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Diamond & Related Materials 15 (2006) 1447 – 1451

DIAMOND AND RELATED MATERIALS

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Growth of branch carbon nanotubes on carbon nanotubes as support

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Received 29 June 2005; received in revised form 28 August 2005; accepted 27 October 2005
Available online 18 January 2006

Abstract

A novel method combining the dense fluidized bed and the floating catalytically chemical vapor deposition method (FCCVD) to prepare carbon nanotubes (CNTs) was proposed. Propylene was decomposed at 660 °C, using the CNTs as supports and the metal particles from the in situ pyrolysis of ferrocene as catalyst. The conversion of propylene in this process was closed to 100% under an optimum condition. By SEM and TEM observations, the growth of new generation of CNTs was proven. It was demonstrated that the short and thin CNT branches exist on the tips or sidewalls of CNTs. Based on the analysis of the formation of catalytic sites in the FCCVD in a fluidized bed, a physical model of the formation of branches was proposed.

Keywords: Carbon nanotubes; Heterojunction; Chemical vapor deposition; Microstructure

1. Introduction

The miniaturization of components and circuits is strategically important for the development of nowadays microelectronics industry. One of the important directions to implement the ‘bottom-up’ approach to the construction of microelectronics architecture is the rational synthesis and utility of nanoscaled wires with the more complex structure than their original 1D form [1]. When the nanotubes/nanowires are connected to form branch or junction structures, some totally new electronic properties may emerge, thus make nano-devices possible [2]. Due to the unique electronic properties of carbon nanotubes(CNTs), e.g. the quantum conductance [3,4] and the conductance depending on their chiral angles [5,6], the CNT-based electronic components [7–9] have been considered as one of the most promising candidates of nano-devices of the future. In 1995, Zhou and Seraphin [10] reported the complicated branches on CNTs in the product by the arc-discharging method, including L, Y and T CNT junctions. From then on, many researchers tried to fabricate the CNTs with branches by various methods. The diverse CNT families, including Y-junction [2,10], heterojuction [11–13], and dentrites [14], have been fabricated by arc-discharge [10], thermal CVD [14,15], and CVD with electric field induction [16]. However, most of these methods still suffer the low formation efficiency of branch and poor controllability of process. Recently, Sun et al. [17] developed a technique to form hierarchical CNT structures by pre-loading of active metal particles on CNTs, by which the second generation of multiwalled carbon nanotubes (MWNTs) grew on carbon fibers as support with controllable efficiency, highlighting the idea that CNTs can grow on CNTs as supports to obtain the branch structure.

Some efforts have been made for the synthesis of CNTs using CNTs as supports [17,18]. Generally, the aggregation of pre-loaded nano-sized particles is difficult to eliminate completely, thus the branches do not grow on CNTs. One of the solutions is to adopt thick CNTs as supports [17] at the possible cost of losing some properties on nano-scale. The in situ supporting method, such as FCCVD, is potential to overcome this disadvantage. In conventional FCCVD for the CNT preparation [19–21], the catalysts (often ferrocene) are introduced into a free space where the catalytic reaction takes place. Thus, the traditional FCCVD is a heterogeneous catalytic reaction with dilute catalysts, short residual time and low catalytic efficiency. A combination of a dense fluidized

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doi:10.1016/j.diamond.2005.10.055

bed (FB) [22], with the high throughput and efficiency, and FCCVD, with the flexible and continuous catalyst supply, can be a hopeful solution for the continuous and efficient production of CNTs. The present work will show that MWNTs with branches can be synthesized by the combined FB-FCCVD method proposed in this paper.

2. Experimental

A quantity of MWNTs was put into a nano-agglomerate fluidized bed reactor (NAFBR) that has been described elsewhere in details [23]. The nitrogen gas was introduced into the reactor to fluidize the materials. At an elevating temperature of 660 °C, the reactant gas composed of nitrogen and propylene, with ratio 10:1, was introduced. At the same time, the ferrocene dissolved in benzene was injected into the reactor from the wall of reactor at a rate of 6.5 ml/min. The optimum concentration of ferrocene is 0.1 g/ml. The exhaust was analyzed by a gas chromatogram (GC) to calculate the conversion of propylene. After the reaction, the catalyst supply was stopped but the reactants were fed until the complete deactivation. After cooling the products to room temperature under nitrogen protection, a large quantity of CNT powder was obtained. The CNT sample was examined by the scanning and transmission electron microscopy (SEM, JSM 6700F; TEM, JEOL 2010).

In this process, the initially filled MWNTs not only acted as fluidization intermedium but also provided supports for the catalytic reaction, which will be expatiated in the following text in details. Considering the purity of products, the MWNTs obtained from the decomposition of propylene on Ni/Cu/Al catalysts [24], called CNT1, were adopted as initial filling. There exists 4.2% residual after combustion by TGA (TA2000-TGA Thermal Gravimetric Analyzer) in air from 30 °C to 800 °C at an elevating rate 20 °C/min. However, no any conversion of propylene was detected before the feed-in of ferrocene, demonstrating the remnants Ni was encapsulated in carbon and deactivated in our reaction condition.

3. Results and discussion

The efficiency of ferrocene in the CNT growth has been demonstrated by many researchers [19–21]. A high conversion of propylene in the presence of ferrocene was quantificationally measured by GC. Fig. 1 shows the conversion of propylene and the carbon yield (defined as the mass of carbon deposited per hour) during the process. The dash line indicated the time when the ferrocene feed-in was stopped. When propylene decomposed, carbon deposited and a small amount of methane, ethylene and ethane were detected in off-gas as by-products. In the presence of ferrocene, the conversion was high, but a period was needed to reach a completely stable operation because the initial bed was too shallow to provide enough contacting time. After the reaction time of about 80 min, the conversion of propylene approached nearly 100%, and decreased until deactivation in the absence of ferrocene. Above results indicated that a steady and high yield of this process, around 4 kg/h finally, can be reached, suggesting an efficient method for the CNT production on a large scale.

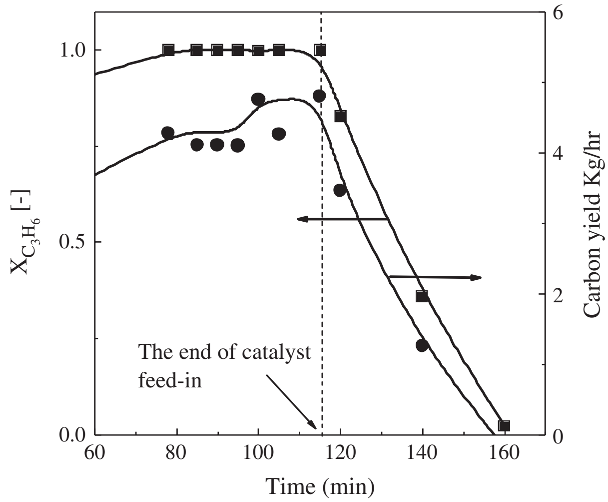

Fig. 1. Variation of the conversion of propylene and the yield of carbon with reaction time.

Black powder with average diameter of 215.5 μm (Marlvern, Master sizer plus) and bulk density of 150 kg/m^3 was obtained after reaction. SEM observation (Fig. 2) showed abundant filaments with diameter on nanometer size. In Fig. 3(a), TEM image indicated that these filaments have hollow cavity, thus newly generated CNTs, called CNT2 were synthesized. The morphology of CNT2 is quite different from that of the initial filling CNT1, as shown in Fig. 3(b). The CNT2 has smaller and more uniform size and has a curling structure. Many zigzags exist along the nanotube axis, as shown in Fig. 4, implicating the re-orientation of growing CNTs. Similar zigzag and Y-junction structure have been reported by Zhu et al. [25]. They assigned the formation of zigzags to the sulfur coverage on metal particles due to the addition of thiophen. However, the zigzag formation in a sulfur-free environment indicated that the process was dominated by a different mechanism in present work. One of the origins of zigzag formation was probably the disturbance from the intensive turbulence in a gas–solid fluidized bed and the collision among the CNT agglomerates [23]. It should be also emphasized that thinner CNTs can be obtained by the FB-FCCVD method than that by the conventional FCCVD [19–21]. The outer diameters of as-grown CNTs range from several nanometers to 20 nm. Their inner diameters are less than 10 nm. Because of the relationship between the sizes of metal particle and CNT [26], it can be expected that smaller metal particles formed in a dense gas–solid flow. Comparing with the conventional FCCVD, the catalyst precursor in a dense fluidized bed may tend to be supported in situ on the suspending particles thus reduce the aggregation in a dilute space, leading to the reduction of CNT diameters.

A more detailed TEM observation revealed some interesting structures in CNT2. As shown in Fig. 4, on a MWNT with diameter of ∼10 nm, a cluster of tussocky CNTs grow at the tips or on the side walls. Based on the TEM observation to tens of branch structures, the diameters of branches are around