The effect of H_2 on the translation of graphene to amorphous carbon by DC arc discharge

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Abstract: Different carbon nanomaterials were prepared in H_2 mixed with Ar by arc discharge method. Naturally crumpled high-purity few-layers graphene with size range of 200~400 nm is prepared under high H_2 concentration. However, carbon nanocages with the diameter of 100~150 nm is synthesized under low H_2 concentration. The diameter of amorphous spherical carbon nanoparticles is found to be about 30~80 nm under Ar atmosphere. The formation mechanism of above different carbon nanomaterials in H_2 mixed with Ar is investigated.

Keywords: Graphene, Hydrogen, Formation mechanism, DC Arc Discharge.

1. Introduction

As we all know, the carbon nanomaterials obtained by arc discharge method is the condensation and growth of carbon vapor consisting of carbon clusters when the anode is evaporated during discharge. Arc current, ambient pressure, the type and ratio of buffer gas, and catalysts are important factors which decides the morphology of carbon nanomaterials. Among them, the type and ratio of buffer gas plays a decisive role in the formation of different products since arc plasma is enhanced by the ionization of buffer gas. Hydrogen and inert atmospheres are the most common buffer atmospheres to synthesize carbon nanomaterials. For example, Subrahmanyam et al [1] prepared few-layers graphene (FLG) with 2~4 layers in the presence of H_2 by DC arc discharge. Qin et al [2] stated that the growth mechanism of high-purity FLGusing the arc discharge method under different environments including He, O_2/He and H_2/He is investigated systematically. Li et al [3] reported a novel method to reduce layer number and structural defects of FLG in He/H_2 arc discharge via rapid cooling treatment. Song et al [4] reported that spherical carbon nanoparticles (SCNs) are synthesized via DC arc discharge in argon atmosphere. Kumar et al [5] demonstrates that FLG, carbon nanotubes (CNTs), and SCNs are synthesized under helium and argon at low pressure. According to the above results, we can conclude: (1) hydrogen facilitates the formation of sheet layers of graphene; (2) inert atmosphere is conducive to the formation of closed structures. However, the mechanism of preparing carbon nanomaterials by arc discharge method in an inert atmosphere mixed with hydrogen is still unclear. Therefore, under the mixed atmosphere of hydrogen and inert gas, the study on the mechanism of preparing carbon nanomaterials by arc discharge method is indispensable.

In this work, we investigate the effect of the different ratio of H_2 to Ar, including 1:0, 2:1,1:1, 1:2, 1:4 and 0:1. According to the morphology of different carbon nanomaterials, the mechanism of preparing carbon nanomaterials by arc discharge method in an inert atmosphere mixed with hydrogen is investigated

2. Experimental

A particular diagram of the DC arc discharge is shown in Fig. 1. A homemade DC arc discharge apparatus, in which two graphite electrodes with purity of 99.999% (Beijing Carbon Plant, China) are installed vertically, is used to prepare nanomaterials. The cathode is a carbon rod with diameter of 10 mm, and the anode is also a carbon rod with same diameter. These two electrodes were placed on the water-cooled holder of a copper pedestal. The graphite cathode with a cone-shape top plane was placed at upper part. The DC arc discharge is generated by applying arc current of 200 A in H_2/Ar atmosphere with different ratios at a total pressure of 70 kPa. These ratios of H_2/Ar include 1:0, 2:1, 1:1, 1:2, 1:4, and 0:1 for synthesis carbon nanomaterials. During the arc discharge, the distance between two electrodes is kept constant at about 2 mm by continuously moving the cathode when it was monitored by oscilloscope.

After evaporating the anode graphite, carbon is deposited onto the inner wall of the reaction chamber to obtain different carbon nanomaterials. The as-obtained powder is collected only in the inner wall of the chamber.

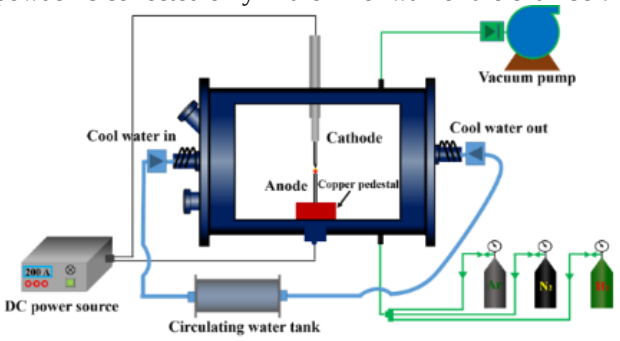

Fig. 1. Schematic diagram of homemade DC arc discharge equipment.

2.1 Characterization

When the discharge ended, the black carbon soot generated from the inner wall of the chamber is collected for analysis without any treatment. The morphologies and microstructures of carbon nanomaterials are characterized using a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) with an accelerating voltage of 200 kV. Raman spectra (Renishaw inVia, Renishaw, UK) are recorded using laser excitation at 514 nm (2.41 eV). The spectra are acquired in the transmission mode in the spectral range of 1000~3000 cm^{-1} at room temperature. Additionally, two different sites are measured for each sample for the accuracy and reliability of Raman spectra data.

3. Results and discussion

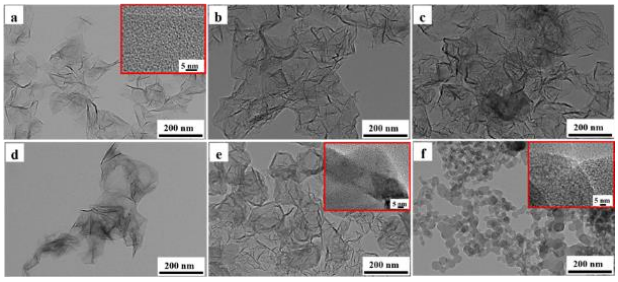

Fig.2. TEM of the carbon nanomaterials prepared in mixing atmosphere of H_2 and Ar with the different ratios of H_2/Ar: (a) 1:0 and insert shows HRTEM image of graphene sheets, (b) 2:1, (c) 1:1, (d) 1:2, (e) 1:4 and insert shows HRTEM image of shell of CNCs, and (f) 0:1 and insert shows HRTEM image of amorphous carbon.

TEM of the carbon nanomaterials prepared in mixing atmosphere of H_2 and Ar with different ratios of 1:0, 2:1,1:1, 1:2, 1:4 and 0:1 can be seen in Fig.2. Three kinds of carbon nanostructures are obviously observed including graphene sheet, carbon nanocages (CNCs), and amorphous SCNs. As shown in Fig. 3(a), the surfaces of the graphene sheets are transparent and have folded layers with wrinkles over the surface and insert image shows graphene sheets with layer numbers of 2~5, which is distinguished by the folded edge. Additionally, the high-purity FLG with size range of 200~400 nm naturally crumpled due to relatively few layers and small size. Fig. 2(b), (c) and (d) also show the graphene sheets gradually become more severely distorted with decreasing the hydrogen content. As shown in Fig. 2(e), plenty of hollow carbon nanocages with a regular circle shape are uniformly distributed. The diameter of carbon nanocages is 100~150 nm. Furthermore, the outer shell is composed of several graphitic layers with tens of nanometers in thickness. The spacing between two neighboring lattice fringes is about 0.34 nm, corresponding to the d_{002} of graphite. As shown in Fig. 3(f), the diameter of SCNs was found to be about 30~80 nm, and these SCNs had amorphous structure. The reason for the above results is that hydrogen inhibited the rolling and closing of graphene sheets by terminating the dangling carbon bonds [3]. However, argon is beneficial to the formation of spherical structures by quenching effect [6].

In Fig.3 (a), the Raman characterization of the specimens show the occurrence of a weak D band at around 1350 cm^{-1}, which is related to the relatively small

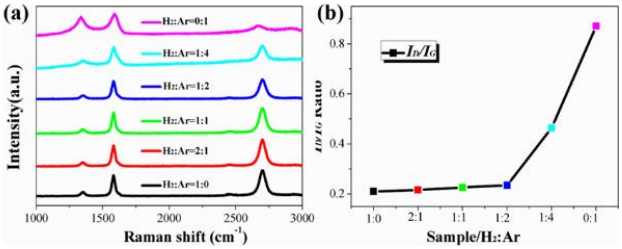

Fig.3. (a) Raman spectra of carbon nanomaterials synthesized at different ratio of H_2/Ar; (b) the relative intensities of the D band to the G band (I_D/I_G) variation with the ratio of H_2/Ar.

amount of defects in sp^2 bonds [7]. The G band at around 1580 cm^{-1} corresponds to the zone centre E_{2g} mode related to phonon vibrations in sp^2 carbon materials. Namely, G peak is related to vibration in the graphene basal planes whose crystalline quality can be assessed by the linewidth of the G band. Normally, the smaller the linewidth of G peak, the higher the crystallinity [8]. The G' band around 2700 cm^{-1} is caused by scattering of phonons with the opposite wave vectors, its shape is sensitive to the number of graphene layer [9]. In addition, the intensity ratio of D band to G band (I_D/I_G) is usually used as a measure of the disorder [10]. As shown in Fig.3 (b), when the ratio of H_2 to Ar is 1:0, 2:1, 1:1 and 1:2, the I_D/I_G value the sample is significantly changed. The results can be explained by the consequence of TEM, the structure of products remain graphene when the ratio of H_2 to Ar is 1:0, 2:1, 1:1, and 1:2. However, the I_D/I_G value of the CNCs is 0.485 under H_2 to Ar with the ratio of 1:4 due to the formation of carbon nanocages [11]. The reason for the I_D/I_G value of SCNs obtained in argon has been explained [6].

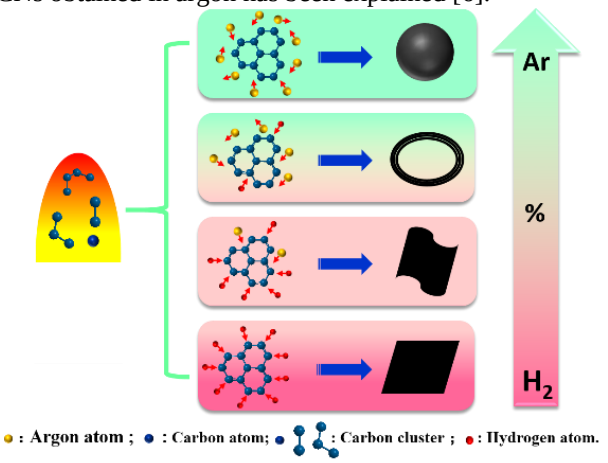

Fig. 4. Schematic illustration of formation mechanism of carbon nanomaterials from inner wall of chamber using different ratio of H_2/Ar by DC arc discharge.

Fig. 4 shows the schematic illustration of the formation mechanism of carbon nanomaterials from the inner wall of chamber using different ratio of H_2/Ar by DC arc discharge method. Anode was evaporated into carbon clusters (C+, C, C_2, C_3, ... C_n). As shown in Fig. 4, the main process of synthesis of carbon nanomaterials under the different ratios of H_2 to Ar could be divided into two stages: (i) formation of precursor; (ii) growth and agglomeration into carbon nanomaterials, such as FLG, CNCs, and amorphous SCNs.

In pure H_2, hydrogen inhibited the rolling and closing of graphene sheets by terminating the dangling carbon bonds. In addition, hydrogen had other function of etching the amorphous carbon [12]. The thermodynamically unstable monolayer graphene sheets were stacking into multiple layers to reduce the energy. Because the arc discharge method had distinct quenching effect, the number of graphene layers obtained was relatively few. However, as the ratio of Ar increasing, graphene sheets gradually wrap owing to just the random combination of the carbon clusters. When the ratio of argon reaches an enough value (the ratio in the paper is 1:4), graphene sheets translate to carbon nanocages, because suitable concentration of hydrogen atom prevents carbon nanocage from forming a two-dimensional structure. Furthermore, carbon precursors combined into amorphous SCNs under Ar atmosphere by quenching effect.

4. Conclusion

In conclusion, the high-purity and 2~5 layers FLG with size range of 200~400 nm resembled naturally crumpled and curly petals is prepared under H_2 to Ar of the ratio of 1:0, 2:1,1:1, 1:2. Although the graphene sheet is gradually distorted as decreasing hydrogen concentration, the graphene structure can still be seen. However, carbon nanocages with the diameter of 100~150 nm is synthesized under H_2 to Ar with the ratio of 1:4. Amorphous SCNs with the diameter of 30~80 nm of are found under Ar atmosphere. According to the above results, the mechanism of carbon nanomaterials in H_2 mixed with Ar is obtained, which refers to hydrogen facilitating the formation of graphene sheet structure, but argon benefiting the formation of spherical structures. Meanwhile, the formation of carbon nanocages is attributed to that suitable concentration of hydrogen atom prevents carbon nanocage from forming a two-dimensional structure.

5. References

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