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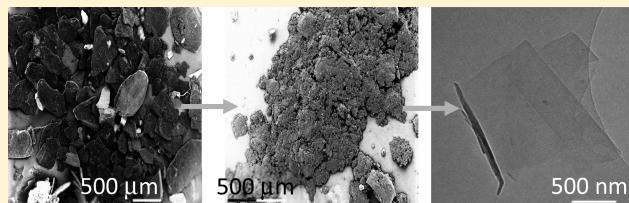
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A Technique To Pretreat Graphite Which Allows the Rapid Dispersion of Defect-Free Graphene in Solvents at High Concentration

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ABSTRACT: We have demonstrated a simple method to pretreat graphite powder resulting in a significant reduction in the time required to produce dispersions of solvent-exfoliated graphene. Sonication of graphite in either stabilizing solvents such as NMP or nonstabilizing solvents such as water results in significant breakage of graphite flakes and considerable exfoliation to give graphene. As expected, much of the graphene produced is stable indefinitely in NMP. Surprisingly, however, in the water-based samples unaggregated graphene was observed up to 26 h after sonication with complete sedimentation only observed after 70–130 h. In both cases, removal of the solvent resulted in a powder consisting of broken graphite flakes and reaggregated graphene. For both water and NMP pretreatments, this powder could be very easily redispersed by sonication in NMP to give good quality, defect-free graphene nanosheets. However, the concentration achievable after a given resonication time depended strongly on the pretreatment solvent and time. Redispersion of NMP-pretreated powder occurred much faster with concentrations of 1 mg/mL achieved after only 1 min resonication. This pretreatment technique will facilitate both the storage and transportation of liquid exfoliated graphene.



INTRODUCTION

Over the past decade graphene has become the most studied of all nanomaterials due to its unprecedented physical properties.^{1,2} It is believed that graphene will be useful in a range of applications from high-frequency transistors to drug delivery vehicles.³ There is an important subset of applications which will require large quantities of graphene nanosheets dispersed in liquid to facilitate solution processing.³ Typical examples are graphene in thin film form for electrodes in batteries,⁴ solar cells,⁵ or supercapacitors,⁶ as a filler or additive in composites^{7,8} or glues,⁹ or as a support for catalysts in fuel cells.¹⁰

Graphene can be exfoliated in liquids to give stable suspensions by a number of methods. Possibly most common is the oxidation and subsequent exfoliation of graphite to give graphene oxide. This material results in nanosheets consisting of a defective 2-dimensional graphitic lattice decorated with oxide groups. While the oxides can be removed by reduction, it is virtually impossible to heal the structural defects in the basal plane.^{11,12} The other main method is direct exfoliation of graphite by sonication in solvents,^{13–17} ionic liquids,¹⁸ aqueous–surfactant solutions,^{17,19–21} or using noncovalently attached small molecules^{15,22–24} or polymers^{25–29} as stabilizers. This results in good quality graphene flakes, free of defects and oxides, typically ~1 μm long by ~1–10 layers thick.³⁰

However, the latter method can be relatively slow. It can take over 100 h bath sonication to prepare a dispersion of graphene at a concentration of 1 mg/mL.¹⁷ Even using a high power sonic tip, at least 2 h sonication is required to reach this concentration.³¹ In addition, when sonating in solvents, care must be taken to avoid heat-related solvent degradation or

sonication-induced polymerization. Another problem is that the concentrations achieved are relatively low (~mg/mL). This makes liquid-exfoliated graphene bulky to store and means for example that to send a given mass of graphene to a collaborator requires sending a dispersion containing up to a thousand times the graphene's volume (i.e., mostly solvent). To solve these problems, we propose a method of pretreating graphite to give a powder which can be stored or shipped easily and yet can be dispersed in solvents quickly and simply to give exfoliated graphene.

The aim of this work is to identify a simple method for pretreating graphite powder to give a starting material which can be very easily exfoliated in solvents to give graphene dispersions. Commercial graphite powder generally consists of flakes which are hundreds of micrometers in size. Exfoliation of graphite to give graphene requires breaking these flakes into graphene nanosheets with lateral dimensions of ~micrometers and thickness ~nanometers. Thus, one possible pretreatment process would be to break up the flakes to much smaller sizes, approaching the final dimensions of graphene flakes. As graphene exfoliation in solvents is often achieved by ultrasonication of graphite in certain stabilizing solvents, we believe ultrasonication of graphite in a solvent environment could be a promising pretreatment technique. However, we suggest that such pretreatment should not be performed in stabilizing solvents such as *N*-methylpyrrolidone (NMP).^{16,30} This is because any graphene formed by sonication of graphite in NMP

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will be stabilized against aggregation and sedimentation by the presence of the solvent. This graphene will remain suspended for very long periods of time, making it difficult to recover as a powder. Such recovery is necessary to achieve a graphene powder which can be stored for later use as a starting material.

Conversely, we suggest a pretreatment that consists of sonicating the graphite in a nonsolvent, e.g., water. In this case, any graphene or small graphitic flakes produced by sonication will not be stabilized and will eventually sediment out facilitating the removal of the water and the formation of a dry powder for later use. However, very little is known about production of graphene by sonication in nonsolvents. For example, it is not known whether exfoliation and stabilization are coupled. If they are coupled then exfoliation will only occur if graphite is sonicated in a good solvent (e.g., NMP). Conversely, if they are not coupled, then sonication should result in exfoliation of the graphite to give graphene regardless of the solvent. However, if sonication is performed in a poor solvent (e.g., water), once the ultrasonic agitation is removed, the exfoliated graphene will not be stabilized, resulting in aggregation followed by sedimentation (or perhaps vice versa). This sedimentation may prove advantageous as it would allow the separation of the pretreated powder from the solvent for purposes of storage or transport.

In this work we have performed pretreatments by sonicating graphite powder in both NMP and water for periods of up to 16 h. After sonication, nonexfoliated graphite quickly sedimented out of both treated liquids. However, while exfoliated graphene remained suspended in NMP, graphene slowly sedimented out of the water-pretreated sample. The resultant powders could be very easily resuspended in NMP. Very high concentrations of ~ 1 mg/mL could be obtained by sonication for only 1 min.

■ EXPERIMENTAL METHODS

The pretreatment consisted of sonication of graphite (Sigma-Aldrich graphite flakes) at a concentration of 100 mg/mL for sonication times of 4, 8, and 16 h. Sonication was performed using a sonic tip (GEX600, solid flat head probe) at 40% of maximum power. This was done in 80 mL of two separate solvents: NMP (Sigma-Aldrich spectroscopic grade) and deionized water. Recovery of the treated graphitic material was achieved via vacuum filtration through porous alumina membranes (Whatman Anodisc 47 mm, pore size 0.02 μm). The resulting powder was then rinsed using IPA and dried in a vacuum oven overnight at 60 °C to ensure as much residual solvent as possible was removed.

In order to investigate the effect of pretreatment, sedimentation studies were performed on the dispersions immediately after switching off the sonic tip (no centrifugation was performed). This was carried out in a home-built apparatus consisting of a cuvette holder and an array of 4 pulsed lasers and photodiodes which measure the optical absorbance as a function of time.³² The data shown were for the laser positioned 1 cm below the top of the cuvette. The sedimenting dispersions were also characterized using TEM by pipetting a few milliliters onto holey carbon grids and obtaining images under bright field TEM (Jeol 2100 operating at 200 kV). After recovery, washing, and drying, the filtered powders were characterized using SEM (Zeiss Ultra Plus). Raman spectroscopy was performed using a Witec Alpha 300 R with an excitation wavelength of 532 nm, with a probe size of ~ 300 nm.

The dispersibility of the pretreated powders was studied by resonating them in fresh NMP at a concentration of 100 mg/mL. These dispersions were sonicated for approximately an hour, removing 1 mL aliquots after fixed time intervals. These aliquots were then diluted and centrifuged at 2000 rpm for 60 min (Hettich Mikro 22R). UV-vis-IR measurements (Varian Cary 6000i with 1 mm quartz cuvettes) were used to measure the concentration of the supernatants (absorption coefficient 3620 mg $\text{mL}^{-1} \text{ m}^{-1}$). In addition, drops were removed and analyzed using TEM. Finally, these resonated, centrifuged dispersions were used to prepare thin films by vacuum filtration. These thin films were then studied using Raman spectroscopy (ten scans recorded at different points, the baseline removed, and the ten scans averaged).

■ RESULTS AND DISCUSSION

In order to test the possibility of pretreating graphite by sonicating in solvents, we have sonicated graphite powder (100 mg/mL) in both water (a nonsolvent) and, for comparison, NMP (a good solvent) for three different times: 4, 8, and 16 h. After sonication, we monitored the fate of the resultant materials by a combination of TEM, sedimentation measurements, SEM, and Raman.

Analysis of Pretreated Dispersions by TEM. Immediately after sonication (no centrifugation was performed), a few drops of the resulting liquid were pipetted from the top of both water pretreated (WPT) and NMP pretreated (NPT) beakers and deposited onto TEM grids for analysis. Shown in Figure 1A,B are examples of the resultant TEM images. In both cases, the dispersions contained large, thick objects which we associate with unexfoliated or partially exfoliated graphite. In addition, in both NMP and water there were large quantities of relatively small objects (\sim micrometers in lateral size) which were electron transparent. By comparison with previous work,^{15–17,30,31} these objects are multilayer graphene nanosheets. While it is not surprising to see such objects in an NMP-based dispersion, it is perhaps surprising to find them in water as water is known to be a poor solvent for graphene.¹⁵ The presence of exfoliated graphene in the WPT sample demonstrates some important points. First, exfoliation (if not stabilization) can be achieved, even in nonstabilizing solvents such as water. This suggests that sonication-induced exfoliation is a brute-force technique where the high energy densities and local shear rates associated with cavitation effects result in breakage and delamination of graphite flakes without and need for surface passivation due to graphene–solvent interactions.

To determine the fate of the objects observed in Figure 1A,B, we removed aliquots of liquid from the top of both NPT and WPT dispersions 25 h after the end of sonication. Optical measurements showed the absorbance of the NPT sample to be 50–60% of its value immediately after the end of sonication. This absorbance reduction is consistent with the sedimentation of large unexfoliated graphite out of the dispersion.³³ The absorbance of the WPT sample was 10–35% of its value immediately after the end of sonication. While this shows that material is sedimenting, what is surprising is that so much material remains dispersed after 25 h.

TEM analysis was performed, with typical TEM images shown in Figure 1C,D. In both cases, large numbers of exfoliated graphene nanosheets were observed. Again this is not surprising for the NPT dispersions; NMP is known to stabilize graphene indefinitely.^{16,17,30} However, this result was not expected for the WPT dispersions. As mentioned above, water

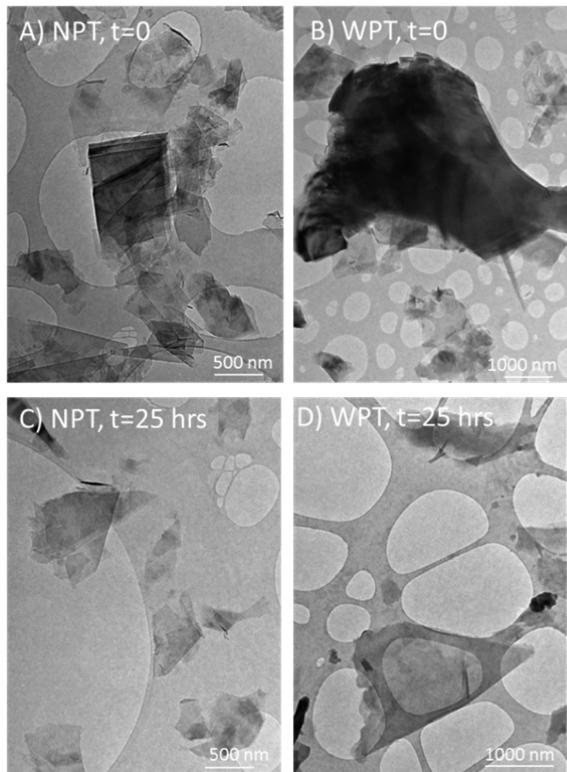


Figure 1. TEM images of dispersed objects found in dispersions immediately after pretreatment (PT) of graphite by sonication in (A) NMP and (B) water ($\tau_{\text{PT}} = 4 \text{ h}$). Also shown are images of objects remaining dispersed 25 h after the end of sonication, for (C) NMP and (D) water pretreated samples ($\tau_{\text{PT}} = 4 \text{ h}$). NB: these dispersions were not centrifuged.

is not a good stabilizing solvent for graphene: when graphite is sonicated in water and subsequently centrifuged, all the graphitic material is removed from the liquid. However, the results presented here show that, contrary to expectation, not only do quantities of graphene remain some 25 h after sonication, they remain unaggregated. This is unexpected as we expect the mismatch between the surface energies of graphene and water to drive aggregation rapidly to minimize the energy of the dispersion.^{15,16} However, we note that the graphene nanosheets observed in the WPT dispersions was not stably dispersed. Observation after long settling times (100–200 h, depending on the sample) showed the dispersion to be transparent, indicating that all the dispersed material had sedimented by that time. In contrast, the NPT dispersions remained black indefinitely, retaining ~30% of their absorbance even >300 h after the end of sonication.

Sedimentation Analysis. We can perform more quantitative analysis by performing sedimentation measurements on the dispersions, starting as soon as the ultrasound was turned off (no centrifugation was applied). These measurements involve monitoring the optical absorbance of the dispersion as a function of time in a dedicated home-built apparatus.³² The data obtained for each treatment time are shown in Figure 2 for dispersions of graphite pretreated in (A) NMP and (B) water. For the NMP pretreated samples, the absorbance decays rapidly reaching a near constant value of ~30% of initial absorbance after ~250 h. Similar results were found for all three pretreatment times. This data is consistent with a portion of the dispersed material falling out under gravity leaving the rest

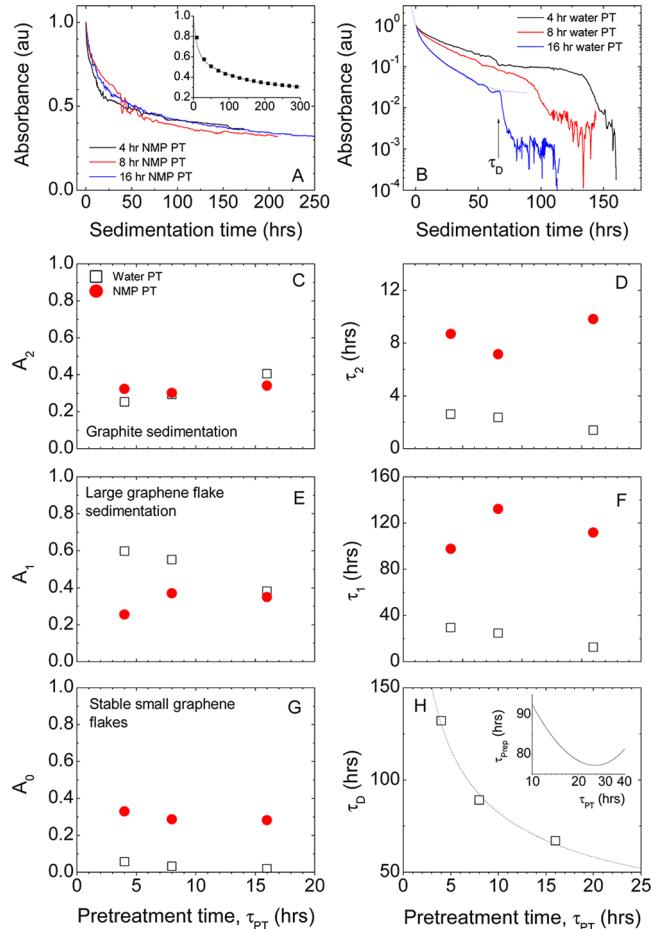


Figure 2. Sedimentation of pretreated dispersions post sonication. (A, B) Absorbance measured as a function of time for dispersions of graphite powder pretreated by sonication in (A) water and (B) NMP for a number of pretreatment times. No centrifugation was applied in either case. The inset in (A) shows a biexponential fit (16 h NPT) where only every 50th data point is shown to enhance visibility. An example of a biexponential fit is also given in (B) (16 h water PT, dashed line). The destabilization time, τ_D , is also indicated by the arrow. (C–G) Measured fit parameters plotted as a function of pretreatment time, τ_{PT} , in both NMP and water: (C) initial absorbance associated with unexfoliated graphite (A_2); (D) sedimentation time constant for unexfoliated graphite (τ_2); (E) initial absorbance associated with sedimenting, large graphene flakes (A_1); (F) sedimentation time constant for sedimenting, large graphene flakes (τ_1); (G) absorbance associated with stably dispersed graphene (A_0). (H) Destabilization time plotted as a function of water pretreatment time. The dashed line is an empirical fit showing $\tau_D \propto \tau_{\text{PT}}^{-1/2}$. Inset: plot of total preparation time, τ_{Prep} , as a function of τ_{PT} .

stably suspended. Rather different behavior is observed for the water pretreated samples. For each pretreatment time the absorbance falls steadily with sedimentation time, albeit at different rates. However, in each case after a well-defined time (which we refer to as the destabilization time, τ_D) which depends on pretreatment time, the absorbance collapses, falling by at least an order of magnitude. In each case the final absorbance is ~0.1% of the initial absorbance.

We can analyze these data quantitatively. We expect any unexfoliated graphite particles to rapidly fall out of dispersion. However, any exfoliated graphene that is not stably dispersed will sediment more slowly due to its smaller size. It is known that the concentration of a sedimenting phase decreases

approximately exponentially with time.³² In addition, the time constant associated with this decay is correlated with the size of the sedimenting particles with larger particles sedimenting faster.^{32,34} This means that a system consisting of a stable phase (labeled 0) and two sedimenting phases (1 and 2) of different sizes should have an optical absorbance which varies with time as³²

$$A = A_0 + A_1 e^{t/\tau_1} + A_2 e^{t/\tau_2}$$

In our case, A_0 represents the absorbance of the stable phase while A_1 and A_2 represent the initial absorbance of any unstable graphene flakes and the unexfoliated graphite, respectively. In addition, τ_1 and τ_2 represent the sedimentation time constants of any unstable graphene flakes and the exfoliated graphite, respectively. Such an expression can be fitted to the data in Figure 1 with examples shown in the inset of Figure 1A and as the dashed line in Figure 1B. Such fits have been applied to all six data sets with the fit constants presented in Figure 1C–G. We note that while the fits apply to the entire temporal range of the NMP-PT samples, they can only describe the water-PT data up to the destabilization time.

The first thing to note is that for all fits the longer time constant (associated with smaller sedimenting objects) was denoted by τ_1 while the shorter time constant (associated with larger sedimenting objects) was denoted by τ_2 . In all cases τ_1 and τ_2 were unambiguously different, varying by a factor of ~ 10 , leaving no doubt that two distinct sedimenting components were present. This labeling is consistent with the labeling of unstable graphene flakes (1) and the exfoliated graphite (2) is described above. This is also consistent with the TEM images in Figure 1 which show large graphitic objects at $t = 0$ which have disappeared after $t = 25$ h. The τ_2 values associated with the rapidly settling graphite were ~ 8 h for the NPT dispersions and ~ 2 h for the WPT dispersions. Any objects settling exponentially with these time constants would be largely gone after 25 h, consistent with TEM observations. In addition, the τ_1 values we associate with sedimenting graphene were ~ 120 h for the NPT dispersions and ~ 20 h for the WPT dispersions. This compares well to previous observations of sedimenting graphene nanosheets with time constants between 10 and 220 h.³³

However, we note that repeating sedimentation measurements for nominally identical samples gives limited reproducibility. We estimate that the relative error associated with the fit constants could be as high as 40%. However, even with this degree of error, some conclusions can be drawn. Shown in Figure 1C are the values of A_2 extracted from the fits. This parameter represents the absorbance associated with unexfoliated graphite at $t = 0$ and is proportional to the concentration of graphite remaining in the sample after sonication. We note that this value is roughly the same for all samples. Assuming that sonication results in a fraction of the graphite being exfoliated to give graphene, this implies that the mass of graphene produced was roughly the same for both water and NMP pretreatments irrespective of pretreatment time. We can test this by noting that A_1 and A_0 represent the absorbance associated with the graphene produced by sonication, be it unstable (A_1) or a stable (A_0) against aggregation. For all samples, the sum $A_1 + A_0$ is between 40% and 65% for all samples with no particular trend observed. This suggests graphene is produced in comparable amounts irrespective of the solvent or the pretreatment time. In addition, we note that while A_0 is close to 30% for the NMP-PT samples, it is close to

zero for all water-PT samples. This confirms that although graphene can be produced by sonication in water, it only remains stably dispersed in the presence of a good solvent such as NMP.

However, when it comes to the sedimentation time constants, considerable differences are observed between water and NMP. As shown in Figure 1D,F, both τ_1 and τ_2 were considerably longer for the NMP-PT samples compared to the water-PT samples. This implies that both the graphite crystallites and unstable graphene flakes which are present after sonication in NMP are smaller than those found in the water-PT samples. That sonication of graphite in a good solvent results in smaller objects may imply that the sonic energy is more efficiently transferred to the solute in the presence of a good solvent. This is contrary to the suggestion that the frictional constant felt by a nano-object under sonication is the fluid viscosity times the objects length.³⁵ If this were the case, sonication in water and NMP would have similar outcomes (their viscosities are similar: $\eta_{\text{NMP}} \approx 1.7 \text{ mPa}\cdot\text{s}$ and $\eta_{\text{water}} \approx 1 \text{ mPa}\cdot\text{s}$). Thus, it appears that the frictional stress transfer must depend on the strength of the interaction between solvent and nano-object. This is consistent with the fact that sonication induced scission is much more effective at cutting graphene nanosheets dispersed in NMP¹⁷ than aqueous surfactant solutions.³⁶ These results suggest that exfoliation and stabilization cannot be completely decoupled from solvent type. It also suggests that the concentration of dispersed graphene may depend on solvent type in a way that depends on sonication effects and not just solvent-graphene interactions.¹⁵

Shown in Figure 2H are the times where the water-PT dispersions become unstable, τ_D , plotted versus the pretreatment time, τ_{PT} . It is clear that τ_D falls off smoothly as τ_{PT} is increased. Empirically, this data matches well to the expression $\tau_D \propto \tau_{\text{PT}}^{-1/2}$ (dashed line). This is of interest because one way of performing the pretreatment would be to sonicate in water and then allow the dispersion to settle until τ_D . At that point destabilization would occur, resulting in the rapid fallout of any remaining dispersed graphene. The majority of the water could then be easily removed by decantation, leaving a damp powder which could be oven-dried. The total time for this process would be $\tau_{\text{prep}} = \tau_{\text{PT}} + \tau_D$. Taking the empirical relationship between τ_D and τ_{PT} gives $\tau_{\text{prep}} = \tau_{\text{PT}} + 261\tau_{\text{PT}}^{-1/2}$. This function is plotted in the inset of Figure 1H and shows a clear minimum for $\tau_{\text{PT}} = 26$ h, suggesting this to be an optimized value.

Because of its stabilization of exfoliated graphene, the treatment described above cannot be used to remove solvent from NMP-PT graphene. Thus, for consistency, for both NMP and water pretreated samples, the graphitic material was separated from the solvent by vacuum filtration. After drying, this resulted in two sets of black powder, both of which visually resembled graphite powder. These treated powders were investigated using SEM and Raman spectroscopy.

Analysis of Powder Prepared by Pretreatment. Shown in Figure 3 are SEM images of (A) the starting graphite powder and graphitic powders pretreated in (B) water and (C) NMP. The stock graphite consists of well-defined flakes with a typical lateral size of $\sim 500 \mu\text{m}$. This is in stark contrast to the pretreated powders which are littered with smaller, poorly defined flakes. While the WPT powder clearly contains $500 \mu\text{m}$ flakes, there are also large numbers of much smaller objects. These have clearly been broken off the starting flakes by the sonication pretreatment process. There also appears to be poorly defined material which may be reaggregated graphene.

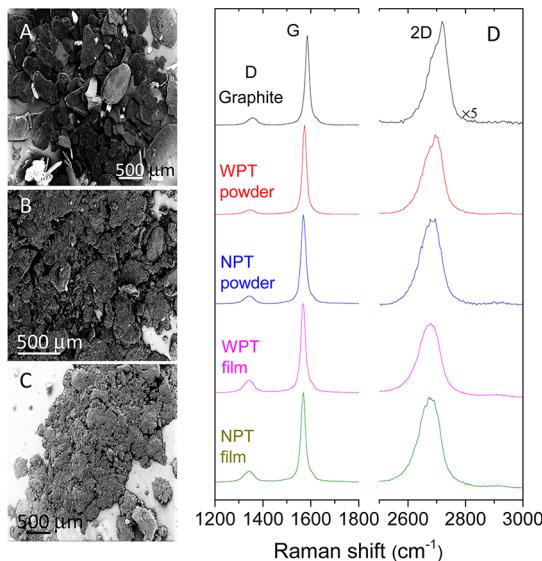


Figure 3. SEM images of (A) starting graphite powder, (B) water pretreated powder ($\tau_{\text{PT}} = 16$ h), and (C) NMP pretreated powder ($\tau_{\text{PT}} = 16$ h). (D) Raman spectra of the starting graphite powder, the water pretreated powder (WPT, $\tau_{\text{PT}} = 16$ h), NMP pretreated powder (NPT, $\tau_{\text{PT}} = 16$ h), and vacuum filtered films prepared from dispersions made by sonication of the pretreated powders in NMP followed by centrifugation to remove any unexfoliated graphite. The films from water and NMP pretreated graphite are labeled WPT and NPT, respectively. In each case, Raman spectra were collected from 10 different points on the sample, and the spectra were normalized and averaged.

In the NPT sample, similar processes appear to have been at work but to a greater extent. While it is clear that this material once consisted of 500 μm flakes, the sonication pretreatment has inflicted great damage. The larger objects are very poorly defined while the powder appears to be dominated by smaller objects of a continuum of sizes. It is likely that the smaller, more poorly defined material consists largely of exfoliated material. We note that the SEM suggests the NMP-PT sample to contain smaller objects in agreement with the sedimentation analysis.

In Figure 3D, the Raman spectra of the pretreated powders are compared to that of the starting stock graphite. All three powders show a well-defined G band ($\sim 1570 \text{ cm}^{-1}$), a small D band ($\sim 1350 \text{ cm}^{-1}$), and the so-called 2D band ($\sim 2700 \text{ cm}^{-1}$).³⁷ These bands are characteristic of graphitic materials with the relatively small intensity of the D band, indicating that the pretreatment has not resulted in large-scale damage to the basal plane. The low-frequency side of the 2D band of the stock graphite spectrum shows a shoulder which is characteristic of Bernal-stacked graphite.³⁷ The 2D band of the WPT powder is similar to graphite with clear evidence of the shoulder, suggesting the powder consists of mostly graphite with small quantities of reaggregated graphene. However, the NPT powder has a more symmetric 2D peak with little evidence of the graphite shoulder. In fact, this peak more closely resembles those observed for few-layer graphene flakes.^{17,37} This suggests again that NMP provides a more effective pretreatment, and the resulting powder consists of a higher proportion of reaggregated graphene. It should be noted that both powders showed a higher D:G ratio than the starting powder, suggesting the average flake size had decreased as would be expected.

Redisposition of Pretreated Powders. So far it can be seen that while both powders consist predominantly of graphite both show evidence of the presence of considerable amounts of small reaggregated graphene flakes. Such flakes would be weakly bound to each other and possibly easily separated from each other.³¹ This would suggest that relative to powdered graphite, these powders should be easier to exfoliate in good solvents such as NMP. This was tested by resonating both the pretreated powders in NMP. After various resonication times, τ_{R} , small aliquots were removed, centrifuged, and the dispersed graphene concentration measured. Shown in Figure 4A is the

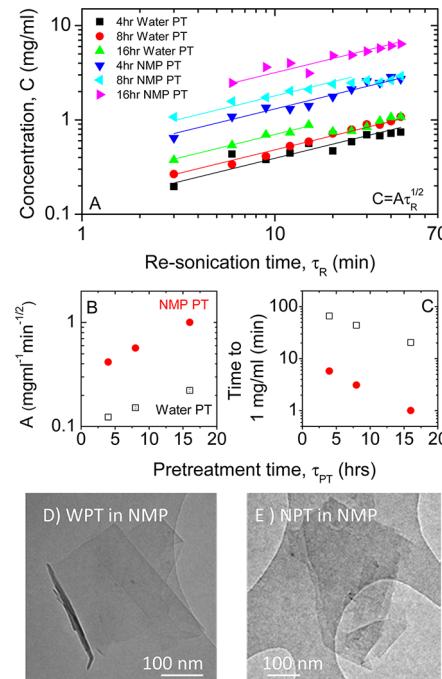


Figure 4. Redisposition of pretreated powders in NMP. (A) Dispersed concentration, C , of graphene, obtained after centrifugation, for pretreated powders resonicated for various times, τ_{R} , in NMP. The solid lines are fits to $C = A\tau_{\text{R}}^{1/2}$. (B) Fit constant, A , and (C) time to reach 1 mg/mL, plotted versus τ_{PT} . (D, E) TEM images of graphene flakes prepared by resonating powder pretreated in (D) water ($\tau_{\text{PT}} = 4$ h) and (E) NMP ($\tau_{\text{PT}} = 8$ h) in the solvent NMP ($\tau_{\text{R}} = 45$ min for both).

resulting concentration versus time data for powder pretreated for various times in both water and NMP. In all cases the dispersed concentration increases with sonication time as is generally observed.^{17,31,33} However, the increase is extremely rapid with a midrange sample reaching ~ 1 mg/mL in ~ 10 min. Previous work on sonication of graphite powder using a similar sonic tip took ~ 2 h to reach 1 mg/mL.³¹ At any given time, the concentration increases with pretreatment time and is significantly higher for NMP-PT powders. From this graph, it can be seen empirically that the concentration increases with time as $C = A(t_{\text{R}})^{1/2}$. Such behavior has been observed on a number of occasions for liquid exfoliation of graphene.^{17,31,33} By fitting the data in Figure 4A, values of A were obtained and are plotted versus pretreatment time in Figure 4B. For the water-PT samples, A increased exponentially from 0.12 to 0.22 mg mL⁻¹ min⁻¹² as the PT time increased from 4 to 16 h. However, for the NMP-PT samples, much higher values were found with A increasing exponentially from 0.42 to 1.0 mg mL⁻¹ min⁻¹² over the same range of PT time. As mentioned

above, such square root time dependence has been observed previously.^{17,31,33} For example, using a sonic bath,¹⁷ values of $A \sim 0.01 \text{ mg mL}^{-1} \text{ min}^{-1/2}$ have been observed while using a sonic tip increases this to $A \sim 0.1 \text{ mg mL}^{-1} \text{ min}^{-1/2}$,³¹ values considerably lower than those found here. Thus, it is clear that sonication-based pretreatment can increase A , and hence the rate of dispersion, 10-fold compared to sonication of untreated graphite. We note these results are consistent with previous experiments on redispersion of reaggregated graphene which attained $A \sim 0.46 \text{ mg mL}^{-1} \text{ min}^{-1/2}$.³¹

A useful metric in preparing high concentration dispersions is the time taken to reach a moderately high concentration, e.g., 1 mg/mL. This time was extracted from Figure 4A and is plotted in Figure 4C as a function of PT time. For both NPT and WPT powder, the time to reach a concentration of 1 mg/mL falls exponentially with pretreatment time. This shows just how effective the NPT can be—the 16 h NMP-PT sample reaching a concentration of 1 mg/mL in only 1 min. This compares to about 90 min being required to prepare a 1 mg/mL dispersion by tip-sonicating graphite in NMP.³¹

We have shown this pretreatment procedure to be highly effective for preparing moderately high concentration dispersions. However, it will be important to show that the long sonication times associated with the pretreatment do not result in any reduction in flake quality. In addition, it is important to assess the final quality of the dispersions, in particular for the dispersions containing flakes pretreated in water. In order to test this, two of the dispersions described in Figure 4A were analyzed using TEM. Both samples contained large numbers of good quality nanosheets as shown in Figure 4D,E. In general, these nanosheets appear indistinguishable from those prepared by sonicating graphite powder in NMP.^{15–17,31}

In order to test the dispersion quality more quantitatively, thin films were prepared by filtering the final dispersions onto alumina membranes and studied using Raman spectroscopy. The Raman spectra for both films (see Figure 3D) show a 2D band consistent with that of few layer graphene with no evidence of the shoulder associated with Bernal-stacked graphite. The D bands are relatively small with mean I_D/I_G ratios of 0.12 and 0.15 for the NPT and WPT films, respectively. Such low values are consistent with micrometer-sized, defect-free flakes, suggesting that the pretreatment procedure has not introduced any basal plane damage.^{17,33}

CONCLUSION

In conclusion, we have demonstrated a method to pretreat graphite, resulting in a powder that can easily be redispersed in solvents such as NMP. This technique involves the sonication of graphene in solvents. We find that sonication of graphite in both NMP and water results in the breakage of graphite flakes and the formation of large quantities of graphene. This shows that the production of graphene does not require sonication in a good solvent (NMP). However, the nature of the graphite breakage and so the size distribution of the resultant graphitic objects does appear to depend on the nature of the solvent. Interestingly, after sonication in water, while the graphene eventually sediments out of dispersion, not all of it aggregates as might be expected from energy minimization considerations.

The powder that is obtained after sonication pretreatment and solvent removal can be exfoliated very easily in NMP. Usually, when tip-sonicating graphite in NMP, it takes ~90 min to reach a concentration of 1 mg/mL. However, for the

graphite pretreated in NMP, 1 mg/mL can be reached after sonicing for only 1 min.

Unlike pretreatment in NMP, treatment in water has the considerable advantage that the graphene produced sediments out of dispersion under gravity, facilitating collection of the treated powder. However, the NMP-pretreated graphite gave considerably higher concentrations of graphene when eventually redispersed in NMP. We suggest that the pretreatment solvent can be chosen depending on the details of the application.

We believe this pretreatment technique will be a valuable for the preparation, transportation and sale of a graphitic material that can be very easily exfoliated to give good quality graphene.

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Notes

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