

The role of per-hydroxyl in the multiwall carbon nanotube growth by PECVD

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Multiwall carbon nanotubes were grown by the plasma enhanced chemical vapor deposition (PECVD) method in downstream at the temperature of c.a. 750°C in Si (100) substrate. Besides the precursor of methane for carbon source and hydrogen as the ablation, ammonia/H₂O was inlet into the reactive chamber at the pressure of 0.05MPa. With the characterizations of the tube structure and the measurement by carbon nano-tube (CNT) yield, the role of perhydroxyl in multiwall carbon nanotubes growth is explored. It is found that in addition of a proper amount of H₂O (~0.1%), a high-purity nanotube can be grown in downstream. But no CNT could be synthesized or even the carbon matrix was appeared in excess H₂O condition. The mechanism of the mutliwall CNT growth controlled by active radical per-hydroxyl is assumed in this paper.

assumption.

Introduction

Since the discoveries of carbon nanotubes (CNTs) [1], intense efforts have been carried out into the technology development of large-scale productions such as laser ablation, vacuum arc discharge, thermal pyrolysis of organic compounds, and plasma-enhanced vapor deposition (PECVD) [2-5]. However, these methods for large-scale productions have shown the disadvantages in high investment, running costs or a still relative slow growth rate, which cannot solve the basic problems of industrial scale production. Recently it was found that adding small amount of water into the reactive gas significantly affected the CNT content in the products [6]. Then numerous endeavors to develop novel low-cost processes for synthesizing CNTs have been conducted, such arc in water method [7], chemical vapor deposition method (CVD) [8]. Besides, it was considered that the mechanism of a small water into the reactive gas hinders the decomposition of CH₄ to amorphous carbon on oxides and carbides, which promotes the growth of main CNT products. Atomic oxygen plays a significant role for the yield. However, in our recent result we noticed the per-hydroxyl (OOH) rather than atomic oxygen seems controlling the CNT growth products. In this study numerous experiments was designed to certify this

Experimental

The species generated by plasma show a high activity at low temperature, which will be benefit for CNT deposition at considerably low substrate temperature. Generally, the CNTs were grown in plasma while the substrates were put on the bottom-electrode where substrate was bombarded directly by species such as electron, ion, and radical. In this experiment, the substrate was designed to place in downstream of plasmas, i.e. a grid down electrode was used and species was allowed to pass through the hole and then arrive to the substrate. In here it is well known the long life radicals is the main reactive radicals and shall be responsible to the CNT growth.

In the CNT growth process, methane the carbon source and hydrogen the reductive gas did not change during whole experiments. But the gas ammonia, liquid ammonia, and mixture of nitrogen and water were added alternatively as an etching agent to suppress the deposition of amorphous carbon from the plasma decomposition of methane.

Fig. 1 is the schematic diagram of the experimental setup. It is consist of an alumina plate anchored on the upper electrode as dielectric and generate plasmas in dielectric barrier discharge (DBD) mode. The substrate, normally p-Si wafer

after cleaning in ultrasonically acetone, was mounted below the grounded grit electrode, where the CH₄ and H₂ as well as ammonia were flowed through a channel ring, just under the dielectric alumina plate for realization of uniform discharge.

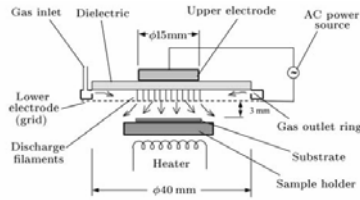


Fig.1 The schematic diagram of DBD plasma setup

A heater was placed under the sample holder to heat the substrate for the CNT growth, and a probe detecting the temperature was just put on the holder surface. The CNT yield was evaluated by the CNT weight. Normalized the weight of CNTs in four levels, best one was in 4 level, the better one in 3, and then to 2, 1 and 0 level was no CNT synthesis.

Results and discussion

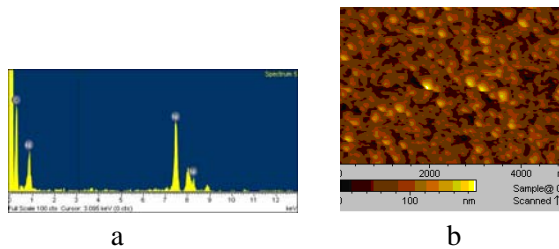


Fig.2 the catalysis of Ni on p-Si substrate (a-XRD pattern of the Ni; b-AFM image of the catalyst surface)

A thickness of 2~5nm Ni layer was evaporated on p-Si surface as catalyst. X-ray diffraction (XRD) shows the catalyst is pure Ni, and atomic force microscopy (AFM) image demonstrates the particles on the substrate are significantly uniform with the diameter of 10nm in Fig.2. Then the CNTs were synthesized on the substrate.

1. CNT deposited in CH₄/ H₂ condition

Firstly a simple schedule was set to grow CNTs in general process. Table 1 is whole contents performed in CNTs growth. From it one is found that at 630⁰C, CH₄ concentration varied from 3.2%

to 25%, the CNTs can be synthesized in the DBD plasma in downstream only in low level.

Table 1 The conditions of CNTs deposition with CH₄/H₂

CH ₄ (%)	CH ₄ /H ₂ (sccm)	Temp (°C)	CNTs level
3.2	10/310	630	1
6.3	20/298	630	2
10	32/288	630	2
15	48/272	630	2
20	64/256	630	2
25	80/240	630	1

2. CNT deposited in CH₄/H₂/NH₃

Table 2 The conditions of CNTs deposition with CH₄/H₂/NH₃

CH ₄ (%)	CH ₄ /H ₂ /NH ₃ (sccm)	NH ₃ (%)	Temp (°C)	CNTs level
15	64/255/0	0	630	2
			750	3
	64/252/3.2	1	630	0
			750	3
	64/246/10	3	630	0
			750	3
	64/240/16	5	750	2
	64/230/26	8	750	0
64/218/38	12	750	0	
64/192/64	20	750	0	

Table 2 shows with adding the etching agent of ammonia it is found the CNTs level is increased obviously at high temperature 750⁰C but not 630⁰C, where without ammonia the CNTs was in 2 level. These results are conflict with previous conclusions that ammonia agent decreased the CNT growth temperature [9, 10] despite Fig.3 TEM images show the CNTs were also grown in bamboo-like structure with a closed end as in previous.

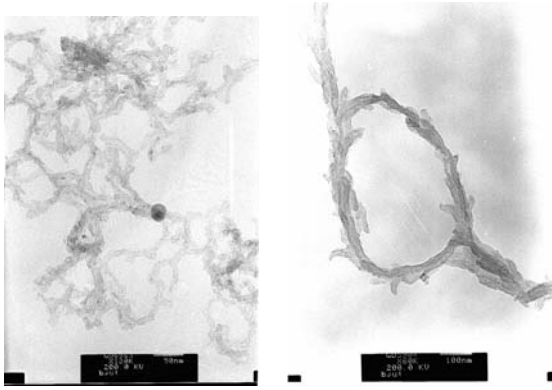


Fig.3 TEM image of CNT in 750⁰C temperature with NH₃ as etching agent

Table 3 The conditions of CNTs deposition with CH₄/ H₂ /NH₃.H₂O

CH ₄ (%)	CH ₄ /H ₂ /liquid ammonia (sccm)	NH ₃ .H ₂ O (%)	Temp (°C)	CNTs level
3.2	10/310/0	0.29	630	0
	10/305/5.0	3.8	630	0
6.4	20/300/0	0.29	630	0
	20/295/5.0	3.8	630	0
10	32/288/0	0.29	630	1
	32/283/5.0	3.8	630	0
15	48/272/0	0.29	630	4
	48/272/0	0.29	750	0
	48/271/0.5	0.63	630	3
	48/271/1.0	1.05	630	2
	48/267/5.0	3.8	630	1
20	64/256/0	0.29	630	4
	64/255/1.0	1.05	630	4
	64/254/2.0	1.7	630	3
	64/253/3.0	2.4	630	2
	64/251/5.0	3.8	630	2
25	80/233/7.0	5.1	630	1

3. CNT deposited in CH₄/H₂/NH₃.H₂O

Now the gas ammonia was replaced by liquid ammonia. From Table 3 and Fig.4 it is noticed that the density CNTs were growth in liquid ammonia

environment even in 630⁰C condition. The TEM images indicate that the CNTs were grown in tip-growth model where the particle Ni catalyst is clearly appeared in the tube tip. Besides that the tubes are smooth with negligible defect on the surface.

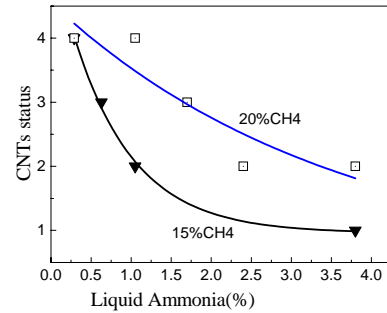


Fig. 4 The growth level of CNTs vs the liquid ammonia concentration

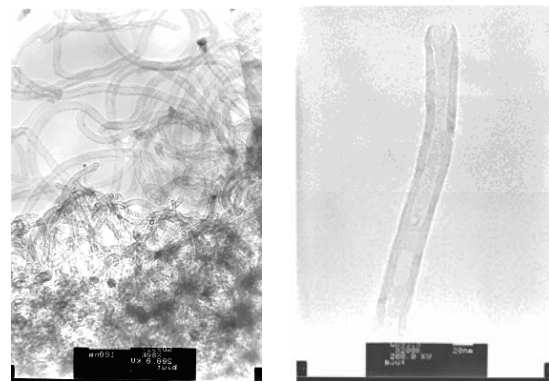


Fig.5 the TEM of carbon nanotube growth with liquid ammonia as etching agent

3. CNT deposited in CH₄/H₂/N₂/H₂O

In this section the mixture of N₂ and water was used as etching agent, where water was inlet into the chamber through carrier H₂ gas, and controllable with the H₂ flowing rate. Fig.6 shows the CNTs in a low water concentration, like 2~4 thousandth, can be fabricated in a high level. Moreover, in this case the CNTs were not grown in bamboo-like structure, instead, it was grown in hollow tube as Fig.7 shows despite its growth mechanism is still following tip-growth model, and the surface was also demonstrates a smooth one. Extending concentration of water in the reactive

gases the etching seemed to determine the whole reaction, CNTs growth rate was decreased.

Table 4 The conditions of CNTs deposition with CH₄/H₂/N₂/H₂O

CH ₄ (%)	CH ₄ /H ₂ /N ₂ (sccm)	N ₂ (%)	carried H ₂ O by H ₂ (sccm)	Temp (°C)	CNTs level
15	64/241/10/5	3	5.0	630	4
	64/220/26/10	8	10	630	0
	64/225/26/5	8	5.0	630	1
	64/228/26/2	8	2.0	630	2
	64/229/26/1	8	10.	630	3
20	64/241/10/5	3	5.0	630	4
	64/254/10/2	3	2.0	630	4
	64/255/10/1	3	1.0	630	4

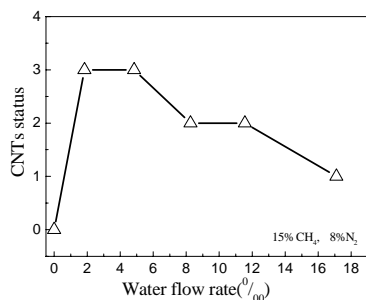


Fig.6 The growth status of CNTs with the H₂O concentration

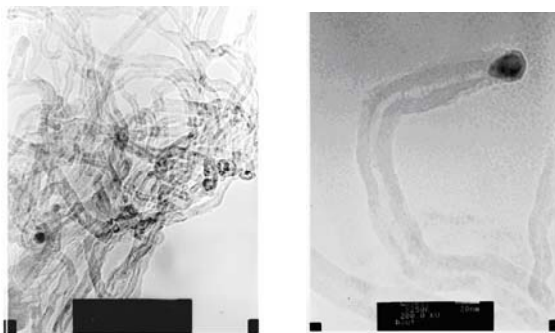


Fig. 7 the TEM of carbon nanotube growth with water as etching agent

Conclusion

In this paper we present the results that with water added in the reactive environment the CNTs showed a remarkable growth rate which seems the

perhydroxyl not atomic oxygen play an important role to promote the CNTs synthesis. The results also demonstrate that water as etching agent can form a new mechanism for CNT growth from bamboo-like to hollow-tube in ammonia condition even the identical tip-growth model still was same.

Acknowledge

This work is supported by National Natural science Foundation of China (No.10475010), PHR (IHLB), Beijing Municipality returned oversee key funds.

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