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Few-layered graphene via gas-driven exfoliation for enhanced supercapacitive performance

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ABSTRACT

High-quality graphene flakes have long been desirable for numerous applications including energy storage, printable electronics, and catalysis. In this contribution, we report a green, efficient, facile gas-driven exfoliation process for the preparation of high-quality graphene in large scale. The gas exfoliation process was realized by the interplay between the expansion of interlayer at high temperature and the gasification of liquid nitrogen within the interlayer. Detailed experiments demonstrated that the higher temperature was critical to the formation of fewer layers. The exfoliated graphene was demonstrated to be of high quality. We further investigated the electrochemical behavior of this exfoliated graphene. As a result, this few-layered graphene demonstrated an enhanced capability as a supercapacitor, much higher than its counterpart parent material.

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1. Introduction

Graphene consisted of carbon atoms arranging in a honeycomb lattice, has been regarded as a harbinger of the both experimentally and industrially coming of next-generation material, because of its remarkable electronic, optical, thermal and mechanical properties [1–4]. Although graphenes, including graphene oxides (Go), reduced graphene oxides (rGo), etc., have shown promising performance in many fields such as catalysis [5–7] electrochemistry [8–10] photochemistry [11,12], even in their disordered forms, one can anticipate that high-quality graphene would demonstrate extensive enhancement in performance [13].

The first discovery of graphene was reported in 2004, Geim and Novoselov harvested graphene monolayers from original graphite crystals by micromechanical cleavage [14]. Since then, a broad range of fabrication methods have been developed. Generally, the production methods of graphene can be summarized as two types: bottom-up process and top-down strategy, i.e., carbonization of organic precursors (bottom-up) and reducing layers by chemical, mechanical, physical methods (top-down) [2,15–17]. While numerous

bottom-up methods have been proposed for generating graphene, the top-down process is still the most versatile strategy for fabricating graphene in mass production [18]. Up to date, several top-down methods, i.e. ball milling, high-shear mixing, ultrasound-assisted liquid exfoliation, have been reported [19–26]. Nevertheless, these pathways struggle from their inherent disadvantages. For example, ball milling, including dry milling and wet milling, was developed for producing graphene from the parent graphite [21,22,27]. However, a high concentration of amorphous carbon is inevitable during the dry milling process and long milling time is required in wet milling procedure [20]. Meanwhile, in both the ultrasound-assisted liquid exfoliation and high-shear mixing methods, liquid medium has turned to be a hurdle. Several issues, including the dispersion of graphene in liquid and subsequent removal of liquid solvent, are usually associated with the liquid medium. As a result, the processes involving the liquid medium generate very poor exfoliating efficiency (usually lower than 3%) and chemical impurity [19]. Thusly, it is of significance to develop a top-down stage which can produce high-quality graphene without a liquid medium.

Recently, our group has developed a gas exfoliation strategy for producing few-layer hexagonal boron nitride from its parent material [28,29]. The operating process employed a gas medium instead of liquid medium for exfoliation, dramatically improved the

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chemical purity of the final products. Additionally, the final products were proved to be in high-quality and high-yield. Inspired by the finding, herein, we employed a gas-driven exfoliation approach to gain few-layer graphene from commercial graphite. The key in the process is treating the pristine graphite under extreme conditions to destroy the Van der Waals' force between graphene layers. Generally, the graphite was treated at a high temperature, leading to the interlayer expansion and enabling exfoliating media (liquid nitrogen, L-N₂) to enter the graphite interlayers. Then the hot graphite was quickly immersed into extreme cold L-N₂, and the L-N₂ entered into the graphene interlayers. Because of the very hot status of graphite, the L-N₂ quickly gasified and consequently destroyed the interlayer Van der Waals' force to generate few-layer graphene. In this contribution, the exfoliation process and mechanism was investigated in detail. We also studied the influence of treating temperature and found that a higher treating temperature is in favor of fewer-layered structure. The gas exfoliation strategy for the preparation of graphene is environmentally benign. We further investigated the electrochemical behavior of the obtained few-layered graphene and demonstrated an enhanced supercapacitive performance at all scan rate. This work provides a new strategy for producing high-quality graphene in large scale to meet the requirements for some electrochemical applications. Also, some other few-layer materials with high quality may be generated by the current procedure as well.

2. Experimental

2.1. Materials

Flake graphite was obtained from Sigma-Aldrich without further treatment. Liquid nitrogen was provided by Suzhou Jinhong Co. Ltd. Ultra-pure water was obtained by a water purifier in our laboratory.

2.2. Preparation process

Typically, 1 g of pristine graphite was placed in a 25 mL of the crucible. After that, the crucible was transferred to a muffle oven with a temperature of 500 °C, 600 °C and 700 °C, respectively. After ~1 min, the graphite turned to be a red-hot status. Then the graphite was poured into a 4 L of Teflon beaker with ~200 mL of L-N₂ inside. Afterwards, shake the beaker until the total gasification of L-N₂. So far, one exfoliation process was completed. Then, the whole process was repeated for ten times. Then, the products were carefully collected and dispersed in 200 mL of DI water. Subsequently, the dispersed solution was centrifuged at 1500 rpm to remove un-exfoliated bulk graphite, and the upper dispersed solution was further centrifuged at 12,000 rpm to obtain the final product. The final product was finally vacuum dried at 50 °C for overnight. With different heating temperature, the exfoliated graphenes were marked as exf-G-500, exf-G-600, and exf-G-700, respectively. The yield of graphene from its parent graphite was measured to be ~0.2–0.3 g, depending on the treatment temperature. Caution that during the preparation process, the high and ultra-low temperature is unavoidable and necessary protection is required.

2.3. Characterizations

In situ X-ray diffraction (XRD) patterns were recorded on an RINT2000 vertical goniometer equipped with Anton-Paar XRK. The scanning voltage and current were 40 kV and 100 mA, respectively; and the scanning range was 5–75°. A D8 ADVANCE X-ray diffraction with Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) was employed for the determination of XRD patterns from 10° to 80° with a scanning speed

of 7° min⁻¹. While the surface morphologies of samples were characterized by a JSM-7001F field emission scanning electron microscope (FE-SEM). Raman spectra were performed on a Thermo Scientific DXR Smart Raman spectrometer, whose excitation wavelength was 532 nm. Atomic force microscope (AFM) was tested by an Asylum MFP-3D from Asylum Research Company. Transmission Electron Microscope (TEM) and High-Resolution Transmission Electron Microscope (HRTEM) were carried out on a Tecnai G2 F30 S-TWIN from FEI Company, USA.

2.4. Electrochemical measurements

The electrochemical measurements were carried out in 1 M KOH solution with a CHI 760D electrochemical analyzer (ChenHua Instruments, Shanghai, China) at room temperature. All the electrochemical performances were tested with a three-electrode system. Platinum foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrodes were prepared as following: Typically, 5 mg of the samples were mixed with 0.5 mg Nafion binder in 1 mL of ethanol to obtain homogeneous slurry. Afterwards, 20 μL of the slurry was doped onto a glassy carbon electrode, whose diameter was 5 mm. Then, the electrode was dried at 80 °C under vacuum for 24 h. The loading amount of samples on glassy carbon electrode was measured to be 0.5 mg cm⁻².

3. Results and discussion

As described in the experimental section, the whole process does not introduce any chemical impurities and produce graphene in large scale. Realization of this strategy mainly relies on high temperature enlarged interlayer distance, triggered weakened Van der Waals' force between layers, and gasification of L-N₂ for overcoming the Van der Waals' force. In situ XRD characterization in Fig. 1 was performed to highlight the impact of the heating process. It is verified that the 2θ degree of (002) peak, representing the inter-layer lattice of graphene, shifted to lower angle gradually from 26.5° to 26.0° with the heating temperature raised from room temperature to 700 °C. Based on Bragg's equation, the interlayer distance enlarged with the increase of heating temperature, facilitating the fluxion of L-N₂ into the interlayer of graphite. Moreover, larger interlayer distance indicates weaker Van der Waals' force between interlayers, making the exfoliation easier than its pristine status.

The whole exfoliation process was summarized in Fig. 2. Firstly, the extraneous heat gave rise to the enlarged interlayer distance, advocating weaker interlayer Van der Waals' force and a larger interlayer space for L-N₂. Subsequently, with the red-hot graphite immersed into L-N₂, L-N₂ entered into the interlayer of graphite.

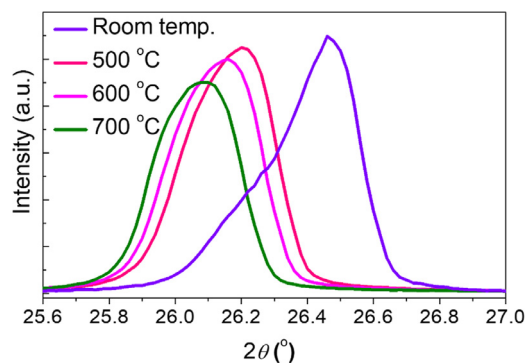


Fig. 1. In situ XRD patterns of graphite at different temperatures.

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