PRODUCTION OF CARBON NANOTUBES FROM COAL IN HIGH YIELDS

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Introduction

The 1985 discovery of the third form of ordered carbon, commonly known as the fullerenes[1], spurred the subsequent discovery of a number of carbon materials. The most famous among these carbons are the nanotubes[2]. These discoveries opened the door to an avalanche of research across the world on fullerenes and related structures. This is chiefly driven by the fact that these novel carbon materials with unique geometrical structure, stable mechanical and chemical properties, could be of potential use in many fields such as rechargeable batteries, superconductors, catalysts, chemical reagents, hydrogen storage medium and composite materials[3].

Graphite has normally been used to synthesise fullerenes and nanotubes. However, coal is one of the cheapest natural resources of carbon, with confirmed reserves of 1001.9 billion tons and an annual production capacity of about 1.4 billion tons in China, and it may be a cheaper and more suitable industrial starting material for production of these novel carbons. It has been reported that unusually high concentration of natural fullerenes (C_{60}/C_{70}) in some Chinese coals has been confirmed[4]. Over the past six to eight years we have been investigating the features and feasibility of producing fullerenes and carbon nanomaterials from Chinese coals varying from brown coals to anthracites[5-8]. Previous research has shown that plasma arcing of coal has other chemical and process advantages over high purity graphite. Here we report the production of carbon nanotubes from eleven bituminous coals with an aim of establishing the cost effective and optimum process parameters for the production of carbon nanotubes from coals.

Experimental

Materials

Ten Chinese bituminous coals were used for this study. In addition, for comparison, one caking coal from New Zealand was also used. The proximate analysis and petrographic analysis of coal samples are shown in Table 1. It can be seen clearly that for Chinese coals used, the volatile matter content varies from 17.3% to 40.86% (on a dry basis) with ash content being in a narrow range of 7.19% to 10.92%. The New Zealand coal with low ash content and high vitrinite content is superb in quality in comparison to Chinese coals. Coals were mixed with phenolic resin (PR) and finely ground moderate coal-derived bitumen with a melting point of 88.9^{o}C as the binder. Details of the bitumen can be found elsewhere [7].

Carbon Rod Preparation

In this work the arc plasma vaporisation method was adopted. The coal samples were pre-treated in such a way that they were converted into rods that are self-supporting and electrically conductive. The crushed coal samples were mixed directly with the bitumen and PR binder, both in a ratio of 10wt%, and subsequently pressed into a stainless steel tube to form rods with a diameter of 8 mm. The coal rod was put into an electric furnace and heated to 500^{o}C for 5 hr under N_2 atmosphere to obtain rod-shaped semi-char. Further carbonisation of the semi-char at 900^{o}C for 5hr in N_2 resulted in the carbon electrode.

Production of Carbon Nanotubes

The carbon electrodes obtained from coals were subjected to vaporisation under arc plasma conditions in Helium atmosphere in a stainless steel chamber[5,7]. The chamber was evacuated and purged four times, first with high purity nitrogen twice then with helium, before being finally filled with helium gas. A DC arc welder capable of delivering 800 A at 80 V was used to supply the power for the experiments. High purity graphite was used as the cathode and the coal-derived coke rod to be vaporised made the anode. The weight of the graphite electrode remained the same before and after the arcing experiments. After completion of reaction, the reactor was opened and the deposit on the cathode was removed,

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and the inner soft core was examined using SEM and HRTEM.

Results and discussion

Preparation of carbon nanotubes (CNT) begins with the arcing of coal-derived carbon electrodes in helium atmosphere. In order to evaluate the suitability of producing CNTs from different coals, the preparation experiments were carried out under the following optimised conditions: the plasma arc current is 100 A with a voltage of 36V, the inter-electrode spacing is 2-6 mm, and the buffer gas pressure is 0.033-0.10MPa.

The SEM and HRTEM studies reveal that nanotubes are an important component of the products from arcing coals. The nanotubes compose most of the inner soft core in the cathode pencil-like deposits though the quantities of nanotubes vary widely depending on the coal samples used in the experiments. For the deposits prepared from Xiangyuan coal and New Zealand coal, there seems to be about the same proportion of nanotubes from high purity graphite. Figure 1 shows three typical SEM photographs of the carbon nanomaterials obtained from Xiangyuan coal and New Zealand coal, respectively. The HRTEM images of these fluffy cotton-like (Figure 1a) or rod-like nanomaterials (Figure 1b and 1c) show that they are multi-walled carbon nanotubes with diameters in a range of 2nm to 15nm and with length from 5μm to 60μm. The nanotubes have a number of graphitic layers, and up to 26 layers have been observed in our experiments. Several novel carbon nanomaterials such as butterfly wing-like nanotubes and fully filled multiwalled nanotubes are also observed.

The yields of carbon nanotubes(CNT) obtained from different coals are shown in Figure 2. For comparison, the yield of CNTs from high purity graphite (H.G.) is also shown. It can be seen that the CNT yields from different coals vary in a wide range from 23.5% to 62.2%. Among the eleven coals tested, the lowest CNT yield was obtained from Tonghua coal, which is only 23.5%. The New Zealand coal gives the highest CNT yield among all coal samples, that is 62.2%, with the CNT yield from Xiangyuan coal being the second highest, that is 60.4%. While under similar experimental conditions the CNT yield from high purity graphite is only 58.4%. This means that the CNT yields from some good caking coals are comparable to that obtained from high purity graphite. This leads us to believe that with the present cost of Chinese coals of ca $5-35 per tonne, its use for carbon nanotubes production should be economically more attractive.

In addition to carbon nanotubes, significant quantities of fullerenes including C_{60}, C_{70} and higher fullerenes such as C_{104}, C_{106}, and C_{108}, which are present in the soot deposited on the inner surface of the arc plasma reactor, were also obtained. The ratio of C_{60}, C_{70} and C_{104} in the crude fullerene sample is estimated to be about 100:26:6. These results are also presented in this conference.

The CNT yield from different coals are plotted against coal properties including fixed carbon content (FC_{daf}) and volatile matter content (V_d) as well as ash content (A_d) which are the indicative of the coal rank and mineral matter in coals, respectively. The variation of CNT yield from coals is also discussed in terms of the maceral composition in coal. It has been found that that the CNT yield increases as the fixed carbon content in coal increases or as the volatile matter content decreases. In other words, higher fixed carbon content or lower volatile matter content in the starting materials (coals) means that more carbon ion species in the plasma zone are available for nanotube formation. The presence of mineral matter (ash content, A_d) in the coal results in a reduced yield of nanotube, which implies that removing the mineral matter will help to further increase the nanotube yield. The CNT yield passes through a minimum value as the semi-vitrinite content in coal increases, but varies in a C shape curve with the vitrinite content in coal.

Conclusions

Carbon nanotubes with yields between 23.5-62.2% have been synthesized from eleven bituminous coals. The yields from three good caking coals are comparable to that obtained using graphite under similar experimental conditions. The morphology and purity of the products were examined using SEM and TEM. The purity of carbon nanotubes from Xiangyuan coal is very high with about 75% of that being multiwalled nanotubes. Several novel carbon nanomaterials such as butterfly wing-like carbon nanotubes and fully filled multiwalled carbon nanotubes are obtained. The yields of carbon nanotubes are closely related to coal properties such as fixed carbon and ash content, vitrinite and semi-vitrinite content. With the present cost of Chinese coals of about $15-35 per tonne, its use for carbon nanotubes production is economically more attractive. Thus, if a large-scale commercial process for carbon nanotubes production can be justified in the future, coal will be a favourable option.

Acknowledgements

This work was jointly supported by the National Natural Science Foundation of China (No.29976006), the Natural Science Foundation of Liaoning Province, China (No.9810300701), the State Ministry of Education of China and the Royal Society of the UK in London.

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Table 1 Analysis data of coal samples

Coal sample	Proximate analysis /%			Maceral composition /%				
	A_d	V_d	FC_{daf}	Vitrinite	Semivitrinite	Liptinite	Fusinite	Mineral
1 Taiji	9.16	37.26	58.98	74.2	10.8	0.5	11.0	3.5
2 Fushun	7.19	40.86	55.98	93.2	5.0	0.2	0.0	1.7
3 Tonghua	8.91	32.40	64.43	79.1	10.9	2.3	4.1	3.6
4 Sanbao	9.66	23.34	74.16	75.1	12.1	0.0	9.9	2.9
5 Gujiao	10.28	20.10	77.60	60.3	13.2	0.6	19.0	7.6
6 Xiaoyi	8.05	30.20	67.16	67.9	12.0	2.4	13.6	4.1
7 Kailuan	10.92	25.68	71.17	74.0	7.8	0.0	12.2	6.0
8 Xiongtai	8.34	34.59	62.26	59.2	11.7	6.2	18.6	4.4
9 Pangzhuang	7.98	31.58	65.68	52.3	11.9	11.0	20.6	4.1
10 Xiangyuan	9.10	17.30	80.97	69.7	5.3	0.0	19.1	5.9
11 New Zealand	0.94	31.69	68.01	96.6	0.5	0.6	0.5	1.8

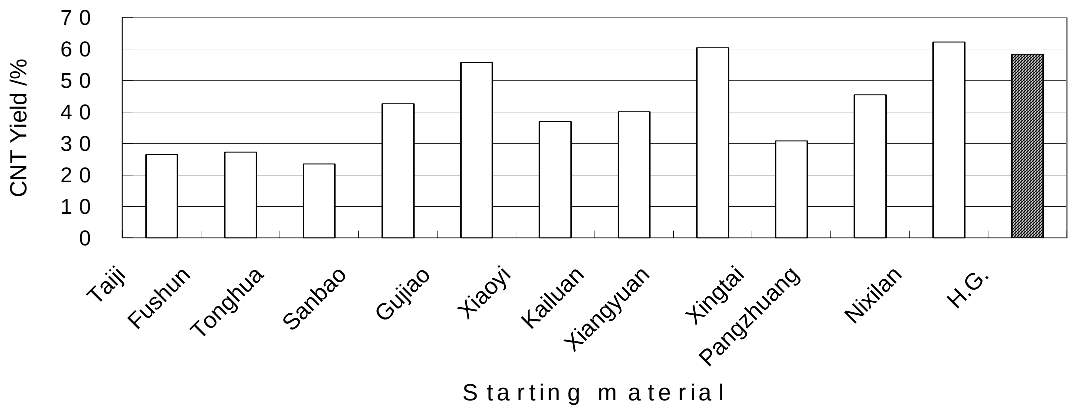

Figure 2 Yield of carbon nanotubes from different coals

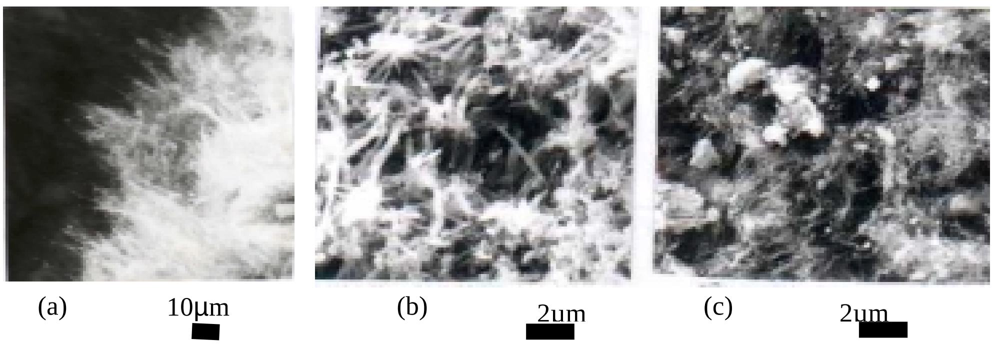

Figure 1. SEM photographs of carbon nanotubes from Xiangyuan coal and New Zealand coal
(a) Xiangyuan coal, 0.03MPa; (b) Xiangyuan coal, 0.0665MPa; (c) New Zealand Coal, 0.03MPa