Liquid exfoliated graphene offers the potential of an easy, simple, and scalable means for the production of high quality graphene sheets. Increasing the loading of exfoliated graphene dispersions is necessary to increase efficiency and make liquid exfoliation a practical method for graphene synthesis. This publication demonstrates the use of NH$_3$ as an additive to significantly increase the loading of graphene within 1-methyl-2-pyrrolidinone (NMP) dispersions. Simple synthesis of graphene films by addition of the dispersion to water is also demonstrated. The films, made from a disordered collection of graphene flakes, are predominantly constructed from few, <5, layered graphene.

There have been several publications$^{19,22}$ and reviews$^{20}$ that describe the sonication and centrifugation dependence of liquid exfoliation on final graphene loading. Sonication produces a dispersion containing sheets of thickness ranging from single layer graphene to multi-layered graphene, including expanded graphene. Centrifugation, at appropriate rates, precipitates the heavier layers and can preserve predominantly single layer graphene within the dispersion, though some multilayered graphene, <5 layers, may persist.$^{19-22}$

This publication reports the inclusion of ammonium hydroxide [NH$_4$OH] within the liquid exfoliation process to increase graphene loadings. The inclusion of ammonia [NH$_3$] within dispersions has most notably been reported for graphene oxide reduction$^{23}$ as a means of preventing sheet aggregation during reduction with hydrazine [N$_2$H$_4$]. The addition of [NH$_4$OH] provides a facile means of including NH$_3$ in order to prevent aggregation of liquid exfoliated graphene, increase graphene loading and improve dispersion stability. Dropping the highly loaded graphene dispersions into water is demonstrated as a simple method of graphene film formation and provides a qualitative means of comparing dispersion concentrations. The effect of NH$_3$ on graphene loading and film forming capacity of the dispersions were the main focus of this work; details as to the role of sonication and centrifugation have been well documented elsewhere.$^{19}$

### Experimental

Liquid exfoliation was carried out in what are considered two of the most commonly used solvents for the exfoliation of graphite; 99.5% anhydrous 1-methyl-2-pyrrolidinone (NMP) [C$_5$H$_9$NO] and 2% sodium cholate [C$_24$H$_40$O$_5$] solution produced from purchased sodium cholate hydrate. Ammonia [NH$_3$] was added to select dispersions in the form of an ammonium hydroxide [NH$_4$OH] solution, ≥25% NH$_3$ in H$_2$O. The concentration of NH$_4$OH added to the select dispersions was 7.5% of the total volume and the addition occurred prior to sonication unless otherwise stated. Graphite flakes, +100 mesh, were then loaded into 60mL of each solvent at a concentration of 75g/L. All chemicals were used as purchased from Sigma Aldrich.

Sonication of the solution occurred using a Qsonica Q500 sonicator with a 1/2” (12.7 mm) diameter probe tip. Power delivered to the dispersions was maintained between 50–54 Watts with oscillations maintained at 54% amplitude. The glass beaker containing the graphite/solvent mixture was submerged in an ice water bath in order to limit heating during sonication. The resulting colloidal mixture was loaded into 2 mL centrifuge tubes and the solution was centrifuged within an Eppendorf 5430 centrifuge. A summary of NH$_4$OH inclusion as well as sonication and centrifugation rate and times are shown in Table I.

**Following centrifugation, the top 50% of the tubes was decanted and collected. The remaining liquid and slurry mixture was collected in a separate vessel. The NMP dispersions 2 and 3 were created by the**

| Dispersion | NH$_4$OH Inclusion | Sonication Time | Centrifugation Rate | Time |
|------------|--------------------|----------------|---------------------|------|
| 1          | None               | 30 min         | 750 rpm             | 30 min|
| 2          | 7.5%               | 30 min         | 750 rpm             | 30 min|
| 3          | 7.5%               | 30 min         | 750 rpm             | 30 min|
| 4          | None               | 60 min         | 750 rpm             | 10 min|
| 5          | 7.5%               | 20 min         | 750 rpm             | 30 min|
| 6          | 7.5%               | 30 min         | 750 rpm             | 30 min|
| 7          | 7.5%**             | 30 min         | 750 rpm             | 30 min|

### Table I. Graphene dispersions in NMP and 2% sodium cholate solutions.

*Denotes inclusion of 2.0 mL of NH$_4$OH prior to sonication and 2.5 mL of NH$_4$OH prior to centrifugation.

**Denotes addition of additional 2.0 mL of NH$_4$OH following centrifugation.

Denotes dispersion was created by reprocessing centrifuged material from the previous dispersion.

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**Conflict of Interest:** The authors declare that they have no conflict of interest.

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Graphene films were produced on laboratory glass slides and silicon wafer substrates by dripping a few drops of the dispersions into a distilled water bath and lifting the floating films directly onto the various surfaces. Video of this process is available in supplemental information; video was taken using the camera on a model ICONIA A510 Acer tablet computer. The films on silicon and glass surfaces were imaged using a Canon 4400 scanner at a quality of 600 dpi (dots per inch) for macroscopic images. Scanning electron microscopy (SEM) images were obtained using a SEM is a JEOL 6700 SEM with Field Emission Gun at an applied potential of 10.0 kV. Elementary information of the films was obtained using energy-dispersive X-ray spectroscopy (EDS) provided by a model Apollo EDAX device attached to the SEM. Raman spectroscopy, which provides a powerful tool to characterize the uniformity of the graphene material, for the thin films was obtained using a T64000 Jobin-Ivon Horiba triple monochromator spectrometer with CCD LN2 cooled detector. Resolution of Raman shifts down to 5 cm\(^{-1}\) was obtained using a monochromatic 514.5 nm Ar+Kr ion Spectra-Physics laser.

**Results**

*NMP solvents.*—The dispersion of exfoliated graphene produced in NMP Dispersion 1 follows the traditional method of producing liquid exfoliated graphene in NMP.\(^{21}\) The slight yellowish tinge of the dispersion, Figure 1, is the only indication of the presence of exfoliated graphene within the high transparency of the NMP dispersion. The appearance of the dispersion is consistent with others produced in NMP and the dispersion is presumed to have a graphene concentration of, at most, around 6 μg/mL consistent with other reports.\(^{21}\)

The inclusion of NH\(_4\)OH within NMP dispersions produced a darkly colored liquid after the sonication and centrifugation processes were carried out. The dark coloring of the dispersion was maintained independent of whether the NH\(_4\)OH was added to the NMP solvent prior to graphite loading or prior to sonication of reprocessed material, such as NMP Dispersion 2. The dark color, which was determined to not be a chemical reaction as it is not observed until after sonication, suggested an increased loading of graphene within the dispersion. Following centrifugation at 750 rpm for 30 minutes, the same rate and duration used for NMP Dispersion 1, NMP Dispersion 2 retained the dark coloring compared to NMP Dispersion 1.

*Graphene film formation and analysis.*—Evidence of an increased loading in NH\(_3\) containing NMP dispersions was established by adding a few drops of the dispersion to distilled water. The addition of drops of NMP Dispersions 2, 5, 6, or 7 to water produced thin, transparent, silver colored islands, on the water’s surface, Figure 3. The instantaneous formation of the graphene films by dripping the dispersion into water is consistent with the reported hydrophobic nature of graphene sheets.\(^{22}\) Thicker, more continuous, sheets may be produced with the additional dripping of the dispersion into water. The introduction of the graphene dispersions under the surface of the water resulted in a dispersed particulate mixture with no sheet formation on the surface. The lack of sheet formation is thought to be a result of coordination of the water around NMP encasing the exfoliated graphene. Despite the dark coloring of NMP Dispersion 3, no sheets were formed by dripping the dispersion into water. The inclusion of NH\(_4\)OH within NMP dispersions produced a darkly colored liquid after the sonication and centrifugation processes were carried out. The dark coloring of the dispersion was maintained independent of whether the NH\(_4\)OH was added to the NMP solvent prior to graphite loading or prior to sonication of reprocessed material, such as NMP Dispersion 2. The dark color, which was determined to not be a chemical reaction as it is not observed until after sonication, suggested an increased loading of graphene within the dispersion. Following centrifugation at 750 rpm for 30 minutes, the same rate and duration used for NMP Dispersion 1, NMP Dispersion 2 retained the dark coloring compared to NMP Dispersion 1.

A second reprocessing of the remaining material from NMP Dispersion 1, or equally the first reprocessing of the remains of NMP Dispersion 2, was conducted to determine whether continuous reprocessing of the waste material was possible. As expected, post-sonication NMP Dispersion 3 remained dark and was effectively indistinguishable from NMP Dispersion 2. Increasing the centrifugation step 10 fold, compared to dispersions 1 and 2, to 7500 rpm demonstrated the superior capacity of the solvent to retain graphene. This capacity was further demonstrated upon subsequent centrifugation of the material at 14000 rpm.

In cases where NH\(_4\)OH was added prior to sonication it was observed that the dispersion retained little scent of NH\(_3\) post-sonication. As the presence of NH\(_4\)OH, and thereby NH\(_3\), was observed to improve loading, the NH\(_4\)OH addition to NMP Dispersion 5 was split both before and after the sonication step. The splitting of the NH\(_4\)OH to before and after sonication allows the final dispersion to retain more NH\(_3\) which easily evaporates during sonication. The increase in the NH\(_3\) content in the final dispersion was associated with a shimer to the dispersion when it was shaken, implying greater loadings of graphene. Notably, the shimer of NMP Dispersion 5, with the addition of NH\(_4\)OH prior to each exfoliation step, was more pronounced than those produced with NH\(_4\)OH added prior to centrifugation; including NMP Dispersion 7 which contained additional NH\(_4\)OH added post-centrifugation decanting.

*Sodium cholate solvents.*—The production of graphene dispersions within 2% sodium cholate solvents resulted in dark dispersions. Cholate Dispersion 1, centrifuged at 14000 rpm for 60 minutes, was optically transparent and remained stable for over 2 weeks showing no signs of precipitation, Figure 2a, consistent with other reports in literature.\(^{22}\) Shorter and less intense centrifugation, at 750 rpm for 10 minutes, visibly increased graphene loading of Cholate Dispersion 2; however, material began precipitating from the dispersion within 24 hours, Figure 2b. Inclusion of NH\(_4\)OH within 2% sodium cholate solvent dispersions resulted in precipitation of the graphene material immediately after sonication; therefore centrifugation was not carried out.

![Dispersion 1](image1.png)
![Dispersion 2](image2.png)
![Dispersion 3](image3.png)

Figure 1. NMP Dispersions 1, 2, and 3, 2 weeks after centrifugation.

![Dispersion 1 with NH\(_4\)OH](image4.png)
![Dispersion 2 with NH\(_4\)OH](image5.png)
![Dispersion 3 with NH\(_4\)OH](image6.png)

Figure 2. a) Cholate Dispersion 1, and b) Cholate Dispersion 2, 72 hours after preparation.
small size of graphene sheets within NMP Dispersion 3 following 14000 rpm centrifugation is thought to be a factor in the lack of floating graphene material. Similarly, the addition of droplets from NMP Dispersions 1 and 4 produced no visible islands or films on the surface of the water. The lack of films formation suggests that both the size and number of sheets present in the dispersion was small.

The same technique of dripping the dispersion into distilled water did not produce films from 2% sodium cholate dispersions. The lack of film formation is attributed to the presence of an adsorbed cholate layer on the graphene, which counters the hydrophobic nature of the graphene sheets. While cholate dispersions did not produce films on the surface of distilled water, centrifuged graphite/graphene material from all NMP and 2% cholate dispersions did produce films when introduced to water. The films produced from immersion of post-centrifuged precipitated material into distilled water were thick, somewhat reflective, and minimally transparent, Figure 3b. The precipitation of graphitic material was observed alongside the formation of the post-centrifuged material films.

Imaging of the samples, via SEM, confirmed that the floated off materials were composed of a multi-layered pile up of the sheets resulting from the synthesis of the films, Figure 4a. Compositional analysis of multiple films and sites using EDAX continually showed only the presence of carbon and the silicon substrate with oxygen quantities consistent with the background, Figure 4b. The lack of oxygen present in EDS analysis strongly suggests that the graphene sheets were not oxidized by the inclusion of NH4OH within the dispersion. Additionally, the lack of nitrogen and oxygen within EDS results further suggest that the graphene was not functionalized.

Raman spectroscopy of the films floated from the distilled water baths onto silicon and laboratory glass slides confirmed that the material was graphene-like carbon, Figure 5. The G peak of the various samples, situated around 1580 cm\(^{-1}\), is larger than the 2D peak, situated around 2700 cm\(^{-1}\), which is typical of liquid exfoliated graphene. In the case of a pristine single layer of graphene a sharp 2D peak, measuring about 4 times the size of the G peak at...
around 2680 cm$^{-1}$ would be expected.\textsuperscript{25} While the position of the 2D peak is more consistent with that expected of graphite, >2700 cm$^{-1}$,\textsuperscript{25} the clear prominence of a shoulder lying below 2700 cm$^{-1}$, seen across all samples, is consistent with ≤5 layered graphene.\textsuperscript{25} Specifically, the sites analyzed on the film from NMP Dispersion 2 is emblematic of 2 layered graphene whereas sites analyzed on films produced from NMP Dispersion 5 are consistent with 5 layered graphene.\textsuperscript{25}

Raman spectroscopy of samples created by immersing post-centrifuged precipitated material in the distilled water bath appear more graphite-like due in part to the increased thickness of those samples, Figure 5. This is most clearly observed by the 2D peak in bulk graphite consisting of two components 2D$_1$ and 2D$_2$, which are respectively roughly 1/4 and 1/2 the height of the G peak.\textsuperscript{25}

The presence of $D$ peaks about 1350 cm$^{-1}$ within the dispersion is the result of edge effects. For a single layer of pristine graphene, the $D$ peak is sharp and situated just below 1350 cm$^{-1}$.\textsuperscript{25} For graphite, the $D$ peak is composed of two peaks, $D_1$ and $D_2$, where the peak $D_1$ is just below 1350 cm$^{-1}$ and peak $D_2$ is situated around 1365 cm$^{-1}$.\textsuperscript{25} The situation of $D$ peaks below 1350 cm$^{-1}$ for the dispersion films further suggests a few-layered graphene structure rather than a graphite film. Conversely, the lack of $D$ peak along with the shape of the 2D peak for films produced using post-centrifuged material seems to suggest larger and thicker graphene structures. Given that 10 layers of graphene have a very similar spectrum to graphite,\textsuperscript{25} the film appears to be composed of several, 5 to 10, layers of graphene. The precipitation of graphitic material observed when introducing the post-centrifuged material to the distilled water bath further suggests the post-centrifuged films are thinner than the initially loaded graphite.

**Discussion**

Analysis using Raman spectroscopy clearly indicates that the film produced by dripping the dispersion into distilled water is neither graphite nor single layer graphene. As graphene is defined as single hexagonal lattice of carbon atoms, the term few-layered graphene is best suited for describing the graphene produced by liquid exfoliation.\textsuperscript{21,22} Specifically, the films produced within this work are best described as a disordered collection of few-layered and single layered graphene sheets.

The inclusion of NH$_3$ in NMP solvent dispersions was found to increase the loading of graphene within the dispersion based on both coloring as well as the capacity to form a thin film on the surface of water. Including H$_2$O within the dispersion in place of NH$_3$ was investigated in order to determine whether H$_2$O, the solvent for NH$_3$, played any role in the darkening of the dispersion. While the inclusion of H$_2$O within the dispersion initially produced an identical result as the inclusion of post-centrifugation material within water has utility as a means of producing higher quality graphene dispersions. The liquid exfoliated few-layer graphene dispersions produced using NH$_3$OH are stable and free of oxides which is fundamentally different compared to the stable, strongly hydrophilic oxides of both graphite and graphene,\textsuperscript{27,28}

When the stable few-layer graphene dispersions were introduced to a water bath, a thin film layer of few-layer graphene sheets formed on the surface. The production of graphene thin films by dripping the dispersions into distilled water is thought to be due to the hydrophobic nature of the graphene sheets\textsuperscript{25} as well as a result of high graphene loadings and large relative sheet sizes within the dispersions. The films produced from the precipitates within the NMP/H$_2$O dispersion remained somewhat transparent, though of a lesser quality than NMP/NH$_3$ dispersions. The increased opacity of films from NMP/H$_2$O dispersions compared to those produced from NMP/NH$_3$ dispersions was likely due to the onset of sheet aggregation; a known occurrence in the NMP/H$_2$O dispersions.

While those NMP dispersions containing NH$_3$ were found to produce films, NMP Dispersion 3 proved a notable exception. The inability for NMP Dispersion 3 to produce an obvious film is attributed to the high centrifugation rate, though multiple sonication cycles from reprocessing may have also played a role. The high centrifugation rate of 14000 rpm likely preserved only the smallest graphene nanosheets within the dispersion. The smaller sheet sizes may therefore have been trapped in the NMP solvent and did not effectively disperse when dripped into distilled water. Conversely, the inability of NMP dispersions without NH$_3$ to produce obvious films was associated with the lower loading of the dispersions. Similar to NMP dispersions without the inclusion of NH$_3$, dispersions in 2% sodium cholate were likewise unable to produce graphene films. The lack of film formation in the case of dispersions in 2% sodium cholate are attributed to the presence of an adsorbed cholate layer on the graphene\textsuperscript{25} which counters the hydrophobic nature of the graphene sheets needed to produce the thin film.

The production of films using post-centrifugation material provides an alternative to using dispersions in applications requiring thicker multi-layered graphene structures. Additionally, the immersion of post-centrifugation material within water has utility as a means of sorting graphene sheets below a threshold layer thickness given that graphite, and possibly large multi-layered graphene sheets, precipitate. Specifically, washing post-centrifuged graphene material and collecting the thin films for reprocessing provides advantageous means of producing higher quality graphene dispersions.

**Conclusions**

The inclusion of NH$_3$, by means of a NH$_3$OH solution, within liquid exfoliated dispersions clearly increases the loading of graphene flakes within NMP dispersions. The increase in loading due to the presence of NH$_3$ is most apparent when compared to dispersions not containing NH$_3$. Specifically, this work demonstrates that NH$_3$ inclusion during liquid exfoliation processing helps prevent aggregation of graphene sheets. The inclusion of H$_2$O within NMP dispersions was confirmed to only temporarily increase the loading of the graphene.
flakes, indicating that NH₃ itself was primarily responsible for increased loading.

The production of drop-cast graphene based films on the surface of water was confirmed using NMP/NH₄OH dispersions. The presence of NH₃ does not appear to have any effect on dispersions created with sodium cholate; a result attributed to hydration of the cholate adsorbed on the surface of graphene flakes. The hydration of the adsorbed cholate, apparently resulting in an improved miscibility with water for graphene sheets, appears to inhibit the hydrophobicity of graphene sheets and thus prevent the formation of flakes when drop-cast on water.

Production of liquid exfoliated graphene using NH₄OH as an additive within the NMP solvent increases graphene sheet loading which has many potential applications. Specifically, increased loading of graphene sheets has applications within graphene-inks and reinforcing material in polymer-based composites.

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