LARGE SCALE SYNTHESIS OF CARBON NANOTUBES AND THEIR CURRENT APPLICATIONS

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Introduction

Extra-ordinary chemical and physical properties of carbon nanotubes [1, 6] and also the success of large-scale production by a catalytic chemical vapour deposition method, particularly with the use of a floating reactant technique [2-4], make them applicable in the fabrication of adsorbent, electrochemical electrode, field emitter and functional filler in composite at a possible low cost. Through judicious selection of transient metal, support materials and synthetic conditions (temperature, duration), it is possible to produce different types of carbon nanotubes such as multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs) and single-walled carbon nanotubes (SWNTs) selectively. In this study, we will describe the catalytic synthesis of various carbon nanotubes from the point of synthetic conditions and structural changes by heat treatment will be discussed in terms of structural stability, and finally their practical applications of these carbon nanotubes will be described from the industrial point of view.

Synthesis of carbon nanotube

It is possible to obtain various fibrous carbons which exhibit a wide range of diameters from 200 to 1 nm, different crystallinity and the angle of graphene sheet with regard to tube axis through exact control of synthetic conditions of CVD method. In recent years, much attention has been focused on the growth control of carbon nanotubes. In this sense, it is very important to understand the manufacturing parameters for the purpose of obtaining fibrous materials with optimum properties for specific applications. Among these parameters, carrier gas, flow rate and feeding method show major effects on the carbon product that are obtained when a benzene solution containing ferrocene was used as the feedstock. Especially, the development of

the floating reactant technique made possible to the large-scale production of CNF and MWNTs [4]. In the synthesis of SWNTs, nano-sized SiO_2 impregnated with Fe-containing compounds (seeding method) were fed into the reactor (around 1000^{o}C) with benzene as carbon feedstock, and with hydrogen as the carrier gas [7]. In contrast to current CVD methods, this combinational technique allows high yield efficiency of the nanotubes. A detailed TEM and Raman studies revealed that there are large variations

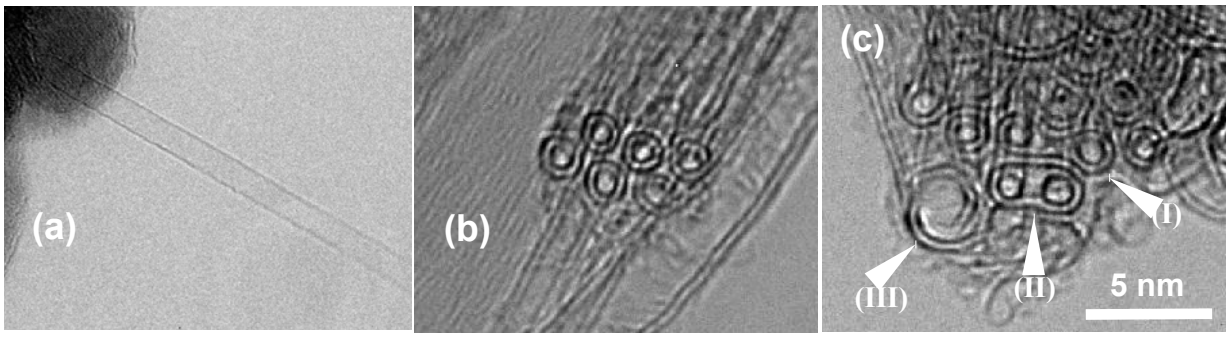

Fig. 1 (a) typical HRTEM image of single wall carbon nanotubes, (b) Typical high resolution transmission electron microscopy (HRTEM) image of DWNTs in a bundle state, (c) HRTEM image of DWNTs at 2100^{o}C. This image exhibits a sequential reconstruction process of a DWNT: (I) two outer tubes start to merge, through a zipping mechanism, (II) two outer tubes are completely combined into a single large outer tube with an oval shape containing two SWNTs, and (III) two inner SWNTs in a confined space might decompose along the inner wall of an outer shell, to form one inner single shell, like the formation of a DWNT derived from a peapod

in textures (isolated and bundle) and also diameters (see Fig. 1 (a)). The recent hot topic is the synthesis of DWNTs because these tubes are more thermally and chemically stable when compared to SWNTs; they also exhibiting the 1D character of a quantum wire. In addition, DWNTs could also be used in the fabrication of electron field emitter and nano-composites. Fig. 1 (b) exhibit cross sectional image of HR-TEM images of DWNTs bundles, which is obtained by the catalytic decomposition of methane over Fe/MgO at 875^{o}C for 10 minutes. HRTEM image (Fig. 1 (c)) exhibiting a sequential reconstruction behaviours of DWNTs at 2100^{o}C [8]. Here, two adjacent outer shells start to merge (see, (I) in Fig. 1 (c)) via a zipping process, similar to the coalescence of SWNTs under electron beam irradiation, and a large single outer shell with an oval shape is formed (see, (II) in Fig. 1(c)). The process occurs due to the coalescence and reconstruction of the outer shells of DWNTs, leaving the inner cylinders almost intact, the latter being encapsulated inside the large diameter coalesced tubule (bi-cable). We

propose that the coalescence process within a bundle of DWNTs is due to: (1) the thermal activity of the outer shells, which is driven by a surface energy minimization process, and (2) a zipping mechanism followed by atom reconstruction, in which two outer shells establish interactions and rapidly anneal.

References

[1] M.S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego (1996).
[2] A. Oberlin, M. Endo, T. Koyama, J. Cryst. Growth, 32, 335 (1976).
[3] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi and H. W. Kroto, J. Phys. Chem. Solids 54, 1841 (1993).
[4] M. Endo, Chem. Tech. (Leipzig) 18, 568 (1988).
[5] M. Endo, Y. A. Kim, T. Hayashi, K. Nishimura, T. Matushita, K. Miyashita and M. S. Dresselhaus, Carbon, 39, 1287 (2001).
[6] S. Iijima, Nature, 354, 56 (1991).
[7] T. Hayashi, Y. A. Kim, T. Matoba, M. Esaka, K. Nishimura, M. Endo and M. S. Dresselhaus, Nanoletters, 3, 887 (2003).
[8] M. Endo et al, submitted to PRL.

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