Preparation of graphene oxides with different sheet sizes by temperature control*

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The sheet size of a graphene oxide (GO) can greatly influence its electrical, optical, mechanical, electrochemical and catalytic property. It is a key challenge to how to control the sheet size during its preparation in different application fields. According to our previous theoretical calculations of the effect of temperature on the oxidation process of graphene, we use Hummers method to prepare GOs with different sheet sizes by simply controlling the temperature condition in the process of the oxidation reaction of potassium permanganate ($KMnO_4$) with graphene and the dilution process with deionized water. The results detected by transmission electron microscopy (TEM) and atomic force microscopy (AFM) show that the average sizes of GO sheets prepared at different temperatures are about 1 μm and 7 μm respectively. The ultraviolet–visible spectroscopy (UV-vis) shows that lower temperature can lead to smaller oxidation degrees of GO and less oxygen functional groups on the surface. In addition, we prepare GO membranes to test their mechanical strengths by ultrasonic waves, and we find that the strengths of the GO membranes prepared under low temperatures are considerably higher than those prepared under high temperatures, showing the high mechanical strengths of larger GO sheets. Our experimental results testify our previous theoretical calculations. Compared with the traditional centrifugal separation and chemical cutting method, the preparation process of GO by temperature control is simple and low-cost and also enables large-size synthesis. These findings develop a new method to control GO sheet sizes for large-scale potential applications.

Keywords: graphene oxide, sheet size, temperature control, degree of oxidation

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1. Introduction

As one of the most important derivatives of graphene, graphene oxide (GO)[1,2] can be synthetized by oxidizing the natural graphite with strong oxidizers, and the monolayer sheet of GO dissolved in water or other organic solvents can be exfoliated by certain treatments such as centrifugation and ultrasonication in the absence of the Van der Waals' force.[3] In the oxidization process, various types of functional groups appear, such as epoxy, hydroxyl, carboxyl, and carbonyl, on the surface of the graphene oxide.[4] These functional groups are randomly distributed over the GO surface, with some unoxidized regions still exposed. Because of the presence of these unoxidized regions, the GO may retain some characteristic features of graphene, such as hydrophobicity, and its electric and photonic properties. The coexistence of these oxidized and unoxidized regions allows the GO to possess some special electrical,[5] optical,[6] and mechanical[7] properties which graphenes are short of. For the special atomic structure, GO plays a key role in the application of cryopreservation,[2] nanoporous membrane,[8] biosensor,[9] catalysis,[10] composites,[11] drug delivery,[12] next-generation optoelectronic nanodevices,[13] and in other fields.

The GO has a size effect, and its properties are closely related to the sheet size. The size of sheet is not only crucial to determine the size of the GO, but also directly related to the number of hydrophilic and hydrophobic groups on the surface of sheets: the smaller the sheet size, the more hydrophilic groups the sheets will possess. The sheets also feature stronger water solubility[14] and biocompatibility.[15] In the case of large sheet size, the number of the oxygen-containing functional groups on the surface of sheet will decrease, the hydrophobicity becomes strong and the surface defects will decrease, and the mechanical strength will thus be enhanced.[16] Therefore, the size of the GO sheets plays an important role in various applications of GOs.

At present, there are a variety of preparation methods of graphene oxides, most of which are modified on the basis of the Hummers method.[17] In this method, the natural graphite powder is oxidized to a GO via an anhydrous mixture consisting of concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), and the main oxidant potassium perman-

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ganate ($KMnO_4$). However, the oxidation mechanisms of these methods are not yet clear. By theoretical calculation, our group recently found that the oxidation process of pre-oxidized graphite and the oxidant $KMnO_4$ was highly correlated with three crucial effects: breaking of delocalized π bonds, steric hindrance, and hydrogen-bond formation. The breaking of delocalized π bond in the pre-oxidized structure and the hydrogen bond between the hydroxy (–OH) group and the oxidant will reduce the oxidation barrier, while the existence of steric repulsion between the pre-oxidized group and the oxidant will increase the reaction energy barrier. High temperatures will weaken the steric hindrance and reduce the oxidation barrier and further promote the breaking of delocalized π bond and the formation of hydrogen bond.[1] In this work, we propose a hypothesis by the theoretical results that low temperature can increase the oxidation barrier and lead to a low oxidation degree of graphene oxide, a small number of functional groups and a larger size of the GO sheets.

In this paper, we further modify the preparation process of the GO, based on the Hummers method established by Marcano *et al.* to verify our results of theoretical calculation.[18] In order to prepare GOs with different sheet sizes, we use a stirring and ice bath method to strictly control the temperature conditions during oxidation reactions of $KMnO_4$ with graphite and the dilution process with deionized water (DI). According to the results of the TEM detection and other characterizing techniques, we find that the sheet size of the GO is significantly increased when prepared under low temperatures during the oxidation process of graphite. Then we make the membranes with two GO solutions prepared under different temperature conditions. It is found that the GO membranes with large sheet sizes featured high mechanical strengths and remain stable for a long time ($>$ 10 min) in the ultrasonic cell with a power of 500 W and ultrasonic frequency of 70 kHz. While the GO membranes with a small sheet size are broken within the first 5 min in the ultrasonic process.

2. Materials and experiments

We prepared GOs through an improved method under different temperature conditions. For the low temperature method, $K_2S_2O_8$ (2.5 g) and P_2O_5 (2.5 g) were dissolved in concentrated H_2SO_4 (12 mL), followed by ultrasonication. Natural graphite (3 g) was added to the above solution and stirred at a constant temperature of 80 °C. When the mixture was cooled to room temperature, it was diluted with DI water (500 mL) and left overnight. The supernatant was decanted away and the remaining material was filtered through a 0.45-μm filter to remove the impurities and then vacuum dried at 60 °C overnight.

The dried pre-oxidized graphite was further added to concentrated H_2SO_4 (120 mL) with the temperature strictly controlled under 5 °C. The $KMnO_4$ (15 g) was added to the above solution slowly in the ice bath and the temperature was controlled at about 6 °C. The solution was stirred at 35 °C for 2 h and then diluted with DI water (250 mL) at 20 °C. The temperature conditions of the dilution process were controlled through a dropping method under the ice bath and it was made sure that the environment was stable and the temperature was under 20 °C upon each dropping. The solution was stirred under room temperature for 2 h and then was added into H_2O_2 (20 mL) whose concentration is 30% immediately after diluted with deionized (DI) water (700 mL). The mixture bubbled, and the color changed from brown to a brilliant yellow. The solution was stirred for 0.5 h and then left overnight.

For the higher temperature method, the temperature condition during the process when the $KMnO_4$ powder was added to concentrated H_2SO_4 was controlled at about 20 °C, 40 °C, and 60 °C and the temperature controlled condition was changed to 35 °C, 60 °C, and 80 °C when the solution was diluted with DI water.

The product was achieved by multi-step centrifugation and ultrasonication. All of the solutions prepared under different temperature conditions were allowed to be left overnight. After the supernatant removed, the precipitate was diluted with DI water (1 L), followed by centrifugation at 10^4 rpm. After the layer was separated, the precipitate was washed with a 1:10 HCl solution and DI water (1 L) to remove metal ions and acid, followed by centrifugation. The operations of washing and centrifugation were repeated until the solution could not be clearly precipitated anymore, the GO solution was collected and diluted with DI water (1 L), followed by ultrasonication treatment. The concentration of the resulting GO solution was about 5 mg/mL. We call this GO solution samples A, B, C, and D as the temperature conditions improved.

3. Results and discussion

TEM is the most intuitive and effective method of characterizing the sheet size of graphene oxide. Figure 1 shows the TEM images of GOs which are prepared under different temperature conditions. In Figs. 1(a) and 1(b), the GO sheets are prepared under low temperature conditions. The sizes of sheet with obvious crimp are about 10 μm (in Fig. 1(a)) and 2 μm (in Fig. 1(b)). Figures 1(c) and 1(d) show the sheet sizes of sample B to be about 0.8 μm and 1.9 μm respectively, and the sheets are relatively flat compared with those low-temperature sheets. Figures 1(e) and 1(f) show the sheet sizes of sample C. We can see that the sheets are widely distributed from 0.2 μm to 1.0 μm. Figures 1(g) and 1(h) show the sheet sizes of sample D whose sheets are mainly distributed from 0.1 μm to 0.6 μm. We can also see some sheets that are less than 0.1 μm in Fig. 1(g). The sheet size distribution of GO is shown in

Fig. 2. It can be obviously seen that the sheet sizes of sample A which is prepared at 6 °C, are mainly distributed in a wide range of 4 μm–10 μm with an average size being about 7 μm, which is significantly larger than those of those higher-temperature sheets. The sheet size distribution ranges of samples B, C, and D prepared at 20 °C, 40 °C, and 60 °C are 0.6 ∼ 1 μm, 0.2 ∼ 1.0 μm, and 0.1 ∼ 0.8 μm respectively. Their corresponding average sizes are about 1 μm, 0.6 μm, and 0.4 μm.

The results are consistent with our previous theoretical predictions. When graphite is oxidized by $KMnO_4$ under low temperature condition, it is not easy to break through the oxidation barrier due to the lack of energy, so the graphene surface presents low oxidation degree, which contains a small number of oxygen functioning groups. The sheet size of GO is thus largely dependent on the process of centrifugation and ultrasonication. Due to the large area of the unoxidized region on the surface, the hydrophobicity of the largesize GO sheet is strong, resulting in a large-size GO sheet prone to curling in the aqueous solution. While the oxidation degree of higher-temperature sheet surface is high, there are more oxygen functional groups on the surface and it becomes more hydrophilic. It is not prone to curling compared with the same-size low-temperature sheet, even the sheet size is as large as about 2 μm as shown in Figs. 1(b) and 1(d).

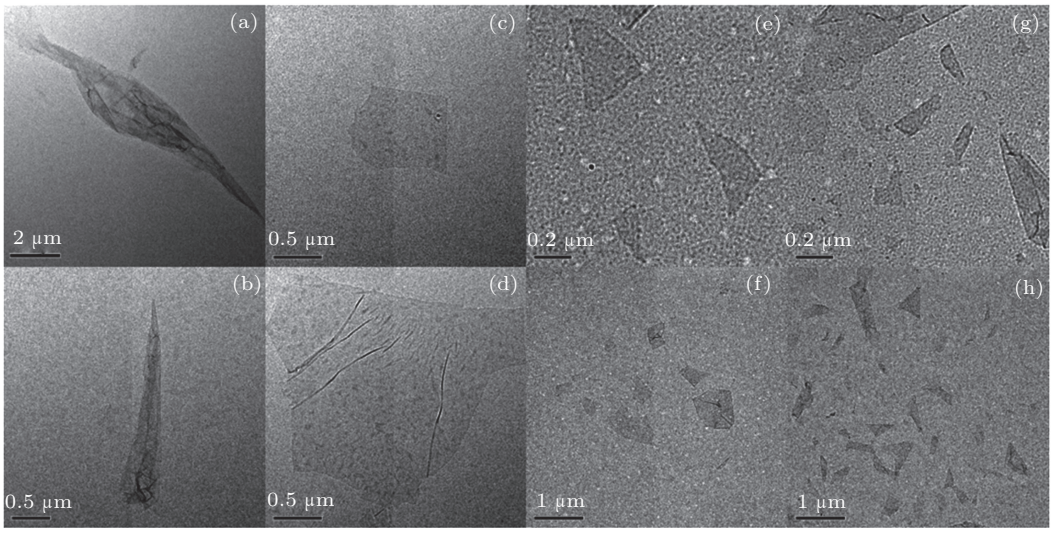


Fig. 1. TEM images of graphene oxide sheets of (panels (a) and (b)) sample A prepared at 6 °C, (panels (c) and (d)) sample B prepared at 20 °C, (panels (e) and (f)) sample C prepared at 40 °C, and (panels (g) and (h)) sample D prepared at 60 °C.

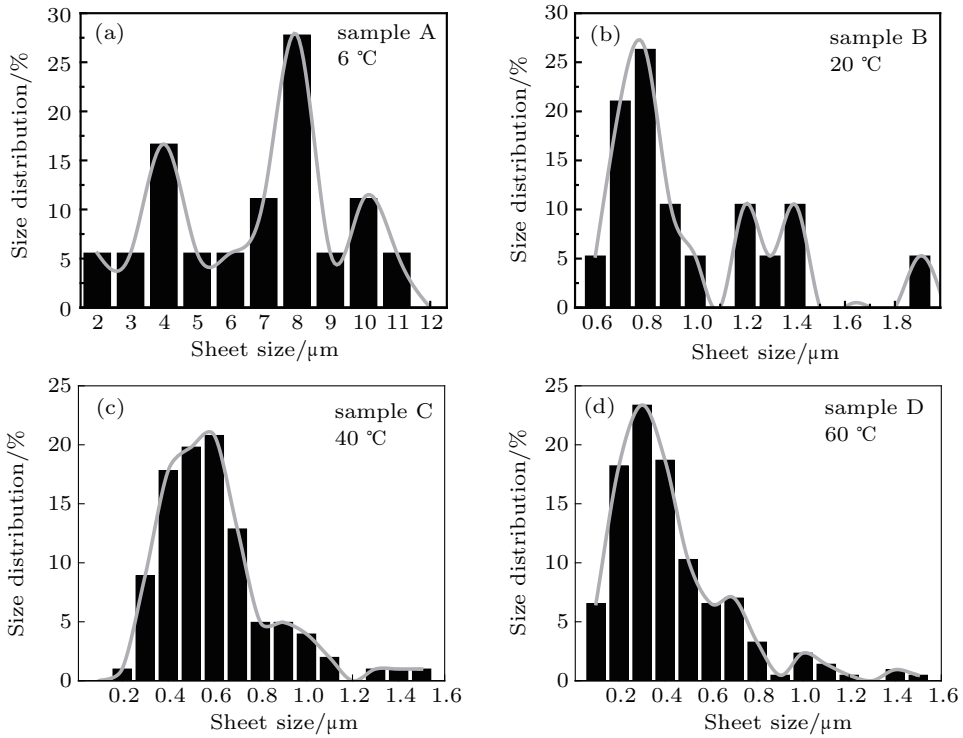


Fig. 2. Size distributions of graphene oxide sheets of samples A. B, C, and D prepared at (a) 6 °C, (b) 20 °C, (c) 40 °C, and (d) 60 °C, respectively.

After normalizing the curves, the ultraviolet–visible (UV-Vis) spectra of GOs prepared under different temperatures is shown in Fig. 3. The solid line is for the low-temperature (6 °C) sheet, and it shows two absorption peaks at 230 nm and 305 nm respectively. The dotted line is for the high-temperature (20 °C) sheet, and the two absorption peaks are slightly shifted to 231 nm and 304 nm. In addition, the difference in absorbance intensity between the two absorption peaks also indicates that a difference exists in sheet size distribution between the GOs prepared under different temperatures. Table 1 shows the absorbance intensities at 400 nm and 700 nm (Abs 400 nm, 700 nm), and the ratio of the absorbance intensity at 400 nm to that at 700 nm (Ratio 400/700). The small GO sheet shows a much lower absorbance in the visible range of 400 nm–700 nm, while the visible absorbance of the large-size sheet increases significantly, and with the increasing of absorbance in the visible range, the ratio of the absorbance intensity at 400 nm to that at 700 nm (denoted as Ratio 400/700) decreases.[19] When the ratio is 1.4:1, the absorbance curve is almost flat and similar to that of the "pristine" graphene made by intercalation and exfoliation without oxidation;[19,20] when the ratio is 4.5:1, the curve is similar and comparable to that observed for fully oxidized GO.[21] In our experiments, the values of Ratio 400/700 of the low and high temperature sheet are 1.38 and 1.50, respectively, indicating that the sizes of the GO sheet made under different temperature conditions are different, and the size of the low temperature sheet is larger than that of the high temperature sheet. The red shift of the absorption peak can also prove this conclusion. The results of the UV-vis are consistent with the results of TEM.

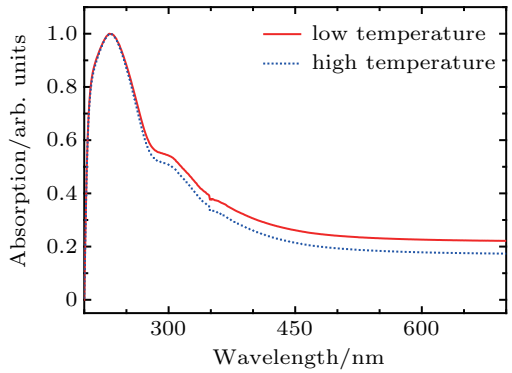


Fig. 3. (color online) UV-vis images of different graphene oxide sheets.

Table 1. UV-vis data of different graphene sheets.

Temperature	Abs 400 nm	Abs 700 nm	Ratio 400/700
Low	0.31	0.22	1.38
High	0.26	0.17	1.50

AFM is another intuitive and effective method of characterizing the sizes of graphene sheets. The AFM image of the GO sheet prepared under low temperature is shown in Fig. 4(a). It can be obviously seen that the low temperature GO is broken and the sizes of the sheet are different, ranging from 2 μm to 7 μm. Figure 4(b) shows the GO sheet prepared at high temperature and its size is about 0.7 μm.[19] This results are also consistent with those of our TEM image.

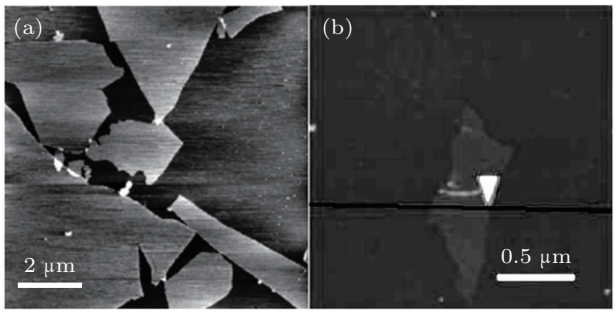


Fig. 4. AFM images of graphene oxide sheets prepared at (a) low temperature and (b) high temperature, respectively.

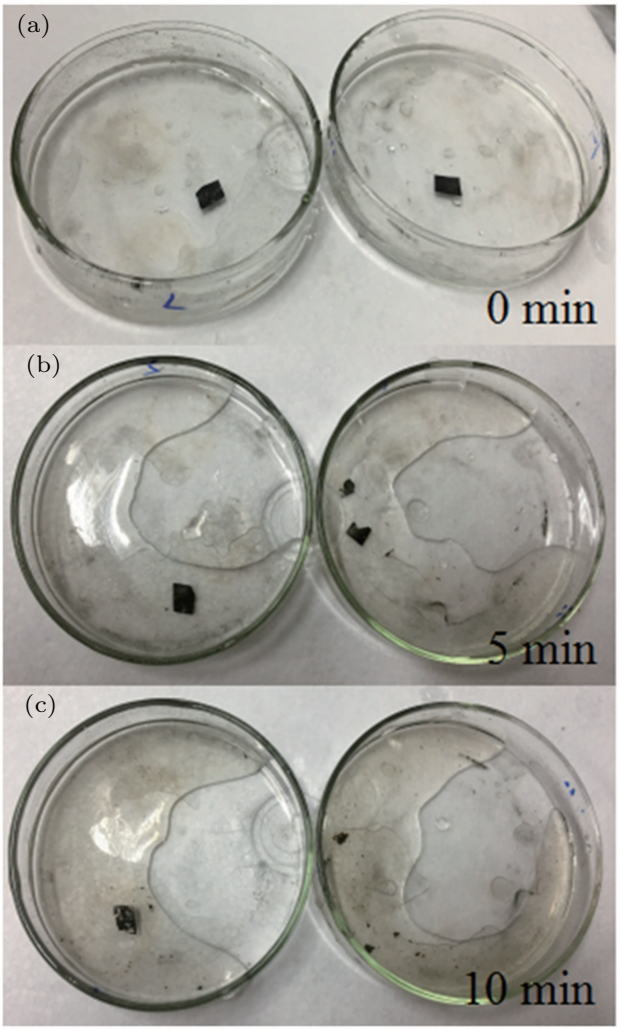


Fig. 5. (color online) Images of different ultrasonically-treated graphene oxide membranes. The Petri dishes on the left-hand side contain the low temperature membranes and the Petri dishes on the right-hand side contain the high temperature membranes. Panel (a) is for the initial state, panel (b) the state after a 5-min ultrasonication treatment, and panel (c) the state after a 10-min ultrasonication treatment.

The GOs with different sheet sizes show different mechanical strength properties. The GO with a large sheet is con-

ducive to the synthesis of high-strength two-dimensional materials, such as filters and electrical/thermal conductivity materials. We prepare freestanding GO membranes with samples A and B, followed by ultrasonication to test the mechanical properties of the GOs with different sheet sizes. The GO solutions whose concentration is about 5 mg/ml is dried at 70 °C to prepare freestanding GO membranes. The GO membranes of different sheet sizes are cut into small squares with the same size and placed in two Petri dishes containing NaCl solution (2.5 mol/L) respectively. The two dishes are placed in an ultrasonic cell and treated ultrasonically at a power of 500 W and a frequency of 70 kHz. Figure 5 shows the fracture degrees of the GO membranes at different temperatures in the salt solution as the ultrasonic time elapses. Figure 5(a) shows the initial states of the two membranes where both of them are intact; figure 5(b) exhibits the state after a 5min ultrasonication treatment. The low temperature membrane is still intact, while the membrane prepared at the high temperature is partially broken; figure 5(c) displays the state after a 10-min ultrasonication treatment. The low temperature membrane is still relatively intact, however the high temperature membrane is completely broken, leaving only small pieces suspended in the solution, with the solution becoming turbid. Therefore, we believe that the mechanical strengths of low temperature and large-size GO membrane are significantly stronger than that of small-size GO membrane prepared at high temperature, which has great application values in two-dimensional materials.

4. Conclusions

In this study, we find that the graphene oxides with different sheet sizes can be synthetized simply through temperature control. The average sheet sizes of GOs prepared at 6 °C, 20 °C, 40 °C, and 60 °C during the oxidation process of $KMnO_4$ are about 7 μm, 1 μm, 0. 6 μm, and 0.4 μm respectively. The obtained freestanding GO membranes show that the mechanical strength of low-temperature membrane is higher than that of the high-temperature membrane. Our study not only elucidates the mechanism responsible for temperature conditions to be able to influence the sheet size of GO during the oxidation process, but also present a simple and effective method of controlling and preparing different-scale GO sheets, which has a promising application in the field of two-dimensional materials.

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