Low-temperature expanded graphite for preparation of graphene sheets by liquid-phase method

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Abstract: A facile and scalable preparation of aqueous solutions of isolated, sparingly graphene sheets from low-temperature expanded graphite by liquid-phase method is reported. And the influence of expansion temperature on the property of graphene sheets in expanded graphite is discussed by several characterization methods. The TEM scans also indicate that graphene sheets exfoliated from expanded graphite has been restored to an extended conjugated sp2 network.

1. Introduction

Known as “the thinnest material in our universe”\(^1\), graphene, a single-atom-thick sheet of hexagonally arrayed sp2-bonded carbon atoms, promises a diverse range of applications from composite materials to quantum dots\(^2\text{-}^7\). However, just as with other newly discovered allotropes of carbon (fullerenes and single-wall nanotubes), material availability and processability will be the rate-limiting steps in the evaluation of putative applications of graphene. For graphene, the availability is encumbered by having to surmount the high cohesive van der Waals energy (5.9 kJ mol\(^{-1}\))\(^8\) adhering graphene sheets to one another. Herein, the developments of various methods for producing graphene sheets have stimulated a vast amount of research in recent years\(^9\). As described in the reference\(^10\), certain organic solvents would be suitable for preparation of graphene sheets directly from flake graphite, which has been named as the liquid-phase method. Here, we extend the raw materials of method from flake graphite to low-temperature expanded graphite (EG), which has been produced by thermal shocked in 300°C. The influence of expansion temperature on the property of expanded graphite was also discussed.

2. Experimental Section

The flake graphite powder used in the majority of experiments was purchased from Sigma-Aldrich (Product Number 332461) and sieved through a 0.5 mm mesh sieve to remove the larger particles. All solvents and reagents used in experiment were obtained from Sinopharm Chemical Reagent Co., Ltd and used as received. The raw graphite oxide material was prepared by modified Hummers-offeman method\(^11\). And expanded graphite was produced by thermal shock of graphite oxide under forming gas. Samples of expanded graphite were produced in three different expansion temperatures: 300°C, 600°C, 900°C with same exposure time (30 seconds). TGA/DSC, XRD, FT-IR, XPS and Rama spectra have been used to characterize the expanded graphite with flake graphite as control.
All materials, including flake graphite and prepared expanded graphite, were stored in a drying basin with P2O5 for five days before characterization and preparation of graphene sheets by liquid-phase method. For preparing graphene sheets, flake graphite and expanded graphite were dispersed in the relevant solvent (N-methylpyrrolidone (NMP) and γ-butyrolactone (GBL)) at a concentration of 0.1 mg/ml by sonicating with a low power tip sonication (KS900c, Hanshu kesheng Ultrasonic) for 1 hour. Care must be taken as excessive sonication can lead to destruction of the graphene. The resultant dispersion was then centrifuged using a TF-2-B centrifuge for 90 minutes at 500 rpm. After centrifugation, decantation was carried out by pipetting off the top half of the dispersion. TEM measurements were made by drop casting from the dispersion onto holey carbon grids (400 mesh size). Initial sample drying was carried out in a vacuum oven at room temperature at a pressure of \( \sim 10^{-3} \) mbar. Subsequently, annealing was carried out to remove residual solvent. The samples were heated to 210°C for 4 hours in vacuum.

Thermal gravimetric analysis (TGA) and differential scanning calorimeters (DSC) was carried out in an NETZSCH STA 409 PC/PG under Ar gas flow (100mL/min) and at a heating rate of 10°C/min. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer using pellets in KBr. The recorded spectra were the result of coadding 64 interferograms obtained at a resolution of 4 cm\(^{-1}\). XRD patterns were obtained with Rigaku MiniFlex diffractometer (D/MAX 2550 VB/PC, GuK\(\alpha\) radiation, \(\lambda=1.5406\)Å). SEM images were taken with JSM-6360LV (JEOL). XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K\(\alpha\) radiation (h\(\nu=1253.6\) eV) for powder. Bright Field TEM images were taken with a Jeol 2100F. Some bright field images (figure 6(d)) and associated ED patterns were taken using a Jeol 2010.

### 3. Results and Discussion

As reference reported\(^{10}\), graphene sheet could be dispersed in a small number of solvents stably. Such exfoliation occurs because the strong interaction between solvent and graphene sheets means that the energetic penalty for exfoliation and subsequent solvation becomes small. Thus, researching the influence of expansion temperature on property of expanded graphite and comparing the prepared expanded graphite with pristine flake graphite would be meaningful.

![Figure 1](image1.png)

**Figure 1.** (A) TGA/DSC scans of graphite oxide. There is a sharp mass loss at an onset temperature of approximately 200°C accompanied by a strongly exothermic DSC peak. (B) SEM image of expanded graphite expanded in 215°C, which appeared the classic “worm-like” structure.

In the beginning, TGA/DSC has been used for characterizing the expansion process of graphite oxide. Figure 1 (A) shows the thermogravimetric (TGA) plot of prepared graphite oxide, together with its DSC plot. In agreement with previous reports in the literature for graphite oxide\(^6\), the main mass loss (\(\sim 30\%\)) takes place around 210°C and is ascribed to the decomposition of labile oxygen-containing groups present in the material. There is also a mass loss (\(\sim 5\%\)) below 100°C attributed to the removal of absorbed water and a slower, steady mass loss (\(\sim 20\%\)) over the whole temperature range above 300°C, which can be assigned to the removal of more stable oxygen functionalities. Further experiment also supports the TGA result: as shown in Figure 1(B), we have got expanded graphite with classic “worm-like” structure at a much low expansion temperature 215°C, which is
always believed to be higher than 900 °C. As for the endothermic peak of DSC curve at about 600 °C in Figure 1(A), it might be ascribed to the decomposition of more stable oxygen-containing groups, which we will discuss in FT-IR spectra.

As TGA/DSC analysis, the main expansion process of graphite oxide happens in the temperature range 200–300 °C. For further investigating the expansion result of graphite oxide in different temperature, XRD data was also used to characterize the exfoliation degree of expanded graphite. As Figure 2 shows, pristine flake graphite exhibits a diffraction peak at 2θ = 27°. For a successful exfoliation process, we have found it necessary to first increase the c-axis spacing of graphite oxide by oxidation to 0.7-1.2 nm and completely eliminate the 0.34 nm graphite interlayer spacing, as shown as line 2. For expanded graphite, there was no significant diffraction peak, which indicates a full exfoliation of graphite flakes. On the other hand, all expanded graphite samples, even prepared at 300 °C, exhibit the same diffraction curve as the other samples. The inset XRD curves of expanded graphite indicate the farthing diffraction peak at 2θ = 24°, which might be ascribed to the collapse of exfoliated graphite flakes because of the weak interaction. In all, the high expansion temperature shows no significant influence on the exfoliated structure of graphite in XRD pattern.

Considering the oxygen-containing groups remained in expanded graphite, FT-IR was used. Figure 3 shows the FT-IR spectrum obtained from flake graphite and expanded graphite. The most characteristic features are the broad, intense band at 3430 cm⁻¹ (O-H stretching vibrations), the bands at 2650 cm⁻¹ and 2920 cm⁻¹ (vibrations of O-H in H₂O and dimeric COOH, but no clear distinction seems possible between C-OH and H₂O peaks.), and 1103 cm⁻¹ (C-O stretching vibrations). In addition, there are other band at 1414 cm⁻¹ (carboxyl C-O stretching vibrations), 1560 cm⁻¹ (skeletal vibrations from unoxidized graphitic domains), and 1726 cm⁻¹ (C=O stretching vibrations from carbonyl and carboxylic groups). It is well known that the flake graphite would contain some physical absorbed water to maintain the lubrication property. Herein, water molecular can intercalate into the interlayer of graphene sheets in graphite. While for the expanded graphite exfoliated by thermal shock, the most oxygen-containing groups should ascribe to the residual of groups on graphite oxide flakes. Here, a band at 1414 cm⁻¹ disappears in curve 2, corresponding to the expansion temperature 900 °C. The phenomenon can be explained based on the expansion theory of graphite oxide12: the exfoliation takes place when the decomposition rate of the epoxy and hydroxyl sites of graphite oxide exceeds the
diffusion rate of the evolved gases, thus yielding pressures that exceed the van der Waals forces holding the graphene sheets together. Because of the relative short exposure time of graphite oxide, it is hard for all oxygen-containing groups to decompose completely. Therefore, the expansion temperature is hard to determine the amount of residual oxygen-containing groups on expanded graphite. The main difference of the three curves of expanded graphite is the disappearance of absorb band at 1414 cm\(^{-1}\), which might be ascribe to the complete thermal decomposition of carboxyl C-O band. However, it is hard for FT-IR measurement to exactly determine the amount of carbon and oxygen atoms on the graphene sheets of expanded graphite. In this view, XPS experiment was taken for investigate the atomic ratio of carbon and oxygen of graphene sheets. Three samples were taken, including graphite oxide and expanded graphite with expansion temperature 300\(^\circ\)C and 900\(^\circ\)C.

| Material                  | C1s  | O1s  | Area atomic ratio (C/O) |
|---------------------------|------|------|-------------------------|
| Graphene oxide            | 69.16% | 30.84% | 2.243                  |
| Expanded graphite A(300\(^\circ\)C) | 84.94% | 15.06% | 5.644                  |
| Expanded graphite B(900\(^\circ\)C) | 89.96% | 10.04% | 8.960                  |

As Table 1 shows, the area atomic ratio of carbon and oxygen increased significantly from graphite oxide (2.243) to expanded graphite (900\(^\circ\)C) (8.960). The raise of atomic ratio (C/O) indicates that the decomposition degree of graphite oxide increases with the expansion temperature raise. On the other hand, the percentage of carbon atoms does not have great variation, which might be ascribed to the exfoliation process. We suppose that the high expansion temperature would increase the decomposition rate of oxygen-containing groups, and in a certain degree influence the decomposition degree of graphite oxide. Thus, it is interesting to investigate the microstructure changes of expanded graphite in different expansion temperature.

Figure 4. Raman spectra of expanded graphite (EG) prepared in 300\(^\circ\)C, 600\(^\circ\)C, 900\(^\circ\)C.

Raman spectroscopy is also used to investigate the microstructure of expanded graphite. Figure 4 shows the Raman spectrum curves of flake graphite and prepared expanded graphite. The bottom curve, corresponding to flake graphite exhibits prominent G and 2D peaks at 1600 cm\(^{-1}\) and 2700 cm\(^{-1}\), respectively. The G peak relates to the E2g vibrational mode within aromatic carbon rings and gives some insight into the degree of graphitization for the area of excitation. The 2D peak represents an out of plane vibrational mode. Near the edge of both single sheets and bulk graphite, an additional peak is present around 1350 cm\(^{-1}\). This D peak is forbidden in pristine systems of \(\pi\) conjugation, but allowed in small and isolated domains of aromaticity, ultimately giving a relative measure of the amount of sp\(^3\) carbons in the surroundings\(^{13}\). Representative Raman spectra for prepared expanded graphite are presented by the curves on the top of the pattern. We can observe an increase in the D/G ratio and disappearance of 2D band. The disappearance of 2D band can be explained by the exfoliation of graphite oxide, which induces the interlayer spacing of expanded graphite flakes. The increase of D/G ratio can be ascribe either to oxidization of graphene sheets during the preparation of graphite oxide, or to the violent decomposition of oxygen-containing groups in graphite oxide. As the observation of spectra, three expanded graphite samples have exactly the same Rama curves, which might be supposed an indication of the same microstructure of graphene sheets in expanded graphite.
Verifying the supposition, SEM images were referenced. The Figure 5 shows the SEM images of flake graphite and prepared expanded graphite in three different expansion temperatures. Image (a) shows the compact layers of graphene sheets, while images (b) (c) (d) show the “worm-like” structure of expanded graphite. It can be obviously observed that the interlayer spacing of graphene sheets has been greatly extended, which can be valued cursorily by the determining the expansion ratio of graphite oxide. But for the thickness of graphene sheets separated in expanded graphite, there is no significant difference for the three samples.

Based on the researches above, it can be inferred that the expansion temperature of graphite oxide has influence on the decomposition of oxygen-containing groups and evaporation of absorbed and intercalated water molecular. But for the exfoliated graphene sheets, the temperature exhibits no significant influence on either the oxygen-containing groups’ residues or the structure of graphene sheets in expanded graphite, except the influence of contain of carboxyl C-O band on graphene sheets. Thus, we take the expanded graphite prepared in 300°C as the raw material for preparation of graphene sheets by liquid-method. There are two reasons, (1) the thermal expansion of graphite oxide would induce a graphitic material crystal structure as pristine flake graphite, or a pre-exfoliation of graphene sheets, which might be useful in mass production of graphene sheets,(2) the optimization of expansion temperature would largely reduce the cost of preparation. Even if the expansion of graphite oxide at 215°C can reach classic “worm-like” structure, we would like to prefer to take 300°C as expansion temperature based on the TGA/DSC plots. At the low temperature 300°C, most of oxygen-containing groups would decompose and induce a relatively stable mass residence.
Figure 6. TEM images of graphene sheets (darker gray areas) supported by a holey carbon grid and corresponding Electron Diffraction patterns. (a) Monolayer of graphene sheet prepared in NMP from flake graphite, and corresponding Electron Diffraction pattern (b). (c) Graphene sheet prepared in GBL from flake graphite. (d) Bilayer graphene sheet prepared in NMP from expanded graphite prepared in 300°C and corresponding Electron Diffraction pattern (e). (f) Graphene sheet prepared in GBL from expanded graphite prepared in 300°C.

By liquid-method, graphene sheets were prepared in NMP and GBL from pristine flake graphite and expanded graphite prepared in 300°C, respectively. As shown in Figure 6, image (a) and (c) corresponds to graphene sheets prepared from pristine flake graphite, image (d) and (f) correspond to graphene sheets prepared from expanded graphite. There are wrinkled sheet structure resulting from reaction sites involved in oxidation and reduction processes for graphene sheets in image (d) and (f), significantly comparing to the smooth surface of graphene sheets in (a) and (c). On the other hand, the ED patterns in image (b) and (e) indicates the crystal structure of prepared graphene sheets. However, (b) indicates a structured single crystal structure, while (e) indicates a crystal structure with defects. The result of ED pattern investigation supports the former Rama Spectrum results, which explains the increased D/G band ratio of expanded graphite. Although it has been observed that there are lots of “wrinkle” structures on the graphene sheets of graphite oxide, but in microns scale it is hard to observe “ripples” on the surface of graphene sheets. Thus it is reasonable to suppose that the thermal shock of graphite oxide that induces violent decomposition of oxygen-containing groups should be responsible for the micron scale wrinkle structure of graphene sheets in graphite oxide. Thus, it is interesting to investigate the expansion process of graphite oxide in different expansion temperature, which would be performed in our next work.

4. Conclusions
We discussed the influence of expansion temperature on expanded graphite by thermal shock of graphite oxide. It indicates that the rise expansion temperature improves the expansion ratio of graphite oxide, but has little to do with the amount and species of residual oxygen-containing groups and microstructure of graphene sheets in expanded graphite. Meanwhile, by strong interaction between solvent and expanded graphite flakes, we have demonstrated a scalable method to produce aqueous solutions of isolated, sparingly graphene sheets from low-temperature expanded graphite. Using certain solvents, graphene sheets can be dispersed at concentrations of up to 0.1 mg/ml stably. These dispersions can then be used to deposit flakes by spray coating, vacuum filtration or drop casting. Otherwise, by thermal shock, graphite oxide will be able to transform to defected single crystal structure. The defects might ascribe to the violent expansion of graphite oxide in high expansion temperature, which might induce a wrinkle structure on graphene sheets as observed.

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