IOP Conf. Series: Materials Science and Engineering **735** (2020) 012011 doi:10.1088/1757-899X/735/1/012011

# Research on Preparation Process of Graphene by Modified Ball Milling and Its Thermal Properties

**Quanmao Yu[1,*], Qiurong Liu[1], Xiaoxia Li[1], Zhong Chen[2], Tao Ren[1], Zhenyu Chen[1] and Zhengyi Huang[1]**

1 Institute of Functional Materials, School of Software and Internet of Things Engineering, Jiangxi University of Finance and Economics, Nanchang 330013, PR China
2 School of Materials and Mechanical and Electrical Engineering, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China
* Corresponding author. Email: bsyqm@163.com

**Abstract.** Graphene is a focus for its excellent properties. The high efficient low cost preparations of high pure Graphene are bottlenecks in Graphene application field. This paper reports a modified mechanical milling high pure Graphene preparation method. The method has the characteristics of less cost and can scale-production. The XRD, TEM and TG/DTA are used to character the properties, especially the thermal properties of Graphene prepared by the method.

## 1. Introduction

Carbon materials are well-known for their superior properties. A single layer of graphite (also called Graphene) is one of the focus materials of this type of material [1]. Graphene is the basic unit for forming two-dimensional carbon materials. With a single layer of graphite, we can get graphite, 0-dimensional fullerenes, 1-dimensional carbon nanotubes and so on. In recent years, two-dimensional materials have attracted more and more attentions, mainly because of their potential applications [2]. Graphite has many unique characteristics and distinctive properties because of its unique and stable crystal structure [3,4]. These rich and unique phenomenon arouse the world research and development community wide interests [5]. Graphene not only has excellent electrical properties, outstanding thermal conductivity (up to 5000 $wm^{-1}k^{-1}$), extraordinary specific surface area (2630 $m^2/g$), ultra-high carrier mobility at room temperature (over 15000 $cm^2/Vs$ , the theoretical value is more than 1 million $cm^2/Vs$) [6], its young's modulus and fracture strength can also be equivalent to carbon nanotubes. Hence, Graphene has a broad application prospect in such aspects as flexible materials, photoelectric materials, semiconductor materials, electronic information materials, drug carriers, etc [7,8].

In 2004, Geim et al. prepared stable monolayers Graphene using a method called mechanicstripping at the University of Manchester [9]. Since 2004, the researches on Graphene become hot topic. The researches mainly focus on the Graphene preparation and application performance [10]. At present, there are many methods to prepare Graphene, and we can divide them into physical and chemical methods. Among them, the physical methods mainly include mechanical exfoliation method, liquid phase stripping method [11], ball-milling method, and so on. The chemical methods mainly include epitaxial growth method [12,13], oxidation-reduction method [14], chemical vapor deposition method [15,16], electric arc synthesis, in situ self-generated template method, etc. In comparison, the preparation process of Graphene by mechanical ball mill is simple, with low cost. However, there is no ideal method for preparing high-quality Graphene at low cost [17]. Therefore, the

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

IOP Conf. Series: Materials Science and Engineering **735** (2020) 012011 doi:10.1088/1757-899X/735/1/012011

low cost produce method of high quality Graphene becomes a bottleneck in Graphene researches and application fields [18,19]. In this paper, we report a modified low cost mechanical milling method for preparing high pure Graphene and character the XRD, TEM and thermal properties of Graphene prepared by the method.

## 2. Experimental

### *2.1. Materials*
The raw materials were natural graphite powder (analytical-grade, purchased from market), deionized water and some certain agents. All agents used in this work were analytical-grade reagents (A.R.) and purchased from Sinopharm Chemical Reagent Co., Ltd.

### *2.2. Synthesis*
The process of preparing Graphene by our modified ball milling method is shown in Figure1. Firstly, the raw materials are pretreated, and then the processed raw materials and functional agents are mixed and added to a mechanical ball mill. After been grinded in a mechanical mill for the definitely time at the setting speed, samples are taken out and purified to high pure Graphene.

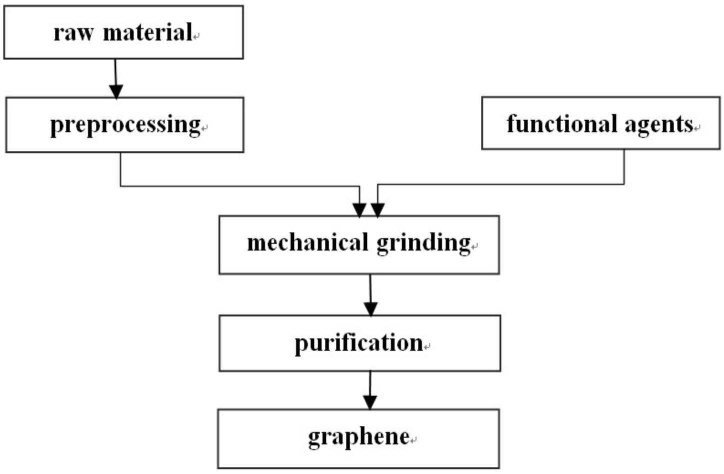



**Figure 1.** Schematic Diagram of Experimental Process

### *2.3. Characterizations*
X-ray diffraction data were obtained by X-ray diffractometer (Shimazu XRD-6100 Lab, Japan, CuKα1) with the scanning speed 2°/min and step 0.02° in the range of (2θ=20°-70°) at room temperature. Transmission electron microscopy images were obtained using TEM (Tecnai G2 20 S-Twin). The thermal performance was performed by the EXSTAR6000 TG/DTA synchronous thermal analyzer (Japan) with the heating speed 5°/min and step 0.02° in the range from 50°C to 1000°C.

## 3. Results and Discussion
Figure 2 shows the Graphene samples (the content about 2.0% (Wt.)) produced by our modified ball milling method. The samples are visible light perspective. In order to enhance the stability and prevent the secondary lamination, the Graphene pretreated by functional agents are dispersed in liquid (in this research, we use water). The content of Graphene produced by our method can rich to 5.0% (Wt.).

Figure 3 shows the XRD patterns of raw materials (untreated graphite) and our Graphene samples. For the original graphite, there is a strong sharp diffraction peak at 26.5°, and the corresponding layer spacing is 0.34 nm. Because the samples using in XRD characterization are accumulations of Graphene flakes (as shown in figure 4), the XRD strength of our Graphene samples is very slight, the diffraction peak is wide peak around 23.5° (as shown in the figure), and the corresponding layer spacing is about 0.38 nm. The XRD patterns and the increase of layer spacing indicate that most of the graphite is mechanical stripping into a few layered Graphene flakes by ball milling.

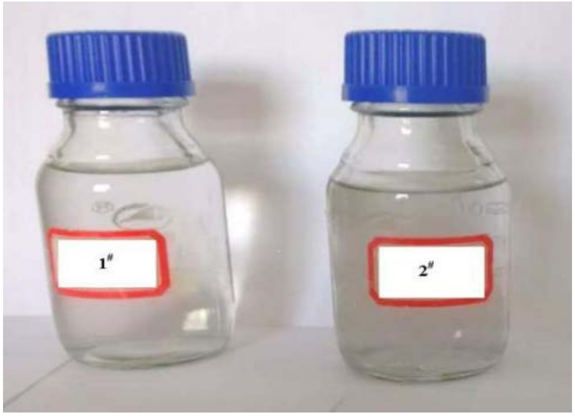
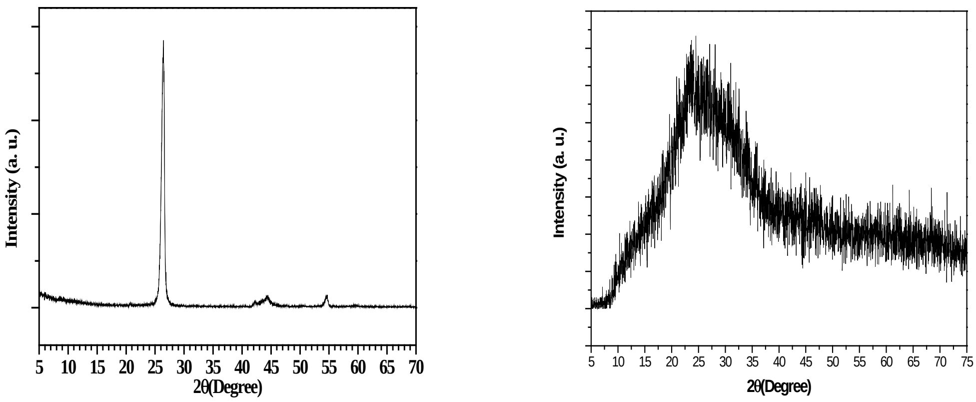



**Figure 2.** Graphene Produced by Modified Ball Milling Method (the Content about 2.0% (Wt.))

Figure 4 is TEM photographs of Graphene prepared by our modified ball milling method. The Graphene are two-dimensional flakes accumulated together. We can clearly see the number of layers of Graphene flakes, and most of them are below 5 layers.




(a) (b)

**Figure 3.** XRD Patterns of Untreated Raw Materials (a) and Graphene (b)

Figure 5 shows the DTG characterization results of Graphene and pretreated raw materials (graphite). The line (A) represents the pretreated raw material and the line (B) is Graphene. It can be seen from the figure that the pretreated graphite raw material has a good heat resistance before 500°C (though the untreated graphite has thermal stability to over 1000°C, as all known), and when the temperature is higher than 500°C, the pretreated graphite raw material begins to decompose. The Graphene sample has a peak at a temperature below 90°C, where the weight loss is the evaporation of the adsorbed water in the sample. There is a peak between 250°C and 400°C, and the peak is 350°C, which is the decomposition of Graphene. After 400°C, the Graphene is broken down, so there is no weightlessness. This means the Graphene produced by our modified ball milling method should be applied under 250°C.

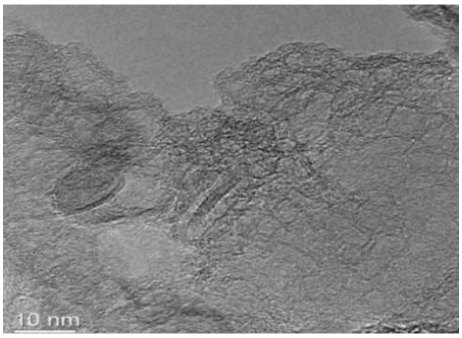



**Figure 4.** TEM Images of Graphene

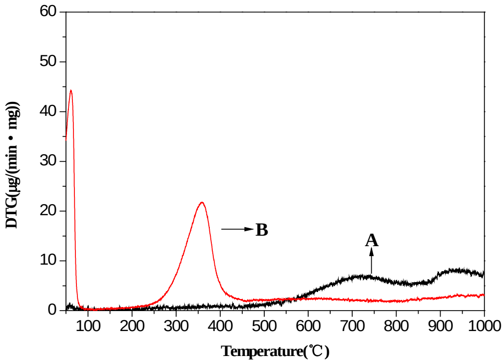



**Figure 5.** The DTG Curves of Graphene and Pre-treated Raw Materials

## 4. Conclusions

In this paper, few-layer Graphene were prepared by a simple low cost modified ball milling method. The Grapheme is less than 5 layers. The Graphene has stable thermal properties under 250°C. The Graphene and its preparation method should have great potential application.

## 5. Acknowledgements

This work was supported by the Key Science Project of Jiangxi Provincial Department of Education (No. GJJ180246).

## 6. References

[1] Geim A K and Novoselov K S 2007 *J. Nat. Mater.* **6**(3):183-91
[2] Sakamoto J, Van H J, Lukin O and Schlüter A D. Two-dimensional polymers: just a dream of synthetic chemists? 2010 *J. Angew Chem Int Ed Engl.* **48**(6):1030-69
[3] Geim A K. Graphene: status and prospects 2009 *J. Science.* **324**(5934):1530-34
[4] Wu J, Pisula W and Müllen K. Graphenes as potential material for electronics 2007 *J. Cheminform.* **38**(26):718
[5] Lu N, He G, Liu J, Liu G, Li J. Combustion Synthesis of Graphene for Water Treatment *2017 J. Ceramics International,* **44** (2017) 2463-2469
[6] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D and Miao F. Superior thermal conductivity of single-layer graphene 2008 *J. Nano Letters.* **8**(3):902
[7] Kuila T , Bose S, Mishra A K, Khanra P , Kim N H and Lee J H. Chemical functionalization of graphene and its applications 2012 *J. Progress in Materials Science.* **57**(7):1061-105
[8] Chen K, Li Y. Progress in preparation methods of graphene 2018 *J. Scientific and technological innovation Information,* (20):1-2
[9] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva V and Firsov A A 2004 *J. Science.* **306**: 666-9
[10] Lerf A, He H and Forster M. Structure of graphite oxide revisited‖ 1998 *J. Journal of Physical Chemistry B.* **102**(23):4477-82
[11] Bepete G, Anglaret E, Ortolani L, Morandi V, Huang K, Pénicaud A and Drummond C, Surfactant-free single-layer graphene in water 2017 *J. Nature Chemistry.* **9**:347-52
[12] Yang Z, Xu S, Zhao L, Zhang J, Wang Z, and Chen X. A new direct growth method of graphene on Si-face of 6H-SiC by synergy of the inner and external carbon sources 2018 *J , Applied Surface Science.* **436**:511-8

[13] Kim K S, Park G H, Fukidome H, Takashi S, Takushi I, Fumio K, Iwao M and Suemitsu M. A table-top formation of bilayer quasi-free-standing epitaxial-graphene on SiC(0001) by microwave annealing in air 2018 *J. Carbon*. **130**:792-98

[14] Voiry D, YangnJ, Kupferberg J, Fullon R, Jeong H Y and Chhowalla M. High-quality graphene via microwave reduction of solution-exfoliated graphene oxide 2016 *J. Science*. **353** :1413-16

[15] Tang Y, Peng P, Wang S, Liu Z, Zu X and Yu Q. Continuous production of graphite nanosheets by bubbling chemical vapor deposition using molten copper 2017 *J. Chemistry of Materials*. **29**(19):8404-11

[16] Komissarov I V, Kovalchuk Nikolai G, Labunov Vladimir A, Girel Ksenia V, Korolik Olga V, and Tivanov Mikhail S. Nitrogen-doped twisted graphene grown on copper by atmospheric pressure CVD from a decane precursor 2017 *J. Beilstein Journal of Nanotechnology*, **2017**(8):145-58

[17] Du M, Zhang G. Progress in preparation and application of graphene 2019 *J. Inorganic Chemicals Industry*, **51**(3):12-5

[18] Ren S, Rong P, Yu Q. Preparations, properties and applications of graphene in functional devices: A concise review *2018 J. Ceramics International*, **44**(11): 11940-55

[19] Gu X, Zhao Y, Sun K, et al. Method of ultrasound-assisted liquid-phase exfoliation to prepare graphene 2019 *J. Ultrasonics Sonochemistry*, **58**:104630