersion in chloroform by filtration. The film is flexible and electrically conductive with a conductivity of 214.0 S/m. Graphene/ENC composites of different graphene loading (1.0-5.3 wt %) have also been prepared from a highly concentrated dispersion by solution blending. The composites show enhanced thermal stability and dynamic moduli with the increase of graphene loading.

ASSOCIATED CONTENT

Supporting Information

TGA curves for graphene products without free HBPE prepared in both chloroform and THF, TGA and DSC results, wide-angle XRD patterns, and storage modulus (E') results for the graphene/ENC composites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(2) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* 2007, *6*, 183–191.

(3) Geim, A. K. Graphene: Status and Prospects. *Science* 2009, 324, 1530–1534.

(4) Geim, A. K. Random Walk to Graphene (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6966–6985.

(5) Novoselov, K. S. Graphene: Materials in the Flatland (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6986–7002.

(6) Fuhrer, M. S.; Chun, N. L.; MacDonald, A. H. Graphene: Materially Better Carbon. *MRS Bull.* **2010**, *35*, 289–295.

(7) Dreyer, D. R.; Ruoff, R. S.; Bielawski, C. W. From Conception to Realization: A Historial Account of Graphene and Some Perspectives for Its Future. *Angew. Chem., Int. Ed.* **2010**, *49*, 9336–9344.

(8) Castro Neto, A. H.; Novoselov, K. New Directions in Science and Technology: Two-Dimensional Crystals. *Rep. Prog. Phys.* **2011**, *74*, 1–9.

(9) Schwierz, F. Graphene Transistors. *Nature Nanotechnol.* 2010, *5*, 487–496.

(10) Avouris, P. Graphene: Electronic and Photonic Properties and Devices. *Nano Lett.* **2010**, *10*, 4285–4294.

(11) Bonaccorso, F.; Sun, T.; Hasan, T.; Ferrari, A. C. Graphene Photonics and Optoelectronics. *Nature Photon.* **2010**, *4*, 611–622.

(12) Sun, Y.; Wu, Q.; Shi, G. Graphene Based New Energy Materials. *Energy Environ. Sci.* **2011**, *4*, 1113–1132.

(13) Hou, J.; Shao, Y.; Ellis, M. W.; Moore, R. B.; Yi, B. Graphene-Based Electrochemical Energy Conversion and Storage: Fuel Cells, Supercapacitors and Lithium Ion Batteries. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15384–15402.

(14) Pumera, M. Graphene-Based Electrochemical Energy Conversion and Storage: Fuel Cells, Supercapacitors and Lithium Ion Batteries. *Energy Environ. Sci.* **2011**, *4*, 668–674.

(15) Brownson, D. A. C.; Kampouris, D. K.; Banks, C. E. An Overview of Graphene in Energy Production and Storage Applications. *J. Power Sources* **2011**, *196*, 4873–4885.

(16) Kim, H.; Abdala, A. A.; Macosko, C. W. Graphene/Polymer Nanocomposites. *Macromolecules* **2010**, *43*, 6515–6530.

(17) Potts, J. R.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S. Graphene-Based Polymer Nanocomposites. *Polymer* **2011**, *52*, 5–25.

(18) Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A. Graphene Filled Polymer Nanocomposites. *J. Mater. Chem.* **2011**, *21*, 3301–3310.

(19) Kuilla, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H. Recent Advances in Graphene Based Polymer Composites. *Prog. Polym. Sci.* **2010**, 35, 1350–1375.

(20) Cai, D.; Song, M. Recent Advance in Functionalized Graphene/ Polymer Nanocomposites. J. Mater. Chem. 2010, 20, 7906–7915.

(21) Huang, C.; Li, C.; Shi, G. Graphene Based Catalysts. *Energy Environ. Sci.* 2012, 5, 8848-8868.

(22) Machado, B. F.; Serp, P. Graphene-Based Materials for Catalysis. *Catal. Sci. Technol.* 2012, 2, 54–75.

(23) Park, S.; Ruff, R. S. Chemical Methods for the Production of Graphenes. *Nature Nanotechnol.* 2009, *4*, 217–224.

(24) Coleman, J. N. Liquid Exfoliation of Defect-Free Graphene. *Acc. Chem. Res.* **2013**, *46*, 14–22.

(25) Cui, X.; Zhang, C.; Hao, R.; Hou, Y. Liquid-Phase Exfoliation, Functionalization and Application of Graphene. *Nanoscale* **2011**, *3*, 2118–2126.

(26) Cai, M.; Thorpe, D.; Adamson, D. H; Schniepp, H. C. Methods of Graphite Exfoliation. J. Mater. Chem. 2012, 22, 24992–25002.

(27) Valentini, L.; Bon, B. S.; Kenny, J. M. Emerging Methods for Producing Graphene Oxide Composites in Coatings with Multifunctional Properties. *J. Mater. Chem.* **2012**, *22*, 21355–21361.

(28) Chen, D.; Feng, H.; Li, J. Graphene Oxides: Preparation, Functionalization, and Electrochemical Applications. *Chem. Rev.* 2012, *112*, 6027–6053.

(29) Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The Chemistry of Graphene Oxide. *Chem. Soc. Rev.* 2010, 39, 228–240.

(30) Kim, J.; Cote, L. J.; Huang, J. Two Dimensional Soft Material: New Faces of Graphene Oxide. *Acc. Chem. Res.* **2012**, *45*, 1356–1364.

(31) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z. Y.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; et al. High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nature Nanotechnol.* **2008**, *3*, 563–568.

(32) Khan, U.; O'Neill, A.; Lotya, M.; De, S.; Coleman, J. N. High-Concentration Solvent Exfoliation of Graphene. *Small* **2010**, *6*, 864–871.

(33) Khan, U.; Porwal, H.; O'Neill, A.; Nawaz, K.; May, P.; Coleman, J. N. Solvent-Exfoliated Graphene at Extremely High Concentration. *Langmuir* **2011**, *27*, 9077–9092.

(34) Khan, U.; O'Neill, A.; Porwal, H.; May, P.; Nawaz, K.; Coleman, J. N. Size Selection of Dispersed, Exfoliated Graphene Flakes by Controlled Centrifugation. *Carbon* **2012**, *50*, 470–475.

(35) Hasan, T.; Torrisi, F.; Sun, Z.; Popa, D.; Nicolosi, V.; Privitera, G.; Bonaccorso, F.; Ferrari, A. C. Solution-Phase Exfoliation of Graphite for Ultrafast Photonics. *Phys. Status Solidi B* **2010**, *247*, 2953–2957.

(36) Blake, P.; Brimicombe, P. D.; Nair, R. R.; Booth, T. J.; Jiang, D.; Schedin, F.; Ponomarenko, L. A.; Morozov, S. V.; Gleeson, H. F; Hill, E. W.; et al. Graphene-Based Liquid Crystal Device. *Nano Lett.* **2008**, *8*, 1704–1708.

(37) Hamilton, C. E.; Lomeda, J. R.; Sun, Z.; Tour, J. M.; Barron, A. R. High-Yield Organic Dispersions of Unfunctionalized Graphene. *Nano Lett.* **2009**, *10*, 3460–3462.

(38) Liu, N.; Luo, F.; Wu, H.; Liu, Y.; Zhang, C.; Chen, J. One-Step Ionic-Liquid-Assisted Electrochemical Synthesis of Ionic-Liquid-Functionalized Graphene Sheets Directly from Graphite. *Adv. Funct. Mater.* **2008**, *18*, 1518–1525.

(39) Wang, X. Q.; Fulvio, P. F.; Baker, G. A.; Veith, G. M.; Unocic, R. R.; Mahurin, S. M.; Chi, M. F.; Dai, S. Direct Exfoliation of Natural Graphite into Micrometre Size Few Layers Graphene Sheets Using Ionic Liquids. *Chem. Commun.* **2010**, *46*, 4487–4489.

(40) Nuvoli, D.; Valentini, L.; Alzari, V.; Scognamillo, S.; Bon, S. B.; Piccinini, M.; Illescas, J.; Mariani, A. High Concentration Few-Layer Graphene Sheets Obtained by Liquid Phase Exfoliation of Graphite in Ionic Liquid. *J. Mater. Chem.* **2011**, *21*, 3428–3431.

(41) Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. A.; Stubos, A. K. Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes. *Small* **2009**, *16*, 1841–1845.

(42) Hernandez, Y.; Lotya, M.; Rickard, D.; Bergin, S. D.; Coleman, J. N. Measurement of Multicomponent Solubility Parameters for Graphene Facilitates Solvent Discovery. *Langmuir* **2010**, *26*, 3208–3213.

(43) O'Neill, A.; Khan, U.; Nirmalraj, P. N.; Boland, J. J.; Coleman, J. N. Graphene Dispersion and Exfoliation in Low Boiling Point Solvents. *J. Phys. Chem. C* 2011, *115*, 5422–5428.

(44) Choi, E.-Y.; Choi, W. S.; Lee, Y. B.; Noh, Y.-Y. Production of Graphene by Exfoliation of Graphite in a Volatile Organic Solvent. *Nanotechnology* **2011**, *22*, 365601–365607.

(45) Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z. M.; McGovern, I. T.; et al. Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *J. Am. Chem. Soc.* **2009**, *131*, 3611–3620.

(46) Vadukumpully, S.; Paul, J.; Valiyaveettil, S. Cationic Surfactant Mediated Exfoliation of Graphite into Graphene Flakes. *Carbon* **2009**, 47, 3288–3294.

(47) Green, A. A.; Hersam, M. C. Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. *Nano Lett.* **2009**, *12*, 4031–4036.

(48) De, S.; King, P. J.; Lotya, M.; O'Neill, A.; Doherty, E. M.; Hernandez, Y.; Duesberg, G. S.; Coleman, J. N. Flexible, Transparent, Conducting Films of Randomly Stacked Graphene from Surfactant-Stabilized, Oxide-Free Graphene Dispersions. *Small* **2010**, *3*, 458–464.

(49) Lotya, M.; King, P. J.; Khan, U.; De, S.; Coleman, J. N. High-Concentration, Surfactant-Stabilized Graphene Dispersions. *ACS Nano* **2010**, *4*, 3155–3162.

(50) Pupysheva, O. V.; Farajian, A. A.; Knick, C. R.; Zhamu, A.; Jang, B. Z. Modeling Direct Exfoliation of Nanoscale Graphene Platelets. *J. Phys. Chem. C* **2010**, *114*, 21083–21087.

(51) Hao, R.; Qian, W.; Zhang, L.; Hou, Y. Aqueous Dispersions of TCNQ-Anion-Stabilized Graphene Sheets. *Chem. Commun.* **2008**, 6576–6578.

(52) Englert, J. M.; Röhrl, J.; Schmidt, C. D.; Graupner, R.; Hundhausen, M.; Hauke, F.; Hirsch, A. Soluble Graphene: Generation of Aqueous Graphene Solutions Aided by a Perylenebisimide-Based Bolaamphiphile. *Adv. Mater.* **2009**, *21*, 4265–4269.

(53) An, X. H.; Simmons, T.; Shah, R.; Wolfe, C.; Lewis, K. M.; Washington, M.; Nayak, S. K.; Talapatra, S.; Kar, S. Stable Aqueous Dispersions of Noncovalently Functionalized Graphene from Graphite and Their Multifunctional High-Performance Applications. *Nano Lett.* **2010**, *10*, 4295–4301.

(54) Zhang, M.; Parajuli, R. R.; Mastrogiovanni, D.; Dai, B.; Lo, P.; Cheung, W.; Brukh, R.; Chiu, P. L.; Zhou, T.; Liu, Z. F.; et al. Production of Graphene Sheets by Direct Dispersion with Aromatic Healing Agents. *Small* **2010**, *6*, 1100–1107.

(55) Ghosh, A.; Rao, K. V.; George, S. J.; Rao, C. N. R. Noncovalent Functionalization, Exfoliation, and Solubilization of Graphene in Water by Employing a Fluorescent Coronene Carboxylate. *Chem.*— *Eur. J.* **2010**, *16*, 2700–2704.

(56) Malig, J.; Norbert, J. P.-D.; Kiessling, D.; Cid, J.- J.; Vázquez, P.; Torres, T.; Guldi, D. M. Towards Tunable Graphene/Phthalocyanine-PPV Hybrid Systems. *Angew. Chem., Int. Ed.* **2011**, *50*, 3561–3565.

(57) Malig, J.; Romero-Nieto, C.; Jux, N.; Guldi, D. M. Integrating Water-Soluble Graphene into Porphyrin Nanohybrids. *Adv. Mater.* **2012**, *24*, 800–805.

(58) Hsu, C.-H.; Liao, H.-Y.; Wu, Y.-F.; Kuo, P.-L. Benzylamine-Assisted Noncovalent Exfoliation of Graphite-Protecting Pt Nanoparticles Applied as Catalyst for Methanol Oxidation. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2169–2172.

(59) Lee, D.-W.; Kim, T.; Lee, M. An Amphiphilic Pyrene Sheet for Selective Functionalization of Graphene. *Chem. Commun.* **2011**, *47*, 8259–8261.

(60) Dasa, S.; Irina, F.; Tanvir, A. H. S.; Cortinasa, A. B.; Wajida, A. S.; Parviza, D.; Jankowskib, A. F.; Katoc, M.; Green, M. J. Non-Covalent Functionalization of Pristine Few-Layer Graphene Using Triphenylene Derivatives for Conductive Poly(Vinyl Alcohol) Composites. *Polymer* **2012**, *53*, 2485–2494.

(61) Li, F.; Bao, Y.; Chai, J.; Zhang, Q.; Han, D.; Niu, L. Synthesis and Applications of Widely Soluble Graphene Sheets. *Langmuir* **2010**, 26, 12314–12320.

(62) Salavagione, H. J.; Ellis, G.; Segura, J. L.; Gómez, R.; Morales, G. M.; Martínez, G. Flexible Film Materials from Conjugated Dye-Modified Polymer Surfactant-Induced Aqueous Graphene Dispersions. *J. Mater. Chem.* **2011**, *21*, 16129–16135.

(63) Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. A.; Stubos, A. K; Trapalis, C. Aqueous-Phase Exfoliation of Graphite in the Presence of Polyvinylpyrrolidone for the Production of Water-Soluble Graphenes. *Solid State Commun.* **2009**, *149*, 2172–2176.

(64) Liang, Y. T.; Hersam, M. C. Highly Concentrated Graphene Solutions via Polymer Enhanced Solvent Exfoliation and Iterative Solvent Exchange. J. Am. Chem. Soc. 2010, 132, 17661–17663.

(65) Seo, J.-W.; Green, A. A.; Antaris, A. L.; Hersam, M. C. High-Concentration Aqueous Dispersions of Graphene Using Non-Ionic, Biocompatible Block Copolymers. *J. Phys. Chem. Lett.* **2011**, *2*, 1004–1008.

(66) Shen, B.; Zhai, W.; Chen, C.; Lu, D.; Wang, J.; Zheng, W. Melt Blending in situ Enhances the Interaction between Polystyrene and Graphene through $\pi-\pi$ Stacking. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3103–3109.

(67) Wajida, A. S.; Dasa, S.; Irina, F.; Tanvir, A. H. S.; Shelburnea, J. L.; Parviza, D.; Fullertona, R. J.; Jankowskib, A. F.; Heddena, R. C.; Green, M. J. Polymer-Stabilized Graphene Dispersions at High Concentrations in Organic Solvents for Composite Production. *Carbon* **2012**, *50*, 526–534.

(68) May, P.; Khan, U.; Hughes, J. M.; Coleman, J. N. Role of Solubility Parameters in Understanding the Steric Stabilization of Exfoliated Two-Dimensional Nanosheets by Adsorbed Polymers. *J. Phys. Chem. C* **2012**, *116*, 11393–11400.

(69) Ye, Z.; Li, S. Hyperbranched Polyethylenes and Functionalized Polymers by Chain Walking Polymerization with Pd-Diimine Catalysts. *Macromol. React. Eng.* **2010**, *4*, 319–332.

(70) Dong, Z.; Ye, Z. Hyperbranched Polyethylenes by Chain Walking Polymerization: Synthesis, Properties, Functionalization, and Applications. *Polym. Chem.* **2012**, *3*, 286–301.

(71) Xu, L.; Ye, Z.; Cui, Q.; Gu, Z. Noncovalent Nonspecific Functionalization and Solubilisation of Multi-Walled Carbon Nanotubes at High Concentrations with a Hyperbranched Polyethylene. *Macromol. Chem. Phys.* **2009**, *210*, 2194–2202.

(72) Petrie, K.; Docoslis, A.; Vasic, S.; Kontopoulou, M.; Morgan, S.; Ye, Z. Non-Covalent/Non-Specific Functionalization of Multi-Walled Carbon Nanotubes with a Hyperbranched Polyethylene and Characterization of Their Dispersion in a Polyolefin Matrix. *Carbon* **2011**, 49, 3378–3382.

(73) Osazuwa, O.; Petrie, K.; Kontopoulou, M.; Xiang, P.; Ye, Z.; Docoslis, A. Characterization of Non-Covalently, Non-Specifically Functionalized Multi-Walled Carbon Nanotubes and Their Melt Compounded Composites with an Ethylene-Octene Copolymer. *Compos. Sci. Technol.* **2012**, *73*, 27–33.

(74) Ye, Z.; Zhu, S. Newtonian Flow Behavior of Hyperbranched High-Molecular-Weight Polyethylenes Produced with a Pd-Diimine Catalyst and Its Dependence on Chain Topology. *Macromolecules* **2003**, *36*, 2194–2197.

(75) Xiang, P.; Ye, Z.; Morgan, S.; Xia, X.; Liu, W. Tuning Polyethylene Chain Topology via Ring Incorporation in Chain Walking Ethylene Polymerization. *Macromolecules* **2009**, *42*, 4946– 4949.

(76) Xiang, P.; Ye, Z. Alternating, Gradient, Block, and Block-Gradient Copolymers of Ethylene and Norbornene by Pd–Diimine-Catalyzed "Living" Copolymerization. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 672–686.

(77) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; et al. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 187401.

(78) Hao, Y. F.; Wang, Y. Y.; Wang, L.; Ni, Z. H.; Wang, Z. Q.; Wang, R.; Koo, C. K.; Shen, Z. X.; Thong, J. T. L. Probing Layer Number and Stacking Order for Few-Layer Graphene by Raman Spectroscopy. *Small* **2010**, *6*, 195–200.

(79) Wang, J.; Ye, Z.; Joly, H. Synthesis and Characterization of Hyperbranched Polyethylenes Tethered with Polyhedral Oligomeric Silsesquioxane (POSS) Nanoparticles by Chain Walking Ethylene Copolymerization with Acryloisobutyl-POSS. *Macromolecules* **2007**, *40*, 6150–6163.

(80) Li, Z. Q.; Lu, C. J.; Xia, Z. P.; Zhou, Y.; Luo, Z. X-Ray Diffraction Patterns of Graphite and Turbostratic Carbon. *Carbon* 2007, 45, 1686–1695.

(81) Baskaran, D.; Mays, J. W.; Bratcher, M. S. Noncovalent and Nonspecific Molecular Interactions of Polymers with Multiwalled Carbon Nanotubes. *Chem. Mater.* **2005**, *17*, 3389–3397.

(82) Nishio, M.; Hirota, M.; Umezawa, Y. The CH/π Interaction: Evidence, Nature and Consequences; Wiley-VCH, New York, 1998.

(83) Sato, T.; Ruch, R. Stabilization of Colloidal Dispersions by Polymer Adsorption; Marcel Deeker, New York, 1980.

(84) Luce, J. E.; Robertson, A. A. The Sorption of Polymers on Cellulose. J. Polym. Sci. 1961, 51, 317–335.

(85) Hiemenz, P. C.; Lodge, T. P. Polymer Chemistry, 2nd ed.; CRC Press: Boca Raton, 2007.

(86) Compton, O. C.; Dikin, D. A.; Putz, K. W.; Brinson, L. C.; Nguyen, S. T. Electrically Conductive "Alkylated" Graphene Paper via Chemical Reduction of Amine-Functionalized Graphene Oxide Paper. *Adv. Mater.* **2010**, *22*, 892–896.

(87) Park, S. J.; An, J. H.; Piner, R. D.; Jung, I.; Yang, D. X.; Velamakanni, A.; Nguyen, S. T.; Ruoff, R. S. Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets. *Chem. Mater.* **2008**, *20*, 6592–6594.

(88) Chen, H.; Müller, M. B.; Gilmore, K. J.; Wallace, G. G.; Li, D. Mechanically Strong, Electrically Conductive, and Biocompatible Graphene Paper. *Adv. Mater.* **2008**, *20*, 3557–3561.

(89) Kim, H.; Macosko, C. W. Morphology and Properties and Polyester/Exfoliated Graphite Nanocomposites. *Macromolecules* **2008**, *41*, 3317–3327.

(90) Zhao, X.; Zhang, Q.; Chen, D. Enhanced Mechanical Properties of Graphene-Based Poly(Vinyl Alcohol) Composites. *Macromolecules* **2010**, *43*, 2357–2363.

(91) Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors. *ACS Nano* **2008**, *2*, 463–470.

(92) Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. Processable Aqueous Dispersions of Graphene Nanosheets. *Nature Nanotechnol.* **2008**, *3*, 101–105.

(93) Khan, U.; May, P.; O'Neill, A.; Coleman, J. N. Development of Stiff, Strong, yet Tough Composites by the Addition of Solvent Exfoliated Graphene to Polyurethane. *Carbon* **2010**, *48*, 4035–4041.

(94) Vadukumpully, S.; Paul, J.; Mahanta, N.; Valiyaveettil, S. Flexible Conductive Graphene/Poly(Vinyl Chloride) Composite Thin Films with High Mechanical Strength and Thermal Stability. *Carbon* **2011**, *49*, 198–205.