High Throughput Exfoliation of Graphene Oxide from Expanded Graphite with Assistance of Strong Oxidant in Modified Hummers Method

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Abstract. The large-quantity (Grams) of graphene oxide (GO) was prepared by modified Hummers method, which the purifying process of GO suspension was much faster by filtering dried GO agglomeration dispersed into deionized water than usually used directed filter. The GO could be easily reduced to graphene.

1. Introduction
As a one-atom-thick two-dimensional crystal, graphene has been considered a basic building block for all sp² carbons including fullerenes, carbon nanotubes and graphite [1]. Since Novoselov peeled a few graphene sheets from highly crystalline graphite by a scotch tape method in 2004 [2], some unique electronic properties of this conceptual matter [3,4] have been found, which indicate potential applications in quantum devices [5–7], nanocomposites with various matrixes [8, 9], and ultrathin membrane materials [10, 11]. Since stable suspension of graphene oxide (GO) can be obtained by ultrasonic treatment of GO platelets in water [12, 13], much effort has been made to assemble these well dispersed oxidized or chemically reduced (under controlled conditions, still water-dispersible) graphene nanosheets into membrane-shaped ordered macrostructures, through flow-directed assembly by filtration and self-assembled free-Standing [10, 11, 14-16]. Recently, molecular templates [17], Langmuir–Blodgett assembly [18, 19], and direct chemical vapor deposition [20] have also been employed to obtain graphene-based or graphene-oxide-based membranes on selected substrates. Though the GO has been used in various investigations and applications, the application range, such as

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Conductive fillers in polymer, barrier material and coating material, is limited because of small-quantity of GO. If the chemically reduced GO is regarded as conductive filler, large-quantity (Grams) of GO may be needed by an experiment of conductive polymer composite [21]. Dongxing Yang has sacrificed the GO purity for gaining large-quantity of GO platelets [22, 23]. The GO platelets contain a few acids, so it is not an ideal nano-material. A new method that could dramatically increase quantity of GO becomes more and more necessary. In the present work, the large-quantity of graphene oxide (GO) was prepared by modified Hummers method, which the purifying process of GO suspension was much faster by filtering dried GO agglomeration dispersed into deionized water than usually used directed filter. The GO could be easily reduced to graphene.

2. Experimental
The expanded graphite powder (20 g) is put into concentrated H₂SO₄ (460 mL). KMnO₄ (60 g) is added gradually with stirring and cooling, so that the temperature of the mixture is not allowed to reach 20 °C. The mixture is then stirred at 35 °C for 2 h, and deionized water (920 mL) is added. In 1 h, the reaction is terminated by the addition of a large amount of deionized water (2.8 L) and 30% H₂O₂ solution (50 mL), causing violent effervescence and an increase in temperature to 100 °C, after which the color of the suspension changes to bright yellow. The suspension washed with 1:10 HCl solution (5 L) in order to remove metal ions by filter paper and funnel. The paste collected from the filter paper is dried at 60 °C, until it becomes agglomeration. The agglomeration is dispersed into deionized water in static state for 2~3 hours and slightly stirred by glass bar. The suspension is washed with much deionized water at 5~7 times for two days by filter paper and funnel, until the PH is nearly 7. The paste collected on the filter paper is dispersed into water by ultrasonication. The obtained brown dispersion is then subjected to 30 mins of centrifugation at 4000 r.p.m. to remove any unexfoliated GO using centrifuge with a rotor radius of 14 cm. The GO platelets are obtained by dehydration at 60 °C in air.

The GO hydrosol is obtained by the GO platelets dispersed into water by ultrasonication and centrifugation at 4000 r.p.m. for 2 hours to remove any unexfoliated GO. Then Atomic force microscopy (AFM) shows that the resulting GO sheets that are cast on a silicon wafer are flat.

3 Results and Discussion

![Figure 1](image_url)

**Figure 1.** (a) Powder of expended graphite. (b) Expended graphite oxidized. (c) GO suspension with acids and metal ions. (d) Paste of GO washed with HCl solution and deionized water.

Figure 1 (a) shows that the expended graphite is dark squamous powder with a little metal shine. It can be known in figure 1 (b) that the expended graphite oxidized by concentrated H₂SO₄ and KMnO₄ is dark paste. The paste can cling on to the glass rod. The paste mixture with a mass of water and a little
H$_2$O$_2$ becomes a brown-yellow suspension in figure 1 (c). If the GO suspension with a lot of acids and metal ions is laid for long time, GO will sink to the bottom and become floccules. The figure 1 (d) indicates that the GO paste without metal ions and acids is dark brown.

Figure 2. The model of filter

In Hummers method [23], little GO could be prepared by laboratory. The most important influencing factor of GO preparation is very slow filtering rate. In other words, the residual acids are hardly wiped away. The suspension with metal ions and acids is washed with 1:10 HCl solution in order to remove metal ions. However the GO paste with acids is dried at vacuum drying oven [22], a few acids remain in the GO. If the GO is continually washed with deionized water, the PH will increase. The suspension gradually becomes colloid. The filtering rate becomes slower and slower and then finishes in the end. The residual acids are hardly completely wiped away. The higher is PH of GO suspension, the larger is the zeta potential of GO as a function and the electrostatic force among GO sheets [14]. If the electrostatic force among GO sheets is greater than or equal to the total of gravity and van der waals force, the GO hydrosol can be stabilize forever. The model in Figure 2 shows that the GO suspension with acids and metal ions is directly filtered, and then the surface of filter will be quickly covered with a layer compact film which could block the water passing. The large-quantity of GO is hardly obtained. For obtaining large-quantity of GO, the purifying process of GO suspension should be modified.

Figure 3. The different process between modified Hummers method and Hummers method.

The large-quantity of GO has been obtained by modified Hummers method. Figure 3 shows that the purifying process of modified Hummers method is different from Hummers method. In Hummers method, the GO suspension is obtained from GO suspension with acids and metal ions that is washed with HCl solution and deionized water. In modified Hummers method, the GO suspension with acids and metal ions is washed with HCl solution and dried at 60 °C. The GO agglomeration is dispersed.
into deionized water, and then the suspension is washed with much deionized water. The GO suspension is obtained from the paste which is collected on the filter paper and dispersed into water by ultrasonication. The dispersion of the GO agglomeration in static state is very slow. Figure 2 shows that few colloids are dispersed into deionized water in the beginning, so the surface of filter paper is not covered a layer compact film which blocks the water passing. The water with residual acids could pass through the interstice of GO film. As the GO is washed with water, the film of GO becomes more and more compact. The filtering rate becomes slower and slower. The residual acids are already wiped away before the compact film formed.

Figure 4. (a) GO platelets. (b) The Tyndall effect confirming the colloidal nature of the GO dispersions.

Figure 5. The AFM image of GO sheets on the Si slice

Figure 4 (a) shows that the GO platelets are dark and flexibility. The GO hydrosol obtained by the GO platelets dispersed into water by ultrasonication and centrifugation at 4000 r.p.m. to remove any unexfoliated GO is brown yellow. The GO hydrosol laid several months in static state has no obvious deposition. The Tyndall effect confirms the colloidal nature of the GO dispersions in figure 4 (b). Figure 5 is an atomic force microscopy (AFM) image of the GO hydrosol. It offers immediate evidence for peeled-off single GO sheets. The thicknesses of the GO layers are about 0.8 nm, as indicated in Figure. As reported previously [24, 25], these GO layers should be mostly monolayer. The sheets are a little bumpier than predicted, which is possibly due to the existence of abundant functional groups, such as epoxy and hydroxyl groups, bonded to both sides of the graphene sheets, which disrupts the original conjugation and introduces lattice defects to result in folds and distortions on the sheets [26]. The AFM image observations indicate that most graphene sheets are of a relatively large size (several hundred nanometers to several micrometers).

4. Conclusion
In modified Hummers method, the purifying process of GO suspension has been studied, which can obtain the large-quantity of GO. More increasing quantity of GO is the next center work. In addition, the device, filter paper and funnel, is inexpensive and simple. The large-quantity of GO prepared in industry may be enlightened by this work.

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