

Graphene Nanoplatelets Prepared by Electric Heating Acid-Treated Graphite in a Vacuum Chamber and Their Use as Additives in Organic Semiconductors

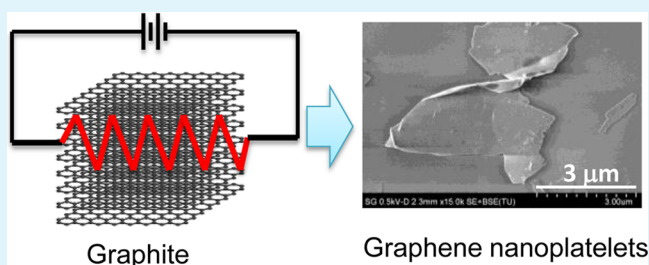
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ABSTRACT: Graphene nanoplatelets (GNPs) were prepared from acid-treated expandable graphite using a novel method of electric heating the graphite in an evaporation chamber under high vacuum, followed by solvent exfoliation. Such prepared graphene nanoplatelets, the eGNPs, were compared to GNPs prepared from two conventional methods: thermal expansion in an isothermal oven followed by solvent exfoliation (oGNPs), and direct solvent exfoliation (sGNPs), using various characterization techniques including UV–vis spectroscopy, scanning electron microscopy, and atomic force microscopy. It was found that the eGNPs were very thin, with a thickness of 4–16 nm, and showed no oxidation. On the other hand, oGNPs exhibited much thicker sheets, upward of 40 nm, and the sGNPs showed a high degree of oxidation. Utilizing the high purity eGNPs as an additive in PQT-12 semiconductor layer has been shown to improve the mobility by a factor of 2 in thin-film transistor devices.

KEYWORDS: graphene nanoplatelets, graphite, electric heating, exfoliation, organic thin-film transistor



1. INTRODUCTION

Graphene, a one layer thick sheet of sp^2 hybridized carbon molecules densely packed in a hexagonal honeycomb structure, has garnered a large amount of research interest lately due to its extraordinary mechanical, optical, and electrical properties.^{1–4} Most research conducted so far on graphene has studied single graphene sheets created by micromechanical cleavage of graphite, or through chemical methods, usually utilizing a modified Hummers method.^{5–11} These methods predominantly create graphene oxide, which must then be reduced back to graphene (i) thermally by annealing in a forming gas at temperatures in excess of 1000 °C,⁴ (ii) chemically using toxic reducing agents,⁸ or (iii) through dehydration as catalyzed by the intercalated sulfuric acid.¹² All methods can create graphene, but because the reduction step will always leave behind residual oxide, the purity of the product is never immaculate. This is also true for production of nanoparticle stacks of a few layers of graphene, called graphene nanoplatelets (GNPs).^{10–16} High purity graphene and/or GNPs are required as conductors,^{17,18} semiconductors,¹⁹ or additives for polymeric nanocomposites.^{20–24} To overcome some barriers to graphene and GNPs production, we report here a novel method for graphite expansion utilizing electric heating in a vacuum evaporation chamber. Using this ubiquitous laboratory equipment, acid-treated expandable graphite can be quickly expanded in a short time in a vacuum to deter oxidation of graphite. It was also postulated that due to the presence of a vacuum, the

expansion of the graphite could be enhanced due to increased likelihood of acid molecules being expelled from adjacent graphene layers. The goal of this investigation was to compare the novel and conventional expansion methods on their ability to expand acid-treated graphite, and to utilize the larger interlayer spacing between graphene sheets after expansion to enhance exfoliation and produce a higher concentration of GNPs within suspension. Such prepared GNPs were also attempted as additives for organic semiconductors in thin-film transistor devices.

2. EXPERIMENTAL SECTION

2.1. Expansion. Acid-treated expandable graphite was provided by Asbury Carbon Co. The material was used as received. A small amount of the graphite was loaded into a tungsten boat in an Edward Auto 306 vacuum evaporator. A cover was applied to the boat to reduce the chance of material being lost in the expansion process. The evaporator was pumped to 2×10^{-6} torr before expansion was conducted. The current applied to the boat was increased so that a temperature of 800 °C was reached. The temperature was held at this value for 1 to 5 min before removing the current applied to the boat. The sample was left to cool in the vacuum for 15 min before equalizing the pressure and retrieving the sample. The same expandable graphite source was placed into a conventional oven and heated to 800 °C in the presence of a forming gas (5 vol % hydrogen in nitrogen). Once the

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temperature was reached, the sample was cooled to room temperature (about 2 h) while still exposed to the forming gas atmosphere.

2.2. Exfoliation. The vacuum expanded graphite and the conventional oven expanded graphite were exfoliated in the same manner. The samples were added to *o*-dichlorobenzene (DCB) solvent at a concentration of 0.1 wt % and bath sonicated for 30 min to break up the very large expanded pieces. Further sonication was done by probe (Cole Parmer, 750 W, 50% amp, 5 min) to further reduce the GNP size and thickness. Suspensions were then centrifuged (3500 rpm, 15 min) to remove any remaining large particles or impurities. For direct solvent exfoliation, unexpanded graphite was added to *N*-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and DCB solvents at 1–5 mg/mL concentrations. The sonication and centrifugation procedure was kept the same as that for the expanded source.

2.3. Characterization. AFM analysis was performed in tapping mode on a MultiMode SPM with a NanoScope IIIa controller by Digital Instruments. Scanning electron microscopy (SEM) was done on Hitachi SU-8000 field emission scanning electron microscope operating in deceleration mode with a landing voltage of 700 V. UV–vis spectra were collected on a VARIAN CARY 5 UV–vis-NIR spectrophotometer.

2.4. OTFT Fabrication. A heavily doped silicon wafer with 200 nm thermal oxide as the gate dielectric layer was used for device fabrication. The silicon oxide layer was modified with octyltrichlorosilane (OTS-8) using previously reported methods.²⁵ PQT-12 powder was dissolved in suspensions of GNPs in DCB solvent at a concentration of 0.3 wt %. The final suspensions were spin-coated on OTS-8 modified silicon wafers at a speed of 2500 rpm for 120s. The film was then vacuum-dried at 70 °C for 30 min, followed by annealing at 140 °C for 10 min.

Gold electrodes were thermally evaporated on the films at 2×10^{-6} mbar (torr). Transistors were patterned at 90 μm channel length and 1 mm channel width in all the cases. Electrical characterization of the devices was carried out in ambient conditions at room temperature under UV protected light using a Keithley 4200 semiconductor characterization device. Mobility was calculated from the slope of $\sqrt{I_{ds}}$ vs V_G using $\mu = \frac{2L}{WC_i} \left(\frac{d\sqrt{I_{ds}}}{dV_G} \right)^2$, where C_i is the gate dielectric capacitance per unit (15 nF/cm²).

3. RESULTS AND DISCUSSION

Expandable graphite, or acid-treated graphite, has been utilized in the production of graphene ribbons and graphene nanoplatelets.^{13,14} In most experiments utilizing this starting material, the expandable graphite was heated in a tube oven in the presence of a forming gas to expand and increase the interlayer spacing without oxidizing the material.⁴ The resultant graphene material after exfoliation can range from narrow graphene ribbons to graphene nanoplatelets. This conventional method was used as a comparison reference for our novel process of electric heating expansion in vacuum. In our proposed method, a vacuum evaporation chamber was utilized to heat the material to the necessary temperatures for expansion. Using electric heating in vacuum can inhibit the oxidation of the material without the use of a forming gas.

Expandable graphite with an average flake length of 300 μm was provided by Asbury Carbon Co. The material was treated with sulfuric and nitric acid. Heating the material caused the acid molecules that intercalated between the graphene sheets to gasify, expelling them from adjacent graphene sheets and increasing the adjacent graphene layer spacing. The material was loaded in a tungsten boat in the vacuum chamber at a vacuum of 2×10^{-6} torr. Current was applied to the boat for 1 to 5 min, so that the temperature of the graphite and the boat would reach ~ 800 °C to fully expand the material. After

sufficient time for the sample to cool, the vacuum was released and the material was added to solvent for exfoliation in an ultrasonic bath. Visually observing the material before and after expansion shows a large volume change (Figure 1A,B).

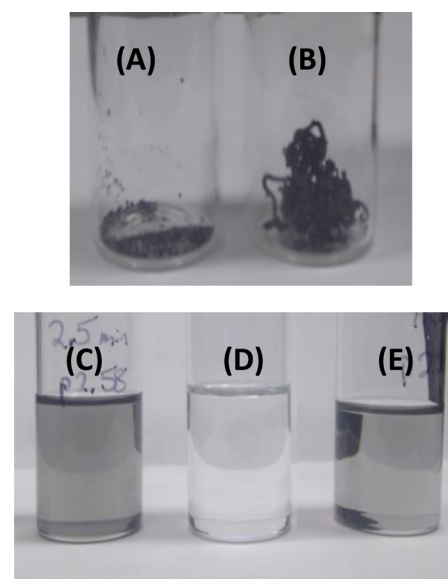


Figure 1. (A) Expandable graphite, (B) graphite after electric heating expansion in vacuum evaporator, (C) eGNPs in DCB, (D) DCB solvent, and (E) oGNPs in DCB after centrifugation.

Conventional oven expansion was used as a comparison method. The same expandable graphite was heated to 800 °C in an isothermal oven under a forming gas (5% H₂ in N₂) to prevent oxidation. Similarly, a large volume change was observed, and no visual difference could be detected for both expanded graphite.

o-Dichlorobenzene (DCB) was chosen as the solvent to exfoliate the expanded graphite, as it is one of the most commonly used solvents for fabrication of organic electron devices.²⁵ The expanded graphite was added to DCB solution at a concentration of 0.1 wt % for exfoliation. The suspension was first sonicated by bath for 30 min, followed by probe sonication for 5 min. Directly probe sonicating the expanded material could produce thin graphene nanoplatelets, but it reduced the sheet length to below 1 μm . Therefore, two types of sonication were employed to produce relatively large GNPs. The low power sonication was used to initially break up the very large pieces of expanded graphite. This step would exfoliate the material into platelets that would have large thicknesses and sheet lengths. The second sonication step was to further exfoliate the platelets to the minimal thickness, although it could break the sheets into smaller lengths. After sonication was completed, the suspensions were centrifuged to remove unexfoliated material and impurities. A comparison of GNP dispersions obtained from both the electric-heating expansion in vacuum chamber (eGNPs) and the conventional oven expansion method (oGNPs) can be seen in Figure 1C,E. The eGNPs dispersion was considerably darker than the oGNPs suspension. Because both the exfoliation and centrifugation steps were consistent, it appeared from qualitative analysis that the electric heating method expanded graphite to a larger degree because more GNPs stayed within the suspension.

To quantify this statement, GNP concentrations were estimated using the absorbance spectra of the suspensions in a UV–vis–NIR spectroscope. The extinction coefficient of graphene has been reported as $2460 \text{ L}/(\text{g}\cdot\text{cm})$.²³ Using this value and basing on the absorbance at 660 nm, we can estimate the concentration based on the Lambert–Beer law ($A = \epsilon lc$ where ϵ is the extinction coefficient, l is the length of light traveled (cell length), and c is the concentration). Table 1

Table 1. Concentrations of GNPs in DCB Calculated Using the Lambert–Beer Law with the Absorbance at 660 nm in UV–Vis Spectra

GNPs	absorbance at 660 nm (au)	estimated concentration (mg/mL)
eGNPs	0.412	0.017
oGNPs	0.169	0.007

summarizes the absorbance at 660 nm and the calculated concentrations of eGNPs and oGNPs in DCB. The oGNPs showed a similar concentration as that of the previous report,²⁶ which is typically $<0.01 \text{ mg/mL}$. On the other hand, the eGNPs showed a much higher concentration up to 0.017 mg/mL , about 2.5 times of the oGNPs concentration. The electric heating time was investigated in detail. No significant concentration difference was found for electric heating from 1 to 5 min, revealing that the electric heating expansion is instant and can be accomplished in very short period of time. Estimated concentrations using UV–vis spectroscopy confirmed that the electric heating in vacuum chamber exfoliated the graphite easier and produced more concentrated suspensions than conventional oven expansion methods. To our knowledge, this is the first demonstration of electric heating expansion graphite under high vacuum for producing a high concentration of GNP dispersion.

Microscopes were used to characterize the difference in sheet length, thickness, and substrate coverage. SEM was used to image suspensions of both eGNPs and oGNPs materials after being drop cast onto silicon wafer substrates (Figure 2). It was confirmed that the expansion and subsequent exfoliation reduced the sheet length and thickness substantially. The eGNPs had very smooth sheet surfaces with sheet lengths, across a variety of images, consistently between 1 and $5 \mu\text{m}$ (Figure 2A–D). This was a large reduction from the initial sheet length of $300 \mu\text{m}$, which was caused by the sonication of the expanded material. It was interesting to note from the images that not all eGNPs lied flat on the substrate surface. In many images, eGNP sheets could be seen having edges or facets protruding away from the substrate surface without an underlying support (Figure 2C,D), possibly an indication of flexibility of the GNPs. Average oGNPs shape and smoothness were very similar to the eGNPs, but the surface coverage was less due to a lower dispersion concentration. The length of oGNPs from this source was slightly larger than that of eGNPs, with average sheet lengths close to $5 \mu\text{m}$. During the SEM investigation of this material, a broken edge of an oGNPs was observed. This edge shows a few layers of graphene that make up the platelets found on the substrate (Figure 2F). This was not observed in the eGNPs, which leads us to suspect that eGNPs are thinner than oGNPs.

AFM was used to measure the thickness of the GNPs on the same drop-cast samples. AFM investigations on the two GNP materials reveal differing sheet thicknesses (Figure 3). For the eGNPs, the largest thickness observed was 16 nm whereas the

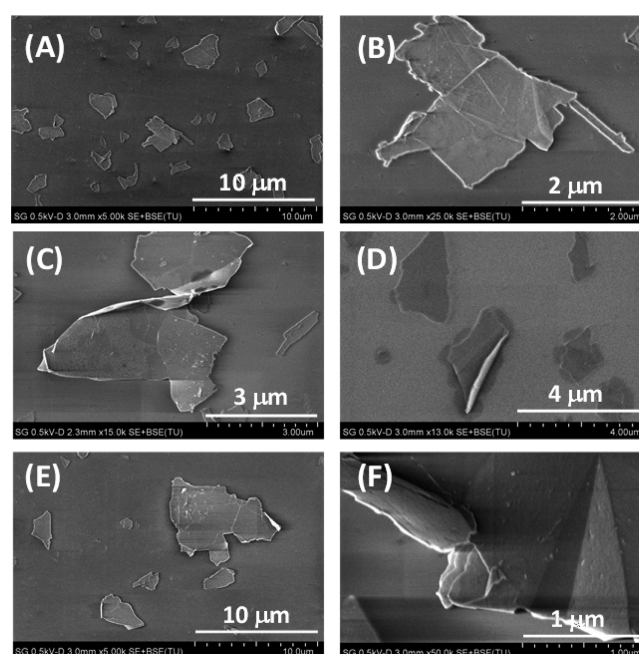


Figure 2. SEM micrographs of GNP sheets casted on silicon substrate. (A–D), eGNPs at different scales and locations; (E,F), oGNPs at different scales.

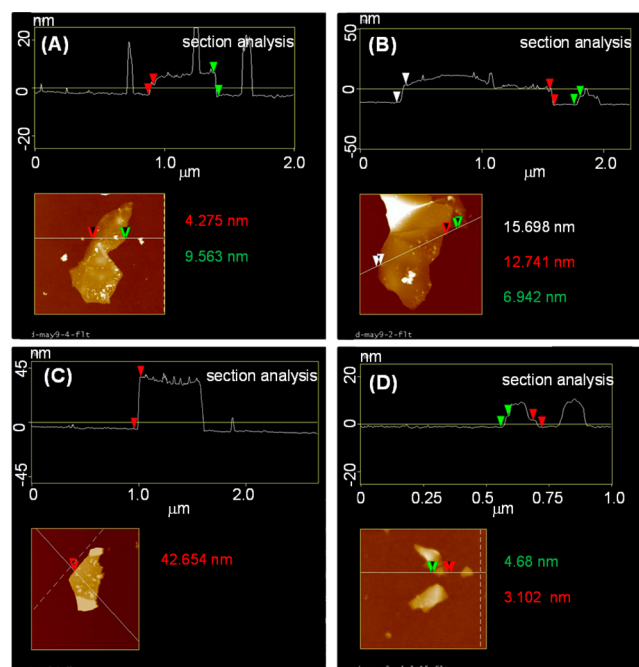


Figure 3. AFM images and height measurements for various GNPs. (A,B) eGNPs, (C) oGNPs, and (D) sGNPs. The scanned area is $2 \times 2 \mu\text{m}$ for images A, B, and C, and $1 \times 1 \mu\text{m}$ for image D.

thinnest was about 4 nm, with most being in the 10 nm range, statistically (Figure 3A,B). This thickness corresponds well to other GNPs reported in literature or commercially available.²⁷ On the other hand, the oGNPs had a very thick nanoplatelets with the largest thickness of $\sim 50 \text{ nm}$, and the thinnest thickness of $\sim 35 \text{ nm}$. The average thickness of the oGNPs is close to 40 nm (Figure 3C). Because the starting material and exfoliation conditions were the same, the thinner thickness of eGNPs may be attributed to the superior expansion of the graphite in the

presence of high vacuum. Instant heating and more homogeneous heat distribution could be the additional advantages of the electric heating method, as the graphite can conduct the current and generate heat within. The exfoliation step was investigated in attempts to further reduce the GNP thickness by extending the probe sonication time; however, further sonication reduced the sheet length but not the thickness. The minimal thickness of 4–16 nm might represent the limit of the electric heating method in expanding this specific acid-treated graphite. In other words, this minimal thickness could be a result of the initial acid treatment, as acid molecules may not have intercalated between every adjacent graphene sheets. Nevertheless, the electric heating expansion in vacuum chamber produced much thinner GNPs than the conventional isothermal oven heating method.

It has been reported that graphene sheets or GNPs could be produced by direct exfoliation of graphite in suitable organic solvents.^{26–29} With some additives such as NaOH, a high concentration up to 0.07 mg/mL was obtained.²⁹ We therefore tested if the acid-treated graphite could be directly exfoliated in DCB. The solvent is preferred for future organic semiconductor composite study. The same acid-treated graphite from Asbury Carbon Co. was added to DCB at various concentrations and sonicated using the same procedure as that of the expanded graphite. As a comparison, the polar aprotic solvents NMP and DMF, which were identified previously as good solvents to directly exfoliate graphite, were used as well. It was found that a 5 mg/mL starting concentration resulted in the largest amount of GNPs in suspension, as measured by UV–vis spectroscopy. Further increasing the starting concentration did not result in more GNPs in the suspension. Figure 4 shows a visual

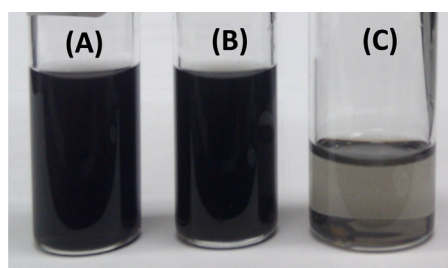


Figure 4. Vials containing sGNPs in (A) NMP, (B) DMF, and (C) DCB. Starting from a 5 mg/mL solution of the expandable graphite.

comparison of the direct solvent exfoliated GNPs (sGNPs) in different solvents. The sGNPs suspension in DCB had the similar darkness to the eGNPs in DCB, while a much higher concentration of sGNPs could be obtained in NMP and DMF. The concentrations of the sGNPs in the suspension were again estimated from the UV–vis absorbance spectra using the Lambert–Beer law. The concentration of sGNPs in DCB was 0.015 mg/mL, which is slightly lower than the eGNPs dispersion and the dispersion of microcrystalline synthetic graphite in DCB.²⁹ As expected, the concentrations of sGNPs in NMP and DMF were much higher, calculated to be 0.08 and 0.11 mg/mL for DMF and NMP suspensions, respectively. The concentrations surpassed the values reported in literature for graphene nanoplatelets exfoliated directly using the same solvents but NaOH additive.²⁸ These results indicated that both acids and bases can exfoliate the graphite and help stabilizing the GNPs in polar aprotic solvents.

SEM characterization was again performed on the sGNPs. Figure 5 shows images of sGNPs produced in different solvents

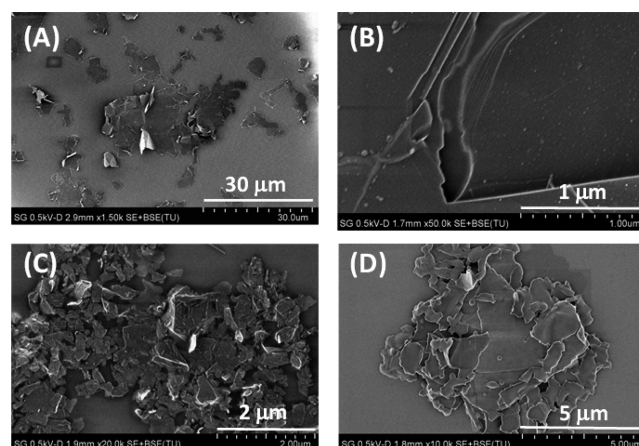


Figure 5. SEM images of sGNPs exfoliated in (A,B) DCB, (C) NMP, and (D) DMF solvents.

and drop cast on a substrate. Although the acid-treated graphite was directly exfoliated in all three solvents, the resulted sGNPs were dramatically different. The GNPs obtained in DCB were flat and very large, from a few micrometers up to $\sim 30 \mu\text{m}$ in sheet size (Figure 5A). In addition, these GNPs were very thick, composed of more than 10's of graphene layers, as shown in Figure 5B. On the other hand, the GNPs obtained in NMP solvent were granular and had very small sizes, typically no more than $1 \mu\text{m}$ (Figure 5C). Exfoliation in DMF yielded flat GNPs of about 1 to $5 \mu\text{m}$ in size, which is in between those for the DCB and NMP solvents. The solvent effect on GNP morphology is very interesting, but not fully understood. Polarity of the solvent and dielectric strength may play an important role. Further AFM study on the smaller sGNPs obtained from NMP showed many steps or sharp ledges on their surfaces (Figure 3D). Although some very thin sGNPs down to 2–3 nm were obtained, each GNP sheet was not flat, containing both thin and thick regimes, when compared to the flat and smooth surfaces of the eGNPs.

We further studied purity of the produced GNPs using EDX. GNPs with high purity should show a carbon peak only, while impurities such as the residual acid molecule and a large degree of oxidation could be present in chemically impure GNPs. Figure 6A shows the energy-dispersive X-ray (EDX) spectrum corresponding to the eGNPs. As expected, a large carbon peak was observed. The presence of a silicon peak should be ascribed to the silicon substrate, while the oxygen peak could be from either the substrate (native silicon oxide) or oxidation of the eGNPs. To figure this out, eGNPs were casted on a silicon wafer with a 200 nm silicon nitride surface layer. As shown in Figure 6C, the oxygen peak vanished below the noise level, indicating that we had very pure eGNPs. The oxygen content was estimated to be less than 1 at. %, based on the areas of the oxygen and carbon peaks using a semiquantitative analysis. This proves that the electric heating expansion process in vacuum successfully expands the material and removes any acid molecules while also preventing oxidation of the material at the high temperatures. In contrast, the sGNPs were not chemically pure. Figure 6B shows EDX spectrum performed on multiple sGNPs cast on the silicon wafer substrate. Besides the carbon, oxygen, and silicon peaks, sulfur, nitrogen, and chlorine

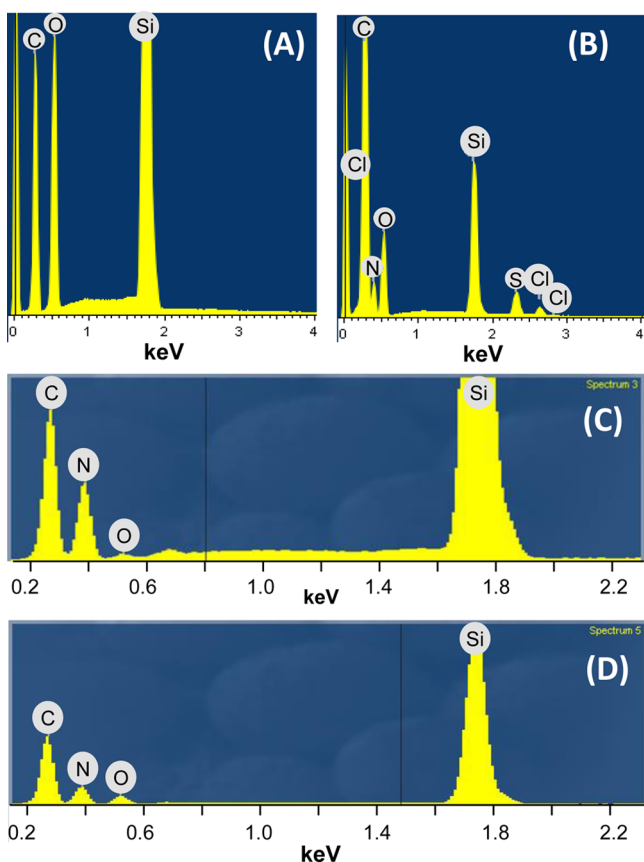


Figure 6. EDX spectra of (A) eGNPs and (B) sGNPs drop cast on silicon wafer substrates, (C) eGNPs and (D) sGNPs drop cast on silicon wafer with 200 nm silicon nitride surface layer.

peaks were detected, revealing the existence of acid molecules in the film. This is expected as graphite was treated with sulfuric and nitric acids, and subsequently washed with hydrochloric acid and water. To further confirm if the sGNPs have oxidation sites, EDX was performed on sGNPs cast on silicon wafer having the silicon nitride surface layer. Because it has been confirmed that there were acid molecules in the sGNP film, to eliminate the interference of oxygen from SO_4^{2-} , we carefully focused the electron beam on single sGNP sheet. As shown in Figure 6D, a significant oxygen peak was observed, indicating the sGNPs have a high degree of oxidation. The oxygen content was estimated to be $\sim 9\%$. Although direct solvent exfoliation produces a higher concentration of sGNPs in suspension, they are not as desirable for some applications due to the presence of acid impurity and heavy oxidation. For use as additives in electronic materials, the eGNPs with high purity and smooth surface from the novel electric heating process would result in better electrical properties.

To test conductivity of the GNPs prepared from the different methods, the GNP suspensions were vacuum filtered to form a film on glass fiber filter paper. Different amounts of suspensions were used for eGNPs, oGNPs, and sGNPs so that the final amount of GNPs on the filter paper was about the same. After vacuum filtration and drying, GNP thin films with an estimated thickness of 60 nm were obtained. Although the glass fiber paper has a very large surface roughness, low resistances were still obtained for such GNP thin films, most likely due to the GNPs lying flat down on the filter paper. It is interesting that the eGNPs provided the lowest resistance of 10 Ohm across

the 1 cm diameter filter paper, while both oGNPs and sGNPs had similar resistances in the 30–50 Ohm range. The low resistance of the eGNP film is probably due to the fact of high purity and thinner GNP sheets.

A major application of GNPs is to be incorporated into polymers to form nanocomposite materials for electronic applications.^{20–24,30,31} As such, the GNPs produced by both expansion methods were utilized as an additive for polythiophene organic thin-film transistors (OTFTs). PQT-12 was chosen as the matrix polymer,²⁵ as it has been shown to stabilize and create nanocomposites with single-walled carbon nanotubes (SWCNTs) for improving device performance.³² The sGNPs were not investigated for OTFT applications due to the high degree of oxidation and the presence of acid impurities which would deteriorate the performance of polythiophene semiconductors through acid doping effect. Suspensions of both eGNPs and oGNPs were prepared as discussed above. DCB was added to the suspensions to dilute the GNP concentration to get a range of GNP:PQT-12 ratios. Then, PQT-12 powder was added to create a 0.3 wt % polymer solution. The solutions were bath sonicated for 30 min to ensure a homogeneous mixture before spin coating. OTFTs with the GNP nanocomposite semiconductor layers showed an improved effective mobility over the pure polymer reference. Figure 7 shows the transfer curves of the OTFTs with pristine

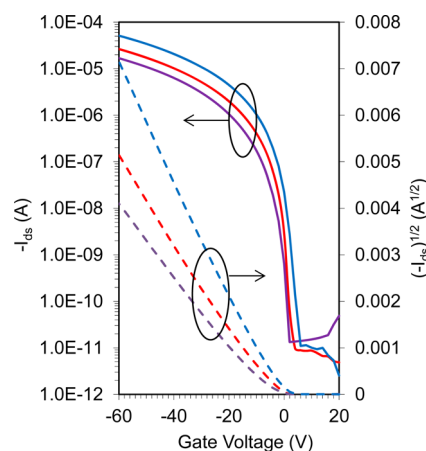


Figure 7. Transfer curves of OTFTs in saturation region ($V_{ds} = -60$ V) with PQT-12 (purple), oGNPs/PQT-12 (red), and eGNPs/PQT-12 (blue) semiconductors. The OTFTs have a channel length of 90 μm and channel width of 1000 μm .

PQT-12, and PQT-12 having 1.0 wt % oGNPs or eGNPs in the semiconductor layer. The current increased dramatically when GNPs were added, especially for eGNPs. Similar to SWCNTs used as the additive in organic semiconductor,³² the GNPs create a “fast lane” for charge carriers to move in the transistor channel. The GNPs had a little effect on the turn-on voltages. The threshold voltages were calculated to be -7.8 , -5.6 , and -4.1 V for devices with PQT-12, oGNPs/PQT-12, and eGNPs/PQT-12, respectively. Figure 8 summarizes the mobility and current on/off ratio results of OTFT devices having eGNPs/PQT-12 and oGNPs/PQT-12 nanocomposites with different GNP contents. Devices with eGNPs exhibited a significant improvement of the mobility. With 1.0 wt % eGNPs in the semiconductor film, the mobility was up to $0.215 \text{ cm}^2/(\text{V s})$, a factor of 2 over the pristine PQT-12, while the current on/off ratio remained very high ($>10^6$). This was a vast

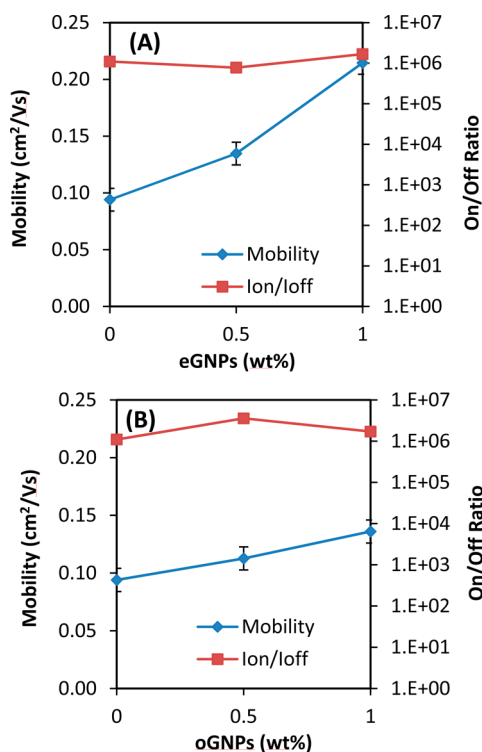


Figure 8. Field-effect mobility and current on/off ratio of OTFTs with PQT-12 semiconductor layers having (A) eGNPs and (B) oGNPs.

improvement in mobility with such a small amount of the eGNPs. On the other hand, use of the oGNPs only resulted in about 50% improvement of the mobility. This was most likely due to thinner thickness and higher chemical purity of the eGNPs. It is postulated that further optimization and increasing the amount of the eGNPs could further enhance device performance.

4. CONCLUSION

We have demonstrated a novel method to prepare graphene nanoplatelets (GNPs) by electric heating acid-treated graphite under high vacuum, followed by solvent exfoliation. This electric heating in a vacuum method produces high purity GNPs with thicknesses ranging from 4 to 16 nm, and sheet length varying from 1 to 5 μm . Comparison studies revealed that the electric heating in vacuum method produces thinner graphene nanoplatelets, thus, a significant higher suspension concentration, than the conventional isothermal oven expansion. Although direct solvent exfoliation of unexpanded graphite created GNPs with a higher concentration than the electric heating in a vacuum method, these GNPs showed a high degree of oxidation and an uneven sheet thickness, which are undesirable for electronic applications. Incorporating the electric heating expanded GNPs in a semiconducting layer of PQT-12 has been shown to improve the mobility of the semiconductor layer by a factor of 2, while retaining a high current on/off ratio $>10^6$.

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Notes

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