



# Arc plasma-assisted hydrogenation of few-layer graphene in methane-hydrogen atmospheres



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## ABSTRACT

Aiming towards high-efficiency hydrogen storage, pristine graphene is usually modified with atomic hydrogen by chemical or physical methods. However, the synthetic procedures of both methods are usually complex and requires specialized equipment. Here, a facile way to produce highly hydrogenated graphene (HG) via DC arc discharge plasma in methane-hydrogen atmosphere is reported. In addition, comparative experiments were also carried out in pure methane and methane-helium systems to probe the effects of chemical nature of buffer gases on the formation of arc nanocarbons. Our studies demonstrate that hydrogen not only leads to a planar growth of carbon radicals, but also plays a crucial role in the conversion from  $sp^2$ - to  $sp^3$ -carbon configuration of graphene lattice in methane-mixed gas discharge. While the addition of helium only facilitates the pyrolysis process of methane and enhances the evaporation efficiency of arc plasma. Based on the experimental results, the growth mechanism of HG in methane-hydrogen arc plasma has been discussed rationally in terms of hydrogen plasma and methane pyrolysis.

## 1. Introduction

Graphane, a novel derivative of graphene, has attracted extensive attention of theoretical and experimental researchers [1]. As a fully hydrogenated analogue of graphene, graphane has a diamond-like structure with purely  $sp^3$  bonding and a hydrogen atom bonded to each carbon atom. Whereas for partially hydrogenated counterparts, hydrogenated graphene (HG) is a general term to address graphene with varying hydrogenation levels. Graphane and HG are predicted to have interesting properties such as chemical storage of hydrogen, ferromagnetism, fluorescence and a tunable band gap [1]. Currently, three main methods have been reported for the preparation of HG, including chemistry reduction reaction (e.g. Birch reduction) [2], exposure to hydrogen plasma [3] and high pressure hydrogenation of graphene or graphene oxide [4]. However, the chemistry-based method requires complex synthetic procedures and skilled chemists and the last two methods need highly specialized equipment which may not be available to all researchers.

The direct-current (DC) arc discharge technique to vaporize graphitic carbon via hot plasma opened a new branch of science and technology of nanocarbons such as fullerene [5], carbon nanotubes (CNTs) [6] and nanohorns [7], and graphene [8,9]. The arc synthesis is

usually performed under gaseous or liquid background, creating arc plasma to evaporate graphitic anode. The evaporated carbon radicals (mainly of carbon atom [C],  $C_2$  and  $C_3$  in plasma zone, whereas  $C_4$ ,  $C_5$ ... in areas distant from the plasma center) coalesce and form various carbon nanostructures depending on the experimental conditions [10]. The central temperature can exceed 4500 K, which thermally anneal the products and remove topological defects, leading to a growth of few-defect arc nanocarbons. Moreover, high temperature is also favorable for the doping of foreign atoms or radicals, such as nitrogen- [11] and fluorine-doped graphene [12]. Generally, DC arc plasma is a facile, versatile and low-cost short cut to material nanosynthesis, especially for nanocarbons. Unfortunately, to our knowledge, there have been few reports on the direct synthesis of HG via this method. Rao et al. once reported their research on the hydrogen storage in few-layer HG and their pristine graphene was fabricated by hydrogen arc discharge, however, the post hydrogenation of graphene was still via Birch reduction [13]. Dong et al. reported their route to directly prepare HG by DC arc discharge in pure hydrogen, but the doped hydrogen atoms is probably located at the sites of edges or defects due to a weak absorption of C-H in FTIR spectra [14]. That is, the simple addition of hydrogen in arcs cannot lead to an effective hydrogenation of graphene sheets.

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For arc nanosynthesis, the chemical nature of buffer gas plays a crucial role in the formation of graphene [15]. According to the understanding on graphene growth and doping in arcs [11,16], HG might be prepared if there is an appropriate gas/gaseous mixture containing high fraction of  $sp^3$  carbon and hydrogen atoms. Reviewing the literature, we noted that methane and methane-mixed atmospheres had been widely used to deposit diamond-like carbon films via chemical vapor deposition (CVD) method assisted by various plasma technologies, such as pulsed-DC discharge plasma [17], radio-frequency plasma [18] and microwave plasma [19]. Thus we supposed that methane molecules may introduce hydrogen atoms into graphene lattice, and the presence of  $sp^3$  carbon may prefer to form diamond-like structure, rather than graphitic structure. In this work, arc nanocarbons were prepared in three groups of atmospheres including pure  $CH_4$ ,  $CH_4$ -reactive gas ( $H_2$ ) and  $CH_4$ -inert gas (He). As expected, the hydrogenation of arc graphene has been validated by the characterizations of transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). It is found that few-layer HG flakes largely exist within the wall-part samples prepared by  $CH_4$ - $H_2$  arc plasma. As for pure  $CH_4$  or  $CH_4$ -He atmospheres, however, the arc nanocarbons are basically amorphous carbon, multi-layer graphene or polyhedral graphite (PG). The comparative studies demonstrate that the additions of hydrogen and helium play different roles in the  $CH_4$ -mixed arcs and the formation of nanocarbons. Moreover, the hydrogenation level of HG could be controlled by  $CH_4$ - $H_2$  pressures. According to the basic theory of arc plasma, including gas decomposition and ionization, as well as nucleation and growth of carbon radicals, a rational mechanism for HG growth has been proposed.

## 2. Experimental

Briefly, a DC arc discharge device was employed to carry out the evaporation of graphite. Commercial pure graphite (99.99%) rods of 6 and 15 mm in diameters were set horizontally as anode and cathode, respectively. Three groups of atmospheres of pure  $CH_4$ ,  $CH_4$ - $H_2$  and  $CH_4$ -He mixtures were filled into the high-vacuum chamber with pressures and ratios as follows: 1) pure  $CH_4$ , total pressures of 25 kPa, 50 kPa and 75 kPa; 2)  $CH_4$ - $H_2$  mixtures, total pressures of 25 kPa (vol. ratio = 1:1), 40 kPa (1:1, 1:3, 3:1), 50 kPa (1:1), 60 kPa (1:1, 1:2, 2:1, 1:5, 5:1), 75 kPa (1:1) and 80 kPa (1:1, 1:3, 3:1, 1:7, 7:1); 3)  $CH_4$ -He mixtures, total pressures of 25 kPa (1:1), 50 kPa (1:1), and 75 kPa (1:1). The direct current was maintained at  $\sim 100$  A and discharge voltage was kept at  $\sim 25$  V by controlling the gap distance between two electrodes. The bright-field imaging was acquired by employing a TEM (JEM-200CX, JEOL) and a HRTEM (JEM-2100, JEOL). The FTIR measurement was performed on a FTIR spectrometer (IRPrestige-21, Shimadzu). FTIR samples were pretreated by vacuum drying, and then compressed into disks by mixing with spectroscopically pure KBr. XPS data was collected from the instrument using monochromatic Al irradiation source (Kratos Axis Ultra DLD). Raman spectra were recorded from 1000 to  $3500\text{ cm}^{-1}$  using  $Ar^+$  laser excitation wavelength of 514.5 nm (HR-800 laser confocal micro-Raman spectrometer, Horiba Jobin Yvon).

## 3. Results and discussion

Fig. 1 exhibits the TEM and HRTEM images of typical arc nanocarbons synthesized in  $CH_4$ - $H_2$  mixture (25 kPa, 1:1), pure  $CH_4$  (25 kPa) and  $CH_4$ -He mixture (25 kPa, 1:1). In  $CH_4$ - $H_2$  mixture, a large number of few-layer graphene-like flakes accompanying with some carbon particles are shown in the wall-part product (Fig. 1(a)), whereas polyhedral graphite (PG) are largely formed within cathode-part product. As shown in Fig. 1(b), the folded edges indicate the interlayer spacing of 0.416 nm for a bi-layer sample, larger than

$d_{(002)} \sim 0.334$  nm for graphite, showing a relaxation of interlayer bonding force. By varying the pressures and ratios of  $CH_4$ - $H_2$  mixtures, we found that low total pressure and higher partial pressure of hydrogen are favorable for the production of graphene-like nanocarbons, while higher partial methane pressure lead to a higher percentage of amorphous carbon phases. In pure  $CH_4$ , the wall-part products are basically amorphous carbon aggregates with micropores as indicated by the arrows in Fig. 1(c). In Fig. 1(d), the amorphous carbon particles with diameters of 30–50 nm consist of small disordered graphenes. For  $CH_4$ -He atmospheres, it is found that the wall-part product at low pressure is complex, including amorphous carbon, small PG particles and multi-layer graphene flakes (Fig. 1(e)). As pressure increase, the fraction of PG particles and graphenes are increasing. Therefore, it can be concluded that hydrogen leads to a selective planar growth of evaporated carbon radicals in  $CH_4$ - $H_2$  arcs. Previous study on CNT growth reveals that the role of hydrogen is to reduce the amount of pentagons which are dispensable in the formation of caps for closing CNTs or fullerene [20]. That is, the presence of hydrogen could terminate the dangling bonds of carbon radicals and results in a 2-dimensional growth.

In Fig. 2, FTIR spectra of wall-part samples synthesized in  $CH_4$ - $H_2$ ,  $CH_4$  and  $CH_4$ -He are compared. The main chemical groups within the materials including C–OH bending vibration ( $\sim 1300$ – $1450\text{ cm}^{-1}$ ), C=C skeletal vibration ( $\sim 1580\text{ cm}^{-1}$ ), C–H stretching vibration ( $\sim 2800$ – $3000\text{ cm}^{-1}$ ), and –OH stretching vibration of water molecules ( $\sim 3000$ – $3700\text{ cm}^{-1}$ ) [13,21]. In addition, some weak absorption is also shown as a set of complex bands between 1000 and  $1300\text{ cm}^{-1}$  arising from multiple C–C or C–O vibrations [22]. In the cases of  $CH_4$ - $H_2$  and pure  $CH_4$ , low pressure is shown to be more preferable for the formation of chemical groups between carbon atoms and other elements or radicals, resulting in strong absorption in their FTIR spectra. In Fig. 2(a), two strong peaks of  $sp^3$  C–H stretching could be further decoupled as  $sp^3$ - $CH_2$  ( $\sim 2855\text{ cm}^{-1}$ ),  $sp^3$ - $CH_3$  ( $\sim 2870\text{ cm}^{-1}$ ) and  $sp^3$ -CH ( $\sim 2920\text{ cm}^{-1}$ ) stretching vibrations coexist within the graphene-like flakes, indicating the high-degree hydrogenation of such graphene flakes [23]. Moreover,  $sp^2$ -carbon configuration of pristine graphene has been transformed into  $sp^3$ -carbon configuration due to a low absorption of C=C skeletal vibration. Additionally, a recent theoretic study demonstrate that the C–H peak appeared at  $2800$ – $2900\text{ cm}^{-1}$  derives from the binding sites of atomic hydrogen with graphene networks, rather than edge sites [24]. The C–H stretching mode in the edge regions could result in a peak at  $3225\text{ cm}^{-1}$ , which may merge with –OH band as a wide-range band from 3000 to  $3700\text{ cm}^{-1}$  in our FTIR spectra. Thus the strong C–H stretching peaks at  $\sim 2800$ – $2900\text{ cm}^{-1}$  in our FTIR spectra is a solid evidence of intraplane hydrogenation of graphene. In Fig. 2(b) and (c), the presence of hydroxyl groups may come from the adsorbed solvent like water molecules in air [25]. In Fig. 2(c), it is noteworthy that an opposite trend that high pressure causes strong absorption is shown in comparison with products synthesized in  $CH_4$ - $H_2$  and  $CH_4$ . This is due to the enhanced effect of inert gas on the molecular excitation, dissociation, and ionization in the plasmas [19]. Such effect is also consistent with the experimental phenomenon of a faster evaporation rate of anode in  $CH_4$ -He in this work.

Fig. 3(a)–(d) exhibit the typical Raman spectra of starting graphite, pristine graphene, cathode-part PG particles and wall-part HG, respectively. Three major peaks are shown as defect-induced D peak ( $\sim 1350\text{ cm}^{-1}$ ), intrinsic vibration peak of G ( $\sim 1580\text{ cm}^{-1}$ ), and 2D peak ( $\sim 2700\text{ cm}^{-1}$ ). The high  $I_D/I_G$  ratio and broader G band of HG indicate the defects induced by hydrogenation and the resulting low-graphitization, which are in a good agreement with the TEM observation and FTIR result, as well as the literature [13,21]. The high D peak relative to G derives from the conversion from –C=C– bonds within graphene plane to out-of-plane C–H bonds, forming a “diamond-like” structure as described in the literature [26]. In contrast, the cathode-part graphite particles exhibit a very low D peak and sharp G peak,

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