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Preparation of few-layer graphene nanosheets by radio-frequency induction thermal plasma

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ABSTRACT

Graphene nanosheets (GNs) are successfully deposited via a radio frequency (RF) induction thermal plasma pyrolysis process using methane as the precursor. Products are characterized by X-ray powder diffractometer (XRD), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and BET measurements. The results illustrate that those few-layer GNs with the number of layer at about 5 and the size at 200–500 nm are deposited. The H_2 atmosphere in the RF induction thermal plasma is the key factor to fabricate the few-layer GNs. The direct conversion of CH_4 to few-layer GNs through RF thermal plasma process suggests that the technique is simple, easy to operate, and is suitable for mass production of few-layer GNs in a continuous and scalable process.

1. Introduction

Graphene possesses many fascinating mechanical, electrical, and thermal properties based on its unique two dimensions structure of monolayer sp^2 hybridized carbon atom arranged in a honeycomb network [1–3]. These properties give rise to various promising potential applications of graphene in composites as photocatalysts [4,5] or ultrasensitive sensors [6], transparent conductive films as next generation roll-up displays or touch screens [7], electrochemical energy storage devices as supercapacitors or electrode materials of lithium-ion batteries [8,9]. Generally, graphene can be prepared by two main kinds of strategies, that is, the so called top-down method and bottom-up method specifically [10,11]. Top-down method involves all the preparation strategies from graphite to graphene through micro mechanical cleavage [12], thermal expansion exfoliation [13], extensive sonication in solvent systems [10], or even unzipping of carbon nanotubes [14]. Whereas, the bottom-up method refers to the growth of graphene from carbon atom by the decomposition of carbonaceous precursors, for example, by the spray pyrolysis of sodium methoxide [15]. The bottom-up method may be more amenable to scale up for graphene synthesis. However, it is difficult to obtain grams scale graphene from these methods.

In the past 30 years, thermal plasmas such as DC or AC arc discharges at atmospheric pressure have been used extensively for pyrolysis and synthesis of chemicals [16–19]. With the features of ultra-high temperature (10^4 K), high reaction ability and the fast quenching rate (10^6 K s^{-1}), thermal plasma is very suitable for the large-scale synthesis of nanomaterials [20,21]. Compared with the arc discharge plasma, the radio frequency (RF) induction thermal plasma is commonly used for the synthesis of high value-added products, for example high purity nanopowders, due to the electrodeless discharge

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and no evaporation of electrodes in the plasma system [22,23]. In recent years, numerous carbon materials such as carbon black [24–27], fullerenes [28,29], and carbon nanotubes [30–34] have been synthesized through the thermal plasma technique. More recently, the synthesis of graphene through thermal plasma technique was focused specially. Matte et al. [35] adopted arc discharge plasma in a mixed atmosphere of H_2/He for the synthesis of graphene nanosheets (GNs). Wu et al. [9] developed a hydrogen arc discharge exfoliation technique for the synthesis of graphene sheets from graphene oxide (GO). Wang et al. [11] realized high yield production of GNs by arc evaporation of a graphite rod in air. Several tens of grams of products were obtained per day. To simply sum-up, these methods belong to the top-down preparation strategy, where the precursors were mainly the graphene oxide obtained through the pre-treatment of graphite, difficult to obtain high purity GNs without oxygen. Moreno-Couranjou et al. [36] has presented a novel approach for the preparation of a broad range of carbon nanoparticles through bottom-up technique by non-thermal plasma. Fewer works were reported on the synthesis of graphene through bottom-up growth mechanisms in a RF thermal plasma system.

Methane, the main composition of natural gas, is the simplest molecule in hydrocarbons. However, the direct conversion of methane is challenging due to its high C–H bond strength (434 kJ/mol), large ionization energy, and low polarizability. Many strategies have been adapted to activate the first C–H bond of CH_4 [37,38]. But these processes often involve multi-step reactions and produce a large amount of CO_2 as by-product. In this work, the RF thermal plasma was used as an ultra-high temperature heat source to activate C–H bond of CH_4 which was converted directly to high-value added GNs.

2. Experimental

The cracking of methane was carried out in a RF induction thermal plasma system similar to that reported in our earlier works [39–41]. The schematic diagram of the experimental apparatus is shown in Fig. 1. The system mainly consists of an RF generator, a plasma torch, a gas delivery system, a precursor feeding system, a quenching chamber, an off-gas exhaust system and an *in situ* optical emission spectroscopy (OES) diagnostic system. The working power of the RF induction thermal plasma system is 10 kW and the excitation frequency is 8–13 MHz.

In a typical experimental procedure, argon is first used to purge the RF induction thermal plasma system to keep the atmosphere inert before generating the thermal plasma. And then the RF induction thermal plasma is turned on using argon as both the plasma working gas and the sheath gas. Argon or hydrogen is used as the carried gas. The thermal plasma is sustained discharged for about 3 min until the thermal plasma discharge reaches a relatively stable state. At this moment methane is mixed with carrier gas and injected perpendicularly into the high temperature zone of the thermal plasma jet. The typical feeding time of pyrolysis process lasts for 15–30 min, and then the thermal plasma jet is quenched. To prevent the pyrolysis products from being oxidized at high temperature collector system after reaction, extra argon supply is necessary till the system is cooled down. The pyrolysis products are deposited and collected on the inner wall of the chamber room. The detailed operation parameters of the RF thermal plasma pyrolysis process are given in Table 1.

OES diagnostic system, introduced in our previous report in detail [40], is used to monitor the pyrolysis process. The phase constituents of the solid products are analyzed by the X-ray powder diffractometer (XRD, D8-Advance, Bruker, Germany) using Cu Kα radiation ($\lambda = 1.54178$ Å) at a fixed power source (40.0 kV, 40.0 mA). Field emission scanning electron microscopy (FESEM, JSM-7401F, JEOL, Japan) is used to characterize the morphologies of the samples. High-resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan, and 120.0 kV) is also used to characterize the morphologies and the microstructures of the samples. To prepare the specimens for TEM, the powders are mixed with absolute alcohol, ultrasonically dispersed for 20 min, and then dropped onto the carbon-coated copper grids. Raman spectrum measurements are carried out at room temperature using 632 nm line of a He–Ne laser as excitation source with a micro Raman spectroscopy (Horibra LABRAM-HR). The N_2 adsorption–desorption isotherms of the samples are measured at 77 K using QuadraSorb Station 1 (Quantachrome, USA) in order to determine the specific surface areas. The specific surface area is calculated from the Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption isotherm.

3. Results and discussion

3.1. *Optical emission spectroscopy*

It is necessary to activate the strong C–H band of CH_4 for direct conversion of methane efficiently. In a thermal plasma system, with the help of ultra-high temperature, methane could be pyrolyzed to active radicals or particles observed by the *in situ* OES diagnostic system. A typical emission spectrum of Ar–H_2–CH_4 plasma at the CH_4 feeding rate of 18×10^{-3} m^3 h^{-1} is shown in Fig. 2. It is similar to other Ar plasma discharge systems that the red/near-infrared spectral region from 690 to 900 nm in OES is dominated clearly by atomic Ar lines due to 4*p*–4*s* transitions [42,43]. However, the intensity of lines in this work is much stronger than the others. It may be due to the ultra-high temperature of the RF induction thermal plasma in the present work. Compared with other non-thermal plasmas, thermal plasma possesses much higher temperature (up to 10^4 K) and much stronger electron energy. Accordingly much more atomic Ar's are excited to the excited state and then the spectra lines are much stronger. As shown in Fig. 2, CH (388.4 nm) and C_2 (516.3 nm), the main radicals of CH_4, are detected in the OES. It was reported that CH_3 radical has longer lifetime in the plasma system, up to several milliseconds [44]. However, we have not observed peaks attributed to CH_2 and CH_3 radicals. It may be due to that CH_3 is not luminescent and thus could not be detected by the OES [45]. CH_2 could not be observed because of the extremely short lifetime and transformation to CH radicals through the route of $CH_2 \rightarrow CH + H$.