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The growth mechanism of few-layer graphene in the arc discharge process



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ABSTRACT

While few-layered graphene (FG) has been synthesized by several different arc-discharge methods, its growing mechanism has hardly been studied by experiment. Here, we have investigated systematically its growth mechanism using the arc-discharge method under different environments including helium, oxygen-helium and hydrogen-helium. The results indicate that FG can only be produced in the presence of reactive gases, implying that the growing mechanism of few-layered graphene involves graphite evaporation and reactive-gas-confining crystallization of the evaporated carbon clusters. The key factor inducing the discrepancies in FG synthesis under different buffer gases can be assigned to the reactivity of corresponding gases.

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1. Introduction

Graphene is one-atom-thick layer of sp²-bonded carbon atoms arranged in two-dimensional honeycomb lattice and is the basic building block for graphitic carbon material [1], and has attracted worldwide interest because of its outstanding electrical, mechanical and chemical properties [2–9]. Micromechanical cleavage of highly ordered pyrolytic graphite (HOPG) was firstly used to obtain graphene with perfect crystal structure [10]. Chemical exfoliation of flake graphite has been used to prepare graphene oxide, which could be reduced to graphene by heat treatment or chemical reduction [11]. The catalytic chemical vapor deposition method could produce graphene with high crystallinity and large size [12]. Other methods such as solvent thermal reaction [13], epitaxial growth of graphene from SiC [14] and bottom-up synthesis [15] have also been reported. However, these methods suffer from either low-output or laborious preparation work or post-treatment process.

Arc-discharge, which has been used to synthesize carbon nanotube (CNT) [16] and is a facile method with high-output to produce graphene with a few layers [17], may overcome these drawbacks to some extent. It was reported that H_2 could react with

carbon-centered radicals at the growing edge of multi-walled CNT (MWCNT), thus preventing tube ends from enclosing [18–20]. Based on such effect of H₂, Subrahmanyam et al. prepared few-layered graphene (FG) samples with 2–4 layers in the presence of H₂ by direct current arc-discharge [21]. Li et al. synthesized N-doped multi-layered graphene sheets using NH₃ as one of the buffer gas [22]. Wu et al. obtained FG in the mixture of CO₂ and He [17], of which the total pressure was much higher than that in H₂–He or NH₃–He. Some other works based on H₂-inert gases were also reported [23–25].

However, despite many reports for the FG arcing synthesis, the growing mechanism have almost not been studied experimentally [26]. In this work, the growth mechanism of FG using the arcdischarge method under different environments including He, O_2 -He and H_2 -He was investigated systematically. The results indicate that FG can only be produced in the presence of reactive gases, implying that the growing mechanism of FG involves graphite evaporation and reactive-gas-confining crystallization of the evaporated carbon clusters. Also, a new method using O_2 -He arc-discharge for the efficient synthesis of FG was developed. The key factors inducing the discrepancies in FG synthesis under different buffer gases can be assigned to the reactivity of corresponding gases.

2. Experimental

In order to demonstrate the reactive-gas-confining growth





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Fig. 1. TEM images of carbon nano materials synthesized at different buffer gases or under different pressure. (a) carbon nanospheres (CNSs) produced in He at 73 kPa. (b) carbon nanohorns (CNHs) generated in He at 169 kPa. (c) (d) OFG synthesized at 169 kPa with P₀₂ at -9 kPa under 120 A. (e) (f) HFG prepared at 73 kPa with P_{H2} at 37 kPa under 140 A.

mechanism of FG, pure He and reactive gas - He $(O_2$ -He, H₂-He) arc-discharge were carried out. The arc-discharge setup was used as previously reported [27]. Two electrodes were both pure graphite, the diameter of cathode and anode were 35 mm and 10 mm respectively.

He arc-discharge synthesis was conducted at 73 kPa and 169 kPa respectively with currents at 120 A. For O₂—He arc-discharge synthesis, the direct currents ranged from 90 to 150 A were studied, the total pressure of O₂—He was studied from 73 kPa to 169 kPa with the partial pressure of O₂ (P_{O_2}) varied from 0 to 18 kPa. The FG

synthesized in O₂–He was denoted as OFG. As for H₂–He arcdischarge, the direct currents of 140–160 A were examined, the total pressure of H₂–He was fixed at 73 kPa in which the partial pressure of H₂ (P_{H₂}) was studied from 0 to 37 kPa. The H₂–He arcdischarge is an intensely researched system for FG synthesis, thus the total pressure of H₂–He was directly chosen according to literature [21,23,24]. The FG synthesized in H₂–He was denoted as HFG. The operating voltages for all acing process were from 25 to 30 V.

Fig. 2. Raman spectra of as-prepared carbon nano materials that correspond to the TEM samples. (A color version of this figure can be viewed online.)

21.10 °

22

24

26

28

30



20

20(°)

18

16

3. Instruments

Intensity (a.u.)

OFG

HFG

12

14

Morphology and structure analysis of FG sheets was carried out on transmission electron microscope (TEM), JEOL JEM2010FEF with accelerating voltage of 200 kV and FEI Tecnai G2 F20 operated at 200 kV. Raman spectra were recorded with a Renishaw inVia Raman microscope with an excitation wavelength of 514.5 nm. Xray diffraction (XRD) measurements were conducted on Rigaku D/ Max-2500 diffractometer with Cu K α 1 radiation (λ = 1.54046 Å) at 40 kV. X-ray photoelectron spectroscopy (XPS) measurements were taken on a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al K α X-ray source (h ν = 1486.6 eV).

4. Results and discussion

Though FG has been successfully synthesized [17,21,22], the

Fig. 4. Wide-scan XPS spectra of as-prepared OFG and HFG. The relative content of O on the surface of OFG and HFG are 4.9 at.% and 2.9 at.%, respectively. (A color version of this figure can be viewed online.)

synthesis mechanism has not yet been clearly understood. To find the key factors for FG synthesis, we select three types of buffer gas with different chemical and physical properties, which are inert gas (He), oxidative gases (mixture of O_2 and He) and reducing gases (mixture of H₂ and He), to try to obtain FG by arc-discharge method.

We have attempted to synthesize FG in inert buffer gas He under different conditions. However, only compact and/or enclosed carbon materials have been produced. The typical products include carbon nanospheres (CNSs) (Fig. 1(a)) and carbon nanohorns (CNHs) (Fig. 1(b)) [28].

 O_2 —He arc-discharge with different direct currents and under different total pressure with varied P_{O_2} was carried out to synthesize OFG. Direct currents ranged from 110 to 120 A with total pressure higher than 152 kPa and P_{O_2} higher than 9 kPa were recommended for OFG synthesis. OFG with the size of 50–200 nm and thickness of 2–10 layers has been produced (Fig. 1(c,d)). AFM image of OFG is shown in Fig. S6(a).

 H_2 —He as one of the most widely used buffer gas for FG synthesis by arc-discharge is also systematically studied here. Direct currents of 140 A are suggested for HFG production. HFG can be produced at ~73 kPa with P_{H_2} at only ~9 kPa that is lower than the reported value [21], and little amorphous carbon is presented in the produced HFG samples as indicated by TEM results, of which the randomly chosen ones are presented in Fig. S1. Nevertheless, when P_{H_2} is lower than 9 kPa such as ~4 kPa, HFG is also found by TEM results but with large quantity of amorphous carbon. Thus, 73 kPa total pressure with P_{H_2} higher than 9 kPa is recommended for HFG synthesis. Typical TEM images of HFG produced at total pressure of 73 kPa with P_{H_2} at 37 kPa are presented in Fig. 1(e,f), showing HFG sheets with the size of 100–300 nm and about 6 layers in thickness. AFM image of HFG is shown in Fig. S6(b).

Some structure information can also be obtained from the Raman spectra of HFG and OFG. Both HFG and OFG show a single Lorentzian profile of G' peak, which is different from the case of FG obtained by microcleaving HOPG. This may indicate that HFG and OFG do not have an ordered AB stacking structure. On the other hand, if just considering the position and full width at half maximum (FWHM) of the G' band, HFG would be estimated to have less than 5 layers according to position of G' band of HFG at ~2678 cm⁻¹ and FWHM of ~66 cm⁻¹ and intensity ratio of G' to G of ~0.59 [29,30].





The structure of HFG and OFG also differ greatly. Raman spectra of OFG sample show higher intensity ratio of D to G peak (I_D/I_G) than that of HFG (Fig. 2), which means that OFG possesses more defects than HFG does [30-32], since O₂ can not only react with carbon to form oxygen-containing groups but also form CO and CO₂ and leave vacancies. Higher I_D/I_G also means more amorphous carbon in the product, and XRD patterns (Fig. 3) supports this ascription. The more obvious broad peak from 13 to 23° in XRD pattern of OFG compared with that of HFG indicates that there is more amorphous carbon in OFG. The weak peaks from 24.58 to 26.32° corresponding to interlayer spacing from 0.362 to 0.338 nm may be assigned to the structure of intra-FG, which is similar to graphite but with larger spacing span due to the disturbance of buffer gases during FG formation process. One possibility of the spacing span may come from the edge of FG [17,33], which may be oxidized by O_2 or reduced by H_2 into sp³ hybridized state that may make the interlayer spacing larger than graphite. Another may originate from the disordered stacking of graphene in FG as analyzed in Raman spectra of FG showing a single Lorentzian profile of G' peak. HFG show more intense diffraction band in this region may mean that HFG possess higher purity than OFG. Two sharp peaks at 21.10° and 23.42° for OFG may be assigned to an organic molecule consisted of hydrocarbon that was produced simultaneously with OFG, because as the scan rate of XRD slows down (from 8 to $2^{\circ}/\text{min}$) the intensity of these two sharp peaks increase in proportion and, for different OFG samples they are always presented (see Fig. S3). XPS results (Fig. 4) show that the surface O content in OFG (4.9 at%) is much higher than in HFG (2.9 at%).

From the above results and the reported literature [17,21,22], it can be seen that FG can only be produced under the atmosphere that contains reactive molecules including H₂, O₂, CO₂ or NH₃. This means that reactive gas is the key factor for FG formation. It has been generally accepted that the growth process of carbon nano materials in arcing is always composed of two stages, that is the formation of carbon vapor (carbon clusters consisted of several carbon atoms [34]) in the center of the arc and the crystallization and growth of carbon clusters during diffusion from the arc-center to side [35]. Reactive gas can react and form bonds with carbon clusters during FG growth and thus terminate carbon-centered radicals and prevent FG from enclosing. For instance, O2 as oxidizing gas can react with carbon-centered radicals and form oxygen-containing functional groups and impede the formation of closed structure, thus OFG are obtained. H₂ terminates carboncentered radicals by forming carbon-hydrogen bond and yield HFG. Inert buffer gas such as He cannot react with evaporated carbon clusters and does not have the ability to quench carboncentered radicals that are generated by arc, thus carbon-carbon bonds will form among these radicals and a closed and folded structure will be created. Hence, the synthesis mechanism of FG by arcing can be described as first formation of carbon vapor in the center of the arc and followed by reactive-gas-confining crystallization of the evaporated carbon clusters during diffusion from the center to side.

5. Conclusions

We have experimentally investigated the growing mechanism of FG in arcing by usage of three types of buffer gases, inert pure He, oxidative O_2 —He and reductive H_2 —He. It should be noted that one of the key factors for FG production in arcing is the reactivity of corresponding buffer gases, implying that the growing mechanism of FG involves graphite evaporation and reactive-gas-confining crystallization of the evaporated carbon clusters. We believe that this will contribute to the understanding of arc-discharge process and desired carbon materials could be within reach by selecting different buffer gas.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.02.074.

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