Getting graphite nano-sheets with different sizes by choosing parent graphite: ultrasonication assisted preparation

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Abstract. In this work, a simple and effective method for preparing graphite nano-sheet (GNS) was investigated. The size choosing of the parent graphite is important to obtain smaller size of GNSs diameter or thickness with the ultrasonication treatment. The ultrasonication treating parameter was confirmed under the optimal preparing condition. The microstructure was characterized with scanning electron microscopy (SEM), high resolution transmission electron microscopy (HTEM). It is The experimental results show that the GNS size decreases decreased sharply at the high power factor stage of ultrasonication and then the decrement trend was slow down with the decreasing power factor of ultrasonication treatment. It is employed that choosing smaller size of parent graphite (>200-mesh) can obtain smaller size GNSs with the diameter value of (<10µm) and thickness value of (~4nm).

Keywords: GNS, Parent graphite, Sizes, Ultrasonication

1. Introduction
Natural graphite flakes are composed of graphene layers that are stacked in a nearly perfect manner. By intercalation and exfoliation, the natural graphite flakes can become expanded graphite (EG), which is composed of partially connected graphite nano-sheets (GNSs) [1-3]. Because the graphite nano-sheets are only weakly connected, they can be separated by using dispersion techniques, such as high speed mixing, sonication, and high shear-strain rate [4]. Both GNSs and CNTs are known for possessing exceptionally high thermal conductivity, with measured values higher than 1200 and 3000 W/m·K, respectively [5]. They are also able to carry an extremely high current density (109 A/cm2) [6]. New methods for graphite nano-sheet (GNS) production have recently emerged. NG turns into a graphite intercalation compound after acid intercalation, easily producing expanded graphite (EG). GNS can be exfoliated from EG via ultrasonic powdering. The thermal conductivity properties of different forms of graphite have been studied with various polymer resins such as polypropylene, polystyrene, polyoxymethylene, high density polyethylene, nylon and polyaniline as well as silicone rubber, and metal hydride [7-10]. However, the effect of GNS size on parent graphite with ultrasonication assisted preparation has seldom been studied.

It is known that the size of graphene sheets plays an important role in controlling their properties and applications. It was also reported that the thermal conductivity of graphene mainly depends on its sheet size [11]. Therefore it is highly demanded to develop simple and efficient methods for the preparation of GNSs with specified size and large quantities for their broad range of technological applications. So far, much effort has been made to study various factors which would affect the size of

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GO sheets, such as post-treatment of parent graphite, oxidation conditions, controlled centrifugation, and pH value [12-15]. However, the large scale preparation of high-quality GNSs with specified size still remains a great challenge. The mechanism of ultrasonication relies on the acoustic phenomenon, of which ultrasonic cavitation is the most important, involving the formation, growth, and implosive collapse of bubbles in liquids [16-17]. During the ultrasound process, extremely high temperature about 5000 K, rapid cooling rate about 1010 Ks⁻¹ and high pressure about 20 MPa are driven by high intensity ultrasound, thus enabling some chemical reactions generally not accessible in the conventional methods [18].

It is worth noting that ultrasonication is an important experimental step in the preparation method to produce GNSs. In order to decrease the high consumption during the preparing GNS, and further simplify the technological process, we proposed a new method, which was choosing parent graphite sizes. So far, however, little attention has been paid to analyze in detail about the effects of ultrasonication to the structure of GNSs. On the basis of the fact that reactions can be accessible by using ultrasonication in preparing nano-materials due to its cavitation and vibration effects, it is motivated to investigate the effects of ultrasonication to the size and structure of GNSs.

2. Experimental

2.1. Materials
Nature graphite power with the average sizes of 80-mesh, 120-mesh, 150-mesh, 200-mesh, was purchased from Qingdao Tai Xing graphite Co., Ltd. Potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄ 98%), hydrogen peroxide (H₂O₂), and glacial acetic acid (CH₃COOH), perchloric acid (HClO₄) were purchased from Kermel Chemical reagent plant (Tianjin, China). All these raw materials were directly used without further purification.

2.2. Preparation of EG
Preparations of graphite sheets from large-size to small-size were synthesized by ultrasonication. The largest-size EG was using 80-mesh expanded graphite powder, and the smallest-size EG was relatively using 200-mesh.

Graphite (10g) was mixed with CH₃COOH (10mL) in HClO₄ (50mL) at 35°C (water bath), then KMnO₄ (2g) was gradually added in 10min while keeping the temperature at 35°C. After that, the reaction mixture was stirred at 35°C for 1.5 h. Next, deionized water (500mL) was rapidly dropped into the reaction system. Then 2L of deionized water was added, to dilute the mixture. In the final procedure, mixture particles washed with deionized water till pH5, leaching remove excess water, then the expandable graphite was produced with drying in oven at 60°C for 6h. The dried graphite intercalation compound was subjected to a thermal shock at 950°C for 50s. The thermal shock vaporized intercalates in the intercalation compound, providing the necessary force to overcome the van der Waals interactions that bind the graphite layers. The exfoliation of the graphite flakes resulted in EG, as shown in Fig.1. The EG is a highly porous material with an extremely low density, occupying a volume about 270-500 cc for 1g of different EG size.

2.3. Preparation of GNSs
The EG is composed of GNSs that are partially and weakly connected. The GNSs can be separated from the EG by using dispersion techniques. The thickness of the GNSs depends on the intercalation and exfoliation processes. In the present study, most GNSs range from 20 to 50 nm in thickness. The mechanism of ultrasonication relies on the acoustic phenomenon, of which ultrasonic cavitation is the most important, involving the formation, growth, and implosive collapse of bubbles in liquids. Different power factor of ultrasonication are employed on producing GNSs. Effect of GNSs sizes relies on parent graphite size and parameters of ultrasonication. The sizes of parent graphite choose on four kinds of 80-mesh, 120-mesh, 150-mesh and 200-mesh. The power factor of ultrasonication is used on 70% (U-70), 80% (U-80), 90% (U-90) and 99% (U-99), corresponding to work 40min.
2.4. Characterization

The morphologies of GNSs were obtained by scanning electron microscopy (SEM), and energy disperse spectroscopy (EDS) was used to confirm elements composition. The Inspect F (FEI) scanning electron microscopy (SEM) with an acceleration voltage of 5 kV was used to measure the size of GNSs. The structure and morphology of the samples obtained were extensively characterized by X-ray powder diffraction (XRD, Rigaku D/max-gB X-ray diffractometer with Cu K radiation ($\lambda=0.154178$nm). Specimens for transmission electron microscopy (TEM) observation were prepared by ultrasonicallyating the as-synthesized products in alcohol for about 20 min, then dipping holey-carbon TEM sample grids into the dispersion. Specific surface area measurements were conducted on a Micrometrics BET 3H-2000PS1 static volume method apparatus with liquid nitrogen at 77K.

3. Results and discussion

3.1. Expanded graphite and GNSs

![SEM images of EG](image1)

**Figure 1.** SEM images of EG (a) 80-mesh (b) 120-mesh (c) 150-mesh (d) 200-mesh. Preparation of EG is using nature graphite power of 80-mesh, 120-mesh, 150mesh, and 200-mesh to produce expanded graphite. Fig.1 shows typical SEM images of EG obtained by the similar exfoliation. It is worth noting that most of the EG are similarity on microstructure, which is similar to this reported recently [2], and expanded graphite with different sizes are vermicular or wormlike in shape. As is apparent from figure 1(a) ~ figure 1(d) reveals that EG has many pores of different sizes ranging from 10 nm to 10μm. There was no difference for all specimens microstructure; vermicular and wormlike in shape are not affected in each group. The Expandable graphite also possesses some closed pores along with a significant amount of open pores. The conductivity of the bulk material is certainly influenced by the expansion of the EG due to the spacing of the graphite layers being increased. In addition, a large number of polar groups, such as hydroxyl, ether and carboxylate groups, on the surface of the
EG layers were easily processed. So multi-pores with some functional groups such as C–O–C, C–OH and–COOH on the surface of EG layers greatly promote the ability of adsorption of other particles. In order to investigate the effects of sizes for EG, different sizes from natural graphite were suitable for grading granulated screening out powder. The expansion volumes are checked for it. Table 1 shows the results of that effect. Measurement of expansion volume shows that expansion volume of different sizes from natural graphite increase with the increase of particle sizes. The best expansion volume of acid treatment is 497mL/g. It is ordered to contrast on imparity of four EG, results of the specific surface area shows in table 1, too. It is shows that specific surface of different sizes from EG increase with the increase of expansion volume. The best specific surface of EG is 220.6 m²/g.

Figure 2 panels a, b, c, and d show SEM images of GNSs obtained from different ultrasonication power factor. In order to obtain size change regularity from ultrasonication power factor, it employs 80-mesh EG for it. Based on the analysis of the SEM images for ultrasonication power factor U-70, U-80, U-90 and U-99, it is found that the size of the GNSs decreases regularly with increasing the power factor of ultrasonication.

**Table 1.** Expanding volume and BET specific surface of EG with different parent graphite sizes.

| Particle size (µm) | Expanding volume (mL/g) | Specific surface BET (m²/g) |
|-------------------|-------------------------|----------------------------|
| 80-mesh           | 180                     | 220.6                      |
| 120-mesh          | 120                     | 108.2                      |
| 150-mesh          | 106                     | 89.3                       |
| 200-mesh          | 74                      | 38.2                       |

**Figure 2.** SEM image of GNS (a) U-70 (b) U-80 (c) U-90 (d) U-99.

The mean size of U-70, U-80, U-90 and U-99 sheets, obtained from the SEM diameter size statistical analysis above, is >30µm, ~20µm, ~10µm, and <10µm, respectively. Moreover, the
different diameter size of U-70, U-80, U-90 and U-99 sheets all exhibit an about similar thickness correspondingly. The thickness are about 10~30nm, the SEM images cannot confirm thickness for each sample of U-70, U-80, U-90 and U-99 sheets, TEM images will be employed to measurement it. The results show that the sheet size decreases sharply at the high power factor stage of ultrasonication and then the decrease slow down with the decrease of ultrasonication power factor. Ultrasonication belongs to high-energy sound waves. Long time of ultrasonication could release large localized amounts of energy and result in the extreme reaction conditions such as high temperature, pressure, rapid cooling times that provide the energy for the peeling off GNSs. Here, it is found that ultrasonication not only can exfoliate and break GNSs, but also increase the shockwaves created from the collapse of cavitating bubbles.

3.2. Layers of GNSs
It is employed that U-99 is to obtain GNSs which come from different parent graphite 80-mesh, 120mesh, 150-mesh, and 200-mesh. Fig.3 and Fig.4 show the low-magnification and high-magnification TEM images of the GNSs. As can be seen from figure 3, the GNSs exhibit a wrinkled paper-like multilayer structure, for example Fig.3 panels a, b, c, and d. The edge thickness of the graphite nano-sheets measured in Fig.4 panels a, b, c, and d, is about 5~20nm. The thickness of U-70, U-80, U-90 and U-99 sheets analysis above, is ~14nm, ~8nm, ~5nm, and ~4nm, respectively. The interlayer spacing can be calculated to be about 0.47 nm which is larger than that of graphite (0.334 nm). It is worth noting that, different from graphite, the adjacent graphene layers of the multilayer graphene derived from chemical exfoliation are not parallel. Figure 4 shows the high-resolution TEM images of synthetic GNSs. The graphite shows twenty or thirty of graphene sheets stacked as shown in figure 4a. Figure 4b shows about ten layers of stacked graphene sheets. Fig.4c and Fig.4d shows about five layers of stacked graphene sheets. All of these GNSs images suggest the formation of exfoliated graphite nano-sheets varying from 5 to ~30 layers similar to that obtained by other chemical methods [19-21].

![Figure 3. TEM image of the GNS with U-99(a)80-mesh (b) 120-mesh(c) 150-mesh (d) 200-mesh.](image)

![Figure 4. High-magnification TEM image of the GNS with U-99 (a) 80-mesh (b) 120-mesh (c) 150-mesh (d) 200-mesh.](image)

3.3. Diffraction peaks of GNSs
The XRD patterns of four GNSs in figure 5. As we know, graphite contained a very sharp and high intensity peak at about 2θ = 26° with the layer-to-layer distance (d-spacing) of 0.334 nm. The feature diffraction peak of 200-mesh GNS appears at about 2θ= 21° after the ultrasonication treatment of 200-mesh EG, moreover other GNSs have no peak at this station. It is indicated that the feature diffraction peak of 200-mesh GNS structure has different character contrast on other three peaks of GNSs. XRD pattern of 200-mesh GNS has not peak of 2θ= 44°, but which appears at 2θ= 45°. The graphite feature diffraction peaks have this characteristic on 80-mesh GNS, 120-mesh GNS and 150-mesh GNS (2θ=26°, 44°, 54°), but 200-mesh GNS has not all peaks for it (2θ=21°, 26°, 54°). This phenomenon is
complying with results of SEM and TEM for smaller size of diameter (<10µm) and thickness (~4nm) of 200-mesh GNS after the ultrasonication treatment.

Figure 5. XRD of the GNS with U-99 (a)80-mesh (b) 120-mesh (c) 150-mesh (d) 200-mesh.

4. Conclusions
A simple and effective method for preparing GNS is presented. GNSs with the diameter of (<10µm) and thickness of (~4nm) have been prepared by the ultrasonication treatment. Under the optimal preparing condition, ultrasonication treatment parameter is 40min for 99% power factor. The results show that the GNS size decreases sharply at the high power factor stage of ultrasonication and then the decrease trend is slow down with the decrease of ultrasonication power factor. It is concluded that the choosing smaller size of parent graphite (>200-mesh) can obtain smaller size GNSs with diameter of (<10µm) and thickness of (~4nm).

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