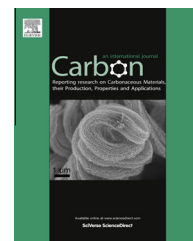


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Review

Towards low temperature thermal exfoliation of graphite oxide for graphene production

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ABSTRACT

Realizing mass production of graphene materials at low cost and high quality is urgently required for their real applications. Thermal exfoliation of graphite oxide (GO) is considered as a promising strategy though it normally requires a high exfoliation temperature together with a fast heating rate, making the produced graphenes suffer from high cost and concentrated topological defects. A mild exfoliation of GO at a far lower temperature than the predicted minimum temperature, has been demonstrated by introducing a high vacuum to exert an outward drawing force which helps effective exfoliation of the stacked graphene layers. In this contribution, together with a discussion on the foundation of thermal exfoliation and the general principle for low-temperature exfoliation, we review current strategies and indicate possible novel approaches. Low cost and easy operability are highlighted for the low-temperature exfoliation and the resulting graphene materials are characterized by low defect concentration, and unique and tunable surface chemistry to promote potential mass applications in energy-related areas.

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1. Introduction

Graphene, as the building block for all types of sp^2 carbon materials [1,2], has attracted extensive attention from academic and industrial fields due to its extraordinary thermal, mechanical, electronic and optical properties, etc.[3–5]. It shows promise in electronics [6], energy storage and conversion [7–9], thermal management [10] and other application fields. The most important issue to realize the potential of graphene is to achieve its mass and controllable production. Thus far, a series of approaches have been developed, which can be classified into two main categories: bottom-up and top-down approaches [11]. The bottom-up approach is to assemble and grow graphene from small carbon-rich molecules such as aromatics, through which the molecular structure and size can be well controlled. However, the mass production of graphene by this approach is difficult to be realized due to the low yield, high cost and long reaction duration [11]. Chemical vapor deposition (CVD) and the organic synthesis method [11–13] can be defined as two typical methods of the bottom-up approach. It is much easier to realize the mass production of graphene through top-down approach by exfoliating graphite, which consists of millions of graphene sheets layer-by-layer stacked with an interlayer distance of 0.335 nm. Since no chemical bond exists between the adjacent layers, the weak interlayer interaction makes such an approach become the first used method for single-layer graphene preparation [1]. Directly exfoliating graphite is a very important method for the preparation and development of graphene, including micromechanical exfoliation [1], organic solvent assisted [14] or surfactant assisted sonication [15]. Another strategy is to decrease the attraction between adjacent layers by expanding the interlayer distance through oxidation or chemical intercalation. This strategy can reduce the van der Waals force significantly, because the force is inversely proportional to the interlayer spacing [16]. Graphite oxide (GO) is the product of the oxidation of graphite, whose graphitic layers are functionalized with oxygen-containing groups, such as hydroxyl and epoxide. The expanded interlayer spacing of GO facilitates the exfoliation significantly. Up to date, many methods have been developed as branches of the top-down approach based on GO, such as chemical exfoliation and reduction of GO [17–20], thermal exfoliation [21–25], electrochemical exfoliation [26,27], etc.

Each of the aforementioned methods has its own set of advantages and disadvantages. Generally, defects and layer numbers of the prepared graphene are two key factors that guide the choice in the graphene preparation process. Mono-layered and few-layered graphene with few defects can be easily prepared by CVD [28], micromechanical exfoliation or epitaxial growth [29,30]. Furthermore, CVD and the epitaxial growth can realize the preparation of graphene with homogeneous layer numbers. However, the mass production

by above three kinds of methods is difficult to achieve due to their low yields and high cost. Meanwhile, thermal or chemical exfoliation of GO always yields graphene with concentrated defects, but it is a convenient method and easy to be scaled up. With the increasing demand for graphene-based materials, especially in the fields of energy storage and catalysis that can endure defects to some extent and uncertainty of the layer numbers, thermal or chemical exfoliation is more appealing. However, the chemical exfoliation, which always employs extra agents, such as hydrazine hydrate [31], NaBH_4 [17], hydroquinone [32], metal Fe [33] or ascorbic acid [34] in the reduction step, often introduces heteroatomic species. Furthermore, the exfoliation in organic solvents often meets the problem of solvent removal since most of them have high boiling point. By contrast, thermal exfoliation is believed to be a promising approach for the mass production of graphene due to the following points. Firstly, thermal exfoliation is a very fast process, for instance, exfoliation at high temperature only takes a few seconds to minutes [18,21], which minimizes processing time. Secondly, thermal exfoliation can produce graphene in the absence of liquid environment which is beneficial for the application of graphene in many fields and avoids the uncontrollable aggregation in the solvent removal and chemical reduction process. And another important reason is that the exfoliation and reduction can be achieved simultaneously without the introduction of heteroatomic impurities in thermal exfoliation [21]. For successful exfoliation, the temperature utilized is of great importance. A high temperature ($\geq 550^\circ\text{C}$) and fast heating rate was predicted theoretically to be necessary for the full exfoliation of GO [21], while a higher temperature (above 1000°C) is usually employed for the fast exfoliation experimentally [18]. This approach requires more energy consumption. And the generated carbon oxides and water vapor may react with the carbon atoms at high temperature, which causes more defects (vacancies) than the case at low temperature. Furthermore, the fast heating rates may also cause more topological defects due to the rapid decomposition of functional groups, such as more ripples. Thus, a mild thermal exfoliation is expected to eliminate the disadvantages caused by the high temperature.

It is obvious that successful thermal exfoliation of GO under mild condition can be achieved only if the functional groups are still eliminated at high rate to allow internal pressure development. Fortunately, the functional groups are sensitive to heating and thermal analyses have proved that most of the functional groups can be removed at a temperature lower than 300°C [35]. Lv et al. firstly proposed a vacuum-promoted low-temperature exfoliation for mass production of graphene, which exhibits excellent electrical double layer capacitor (EDLC) performance [35]. This method was

developed based on understanding of the thermal behavior of GO and provides motivation to find even lower temperatures. The low exfoliation temperature (as low as 200 °C) is a breakthrough for the mass production of graphene, which results in low cost and sustainable energy consumption. More importantly, graphene materials prepared by low-temperature exfoliation show higher thermal stability, indicating the low defects concentration on the graphene sheet, and the properties of the obtained graphene can be precisely tuned by a simple thermal treatment. Besides, the graphene materials show appealing properties in electrochemical energy storage due to the unique surface chemistry [35], which is very important for development of energy storage devices. Thus, following this work [35], several groups have studied thermal exfoliation of GO to scale up the production of graphene at a relative low temperature.

In this contribution, we discuss the mechanism of low temperature exfoliation and review recent progresses on the thermal exfoliation of GO at low temperature with various assistant components. A detailed study is carried out to investigate the relationship between particle sizes of graphite and the properties of resulting graphene, especially the capacitive performance of graphene as electrode materials for supercapacitors. An overall comparison of the exfoliation at low and high temperature is also given both from their features and applications.

2. Foundation of the low-temperature exfoliation of GO

GO [36–40], prepared from the oxidation of graphite, is believed to be an important precursor to prepare graphene. The introduction of oxygen-containing functional groups (such as hydroxyl and epoxide) results in an increase of the *d*-spacing of graphite as well as a change of hybridization of the oxidized carbon atoms from planar sp^2 to tetrahedral sp^3 [21]. While there is only weak van der Waals force between the interlayers in graphite, the intercalation of functional groups further decrease the interlayer interaction,

which lessens the interplanar forces that cause the lamellar stacking; thus the oxidized layers can be readily exfoliated by ultrasonic, thermal, or other energetic conditions [41]. Particularly, the abundant functional groups which are sensitive to heating provide access to the complete exfoliation of GO by the internal force generated from the thermal decomposition.

The thermal exfoliation of GO can be traced back to 1960s, when Boehm et al. prepared thin, lamellar carbon films from GO by thermal deflagration (i.e., exfoliation) [42]. Following the pioneering work, thermal exfoliation has been an appealing method due to the rise of graphene since 2004 [1,2]. The first detailed concept of thermal exfoliation of GO to produce graphene was proposed by Schneipp et al. in 2006 [18]. In this report, a high temperature was employed and the exfoliation occurred at 1050 °C within 30 s, during which a fast heating rate was necessary. After that, the mechanism of thermal exfoliation of GO was investigated systematically by McAllister et al. in 2007 [21]. The thermal exfoliation was described as follows: functional groups which are sensitive to heating will decompose upon heating and generate gases including H_2O , CO_2 , CO , etc. which will diffuse along the lateral direction; the exfoliation occurs only if the decomposition rate of functional groups surpasses the diffusion rate of evolved gases, since, under such a condition, a very large interlayer pressure exists among adjacent layers and pushes the layers separated from others (overcomes the weak van der Waals force that connects the paralleled stacked layers). In general, a minimum temperature of 550 °C was also suggested to be necessary for the successful exfoliation at atmospheric pressure.

According to the mechanism proposed by McAllister, the key factor for successful exfoliation is the generation of enough pressure between the adjacent layers of GO, which can fight against the van der Waals force and thus push graphene layers separated from each other. Obviously, reduction of GO will also be achieved during the thermal exfoliation since the pressure generated comes from the decomposition of functional groups upon heating. But a high temperature is not suitable for real application because of increased energy consumption and underlying danger. Therefore, achieving the

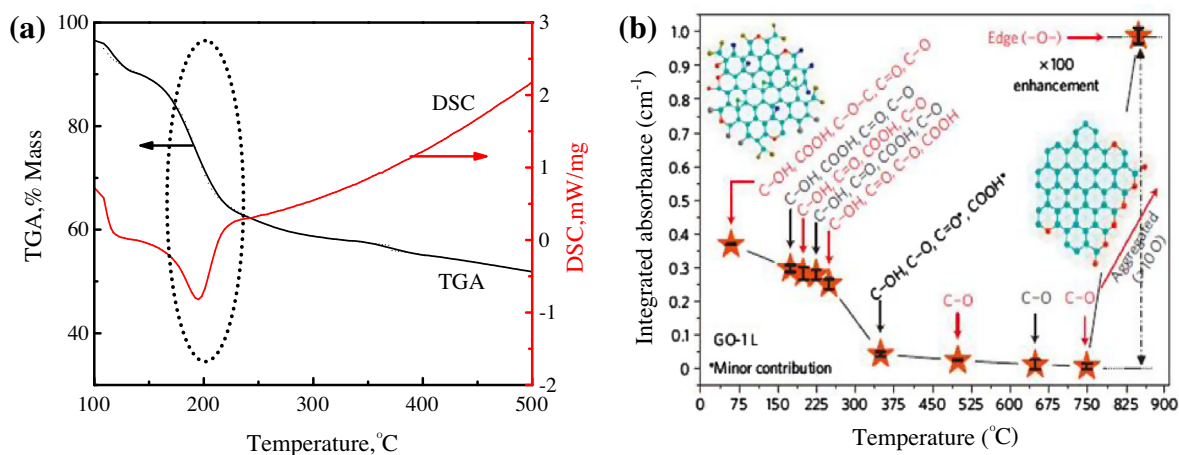


Fig. 1 – (a) Thermal analyses of GO under N_2 atmosphere. Reproduced with permission from [35]. Copyright (2009) American Chemical Society; (b) total integrated absorbance versus annealing temperatures. Reproduced with permission from [43]. Copyright (2010) Nature Publishing Group.

exfoliation at a lower temperature is more attractive and has great practicability. Based on the analysis of thermal exfoliation, the exfoliation can occur only if we can create enough pressure difference between the inner and outer space of GO by particular methods, for instance, the inner/outer pressure difference can be enhanced by the use of vacuum. Actually, the nature of thermal exfoliation is separating GO into individual sheet and deoxidizing under a certain temperature. As revealed in Fig. 1(a), thermal analysis reveals that the functional groups are removed mostly between 150 and 250 °C [35], which is much lower than the reported critical exfoliation temperature (~550 °C) [18,21]. Another study has also proved that most functional groups disappear below 350 °C and only C–O (ether groups) bond exists on the the layers above that temperature [43]. This indicated a possibility for the thermal exfoliation of GO at low temperature. However, such a low temperature can remove volatile gases from the planar graphene sheets but the pressure is not strong enough to fully expand the graphene layers. Hence, enough pressure should be created to separate stacked layers. Up to date, great efforts have been made to realize the low-temperature exfoliation of GO [35,44–48], and some groups have reported exciting results by different approaches on this issue. The basis of all the different approaches is in consistent with the above discussion, in which trying to create enough pressure difference is the key point to lower the exfoliation temperature. Vacuum-promoted exfoliation was the first successful attempt to prepare graphene by low-temperature exfoliation of GO [35], in which vacuum environment brought an extra outer force that can pull the layers from each other. Besides, several attempts have also been proved to be effective for the exfoliation of GO at low temperature, including exfoliation under H₂ atmosphere [44], vacuum-assisted exfoliation [45], acid-assisted exfoliation [46].

3. Thermal exfoliation at low temperature

3.1. Vacuum-promoted exfoliation

Conventional thermal exfoliation is based on the pressure generated from the decomposition of functional groups caused by fast heating to a very high temperature, while vacuum-promoted thermal exfoliation is accelerated by the strong “pulling force” from the vacuum environment. Based on the detailed analysis of thermal behavior of GO, Lv et al. [35] originally proposed a vacuum-promoted exfoliation of GO to produce graphene at low temperature as illustrated in Fig. 2. A low environmental pressure (less than 1 Pa) provided an outside negative driving force that pulled the graphene layers separated while the generated gases upon heating at low temperature provided an inside positive driving force that pushed the graphene layers. In such a vacuum system, the lower exfoliation temperature is attributed to two aspects. Firstly, the abundant functional groups in GO can be removed at a low temperature around 200 °C demonstrated by thermogravimetric (TG) and differential scanning calorimetry (DSC) measurement, while the generated gases can provide pushing forces for the exfoliation; secondly, the vacuum environment provides outer pulling forces for the exfoliation. Both the

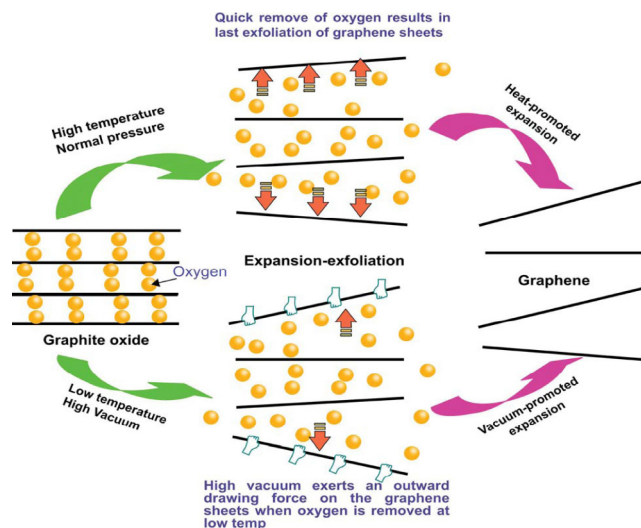


Fig. 2 – Schematics showing exfoliation of GO at high temperature under atmospheric pressure (top) and at low temperature (as low as 200 °C) under high vacuum (bottom). Reproduced with permission from [35]. Copyright (2009) American Chemical Society.

above two conditions promoted the exfoliation of GO at a temperature far lower than the normally employed even lower than the predicted critical exfoliation temperature by McAllister. Statistical analysis revealed that over 60% of the sheets were mono-layered, indicating an effective exfoliation was realized. The produced graphene shows great potentials in energy storage due to the fully accessible surface, acceptable conductivity and unique surface chemistry.

Notably, the exfoliation at low temperature induces fewer defects on the graphene layers, which can be confirmed by TG and the low doping concentration of nitrogen. It is generally accepted that the thermal stability of carbon materials towards high-temperature air oxidation can be used to evaluate its quality or defects concentration. As shown in the TG and differential thermal analysis (DTA) curves of low-temperature exfoliated graphene (Fig. 3(a)), the highest combustion rate temperature is 576 °C, which is higher than that of conventional high temperature thermal exfoliated (507 °C) and Arc discharge-exfoliated graphene (525 °C) [49]. The increase of oxidation temperature suggests that less vacancies/defects exist on our low-temperature exfoliated graphene [49], which can be further demonstrated by the doping results. X-ray photoelectron spectroscopy (XPS) measurements indicate a relatively low doping concentration by nitrogen (thermal doping at 600 °C using the mixture of NH₃ (50 sccm) and H₂ gas phase). In the XPS spectra (Fig. 3(b)), the peaks at 284.8, 401.6, and 531.9 eV correspond to C 1s of sp² C (detailed see Fig. 3(c)), N 1s of the doped N (Fig. 3(d)), and O 1s of the absorbed oxygen, respectively, and the atomic percentage of N in the sample is about 2.3 at.%, which is lower than most of the previous reports (3–5 at.%) [50–52]. In the XPS result of as-prepared graphene, the N 1s peak is absent, while in the N-doped graphene, the N 1s peak has two components, indicating that N atoms are mainly in the two different bonding characters inserted into the graphene network. The small peaks at 398.2 and

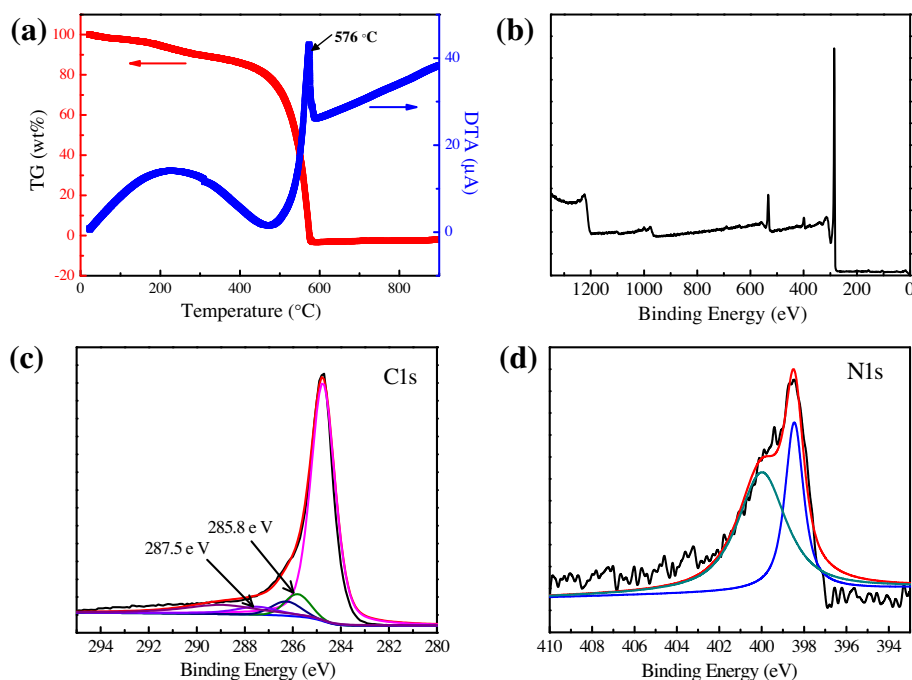


Fig. 3 – (a) TG and DTA curves of low-temperature exfoliated graphene under vacuum; (b) XPS spectrum of N-doped graphene; (c) and (d) C 1s and N 1s peaks of N-doped graphene.

400.1 eV correspond to “pyridinic” and “pyrrolic” nitrogen, respectively (Fig. 3(d)). They refer to the N atoms which are located in a π conjugated system and contribute to the π system with one or two p-electrons, respectively. The peak for “graphitic” N, which usually appears at 401.7 eV, cannot be observed, indicating the N atoms are hard to be doped into the graphene lattice in the form of “graphitic” N.

Inspired by such a vacuum-promoted exfoliation, Zhang et al. [45] developed a vacuum-assisted exfoliation at an even lower temperature of 135 °C (as shown in Fig. 4). In a typical exfoliation process, dry GO powder was placed in a preheated vacuum oven and kept for 24 h to ensure the complete exfoliation. Different temperatures were also employed to investigate the exfoliation process. The graphene sheets obtained at 135 °C (graphene-135) have a specific surface area (SSA) of 758 m² g⁻¹, and the reduction of GO can also be partially achieved simultaneously. It highlights that the exfoliation temperature is further decreased to a large extent, but some improvements still need to be made on this approach, including the long exfoliation duration and the low reduction degree. The reduction degree with C/O ratio being 5.0 only is too low for some applications of graphene due to the low conductivity. Further study based on this method should focus on improving the feasibility of this strategy.

The introduction of vacuum system provides an extra driving force and accelerates the exfoliation at low temperature, which is a promising approach towards the mass production of graphene.

3.2. H₂-induced exfoliation of GO at low temperature

Vacuum-assisted thermal exfoliation concentrates on enhancing the outer pulling force or decreasing the outer

pressure in the decomposition process of functional groups. Since the exfoliation of GO is decided by the combination of inner and outer driving forces, another way to realize the low-temperature exfoliation is enhancing the decomposition rate or the inner pushing forces from the removal of functional groups. Kaniyoor et al. [44] developed a H₂-induced exfoliation of GO at a temperature as low as 200 °C (HEG-200, see Fig. 4). Two key points have a huge impact on the exfoliation process: heating and the use of H₂, since the functional groups are sensitive to both the above two factors. A hypothesis was proposed that hydrogen reacts violently with -OH groups to form water vapor and observations of fire in the reaction further confirm the fast and violent reaction. Upon heating and with the assistance of the fast generated water vapor, GO can be exfoliated and reduced simultaneously at 200 °C. The SSA reaches a value of 442.9 m² g⁻¹, which is comparable to the result reported in the related literatures. This study realized the low temperature exfoliation by a novel gas-assisted approach. The reaction between H₂ and hydroxyl groups can generate stronger inner pressure to fight against the van der Waals force and the atmospheric pressure, thus decreasing the exfoliation temperature significantly. A few familiar methods, which utilized assistant components, were also developed to realize the successful exfoliation.

3.3. HCl-assisted exfoliation of GO at low temperature

Besides the introduction of components which can react with functional groups, the addition of component which is also sensitive to heating is also effective for enhancing the inner pressure. Successful exfoliation was realized with the aid of HCl by Shen et al. [46]. To avoid the employment of special atmosphere, such as vacuum system and H₂, HCl as

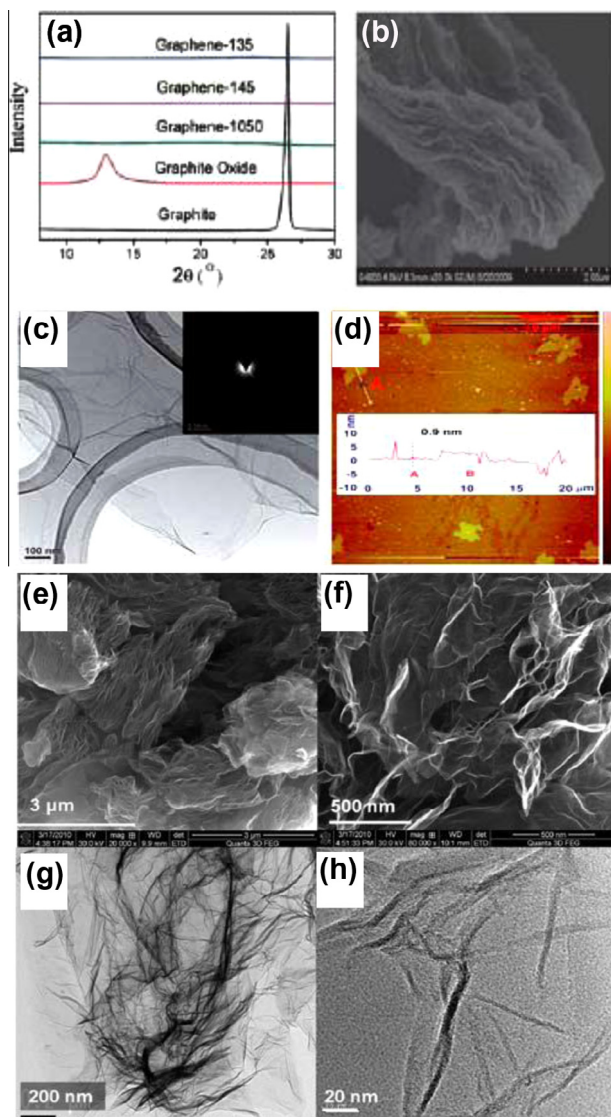


Fig. 4 – (a) X-ray diffraction (XRD) patterns of pristine graphite, GO, thermally exfoliated graphene sheets at different temperatures under vacuum (for graphene-135 and graphene-145) and atmospheric pressure (graphene-1050); (b) scanning electron microscope (SEM) image of graphene-135; (c) transmission electron microscope (TEM) image of graphene-135 with an inset of selected area electron diffraction (SAED), (d) atomic force microscope (AFM) image of single-layered graphene sheets; Reproduced with permission from [45]. Copyright (2011) Royal Society of Chemistry. (e) and (f) Low and high magnification SEM images of HEG-200 showing its fluffy and wrinkled morphology; (g) TEM images of the obtained HEG-200; (h) high resolution transmission electron microscope (HRTEM) images showing the folding in graphene. Reproduced with permission from [44]. Copyright (2010) Royal Society of Chemistry.

a residual in the washing process of GO, was remained and served as an extra source of gases which can accelerate the expansion process because HCl tends to volatilize to

generate extra inner pressure upon heating (as shown in Fig. 5). Compared with exfoliation under high vacuum system, effective exfoliation under ambient atmosphere herein is attributed to the addition of HCl, which provides enough expansion force for the exfoliation of GO. The obtained graphene materials (130 °C) exhibited high SSA of $500 \text{ m}^2 \text{ g}^{-1}$, and the C/O ratio determined by XPS spectra was 7.4, while the C/O ratio of graphene exfoliated at 200 °C was 8.0. It should be noted that both high SSA and high C/O ratio are necessary for real application of graphene, so how to decrease the exfoliation temperature without sacrificing the reduction degree is of great importance in future research. Though the acid-induced exfoliation reduced the exfoliation temperature significantly, the corrosion effect of acid is a serious problem that is too crucial to be neglected in industrial field. Other components free from corrosion effect should be developed to accelerate the exfoliation following the mechanism like HCl vaporization.

3.4. Other strategies

Apart from the mentioned method that requires assistance from other components or technique, the low temperature exfoliation at atmospheric pressure with no assistance was also achieved by several groups [47,48,53]. The mechanism of exfoliation at low temperature under ambient pressure is in consistent with that of approaches assisted by high vacuum, H_2 and so on. Jin et al. reported a successful thermal exfoliation of GO at 270–275 °C under ambient Ar (Fig. 6) [48]. The key point for this method is the high content of functional groups in the as-prepared GO. Higher oxygen content can generate excessive gases which accelerate the exfoliation at low temperature. The abundant functional groups herein play a role similar to that of H_2 or HCl mentioned above.

Some other novel strategies were also developed to realize the exfoliation and reduction of GO at low temperature [54–58], such as microwave-assisted exfoliation, irradiation-assisted exfoliation and so on, which provide an extra energy to GO to cause the decomposition of functional groups and result in the effective exfoliation of GO.

4. Applications of the low-temperature exfoliated graphene

Pristine graphene is hydrophobic due to its non-polarized structure, and is an excellent model and platform for experimental physical investigations because of its two-dimensional structure and unique electronic properties. However, it does not meet the expectation in chemical application like catalysis or electrochemical sensing, where more active sites and controllable structure are ideally suitable. Graphene prepared from low-temperature exfoliation of GO, possess certain amount of functional groups, and thus, it displays various superior properties in chemistry-related fields. Decomposition of oxygen groups on the carbon layers will leave some defects and vacancies, which can provide active sites for the reaction with other components. Another important point is the acceptable oxygen residues under low

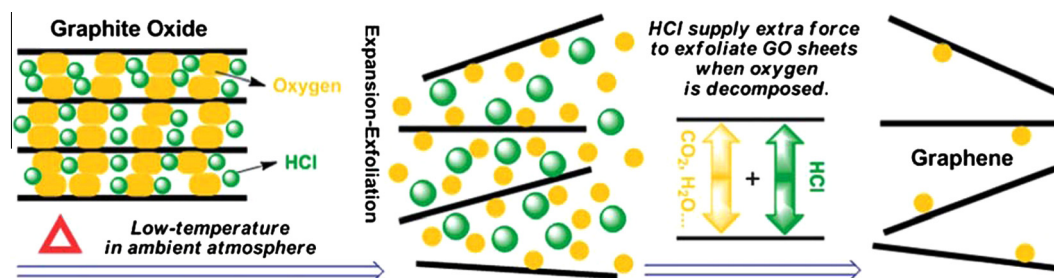


Fig. 5 – Schematic representation of low-temperature exfoliation of GO sheets under ambient atmosphere with the assistance of HCl. Reproduced with permission from [46]. Copyright (2012) Royal Society of Chemistry.

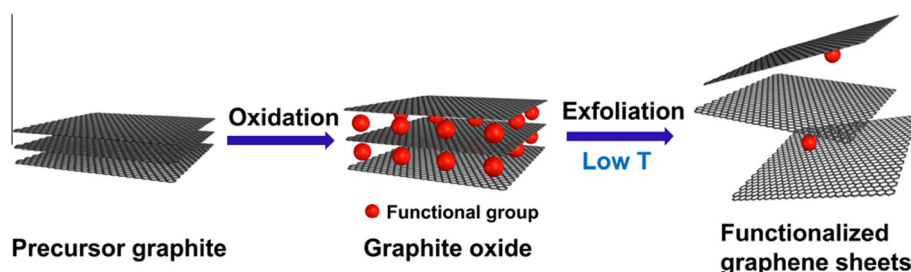


Fig. 6 – Schematic representation of low-temperature exfoliation of GO sheets under ambient atmosphere with the assistance of HCl. Reproduced with permission from [48]. Copyright (2010) IOP Publishing.

Table 1 – EDLC performances of graphene exfoliated at low temperature.

Sample	Method	SSA ($\text{m}^2 \text{g}^{-1}$)	Capacitance (F g^{-1})
G-200 [32]	Vacuum-promoted	368	262 (10 mV s^{-1})
FG200 [50]	Ambient pressure	/	242 (10 mV s^{-1})
GS- CO_2 [61]	DBD plasma	420	257 (100 mA g^{-1})
MEGO [62]	Microwave	/	191 (150 mA g^{-1})

temperature. In the fields of sensors, catalyst, energy storage and adsorption, oxygen-containing groups may impart chemically specific reactivity. For instance, oxygen-containing groups on the graphene layers can contribute to the pseudocapacitance when graphene is used as electrode materials for supercapacitor, and some chemical sensors can also utilize the oxygen-containing groups on graphene layers to detect specific substance.

Huang et al. found that vacuum-promoted low-temperature exfoliated graphene materials exhibited very high adsorption capacity towards metal ions, especially lead ions, which are toxic to humans and many non-human organisms [59]. Due to the large surface area, graphene materials exhibited a high initial adsorption rate, while the adsorption against lead ions can be enhanced by heat treatment, which was ascribed to the increase in the Lewis basicity and electrostatic attraction of graphene.

Another important application of graphene is conductive additives in composites and energy-related applications (e.g., lithium-ion battery). Su et al. employed graphene as two-dimensional soft conductivity additives to replace traditional additives (conductive graphite or carbon black) in cathode system [60], and the results show that graphene can construct flexible conducting network through a “plane to

point” mode. By adding 2 wt% graphene in the cathode of the LiFePO_4 (LFP)-Graphite battery, the performance of the prepared battery is much better than that of LFP-Graphite battery with 7–10 wt% commercial carbon black additives. Though a high temperature exfoliation can endow graphene excellent conductivity, low-temperature exfoliated graphene with acceptable conductivity is more favorable since the tolerant functional groups can enhance the interaction between active materials and conductive additives.

Extensive research has demonstrated that graphene-based materials display an excellent EDLC performance due to its high SSA, flat structure and high conductivity. An important obstacle is the weak wettability of pristine graphene in the aqueous electrolyte, which hinders the contact between the surface of graphene and the ions in the solution, thus decreasing the effective surface of electrode. It has been mentioned that thermal or chemical reduction of GO cannot prepare “ideal graphene” which is free from defects and heteroatoms as mentioned above. Interestingly, the existence of defects and tolerant oxygen-containing groups afford the hydrophobic graphene layers reasonable wettability and active sites which are favorable for EDLC electrode materials. Considering the features and properties of graphene exfoliated at low temperature, which can be described as

reasonable electrical conductivity and tolerable oxygen residuals compared with high temperature exfoliated graphene materials, the obtained graphene materials at low temperature is more attractive than high temperature exfoliated graphene materials as EDLC electrode materials (see details in next section). Table 1 lists the EDLC performances of some low-temperature exfoliated graphenes. Most of the low-temperature exfoliated graphene materials have a relatively high specific capacitance, while the resident oxygen-containing groups play a significant role on contributing to the pseudocapacitance. Some previous studies have shown that the EDLC performance of graphene is closely related to the surface chemistry, which can be tuned by thermal treatment [63]. Detailed discussion will be given in the next section.

5. Further considerations towards some real applications

Based on the aforementioned discussion, the functional groups that are confined on the graphene layers play a determinant role on the generation of the inner pressure, deciding the exfoliation degree of GO upon heating. Generally, the amount and chemical nature of the functional groups are influenced by the oxidation process, including the parent graphite, the oxidation duration, oxidants and so on. More importantly, the oxidation process also determines whether the preparation of graphene is fast and economical. Compared with the factors involved in the oxidation process, parent graphite plays a more important role since it is the starting material and the basis of the following steps. Thus, the graphite utilized is of great importance for the real mass

production of graphene. Generally, natural flake graphite is employed as parent graphite in most cases because its layered structure is much easier for the intercalation of oxygen-containing groups or other components, which will enlarge the interlayer distance and make it possible for the oxidation and the following exfoliation. And it is also cost effective. It is desirable that the properties of graphene can be easily tuned by the parent graphite so that the whole preparation process will be simplified and controllable. The selection of parent graphite with different kinds or particle sizes may have a huge impact on the properties of obtained graphene materials. Wu et al. investigated the effects of different kinds of parent graphite on the microstructure of the obtained graphene based on high temperature exfoliation, and both the lateral size and crystallinity of the original graphite are found to play important roles deciding the number of graphene layers. Graphite with a small lateral size and low crystallinity is appropriate to prepare single-layer graphene, for instance, almost 80% of the graphene layers originated from artificial graphite are single-layer [64]. Apart from the graphite origin and type, the particle size of graphite is also considered to be important to the oxidation degree and the required time.

Following our previous work on low-temperature exfoliation, a detailed study on the particle sizes of parent graphite was carried out, and its influences on the final graphene were characterized by the electrochemical method. Natural flake graphites with the particle sizes arranging from 100 to 5000 mesh are selected for the preparation of graphene. Graphite samples with size of 100 (160 μm), 200 (74 μm), 800 (15 μm) and 5000 (2.5 μm) mesh are denoted as Gr-100, Gr-200,

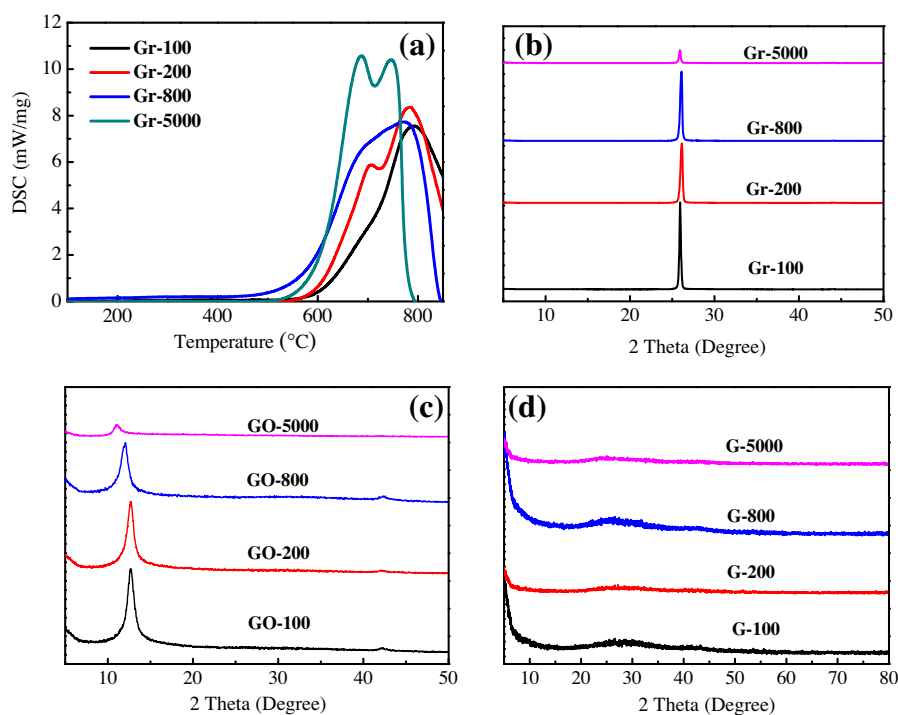


Fig. 7 – (a) DSC curves of Gr-100, Gr-200, Gr-800 and Gr-5000; XRD patterns of (b) Gr-100, Gr-200, Gr-800 and Gr-5000; (c) GO-100, GO-200, GO-800 and GO-5000 and (d) G-100, G-200, G-800 and G-5000.

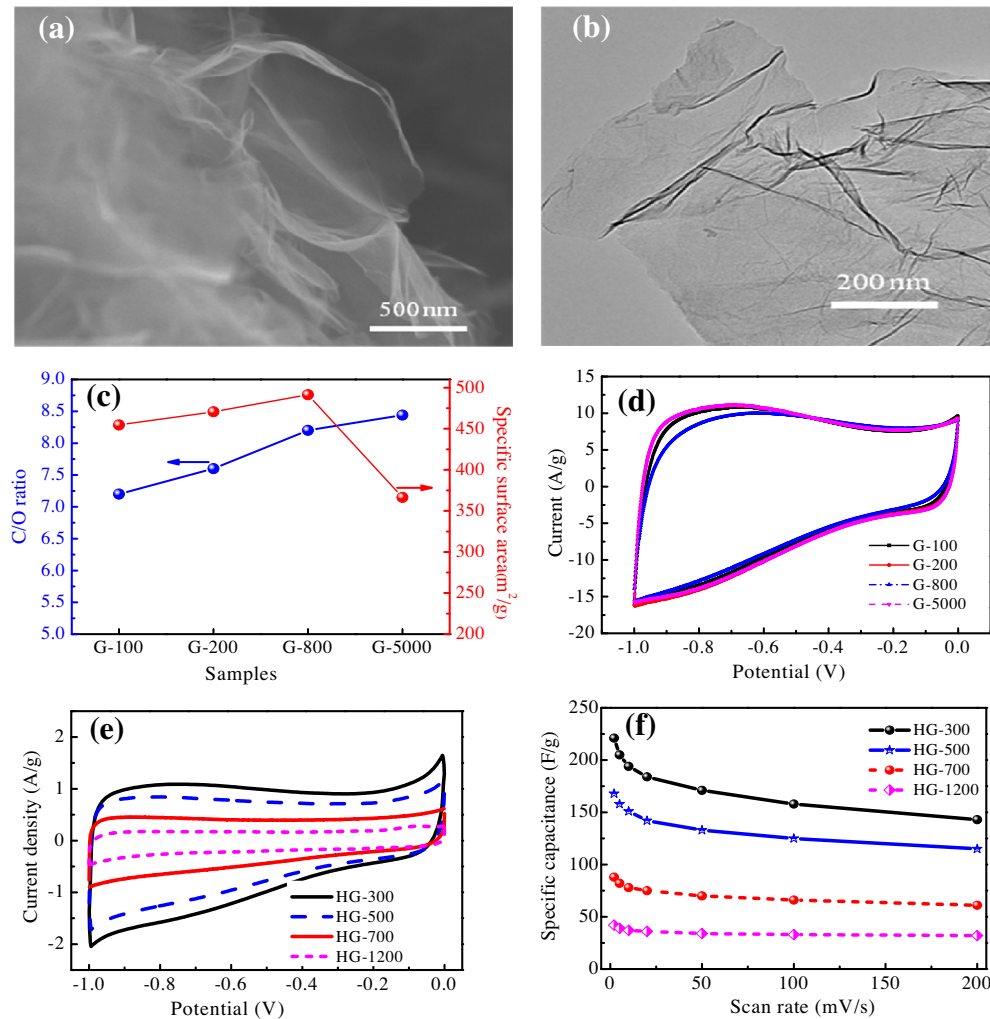


Fig. 8 – (a) Typical SEM image of G-800; (b) TEM image of G-800; (c) C/O ratio and SSA of different graphene samples; (d) CV curves of different graphene samples at scan rate of 50 mV s^{-1} ; (e) CV curves of HG-300, HG-500, HG-700 and HG-1200 at scan rate of 5 mV s^{-1} ; (f) Rate performances of different HG samples.

Gr-800 and Gr-5000, respectively. XRD patterns (Fig. 7(b)) reveal that all graphite samples are well crystallized with a sharp typical diffraction peak (002) located at 26° . Graphite flakes were oxidized to prepare GO by modified Hummers method as demonstrated in our previous work. Graphite flakes with smaller size have a higher aspect ratio which results in more edges exposed to the environment, making it easier to be oxidized. It can be indicated from the DSC curves (Fig. 7(a)) that graphite flakes with smaller particle size react with oxygen at a lower temperature, indicating Gr-5000 has a higher activity towards oxygen and is less thermally stable than graphite with larger sizes. Thus, Gr-5000 is much easier to be oxidized under the same oxidation condition than other samples and the corresponding GO should have the deepest oxidation degree. GO samples prepared from the oxidation of graphite are denoted as GO-X, where X represents the sizes of parent graphite. XRD results of GO samples confirm the above assumption. As shown in Fig. 7(c), the sharp diffraction peak located at around 26° disappeared and a new diffraction peak located at around 12° emerged due to the enlargement

of the interlayer distance. It is obvious that the diffraction peaks shifted to a lower angle with the decreasing of particle size, which hints that GO prepared from graphite with smaller size will have a larger interlayer distance. In general, the interlayer distance is a convincing proof to evaluate the oxidation degree of GO because the enlargement of interlayer distance is caused by the intercalation of the oxygen-containing groups. A fierce volume explosion can be observed during the heat process at around 200°C for these four GO samples, which resulted from the fast exfoliation and reduction of GO. The corresponding graphene samples are denoted as G-100, G-200, G-800 and G-5000. From the SEM and TEM observations, no obvious differences can be found from the morphology of different samples, indicating that different GO can be exfoliated completely by our method and typical SEM and TEM images are represented in Fig. 8(a) and (b). XRD patterns (Fig. 7(d)) also give a result in consistent with SEM and TEM characterization. The diffraction peak at 12° disappeared while a broaden peak with low intensity around 26° can be detected due to the random stacking of graphene layers.

The shift of diffraction peak indicated that GO was completely exfoliated and reduced by our low-temperature exfoliation. Both the morphology and structure of different graphene samples are not affected evidently by different parent graphite. It can be figured out from Fig. 8(c) that the SSA of G-800 is around $490 \text{ m}^2 \text{ g}^{-1}$, which is slightly higher than those of the other graphene samples. Besides, all the graphene samples delivered a type II adsorption isotherm, which means that no micropores existed in the randomly stacked graphene samples. The C/O ratio determined by XPS analysis reveals that G-100, G-200, G-800 and G-500 have almost the same oxygen content, which is irrelevant to the parent graphite flakes. All the above results hints us that the vacuum-promoted low-temperature exfoliation method is effective enough to realize the complete exfoliation for the preparation of graphene and the differences originated from the parent graphite flakes can be minimized in the exfoliation process. Based on the systematic investigations, we can draw a conclusion that all the GO samples have a complete exfoliation and the different oxidation degree of GO does not make a big difference on the morphology and structure of the obtained graphene.

The electrochemical capacitive performance of graphene is mainly determined by its SSA and surface chemistry, while the surface chemistry plays a more crucial role. Investigations on the capacitive performance of different graphene samples were conducted in details. Cyclic voltammetry (CV) and charge/discharge measurements were tested in 6 M KOH solution by three-electrode system. It can be figured out clearly that these four graphene samples displayed almost the same CV performance with a quasi-rectangular shape, which indicated that our graphene materials have a good EDLC performance. A slight difference can be found from the specific capacitance calculated from CV curves that the capacitance of G-800 can reach 274 F g^{-1} at a scan rate of 50 mV s^{-1} , while G-100 and G-5000 had a specific capacitance of around 260 F g^{-1} . Though some differences can be found among different graphene samples, such differences are tolerant and negligible compared with the huge differences among various parent graphites with different sizes. For the industrial applications, such differences are acceptable and it can be claimed that particle size of natural flake graphite does not have a huge impact on the EDLC performance of obtained graphene. Therefore, natural flake graphite can be utilized as a common source for the preparation of graphene in terms of the cost, while a subsequent treatment can be employed to tune its properties. From this point, no further sieving treatment is needed for the raw graphite mixture with different sizes except for a purification process to remove the impurities.

The key point that influences the electrochemical performance of graphene materials significantly is the surface chemistry. Upon heating at different temperatures, graphene materials with different surface chemistry can be obtained and have totally different electrochemical performance. The vacuum-promoted low-temperature thermal exfoliation occurred at around $200 \text{ }^\circ\text{C}$, makes some oxygen residuals still remain on the graphene layers. For further understanding of the EDLC performance of graphene materials, G-800 was employed as a typical sample to investigate the role of heat treatment on the low temperature exfoliated graphene. The

Table 2 – C/O ratio and capacitive performance of G-800 treated at different temperatures.

Samples	Ratio of C/O	Capacitance (F g^{-1} at 5 mV s^{-1})
HG-300	9.88	207
HG-500	10.59	158
HG-700	15.34	82
HG-1200	15.65	39

obtained graphene materials were treated at 300, 500, 700 and $1200 \text{ }^\circ\text{C}$. The corresponding samples were denoted as HG-300, HG-500, HG-700 and HG-1200. Since G-800 has been exfoliated at $200 \text{ }^\circ\text{C}$, the heat treatment at different temperatures will not cause further exfoliation or volume expansion, it will do nothing more than modify the surface chemistry of graphene. As shown in Table 2, the C/O ratio increased dramatically from 9.88 to 15.6 with the increasing treatment temperature up to $1200 \text{ }^\circ\text{C}$, which hints that the heat treatment has an important role in purifying the surface of graphene layers and controlling its conductivity. It has been demonstrated that oxygen-containing groups attached on graphene layers will contribute to the capacity due to its pseudocapacitance. CV curves of the heat-treated samples show quasi-rectangular shape, while the current density decreases with the increasing treatment temperature, which hints the contribution of pseudocapacitance from oxygen groups. An interesting phenomenon is that the shape of CV curve is a quasi-rectangle for HG-300, but it changes to a rectangular shape with no obvious polarization for HG-1200 as shown in Fig. 8(e). This continuous transformation is consistent with the change of surface chemistry of graphene samples. With the increase of the heating temperature, the oxygen content on the graphene surface becomes less and when it is subjected to electrochemical charge/discharge, less redox reaction occurs so that the polarization becomes weaker, an extreme example is that the shape of CV curve for pristine graphene should be a perfect rectangle due to its perfect electrical double layer structure. Considering the capacity of heat treated samples, the specific capacitances of four heat treated samples at a scan rate of 5 mV s^{-1} are 207, 158, 82 and 39 F g^{-1} . The fast drop of the capacitance confirms that the surface chemistry plays a dominant role on the EDLC performance of graphene materials. The rate performances were also investigated as shown in Fig. 8(f). The retentions of HG-300, HG-500, HG-700 and HG-1200 are 64, 68, 69 and 76%, respectively. The increase of capacitance retention demonstrated the improved rate performance under higher treatment temperature. Upon heating at higher temperature, less oxygen groups remained on the surface of graphene and the destroyed sp^2 system can be healed to some extent, which gives a recovery of the electrical conductivity of the graphene materials. As the improved electron transfer process, the graphene samples can have a fast response to the voltage changes, which results in a better rate performance. Different from costly high temperature exfoliation, low temperature exfoliated graphene samples have more functional groups which are beneficial to their EDLC performance, and a controllable multi-step modification can be achieved by heat

treatment to tune the properties of as-prepared graphene. Heat treatment on low-temperature vacuum-promoted graphene can affect its EDLC performance remarkably, which gives a guiding favor for the real application of graphene materials.

Therefore, the vacuum-promoted low-temperature exfoliation provides a versatile way to realize the effective preparation of graphene even if different starting materials are employed. And also the electrochemical performance of the obtained graphene samples can be tuned easily by heat treatment at different temperatures. The post-heat treatment on the low temperature exfoliated graphene will not be responsible for the exfoliation of graphene layers and does not induce fresh defects, which is totally different from the high temperature exfoliated samples, since the high temperature exfoliation causes the explosive expansion and induces concentrated defects. For mass production and real application of graphene, it is more important to modify the preparing process rather than to alter the starting materials.

6. Remarks about the low temperature thermal exfoliation

To guarantee the effective exfoliation at low temperature, foreign forces should be introduced to ensure enough pressure difference between the inner and outer space of graphene layers (as illustrated in Fig. 9). The following versatile strategies are based on our principle discussed above: (1) Enhancing the internal pressure; (2) Increasing the external vacuum environment; (3) Combining the inner pressure and external vacuum together.

The first work on low-temperature thermal exfoliation, namely the vacuum-promoted low-temperature exfoliation [35], follows the strategy 2, where a high vacuum is introduced into the system to create an external pulling force. The followed efforts thus far have been mostly concerning on the strategy 1. Following Strategy 1, the internal pressure mainly come from the evolved gases during the decomposition of functional groups, thus we can enhance this force through the following methods: (I) Increasing the graphite

oxidation degree so that a higher oxygen content can be obtained to generate more gases in a certain duration. (II) Leaving some volatilizable components between the layers of GO such as HCl, CO_3^{2-} , $\text{C}_2\text{H}_5\text{OH}$ and so on. Such components tend to volatilize upon heating so that a stronger pressure can be generated. H_2O is not favorable as such a component since its evaporation process adsorbs much heat decreasing the heating rate which leads to a slow decomposition process of the functional groups. (III) Introducing active components into the thermal exfoliation so that the functional groups in GO can react with the introduced components fiercely to generate enough heat and gases to exfoliate the GO layers, H_2 is an ideal component because the gaseous product is H_2O which is tolerant in the thermal exfoliation. Other components should follow the principle that the products do not pollute the graphene materials. CH_4 or other hydrocarbon may be suitable for this method. (IV) A rapid heating rate will accelerate the decomposition of functional groups further generating enough gases in a second. Microwave irradiation or plasma treatment can create a fast internal heating environment because GO can absorb the heat from the microwave or plasma quickly to give enough energy for the decomposition of functional groups. Pre-heating of the furnace can create a fast external heating environment so that GO can be exfoliated once it was pushed into the furnace. The combination of pulling and pushing forces following strategy 3 can develop a variety of methods that are beneficial to the successful exfoliation of GO. Vacuum atmosphere combined with additional treatment of GO such as HCl or H_2 may result in a better exfoliation.

7. Conclusions

Generally, thermal exfoliation of GO at mild condition (low temperature) is promising for the further development towards the mass production of graphene materials. Low-temperature thermal exfoliation follows the same general mechanism as that for the high temperature case, where the explosive pressure from internal to external space gives birth to the successful exfoliation. What makes the low-temperature exfoliation remarkable and significant is its mild condition, safety, low cost and easy-operation. In this contribution, together with a discussion on the foundation of thermal exfoliation and the general principle for low-temperature exfoliation, we reviewed currently-developed progresses on the thermal exfoliation of GO at low temperature, which is an attractive route for the mass production and real application of graphene. The resulting graphene materials are characterized by low defect concentration, and unique and tunable surface chemistry to promote potential mass applications in energy-related areas. It is also demonstrated that the vacuum-promoted low-temperature exfoliation provides a versatile way to realize the effective preparation of graphene even if different starting materials are employed. And also the electrochemical performance of the obtained graphene samples can be tuned easily by heat treatment at different temperatures.

Further efforts on the mass production of graphene materials are ongoing, and thermal exfoliation at low temperature

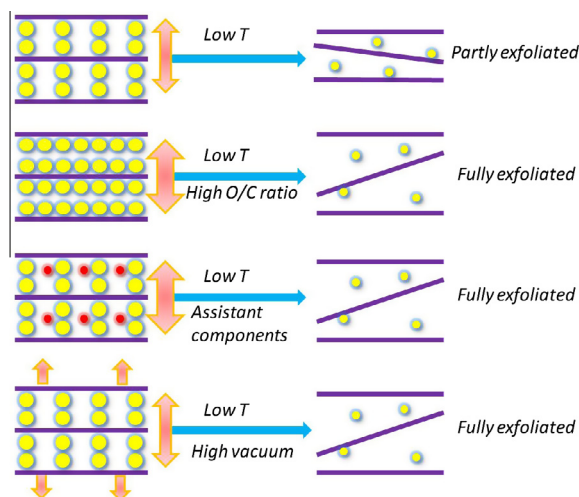


Fig. 9 – Schematic representations of thermal exfoliation mechanism at low temperature.

is proved to be a promising method. However, some problems still need to be solved in the low-temperature exfoliation, including the reduction degree of GO and the controllable conductivity and defect concentration, the subsequent treatment is a good choice for realizing the precise controlling of the low-temperature exfoliated graphene.

For instance, further thermal-treatment of low-temperature exfoliated graphene in an inert (N_2 or Ar_2) or reducing atmosphere (H_2) can greatly improve its conductivity by increasing the reduction degree with no structure changes. Compared to the control of reduction degree and conductivity, the defect control is more complicated in the real preparation process, which can be realized from two aspects. The first one is to control the defect concentration by changing the oxidization degree in the oxidation process of graphite, and graphene with fewer defects can be obtained from the GO with lower oxidation degree. Although the decrease of the oxidization degree induces low internal force upon heating, the pressure differences can also be maintained by increasing the external force. The defect healing, which can be realized by the thermal treatment of the exfoliated graphene in the atmosphere containing H_2 and carbon sources (e.g., $H_2 + CH_4$), is another strategy to decrease the defect concentration on the graphene sheets. In contrast, more defects can be created by the activation (e.g., KOH or CO_2) or corrosion with metal ions at high temperature or the plasma etching technology besides increasing the oxidization degree of the GO.

Also extensive research, both theoretically and experimentally, is underway to answer what the lowest exfoliation temperature is and whether the exfoliation may occur at room temperature. It is desirable that the low-temperature exfoliation can be developed to a significant industrial approach for scale-up production of graphene. Once the graphene with acceptable conductivity can be prepared in large scale, the applications in energy-related (e.g., electrode materials for supercapacitors and the conductive additives in Li-ion batteries) and catalysis fields, will meet a great opportunity, since appropriate defects concentration will serve active sites and help the construction of an ideal interface between graphene and other components. It is noteworthy that certain amount of defects are very important to the electrochemical applications since the ion cannot pass through the ideal two-dimensional graphene nanosheets, and our works have proved this point by exploring the graphene applications in Li-ion battery [60,65]. Also, to further develop the commercialization of graphene, the transportation and storage are critical issues for real applications, so dispersible graphene materials with acceptable density should draw our interests.

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