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# Preparation of high quality graphene using high gravity technology

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ABSTRACT

In this paper, the preparation of graphene from graphite oxide (GO) by high gravity technology in Rotating Packed Bed (RPB) was studied. It was verified that the surface area of graphene oxide exfoliated by high gravity technology was about 7–8 times of that obtained by ultrasonic technology and the layer numbers could be reduced to about two layers with high gravity technology. After reduction, the electric conductivity and specific capacitance of graphene prepared by high gravity technology increased 12.5% and 15.0% compared to that prepared by common method respectively. This technology has obvious advantages in sufficient exfoliation and reduction besides better product qualities and application properties. Moreover, it is easily scaled up.



## 1. Introduction

Graphene, a single sheet of carbon atoms tightly arranged in a two-dimensional (2D) honeycomb lattice [1], has attracted enormous attention from both the basic experimental research and technical application due to its outstanding mechanical, thermal, optical and electronic properties [2,3], which endow graphene a series of potential applications in many different areas, such as sensors [4,5], supercapacitors [6], solar cell [7] and polymer composites [8]. However, there is a big challenge for chemists to develop new effective and scalable approaches to prepare graphene [9]. At present, graphene is prepared by a variety of techniques, including micromechanical exfoliation [10], chemical vapor deposition [11], epitaxial growth [12], cutting carbon nanotubes [13], direct sonication [14], electric arc discharge [15] and chemical reduction of exfoliated graphite oxide (GO) [16], in which the chemical reduction method is advantageous due to being scaled up easily. In general, the chemical reduction method includes three steps: (1) preparation of graphite oxide (GO), (2) exfoliation of GO, (3) reduction of exfoliated GO (EGO). Among them, the preparation technology of GO is very mature, Hummers method as traditional method is widely used. For the step of reduction, although there also were several attempts and research results [17–19], few studies investigated how the exfoliation and reduction methods and their equipment affect the quality and application of graphene. Traditionally, ultrasonic cleaner is usually used in exfoliation process and stirring tank reactor (STR) in reduction, whereas both of them exists some drawbacks that the former is difficult to be scaled up and the latter reduction efficiency is lower.

Recently, it was verified that graphite could be exfoliated in a liquid under shear force to yield defect-free graphene [20]. In comparison with ultrasonic exfoliation, the shear-exfoliation is easily scaled up. Up to now, the used shear-exfoliation equipment includes Rotor-stator mixer [21], Kitchen blender [22], Taylor–Couette flow reactor [23] and balling mill [24] etc. However, these equipment still exist some issues, such as the created shear force inhomogeneous or uncontrollable etc.

- Rotating packed bed (RPB) is a high-gravity apparatus which can generate an acceleration of up to 1–3 orders of magnitude larger than the gravitational acceleration on earth [25]. Its outstanding characteristics are intensive, even and controllable shearing, transfering and micromixing [26], which is very suited to the exfoliation of graphite oxide and the reduction of graphene oxide. More importantly, the process with RPB is easy to be scaled up [27], however, RPB being used to the preparation of graphene has not been reported until now.

In this work, graphite oxide (GO) was prepared according to the Hummers method. The steps of exfoliation and reduction were carried out in RPB. For comparison, the traditional method is also adopted, in which ultrasonic cleaner was used for GO exfoliation and STR for reduction. The as-prepared products were characterized in details. The results indicate the high gravity technology is an effective and promising method for the preparation of graphene with high quality.

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## 2. Experimental

### 2.1. Materials and synthesis

GO was prepared according to the Hummers method [28,29]. The product was then washed copiously with distilled water and 1.0 M HCl solution, followed by centrifugation and freeze-drying. 100 mg of GO was dispersed in 100 mL distilled water to form 1.0 mg/mL brown GO dispersion and then exfoliated (0.5 h) and reduced (90 °C, 0.5 h) in RPB, the products are named as R-GO and R-G respectively. The process is illustrated in Fig. 1. Typically, 100 mL of GO suspension was pumped into RPB by a peristaltic pump at 100 mL/min, which was running at a high-gravity level of 540 m/s$^2$, and the liquid from outlet was then pumped into RPB circularly. The as-prepared R-GO was reduced by chemical reducing agent according to literature [30]. The reduction process was conducted in RPB and the temperature was controlled by a circulating water bath. R-GO and reducing agent were mixed in the flask and the stream was ejected and impinged through the distributor repeatedly. The R-G was gotten after the brown R-GO turned black. For comparison, equal graphite oxide suspension was exfoliated with the aid of intensive sonication (150 W, 40 KHz, 0.5 h) and reduced in STR for the same time, the resulting graphene oxide is named as S-GO and graphene as S-G, respectively.

### 2.2. The measurement of relative specific surface area of GO

According reference [31], we use the adsorption of methylene blue (MB) on GO to characterize the relative specific surface area of GO. 1 mg of the exfoliated GO(EGO) was added into 100 mL of 3 mg L$^{-1}$ MB solution and mixed for 1 h under shaking at room temperature. The supernatant was gotten after membrane filtration. The MB concentration in the supernatant was obtained through the absorbance and the standard absorption carve of MB measured at a wavelength of 664 nm. According to the concentration changes of MB before and after adsorption, the adsorption mass of MB by EGO was gotten. The specific surface area of EGO could be calculated roughly according that the adsorption area of 1 mg MB is 2.54m$^2$ The value of relative specific surface area of GO can reflect the exfoliation effect comparatively and indirectly.

### 2.3. Preparation of electrode and electrochemical measurements

All electrochemical experiments were carried out using a three-electrode system, in which Platinum electrode was used as the counter, saturated calomel electrode (SCE) as a reference electrode and 1 M $H_2SO_4$ solution as electrolyte. The working electrode was made according to the following procedure: electroactive materials and polytetrafluoroethylene (PTFE) were mixed in a mass ratio of 95:5 and dispersed in ethanol to form slurry, which was then coated onto a titanium plate and dried under vacuum at 70 °C for 24 h. Galvanostatic charge-discharge (GCD) curves were carried out in a potential range from −0.2 to +0.8 V. Cyclic voltammetry (CV) measurements were conducted with voltage from −0.2 to +0.8 V and electric current 10 mV s$^{-1}$ to 200 mV s$^{-1}$. For the electrochemical impedance spectroscopy (EIS) measurements, the frequency range was from $10^{-2}$ to $10^5$ Hz.

### 2.4. Characterization methods

The layers of the graphene oxide were analyzed by a NanoScope3D (Veeco, USA) atomic force microscope (AFM). The morphologies and structures of the graphene were characterized by an H-800 (Hitachi, Japan) transmission electron microscopy (TEM) and JEM-3010 (JEOL, Japan) high resolution transmission electron microscopy (HRTEM). Raman spectra were recorded from 200 to 3200 cm$^{-1}$ on a Renishaw 1000 confocal Raman microprobe (Renishaw plc, UK) using a 514 nm argon ion laser. XPS measurement was performed using an ESCALAB 250 instrument (Thermo-Fisher, USA) with Al Kα radiation. The adsorption of MB was tested by a UV/vis spectrophotometer (PerkinElmer, USA). The Fourier transform infrared (FT-IR) analysis was carried out with a Nicolet model 8700 spectrometer (Nicolet Instrument Corporation, USA). The electrical conductivity of graphene was determined using a four-probe technique on a SX1934 digital multimeter (Suzhou Telecommunication Factory, China), and the electrochemical properties were investigated by CHI660E electrochemical workstation (Shanghai Chenhua, China)

## 3. Results and discussion

### 3.1. The properties and characterizations of graphene oxide

#### 3.1.1. Effects of exfoliation time

Fig. 2 is the AFM spectra of R-GO at different time, Fig. 3 is the specific surface area at different time. From Fig. 2, it can be seen that the thickness of graphene reduces first and then increases after 50 min. The thickness gets to 1.9 nm at 50 min, which is close to single or double layer. The thickness increases to 3.76 nm inversely in 60 min. Fig. 3 shows that the surface area of GO increases first and then decreases with increasing exfoliated time, the maximum value appears at about 30 min, whose trend agrees with in Fig. 2. The reasons may be that the equilibrium is set up between exfoliation created by shearing force mainly and

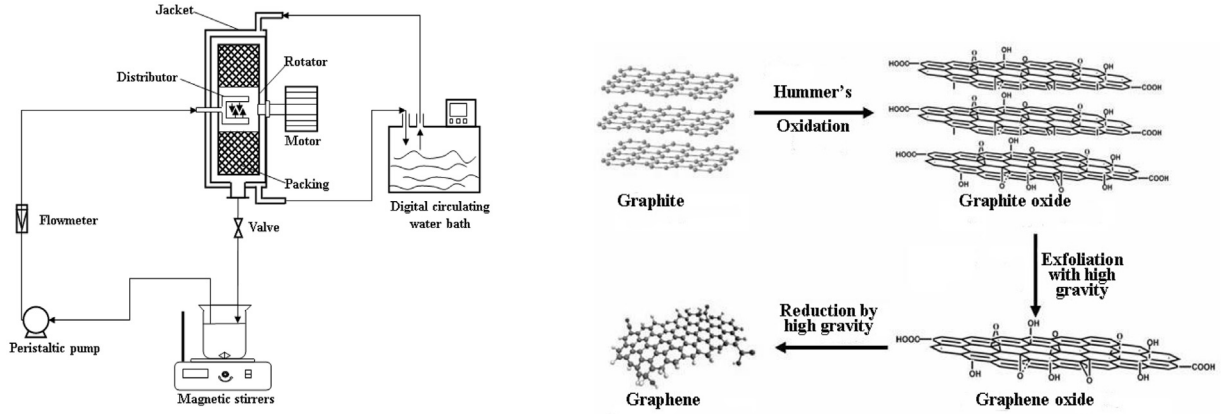


**Fig. 1.** Schematic diagram of exfoliation and reduction process in a RPB.