A layer-by-layer deposition mechanism for producing a pyrolytic carbon coating on

carbon nanotubes

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Abstract:

Pyrolytic carbon (PyC) was deposited on carbon nanotubes (CNTs) in order to modify them by introducing defects to their surface. The deposition of PyC was carried out at temperature between 800 and 1000ºC using propane as carbon source with or without a hydrogen carrier gas at low pressure of 20 kPa. The structure of PyC coatings was examined using transmission electron microscopy. The PyC coating could be distinguished from the original CNT walls due to the difference of the structure, with the coating showing a less orderly layer structure. When H_2 was introduced during deposition, PyC coating started to form at 900ºC, and the deposition rate increased rapidly with increasing temperature. Without H_2, PyC coating with a thickness of a few layers could be formed at temperatures between 800-900ºC in 10 min. The outmost layer of the PyC coating showed a structure of rough and curved carbon fragment. A layer-by-layer mechanism is proposed for the deposition consisting of alternating fragment formation (nucleation) and lateral growth to layer.

1. Introduction

Carbon nanotubes (CNTs) have been attracting extensive researches because they possess many fascinating properties due to their unique nanostructure [1]. CNTs are regarded as ideal nanofillers of polymers in nanocomposites, potentially endowing them with higher mechanical strength as well as electrical conductivity with only small amount addition because CNTs possess high mechanical strength and electrical conductivity with good flexibility and ductility [2-4].

In many applications, CNTs are required to disperse well in solvent or solid media. The inactive graphene surface of CNTs, however, causes a poor dispersion in water or many organic solvents. A good bonding of CNTs with polymer is also necessary to fully exploit their properties in nanocomposites, whereas poor bonding between CNTs and polymer molecules is a main reason why they showed little effect on the properties of the nanocomposites [4].

Although the dispersion could be improved by using amphiphilic molecules [5] that interact with surface of CNTs through their hydrophobic tails or by wrapping with polymer molecules [6], it is more flexible by using chemical modification to functionalize the surface of CNTs through strong oxidation in HNO_3 or H_2SO_4, since further chemical modification on the oxidized CNTs is able to introduce many other functional groups to the CNTs [7-9]. One problem of chemical modification, however, is the introduction of many defects to the CNTs that may degrade their properties.

The edge of graphene is substantially easier to react or functionalize than basal surface. If many defects are induced on the surface of CNTs, chemical modification should be considerably easier. Therefore, a thin pyrolytic carbon (PyC) coating on CNTs should allow facile chemical functionalization. In addition, it is possible for PyC coating to be formed during CVD synthesis of CNTs without significant cost increase to CNTs. However, thick PyC coating on CNTs, which increases the diameter of CNTs and introduces too many defects, may degrade severely the CNTs; therefore, it is necessary to find a way to deposit thin uniform PyC coating with a few atomic layer thick.

On the other hand, chemical vapor deposition of carbon is an important process with many applications, such as the fabrication of highly oriented pyrolytic graphite (HOPG) and isotropic carbon coating, C/C composite materials by infiltration into carbon felt [10, 11], thickening of vapor grown carbon fibers (VGCFs) [12], and preparation of graphenes [13]. The PyCs with a variety of morphology, texture and structure have been obtained, depending on the deposition parameters including deposition temperature, carbon source, types of substrate and even the geometry of reaction chamber. The deposition kinetics and mechanism of pyrolytic carbon have been studied quite extensively by many researchers [14-22]. One of the main mechanisms is the droplet model that polyaromatic hydrocarbon molecules (PAH), which are formed in gas phase, play an important role in the nucleation and growth of PyC. Allouche et al [23-25] reported the deposition of carbon on CNTs, and used the droplet model to

interpret the deposited carbon with various morphology like cones and beads. Pfrang *et al* investigated the carbon nucleation of PyC on planar silicon substrate using atomic force microscopy, but did not describe the details of the nucleation [26]. Smooth deposition of pyrolytic carbon on CNTs was also demonstrated in the preparation of VGCFs [27], implying a different deposition mechanism other than droplet model. Hu and Huttinger examined another model of PyC deposition, which consisted of two different mechanisms: nucleation on the basal plane on graphene and carbon growth at the edge of graphene [28]. They suggested that the two mechanisms could be distinguished at very low supersaturation of gas phase.

Our purpose is to deposit PyC with only a few layers. Apparently, droplet mechanism is not adequate to our purpose because it will lead to very thick coating. Layer-by-layer deposition would be a good choice for our purpose. One advantage by using CNTs as substrate is that it is easy to observe the very initial stage of carbon deposition on CNTs by transmission electron microscopy, in comparison to planar large substrate, as demonstrated by Allouche [23-25]. Therefore, it is possible to examine the details of the nucleation and growth process of PyC on CNTs. In this paper, we report the deposition of PyC on CNTs at low temperature regime and examine the deposition mechanism using TEM.

2. Experimental

2.1 *Synthesis of CNTs*

CNTs were synthesized using Co/MgO catalyst at 700ºC using C_2H_2 as carbon source by CVD method [29]. The as-synthesized CNTs were purified by removing the catalyst particles in 10% HCl aqueous solution. The average diameter of CNTs was about 15 nm, according to the measurement by TEM observation.

2.2 *Deposition of PyC*

The deposition of PyC was carried out in a tubular quartz furnace with inner diameter of 12 mm. The furnace could be heated and cooled rather rapidly, and had a short heating area so that the flight time of gas molecules was short in the furnace. 10 mg CNT powders were loaded in a ceramic boat which was then set in the quartz furnace. The deposition was carried out at low pressure of 20 kPa in order to enhance the diffusion of gases into the CNT aggregates. The two sides of the quartz tube were sealed by glass wool to prevent the CNTs being blown away during suction of vacuum pump. The flow rates of C_3H_8, the carbon source, and argon were set to 20 and 50 ml/min, while the flow rate of H_2 carrier gas was set to 20, 10 or 0 ml/min. The deposition was performed at temperatures from 800ºC to 1000ºC for 10 min.

2.3 *Characterization*

CNTs and PyC coating were observed using transmission electron microscope (TEM, JEOL 2100). The CNTs with PyC coating were dispersed in acetone

ultrasonically. The average diameter of CNTs after PyC deposition was obtained by measuring diameter of 100 CNTs from the TEM images.

3. **Results and discussion**

3.1 *As-synthesized CNT*

CNTs were synthesized using Co/MgO catalyst and purified in dilute HCl aqueous solution to remove the catalyst particles. The purified CNTs still contained about several percent catalyst particles that were wrapped by carbon. Fig.1 shows the TEM image of purified CNTs. The average diameter of CNTs was about 15 nm, obtained by measuring 100 CNTs. It can be seen that the multi-walled nanotubes have almost no amorphous carbon on the surface.
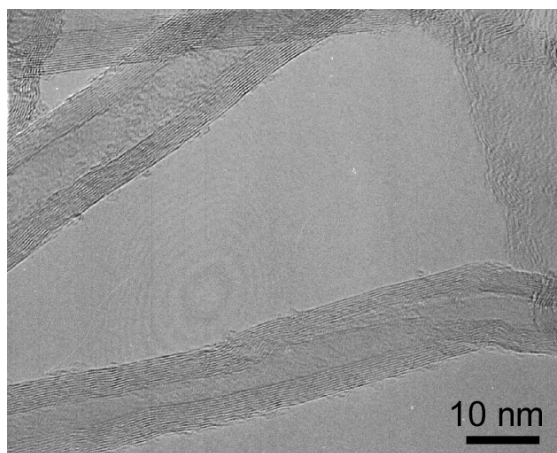

Fig. 1 TEM image of as-synthesized CNTs.

3.2 *Deposition of PyC on CNTs with H_2*

At first, the deposition of pyrolytic carbon was conducted at 800℃, 900℃ and 1000℃, respectively, with flow rates of C_3H_8, H_2 and Ar set to 20, 20 and 50 ml/min. It

was found that no pyrolytic carbon was formed at 800ºC. As shown in Fig. 2, the diameter of CNTs deposited with PyC at 900ºC was larger than that of pristine CNTs, and the CNTs deposited with PyC at 1000ºC became remarkably thicker. It is noted that the surfaces of the CNTs are very smooth, implying a uniform deposition process, which is quite different from that reported by Allouche et al [23-25]. To examine the PyC deposition in detail, the deposition was also carried out at temperatures between 900ºC and 1000ºC.
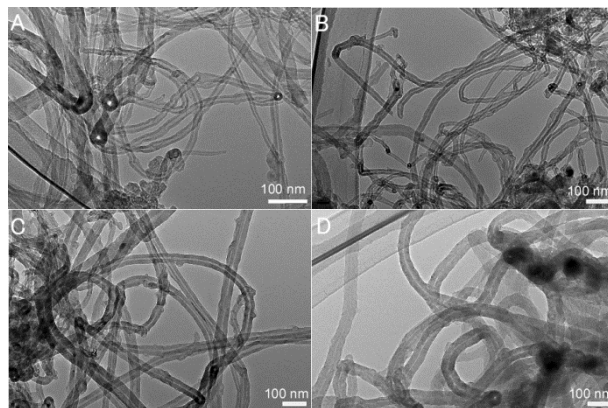

Fig. 2 TEM images of CNTs deposited with pyrolytic carbon at 700 ºC (A), 800 ºC (B), 900 ºC (C) and 1000ºC (D) with 20 ml/min H_2.

Fig. 3 shows the average diameter of CNTs with PyC deposition at different deposition temperature. TEM observation showed that no PyC was deposited on CNTs at 800ºC; therefore, the diameter of CNTs after PyC deposition of 800 ºC was the same as that of original CNTs. The thickness of PyC coating could be calculated by the difference between the average diameters of CNTs with PyC coating and the original CNTs. The thickness of PyC on CNTs with deposition at 900ºC was about 3 nm,

increased very rapidly to about 10 nm for the CNTs at 940ºC. Above 940ºC, the increase

of PyC thickness was slower, probably due to the diffusion rate limitation of gases into

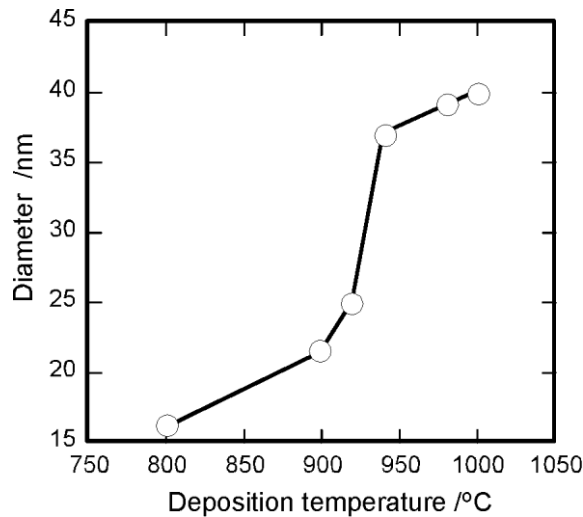the CNTs aggregates as more PyC deposited on the surface of the aggregates.

Fig. 3 The variation of diameter of CNTs with the deposition temperature of pyrolytic
carbon for 10 min with 20 ml/min H_2.

Fig. 4 shows the diameter distribution of CNTs with PyC deposition at 800ºC,

900ºC, 920ºC and 940ºC. Apparently, the diameter distribution of CNTs at 940ºC shows

much broader diameter range than those at lower temperatures. The deposition process

consists of two main steps: the diffusion of gases into the CNT aggregates and the

deposition of PyC on the surface of CNTs. At low temperature, deposition rate is low

and the diffusion rate is relatively fast, uniform coating on different CNTs can be

obtained. At higher temperature, deposition rate is high and the diffusion rate is

relatively slow, the supply of gases is not able to catch up the deposition. As a result,

those CNTs near the surface of the aggregates showed more PyC deposition, whereas

those CNTs in the middle of aggregates showed less PyC deposition, leading to different

PyC thickness. Therefore, the diameter showed broader distribution at high deposition
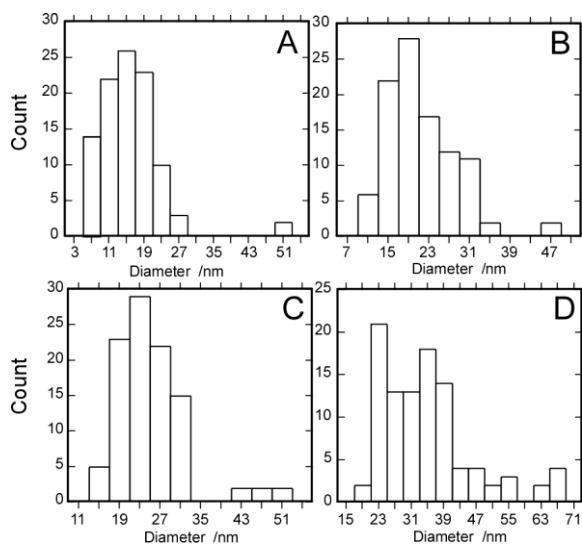
temperature.

Fig. 4 The diameter distribution of CNTs with pyrolytic carbon coating
deposited at different temperature, (A) 800ºC, (B) 900ºC, (C) 920ºC, (D)
940ºC with 20 ml/min H$_2$.

TEM image at Fig. 5 shows the structure of typical CNTs with PyC deposition at

920ºC. The CNTs exhibit double structure: the inner layers have an orderly layer

structure, while the outer layers as marked by white rectangle have less orderly layer

structure, suggesting that the outer layers are due to PyC deposition and inner layers are

the pristine walls of the CNTs. Note that the outermost layer is not continuous, but

consists of curved carbon fragments. This is related to the nucleation and growth

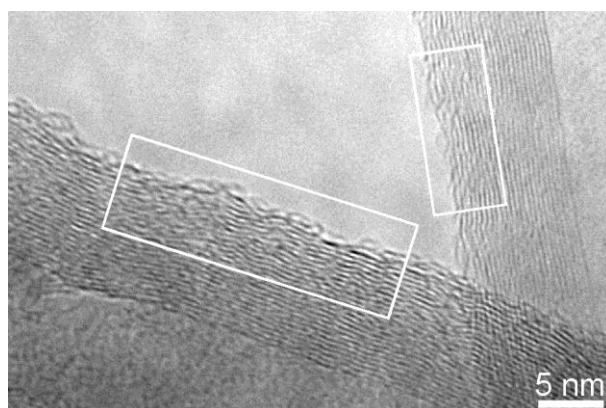mechanism of PyC, and will be discussed in later section.

Fig. 5 TEM image of CNTs with pyrolytic carbon coating deposited at 920ºC with 20 ml/min H_2. The outer pyrolytic carbon layers showed less orderly structure.

When the deposition of PyC was carried with H_2 10 ml/min, no significant difference was found, compared to those obtained with 20 ml/min H_2 in the present experimental conditions. Fig. 6 shows CNTs with PyC deposition at 920ºC. We can clearly see the difference between the outer layers with disorderly structure and the inner layers with orderly structure as in Fig 5. Similarly, the outmost layer was very rough, consisting of discontinuous carbon fragments.
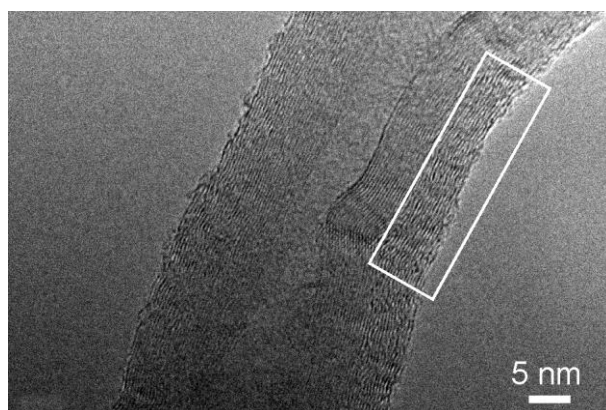

Fig. 6 TEM image of CNTs with pyrolytic carbon coating deposited at 920ºC with 10 ml/min H_2. The outer pyrolytic carbon layers showed less orderly structure.

3.3 *PyC deposition on CNTs without H_2 carrier gas*

Fig. 7 shows the diameter change of CNTs with PyC deposited at different temperatures without H_2 introduced. For detailed examination of mechanism, we also deposited PyC at the temperature between 800 and 900ºC. As mentioned in the previous section, when H_2 was introduced during the deposition of PyC, almost no PyC was obtained on the CNT surface below 900ºC. It is probably because H_2 had inhibited the nucleation of carbon. From Fig. 7, it is known that the thickness increased with deposition temperature. However, the thickness of CNTs at 940ºC was thinner than that in Fig. 3. It is difficult to explain because, in general, H_2 could suppress the formation of carbon. When the deposition rate is high, the outer deposition of CNTs deposited fast, so that the gases consumed at outer part of CNT aggregates, at the same time, it is more difficult for gases to diffuse into the middle of CNT aggregates. In the preparation of sample for TEM observation, there is a tendency to get those easily dispersed CNTs in acetone, that is, thin CNTs. This is probably the reason CNTs at 940ºC showed thin diameter.
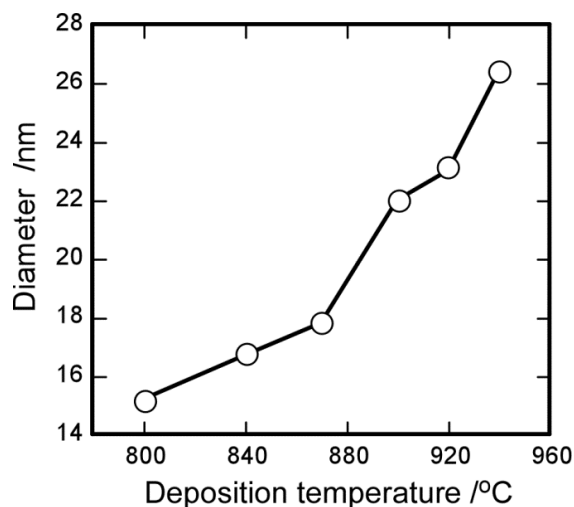
Fig. 7 The variation of diameter of CNTs with the deposition temperature of pyrolytic carbon for 10 min without H_2.

Fig. 8 shows the TEM images of the CNTs with PyC deposition at 800, 840, 870 and 900, 920 and 940°C without H_2, respectively. It can be seen that the samples obtained at 800 and 840°C show rough surface with 1-2 layers curved carbon fragments formed on the surface of the CNTs as shown in Fig. 8A and Fig. 8B. At 870°C, PyC with 2-3 layers were formed on CNTs with less orderly structure as shown in Fig. 8C. In a word, at 870°C or lower temperature, only rough disordered carbon less than 3 layers were obtained. At 900°C, about 8-12 layers of pyrolytic carbon were formed on CNTs, as shown in Fig. 8D. The outer PyC layers had slightly less ordered structure than the original CNT walls, just like those in Fig. 5 and Fig.6. At higher temperature, the PyC showed more orderly structure, similar to carbon nanotubes walls, so it is difficult to distinguish the boundary between original CNT walls and PyC. At 900°C or above, the outmost layer of PyC is still relatively rough and not continuous. In Fig. 8F, it can be

seen that the number of PyC layers was different; this suggests that some layers stopped growing laterally due to the edges of graphenes were blocked by the top layer. From above results, it is known that 1 to 10 layers of PyC could be obtained by deposition at 800 to 900ºC for 10 min. Therefore, it is possible to control the layers of PyC deposition by changing the deposition time and temperature.
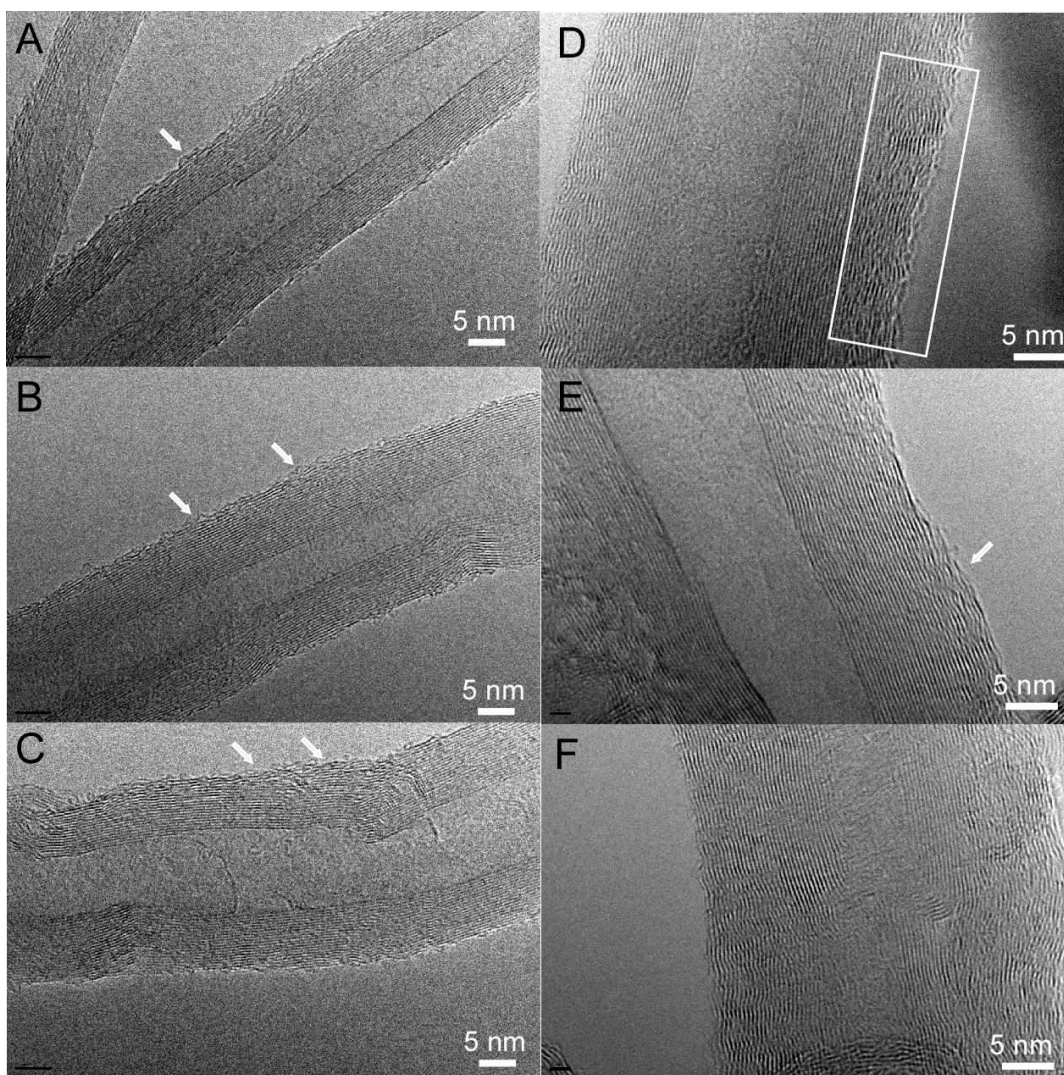

Fig. 8 TEM images of CNTs with pyrolytic carbon coatings deposited at 800ºC (A), 840ºC (B), 870ºC (C), 900ºC (D), 920ºC (E), 940CºC (F) without H_2.

3.4 Discussion

At first, we used CH_4 as carbon source to deposit PyC. However, no PyC was obtained on CNTs up to 1000ºC, although carbon was clearly formed on the alumina boat. This fact suggests it is more difficult to form nuclei on CNTs with a basal graphene surface than alumina surface. Therefore, instead of methane, propane was used as carbon source.

When the flow rate ratio of C_3H_8/H_2 is 20/20 and 20/10, it is difficult to form PyC deposition on CNTs at temperatures below 900 ºC. Without H_2 in the deposition process, carbon even formed on CNTs at temperature as low as 800ºC. It is unlikely for C_3H_8 absorbed directly on the basal plane of CNTs to form carbon nuclei due to weak interaction between C_3H_8 molecule and graphene plane. The reaction of C_3H_8 in gas phase leads to formation of flat polyaromatic hydrocarbon molecules (PAH) that are more easily adsorbed on the basal plane via pi-pi interaction. Increase of H_2 in gas phase inhibits the formation of such PAH molecules so that they are more difficult to form nuclei on the surface of CNTs. Without H_2 in gas phase, PAH molecules are easier to form, and the adsorption of PAH molecules on CNT surface results in the nucleation of carbon fragments on CNTs at low temperature like 800 and 840ºC as shown in Fig. 8A and 8B.

From the results of Fig. 8, it is known that one to 10 layers of PyC can be deposited on CNTs in 10 min. This means that the pyrolytic carbon could be deposited

layer by layer. At temperatures of 800 and 840ºC, only one or two layers amorphous carbon was formed. From the viewpoint of surface modification, the purpose is achieved, for the amorphous structure was easy for further chemical functionalization due to more defects. With increasing deposition temperature, the pyrolytic carbon showed more orderly layer structure with more layers.
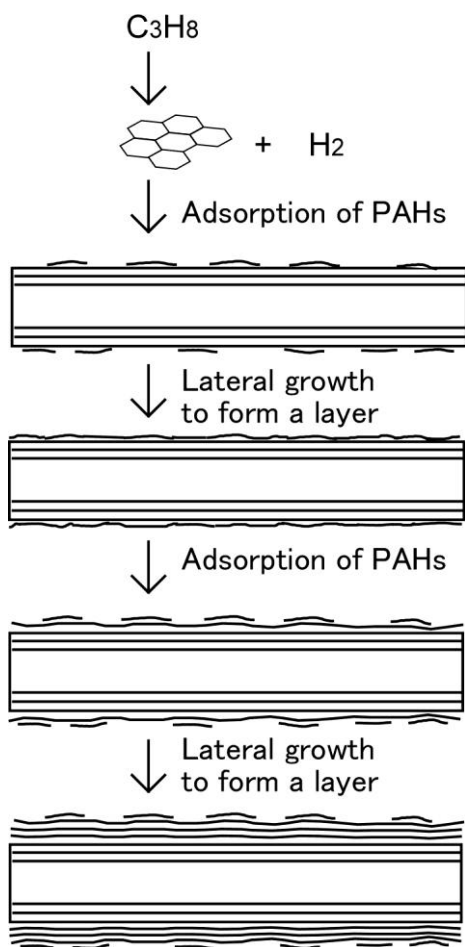

Fig. 9 A layer-by-layer deposition model of pyrolytic carbon on CNT surface.

Although the droplet mechanism is a dominant model to interpret various PyC morphology, texture and structure, it is apparently not applicable to the interpretation of the present results of only a few layers pyrolytic carbon. In the present experiments at

relatively low temperature and low pressure, formation of droplets might not occur in the gas phase before they are blown out due to short residence time.

Hu and Huttinger examined the growth and nucleation mechanism of pyrolytic carbon deposition, and claimed that both mechanisms could be distinguished at low supersaturation [28]. Based on this, a layer-by-layer mechanism is proposed here, as shown in Fig. 9. Since CNTs show only basal plane of graphene on the surface, the interaction between gas molecules and the basal plane is very weak, therefore it is unlikely that propane molecules are directly absorbed on the surface of CNTs to form carbon nuclei. It is more likely that PAH molecules, which are formed in the gas phase, are adsorbed on the surface of CNTs via the pi-pi interaction between PAH and CNT surface. The absorbed PAH molecules on the surface are then changed to carbon fragments, as illustrated in Fig 9. Since the interaction between the basal surface and the carbon fragments is weak, they show a curved morphology. Once these fragments form on the surface, they show much more active sites than original basal surface of CNTs; therefore, the subsequent adsorptions are more likely to occur on the edges of these initial fragments, and the fragments tend to grow laterally rather than grow by stacking layer. In this way, a PyC layer is formed around CNT.

When a layer is formed around the CNT, the pi-pi interaction between the layer and CNT surface makes the layer more orderly, similar to stress graphitization. However, when the continuous layer is not yet formed, they tend to show curved fragments on

surface, which is why the outmost layer shows less orderly structure. After a layer growth is completed, new carbon fragments are formed on the new PyC layer and then laterally grow to a new layer. In this way, PyC is deposited layer by layer.

The layer-by-layer mechanism is applicable to the deposition at the conditions of relatively low temperature regime and low pressure with short residence time in this research, in which the large droplet PAHs are not formed in the reaction zone. This mechanism might be beneficial in understanding the deposition process of a few layers of graphene.

4. Summary

Pyrolytic carbon was deposited on CNTs at the temperatures ranging from 800ºC to 1000ºC using propane as carbon source. The difference between the structure of CNT walls and pyrolytic carbon allowed us to distinguish the pyrolytic carbon layers from pristine CNT walls by TEM observation. In 10 min deposition, one to more than 10 layers of pyrolytic carbon can be deposited, depending on the deposition temperature. A layer-by-layer mechanism of pyrolytic carbon was proposed that the deposition process consisted of carbon fragment deposition of surface, laterally growth to a layer, and further carbon fragment deposition and growth to a new layer.

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