Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 89 (2004) 233–236

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of catalysis on coal to nanotube in thermal plasma

Y.J. Tian [a,*], Y.L. Zhang [b], Q. Yü [a], X.Z. Wang [a], Z. Hu [a], Y.F. Zhang [c], K.C. Xie [c]

[a] Laboratory of Mesoscopic Materials Chemistry, Nanjing University, Nanjing 210093, PR China
[b] Department of Applied Chemistry, Nanjing University of Chemical Technology, Nanjing 210009, PR China
[c] Key Lab of Coal Science and Technology, Taiyuan University of Technology, Taiyuan 030024, PR China

Abstract

Arc/graphite, laser ablation and CVD are three main methods for the production of carbon nanotubes (CNTs). A free coal-based or graphite electrodes method was explored in our lab. In this method, coal powder was directly injected into arc plasma jet instead of arc evaporation of coal-based electrodes, so we called it coal/arc-jet process. It is found that the Cu nano-particles sputtered from copper electrodes played an important role of catalyst for the synthesis of CNTs. Three metal particles (Fe, Co, Cu) with grain size of 120 mesh were mixed into coal powder and injected into plasma jet, respectively. It is found that the yield of CNTs was improved evidently. The difference of their effectiveness of catalysis was discussed. Under the condition of thermal plasma jet with initial temperature of 3700 K, coal was cracked into aromatic fragments, carbon free radicals and light hydrocarbons. Meanwhile, metallic particles were vaporized and then condense to nano-droplet that was the active site for CNTs growth. The generation of carbon precursor and "preparation" of metallic nano-particles was finished within one stage.

Keywords: Carbon nanotubes; Coal; Plasma jet; Catalysis

1. Introduction

The research on carbon nanotubes (CNTs) has been carried out widely in the world since it was discovered in 1991 [1]. Many preparation methods have been developed such as arc/graphite [1,2], CVD [3], and laser technique, etc. [4]. The synthesis of C_{60} and C_{70} from coal was reported in 1991 by Pang et al. The yield as high as 8.6 wt.% was achieved by them using arc discharge method [5]. They group was also the first to identify and then prepare fullerenes and CNTs from a molecular solid, namely coal, rather than graphite which is, relative to coal, an expensive lattice solid [6]. In their research, preparation of coal-based electrode is an important and complex step. A coal/arc-jet method was introduced in this paper. In this process, coal was directly injected into plasma jet, and then the CNTs were rapidly synthesized in plasma reactor. Some coal-based methods reported are similar with the technique of arc/graphite [7–9], but they are different from ours. In our experiments, coal power was injected into arc plasma jet instead of arc evaporation of graphite or coal-based electrodes. Due to the arc was generated by plasmatron separately and litter of electrodes was consumed. Therefore, the process could run steadily for long time. Above all, this process has the advantages of easy operation, stable running and low cost of raw material.

2. Experimental

The experimental equipment is mainly consisted of arc plasmatron, injector, reactor and accumulator as shown in Fig. 1. The plasmatron generates plasma jet, and the feedstock is injected into jet by the injector, and then reactions take place in reactor. Mixture gas of argon and hydrogen is the working gas of arc generator, their flow rate are 2.2 and 5.2 m^3/h, respectively. The arc is ignited between anode and cathode both of them is made of copper and is cooled by water. When working gas is across the arc, it is rapidly heated to high temperature, then forming a plasma jet in which lots of active species is contained. The effective power of plasmatron is 25.2 kW. Coal is injected into jet through an injection tube with diameter of 3–5 mm, the diameter of reactor tube is 20 mm, and length is 350 mm. Argon with the flow rate of 1.7 m^3/h is employed as carry

* Corresponding author. Present address: College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China.
E-mail address: tianyajun@nju.edu.cn (Y.J. Tian).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.11.032

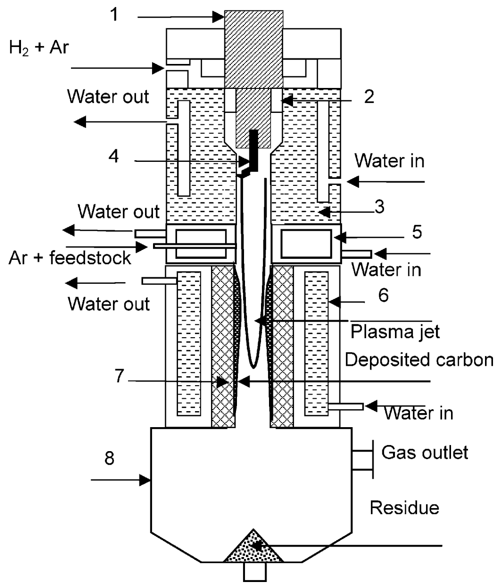

Fig. 1. Sketch of experimental equipment: (1) cathode; (2) insulation; (3) anode; (4) arc; (5) injector; (6) reactor; (7) reactor wall; (8) accumulator.

Table 1
Chemical components of coal used in this work

Proximate analysis (wt.%)				Ultimate analysis (wt.%)			
M_{ad}	A_d	V_{ad}	C_{daf}	H_{daf}	N_{daf}	S_{daf}	O_{daf} [a]
4.43	3.29	40.35	75.82	5.36	1.86	0.74	16.22
Ash subcomponent (wt.%)							
Fe_2O_3	Al_2O_3	CaO	MgO	SiO_2	TiO_2	Na_2O	K_2O
16.74	24.63	2.87	0.77	51.67	0.88	0.97	1.02

[a] O content is by difference.

gas. The feeding rate of coal ranges from 0.5 to 4.0 g/s. The gaseous products mainly consist of C_2H_2 and CO. Partial solid products is deposited on reactor wall, the rest collected in accumulator is the reaction residue. Baode coal with diameter of 5–25 μm is used as raw material. Its proximate analysis, ultimate analysis and ash subcomponent are shown in Table 1. The products are characterized by transmission electron microscopy (TEM, JEOL-JEM-1005, 100 kV) and high-resolution TEM (HRTEM, TEM-4000FXII, 400 kV).

3. Results and discussion

3.1. Parent coal as feedstock

At first, parent coal was used as feedstock. The hard carbon deposited on the upside of reactor wall was selected as sample to be observed by TEM. Fig. 2 illustrates a typical micrograph of the deposited carbon. Clearly, CNTs with diameter about 50–70 nm was found within deposited carbon, the HRTEM inset indicated this kind of tube was well-graphited multi-wall CNTs (MWNT). It is also noticed

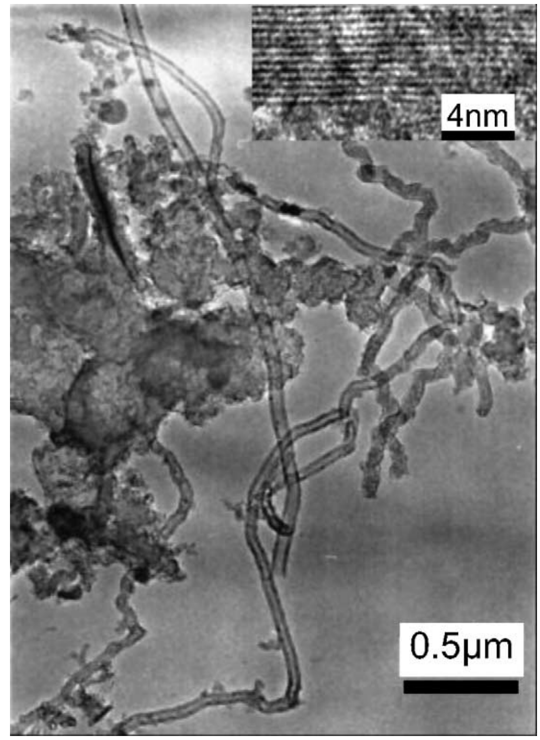

Fig. 2. TEM image of CNTs in the deposited carbon on reactor wall, the inset demonstrates that the product is well-graphited multi-wall CNTs.

that some particles were wrapped within tubes, and the tube diameter was equal to the diameter of particles. Analyzing with EDS, it is shown in Fig. 3 that the components of particle are Cu and Si, sometimes Al was also detected [10]. It is inferred that this kind of alloy particles played the function of catalysis, although catalyst was not necessary for the formation of MWNT [1]. It is needed to point that no anything had been added into coal in our experiments in advance, where did the alloy catalysts come from? In fact, mineral is an essential composition of coal in nature as shown in Table 1. In thermal hydrogen-enriched plasma jet, they might be reduced into simple substance, so Si and Al should come from parent coal. Additionally, considering

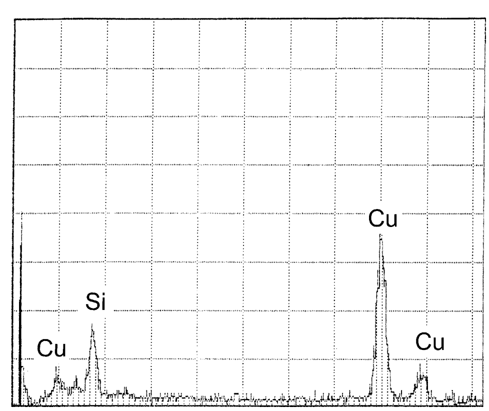

Fig. 3. EDS of the particle wrapped in CNTs found in deposited carbon.

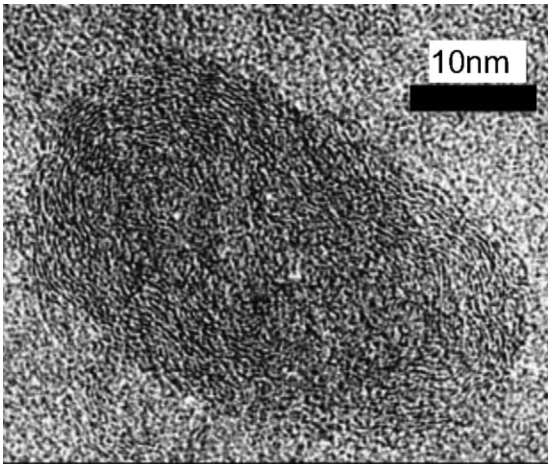

Fig. 4. Onion fullerene that is observed within reaction residue.

the electrodes are made of copper, when the arc was ignited, sputtering electrodes would generate Cu nano-particles that mixed with coal as coal was injected. In a word, many alloy particles were found within CNTs, they probably played key role of catalyst in the formation of CNTs. The main component of alloy was Cu, we believed that it was the Cu that acted as catalyst.

If large quantity of CNTs could be found in reaction residue, the process might become promising. Unfortunately, no CNT was observed by HRTEM in reaction residue. However, treated by high temperature great change of coal structure occurred, because onion fullerene (Fig. 4) and amorphous carbon nanoball with diameter about 20 nm (Fig. 5) were found in the residue.

3.2. Effect of catalyst

Enlightened by the experimental results with coal, we selected Fe, Co, Cu as catalysts to mix with coal (mass ratio was 1:20). The grain of the metal particle was about 120 mesh. After mixture, they were injected into plasma jet together.

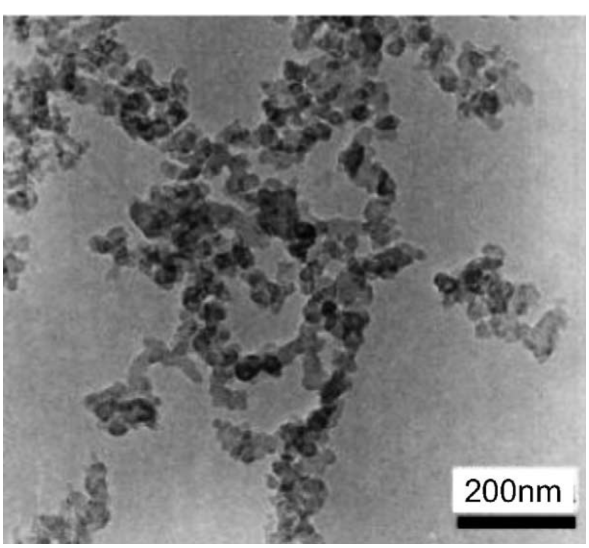

Fig. 5. Carbon nanoball with diameter about 20 nm observed within reaction residue.

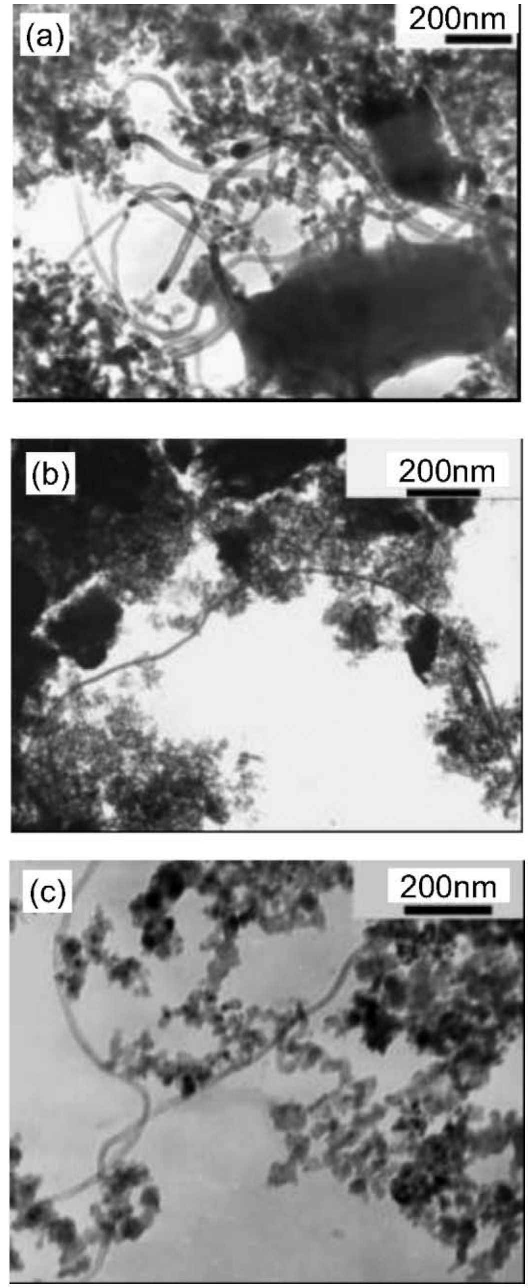

Fig. 6. TEM images of CNTs within reaction residue using (a) Cu particle, (b) Co particle and (c) Fe particle as catalyst. When Cu catalyst is used, many metal particles are wrapped in the tip of a tube. The yield with Cu as catalyst is higher than that with Co and Fe as catalyst.

It was excited that abundant CNTs were found not only within the deposited carbon on reactor wall but also within the reaction residue as shown in Fig. 6. It is estimated by TEM observation that the yield was about 5% with Cu as catalyst and about 1% with Fe or Co catalyst. Although there was not an accurate figure to determine how much the yield was increased, clearly, the yield was improved evidently. It is shown in Fig. 6(a) that catalyst particles were affixed at one end of CNTs, which confirmed that it was the catalyst that improved the yield of CNTs. Generally, Fe and Co had higher activity than Cu [11]. However, in our experimental results, it is found their catalysis activity were different from that reported by the previous publications. The TEM results indicated catalyst of Cu was more active than Co and Fe is shown in Fig. 6(b) and (c), respectively. Two factors probably caused the strange results. Firstly, when coal was pyrolyzed in hot plasma jet, C_2H_2 was one of main product gas [12]. For the structure of copper's outer-shell electron is $3d^{10}4s^1$, it is very easy for Cu to replace the H of C_2H_2. When a C_2H_2 was adsorbed on copper particle's surface, two hydrogen atoms were removed by substitution reaction, and then formed C_2 dimers that might be used as units to build up CNTs [13]. Moreover, the initial temperature of plasma jet was about 3700 K, the boiling points of Cu, Co and Fe were 2840, 3200 and 3134 K, respectively. They should be ideally gasified in plasma jet, and then condensed to nano-metal droplets when temperature decreased. According to VLS mechanism [14], these droplets were the active sites for the CNTs growth. Considering the melting point of Cu, Co, Fe were 1358, 1768 and 1809 K, therefore the lifetime of Cu nano-droplet was the longest, so using Cu as catalyst was more effective than Co and Fe under the condition of H_2/Ar plasma jet.

4. Conclusions

In this coal/arc-jet process, no graphite or coal-based electrodes were employed, and the injector was installed downstream arc generator, the formed jet rushed across its central channel into reactor. Through injection coal can be fed successively into plasma jet and hence this process can successively run for long time. We have speculated the catalysis of metal particles for the synthesis of CNTs by the experiment with parent coal as raw material, and then this speculation was further confirmed by the experiments with mixture of metal particles and coal. Actually, as the mixture of coal and metal powder was injected into plasma jet, metal particles were gasified and then condensed to nano-droplet. According to the VLS mechanism, the nano-droplet was the ideal catalyst for CNTs synthesis once carbon source reaches its surface, simultaneously, within plasma jet coal was pyrolyzed rapidly aromatic fragment, carbon free radical and light hydrocarbons such as CH_4 and C_2H_2. All of these species were the ideal precursor for CNTs. Above all, the preparation of catalyst and the synthesis of CNTs was achieved in one stage in this coal/arc-jet process.

Acknowledgements

We acknowledge financial support by National Natural Science Foundation of China (No. 19935010).

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] T.W. Ebbesen, P.M. Ajayan, Nature 358 (1992) 220–222.
[3] W.Z. Li, S.S. Xie, L.X. Oian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 74 (1996) 1701–1703.
[4] T. Guo, D. Nikolaev, A.D. Rinzler, D. Tomanek, D.T. Colbert, R.E. Smalley, J. Chem. Phys. 99 (1995) 10694.
[5] L.S.K. Pang, A.M. Vassallo, M.A. Wilson, Nature 352 (1991) 480.
[6] M.A. Wilson, H.K. Patney, J. Kalman, Fuel 81 (2002) 5–14.
[7] L.S.K. Pang, M.A. Wilson, Energy Fuels 7 (1993) 436.
[8] K.A. Williams, T. Tachibana, J.L. Allen, et al., Chem. Phys. Lett. 310 (1999) 31–37.
[9] J.S. Qiu, Y. Zhou, L.N. Wang, S.C. Tsang, Carbon 36 (1998) 465–467.
[10] Y.J. Tian, K.C. Xie, Chem. J. Chin. Univ. 22 (2001) 1456–1458.
[11] V. Ivanov, J.B. Nagy, Ph. Lambin, A. Lucas, X.B. Zhang, X.F. Zhang, D. Bernaerts, G. Van Tendeloo, et al., Chem. Phys. Lett. 223 (1994) 329–335.
[12] Y.J. Tian, K.C. Xie, S.Y. Zhu, T.H. Fletcher, Energy Fuels 15 (6) (2001) 1354–1358.
[13] R. Saoti, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Mater. Sci. Eng. B 19 (1993) 185.
[14] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett. 4 (1964) 89.