The Superior Dispersion of Easily Soluble Graphite**

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Graphene is a 2D one-atom-thick layer that has attracted enormous scientific attention on account of its extraordinary electronic and mechanical properties resulting from the hexagonally arrayed sp²-hybridized carbon atom structure.[1,2] Several efforts have been made to use graphene in devices and composites.[3,4] The strong covalent bonds of carbon atoms provide high mechanical and thermal properties and chemical stability. The theoretical Young’s modulus of graphene is approximately 1060 GPa.[5] In addition, the high electrical conductivity (mobility: 20000 cm² V⁻¹ s⁻¹, velocity: c/300) through the π-electron cloud makes graphene a promising material in conducting composites and quantum electronics.[6–8]

As in other new materials (such as carbon nanotubes, various quantum dots, etc.), the development of mass production methods that can support the demand for graphene in a variety of large-scale applications is of high priority. Thus far, several methods for graphene production have been developed and can be summarized into three areas: mechanical exfoliation,[9,10] graphene in solution,[11,12] and epitaxial growth.[13,14] Mechanical exfoliation produces the highest quality graphene, which is suitable for fundamental studies. Epitaxial growth provides the shortest path to graphene-based electronic circuits. Graphene in solution can offer lower costs and higher throughputs and may be used in a wide range of applications because of the significant practical utility of this material. However, the method is quite complicated and involves personnel-dependant procedures due to the requirement of functionalization and reduction processes. Thus far, the most commonly used process for graphene solutions is Hummer’s method,[15] which can produce well-dispersed graphene oxide (GO) in water due to its hydrophilic properties. This method involves the oxidation of graphite in the presence of strong acids and oxidants. The level of oxidation can be varied according to the reaction conditions and chemicals. Recently, some researchers have reported that as-prepared graphite oxide can be dispersed in an organic solvent such as N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) without additional chemical functionalization.[16] However, the as-prepared GO is an electrical insulator and therefore additional chemical reduction processes are necessary to recover its conductivity. In addition, reduced GO still exhibits lower conductivity than pristine graphene.[17] In order to circumvent the oxidation of graphene, some researchers have introduced different re-intercalation or liquid-phase-exfoliation methods.[18,19] However, these methods are quite complicated with long processing times or low yields of normal expanded graphite in organic solvents. The production of stable suspensions of graphene in various solvents is important in the fabrication of graphene-based devices and composites. Previously the preparation of easily soluble expanded graphite (ESEG) has been reported,[20] which can be dispersed in water with sodium dodecylbenzene sulfonate (SDBS) and NMP by ultrasonication. Most sheets were composed of a few layers and were well-dispersed with long-term stability in a manner comparable to that of GO dispersions in water. In addition, due to the absence of an oxidation state, the graphene sheet obtained from the stable suspension showed high conductivity compared to that produced by other solution-based methods without any reduction process. This study examines the dispersion behavior of easily soluble expanded graphite in a variety of organic solvents and surfactants in water. The results are expected to expand the applications of graphene–polymer composites or the development of graphene-based electrical devices.

ESEG was prepared from a fluorinated graphite intercalation compound (FGIC), C₂F₆·nClF₃, containing inorganic volatile intercalating agent CIF₃ as reported elsewhere.[20] FGIC was synthesized using the single intercalation process with CIF₃. Pure natural graphite (5 g) was added to cooled CIF₃ in a Teflon reactor for intercalation and fluorine functionalization for 5 h. After intercalation excess CIF₃ was removed and the intercalation product with a composition of C₂F₆·0.13ClF₃ was obtained.

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[**] This research was funded by the BK21 Project of the School of Advanced Materials Science & Engineering and Seoul Fellowship to J.H.Lee.

DOI: 10.1002/smll.200901556
Figure 1 shows the expanded volumes of commercial expanded graphite (EG) and ESEG. Commercial EG (50 mg) and FGIC was placed into the bottom of a quartz tube, as shown in inset of Figure 1. The samples were then placed into a furnace at 700°C for a few minutes in N2 under ambient conditions. During the “thermal shock” process volume expansion occurred, which is explosive and accompanied by a flash and sound. As shown in Figure 1a, ESEG showed higher volume expansion than commercial EG (approximately double that of EG). Figure 1b shows the intercalated and functionalized graphite structure of FGIC. The main difference in the expanded state of EG and ESEG is the thermal decomposition molecules. In the case of EG, expansion occurs only as a result of the rapid vaporization of volatile intercalated substances, \( R \) (the regime of “thermal shock”). In the case of the ESEG, expansion of the graphite layers occurs as a result of both the rapid increase in the vapor pressure of the volatile intercalated substances and the formation of gaseous fluorocarbons and other gaseous products due to interaction between the carbon matrix and fluorine atoms. Finally, ESEG has a bulk density and specific surface of 1.3–1.8 kg m\(^{-3}\) and 250–280 m\(^2\) g\(^{-1}\), respectively.\(^{[20]}\) The decomposition process is as follows:

\[
C_2F_nClF_3 (\text{solid}) \rightarrow C (\text{solid}) + Cl_2 + C_F_y + C_xF_yCl_z
\]  

Figure 2 shows a scanning electron microscopy (SEM) image of the worm-like ESEG structure and the Raman spectroscopy result of ESEG, which indicates high volume expansion and a partially destroyed graphene structure in exfoliated graphite. In particular, in the 2D peak of ESEG, a red-shift trend was dominant due to the larger space between the two graphenes as compared to that of ordinary expanded graphite.\(^{[20]}\) This severe expansion process provides the material properties essential for easy dispersion. This method can be used in the low-cost mass production of graphene for a variety of applications because of its simplicity and short processing time.

To examine the solubility of ESEG, 0.5 mg of ESEG was dispersed in 50 mL aqueous solutions of both SDBS and sodium dodecyl sulfate (SDS) and 50 mL solutions of diethylene glycol (DEG), DMF, NMP, dichloromethane (DCM), toluene, dimethylacetamide (DMAc), and n-hexane without a surfactant using a tip (cup-horn type) sonication instrument for 30 min. The as-prepared graphene suspensions, except that with hexane, had well-dispersed states (Figure 3, top). A few droplets of SDS in water, DEG, and DMAc were dropped onto the transmission electron microscopy (TEM) grid after the sonication process to measure the number of graphene layers per sheet. In a previous paper, it was demonstrated that the yield of a few layers of graphene in NMP and SDBS in water suspensions was approximately 90%.\(^{[20]}\) Figure 4 shows TEM images of the dispersed ESEG in DMAc and histograms of the number of graphene units in a sheet of SDS in water, DEG, and DMAc. The yields of a few layers of graphene (<5 layers) were approximately 93%, 87%, and 93%, respectively. However, the yields of one layer of graphene were approximately 17%, 7%, and 23%, which are lower than the 32% obtained for NMP. NMP has been reported to be efficient in dispersing graphene because the energy required to exfoliate graphene is balanced by the NMP–graphene interaction, which means the surface energies match that of graphene.\(^{[18]}\) In this study, the NMP suspension had the most well-dispersed state compared to any other solution, as reported elsewhere.

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**Figure 1.** Photographs of (a) volume states of ESEG (right) and commercial EG (left). b) Schematic diagram of the structure of a FGIC and thermal decomposition molecules.

**Figure 2.** a) SEM image of ESEG and b) Raman results of ESEG and EG.
The bottom part of Figure 3 shows the long-term stability of ESEG in various solvents. After 3 weeks, NMP, DMAc, DMF, SDBS in water, DEG, and toluene still showed a very good dispersion state, whereas n-hexane, SDS, and DCM had low dispersibility. Interestingly, there was a significant difference between the SDS and SDBS solutions. SDS and SDBS are well-known and commonly used surfactants for dispersing carbon nanotubes due to their amphiphilic properties. The hydrophobic tails of SDS and SDBS molecules interact with the hydrophobic surface of the nanotubes and the hydrophilic moieties face outward. The dispersion mechanism of ESEG using SDS or SDBS surfactants should be similar to the carbon nanotube case because the lattice structures of graphene and carbon nanotubes are basically the same with a hexagonally arranged carbon structure and both have hydrophobic properties. However, the long-term stabilities of SDS and SDBS are quite different. Even the yield of a few layers of graphene from a just-sonicated graphene suspension in SDS was approximately 93%. The difference in molecule composition between SDS and SDBS is the additional benzene ring of SDBS, which means that the dispersion mechanisms and early states of SDS and SDBS suspensions are similar. However, the steric hindrance effect of the additional benzene ring is a critical factor for the long-term stability of a graphene dispersion.

Using the suspensions after 3 weeks, the dispersibility of each solvent was examined from the relationship between the absorbance ($A$) and concentration ($c$). According to the Lambert–Beer law, $A$ of the suspension is proportional to the absorption coefficient ($a$), the cell length ($l$), and $c$:

$$A = acl.$$  

This means that if $c$ can be obtained for one suspension, $c$ can be determined for the other suspensions because $a$ and $l$ are constant. This method is quite useful for well-dispersed suspensions with no sedimentation. However, there is usually some sediment in carbon nanotubes or graphene. Therefore, it is very difficult to measure $c$ because of the uncertainty of measuring the amount of sediment. Although some researchers use a filtration method, which compares the weight difference between the clean and filtered membrane, the method is quite risky because only 0.5 mg of graphene was used and some surfactant or solvent still remained. Fortunately, there was no sediment in the graphene suspension in NMP even after 3 weeks. It could be assumed that the graphene concentration of the suspension was $10^{-3}$ mg mL$^{-1}$. Before using the Lambert–Beer law, it is important to confirm the uniform dispersion of the suspensions. First, the baseline was made using pure solvents for each solvent and the quartz cell filled by a mixture of the graphene suspension and pure solvent at different ratios such as 1:2, 2:1, and 3:0. Figure 5b shows the uniform dispersion of the suspensions. Then, the baseline was made using pure solvents for each solvent and the quartz cell filled by a mixture of the graphene suspension and pure solvent at different ratios such as 1:2, 2:1, and 3:0. The Lambert–Beer behavior and different slopes of each suspension, which means that each solvent has a uniform dispersion and different dispersibility. The dispersibility of each suspension was calculated using $A$ for the pure graphene suspension in NMP and the other suspensions and the Lambert–Beer law. After 3 weeks, the NMP, DMAc, DEG, toluene, DCM, and SDS suspensions gave $A = 0.629, 0.565, 0.458, 0.38, 0.315, 0.238, 0.092, and 0.012$ and dispersibilities of $10, 8.98, 7.28, 6.04, 5.0, 3.78, 1.46, and 0.19$ mg mL$^{-1}$, respectively.

Using the graphene suspension in NMP, transparent conducting films (TCFs) were made in order to evaluate their use as a transparent electrodes using a filtration and wet transfer method. Figure 6a shows SEM images of the filtered ESEG
After conformal contact between the filtrated ESEG film and polyethylene terephthalate (PET), lateral transfer of the graphene film occurred as a result of water flow through the filter channels in the deionized water bath. The film thickness was controlled simply by varying the filtration volume of the suspensions. As shown in Figure 6c, the sheet resistance of the ESEG film was measured and compared with those of the as-made and acid-treated films. After a nitric acid treatment for a few minutes, the remaining organic material was removed. The obtained multilayered flexible graphene films on the PET substrates had sheet resistances of 2320, 39.3, 8.5, and 4.23 kΩsq⁻¹ at room temperature and transparencies (defined as transmittance at a wavelength of 550 nm) of 88%, 84.4%, 78.5%, and 72.6%, respectively.
In summary, ESEG was synthesized by a one-step exfoliation process using FGIC. Due to the severe expansion state, the obtained ESEG was sufficiently dispersed in an aqueous solution using an ordinary surfactant and various organic solvents. NMP, DMAc, DEG, tolouene, DMF, SDS, DCM, and SDS had dispersibilities of 10, 8.98, 7.28, 6.04, 5.0, 3.78, 1.46, and 0.19 μg mL⁻¹, respectively. A sheet resistance of 4.23 kΩ sq⁻¹ and a transparency of approximately 72% were obtained using filtration-transfer and acid-treatment methods. This one-step exfoliation process can allow the low-cost mass production of graphene because of the very simple procedure and short processing time. In addition, well-dispersed graphene in water and organic solutions have potential use in high-performance, scalable graphene-based applications.

Experimental Section

FGIC production: Step 1: Synthesis of the FGIC C₂F₅-nClF₃. A Teflon reactor was filled with 30 g of liquid ClF₃ and cooled with liquid nitrogen. Pure natural graphite (5 g; ash content <0.05 mass%, particle size = 200–300 μm; Zav’al’evsk coal field, Ukraine) was added to the cooled ClF₃. The reactor was then hermetically sealed. The temperature was increased slowly to 22 °C and kept at that temperature for 5 h. The excess ClF₃ was removed in a nickel vessel cooled with liquid nitrogen until a constant mass was measured. The intercalation product (approximately 11 g) had an approximate composition of C₂F₅–0.13ClF₃. Elemental analysis (mass%): C 94.1; F 3.0; Cl 1.9; H 1.0.

Dispersion, film formation, and transfer process: ESEG (0.5 mg) was dispersed in 50 mL of 1% SDS, 2% SDS dissolved water, DEG, DMF, NMP, DCM, tolouene, DMAc, or n-hexane, and sonicated using a tip (bar-type) sonication instrument at 400 W for 30 min. A few droplets of SDS in water, DEG, and DMAc were added to the Cu micro-TEM grid to measure the number of graphene layers per sheet. After 3 weeks, A was measured for each suspension. After making a baseline with each pure solvent, the quartz cell was filled with the graphene suspension and pure solvent with different concentrations such as 1:2, 2:1, and 3:0. A uniform flexible graphene film was obtained by vacuum filtration using an anodic membrane (Whatman International Ltd.) and transferred to a PET film. The transmittance and sheet resistance of the obtained film were examined by UV–Vis spectroscopy and a 4-point probe, respectively.

Keywords: dispersions · exfoliation · graphene · graphite · solvent effects

Received: August 19, 2009
Revised: September 29, 2009
Published online: