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Bulk production of quasi-aligned carbon nanotube bundles by the catalytic chemical vapour deposition (CCVD) method

Kingsuk Mukhopadhyay ^a, Akira Koshio ^a, Toshiki Sugai ^a, Nobuo Tanaka ^b, Hisanori Shinohara ^{a,*}, Zoltan Konya ^c, Janos B. Nagy ^c

^a Faculty of Science, Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

^b Faculty of Engineering, Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

^c Laboratoire de Résonance Magnétique Nucléaire, FUNDP, 61 rue de Bruxelles, B-5000 Namur, Belgium

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Abstract

The large-scale production of quasi-aligned carbon nanotube bundles is reported. The method includes catalytic decomposition of acetylene over well-dispersed metal particles embedded in commercially available zeolite at a lower temperature (700°C). In-depth studies of this nanotube through scanning electron microscopy and transmission electron microscopy reveal their homogeneity as well as perfect graphitization, along with inner (2.5–4 nm) and outer diameters (10–12 nm) of the tubes. Details of the optimum conditions for producing these nanotubes are also described. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the discovery of carbon nanotubes [1], various synthetic procedures of the nanotubes have been reported, such as carbon arc discharge in the presence of a metal catalyst [1,2], laser vaporization of a graphite electrode in the presence of metal catalysts [3], pyrolysis of hydrocarbon vapour over a transition metal incorporated silica/zeolite support (catalytic chemical vapour deposition, CCVD technique) [4,5], pyrolysis of metallocenes (e.g., ferrocene, cobaltocene and nickelocene) [6], chemical vapour deposition on silicon wafers containing lithographically deposited metal salts and alumina [7] and laser-assisted production of carbon nanotubes from acety-

* Corresponding author. Fax: +81 52 789 2962; e-mail: nori@chem2.chem.nagoya-u.ac.jp

lene [8]. Of these production procedures reported, only the CCVD method leads to a large-scale yield of carbon nanotubes. The lower reaction temperature coupled to the low cost of production, as compared with others, is of fundamental importance for the CCVD method. However, the separation of carbon nanotubes from the support, as well as from the amorphous carbon, has been difficult [9].

It is well known that on proper alignment these carbon nanotubes act as good electron field emitters [10]. Hence, attention has been drawn to align them. Recently, some reports concerning the alignment of nanotubes have attracted much interest. Terrones et al. [11] have reported the formation of aligned nanotubes by the pyrolysis of a triazine compound over well-aligned laser-deposited Co particles. Li et al. [12] have reported the synthesis of aligned nanotubes by the pyrolysis of acetylene over Fe-incorporated mesoporous silica. In the former report, the temperature of the laser deposition system as well as of the furnace is quite high and in both cases the formed nanotubes contain 40–60 graphitic layers, having outer diameters of 30–50 nm and an inner diameter of ~4 nm. Rao et al. [13] have reported the formation of aligned nanotube bundles from ferrocene pyrolysis but in this case also the furnace temperature is high and tubes are ~ 30–40 nm in diameter. Ren et al. [14] have synthesized well-aligned carbon nanotubes by plasma-enhanced hot filament chemical vapour deposition on nickel-coated glass at 666°C but the synthesized nanotubes have many structural defects and have outer diameters in the range of 30–50 nm.

Here, we report the bulk synthesis of thin, quasialigned nanotubes over well-dispersed metal particles on a commercially available zeolite support by the pyrolysis of acetylene at much lower temperature (700°C). We also present the effects of reaction parameters on the quality and quantity of nanotubes.

2. Experimental

The experimental procedure is illustrated schematically in Fig. 1. It involves a horizontal furnace with three thermocouples to regulate and measure the temperatures of the furnace precisely. The length of the furnace is 1 m and has an inner diameter of 10 cm. The quartz tube used to carry out the deposition has a length of 1.5 m with outer (8 cm) and inner (7.5 cm) diameters.

The catalyst was prepared by dissolving cobalt acetate (2.5 wt%) and vanadium acetate (2.5 wt%) in 25 ml of water and then mixing them with a commercially available zeolite support (Y-type zeolite from Zeolyst International). The mixture was vigorously stirred in order to obtain the resulting mixture of semisolid form. This semisolid mixture was then dried overnight at 140°C which was then ground into a fine powder and used in the production process.

The so-prepared catalyst (~ 1.5 g) was spraved over the quartz boat and was placed in the central position of the furnace. It was then activated by passing nitrogen gas (99.99%) through the chamber for 15 min at 120 ml/min flow rate. The temperature of the reaction was fixed at 700°C. It was followed by the flow of acetylene (99.6%) at the rate of 15 ml/min for 1 h through the reaction chamber while nitrogen gas flow was maintained at 120 ml/min flow rate. After the scheduled time, the furnace was cooled to room temperature by the passage of nitrogen gas (120 ml/min). The sample was then collected as a black powder from the quartz boat. In this way, we can synthesize nanotubes in gram quantities ($\sim 500 \text{ mg}$ of carbon nanotubes per hour).

The resulting carbon nanotube samples were characterized by scanning electron microscopy (SEM: Hitachi S-900) and transmission electron microscopy (TEM: Hitachi H-800 and JEOL JEM 2010). Details



Fig. 1. A schematic representation of nanotube production unit: (A) the furnace; (B) a quartz tube with gas inlet and outlet system; (C) a quartz boat for carrying the catalyst during the synthesis; and (D) the thermocouples.

Table 1	Tal	ble	1
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Effect of reaction temperature, flow rate of the gases, support and metal particles on the quality/quantity of nanotubes

Support	Metals used	Reaction time (min)	Temp. (°C)	Gas flow rate: N ₂ flow;	Comment
				C ₂ H ₂ flow (ml/min)	
Y-type zeolite	Co-V	60	700	120; 15	high density and quasi aligned
Y-type zeolite	Co-V	60	600	120; 15	less dense but quasi aligned
Y-type zeolite	Co-V	30	700	120; 15	less dense but quasi aligned
Y-type zeolite	Co-V	45	700	120; 15	less dense but quasi aligned
Y-type zeolite	Co-V	60	700	200; 25	quasi aligned but not homogeneous in nature
Y-type zeolite	Co-V	60	700	85; 25	high amount of amorphous carbon
Y-type zeolite	Co–Fe	60	600	120; 15	high density and quasi aligned
Y-type zeolite	Co–Fe	60	700	120; 15	quasi aligned but high amount of amorphous carbon and also slightly thick nanotubes
Y-type zeolite	Co-Ni	60	700	120; 15	less dense and not aligned
Y-type zeolite	Co-Pt	60	700	120; 15	less dense and not aligned
Y-type zeolite	Co-Y	60	700	120; 15	less dense and not aligned
Y-type zeolite	Co-Cu	60	700	120; 15	not active, almost no nanotubes
Y-type zeolite	Co–Sn	60	700	120; 15	not at all active
Commercial grade alumina	Co-V	60	700	120; 15	high density and quasi aligned
Commercial grade silica	Co-V	60	700	120; 15	high density but not aligned

of the experimental results, along with the optimization of experimental parameters (such as metal particles, flow rate of the reaction gas and temperature of the furnace), are summarized in Table 1.

3. Results and discussion

3.1. SEM / TEM observations

Fig. 2a–d shows the SEM topographs of assynthesized carbon nanotube samples. It clearly illustrates the purity and homogeneity of the tubes, where graphitic particles and nano-capsules are completely absent. Fig. 3 is a low-resolution TEM image of the nanotubes. It shows that the tubes are thin and quasi-aligned. It also depicts the parallel alignment of the tubes on the catalyst support. Fig. 4 shows a high-resolution TEM image (HREM) of the carbon nanotubes. It is clear from these images that the tubes are perfectly graphitized, having ~ 10 graphitic layers on both sides. The as-prepared carbon nanotubes have an inner diameter of ~ 3.5 nm and an external diameter of ~ 12 nm. It should be noted that during TEM, as well as electron-dispersive X-ray (EDAX) analyses of the tubes, we have found no trace of the metal particles, either at the base or at the tip of the tubes, which might be closely related to the growth process of the nanotubes by the present CCVD method [4].

3.2. Optimization of the production yield of the nanotubes

The synthesis of nanotubes by the above-mentioned procedure involves the following parameters: (1) the temperature of the furnace; (2) the flow rate of the gases; (3) the reaction time; (4) the kind of the embedded metal particles; and (5) the composition of the support. In the following, we present the effect of each parameter which is summarized in Table 1.



Fig. 2. SEM images of the sample: (a) and (b) show the overall morphology of the sample while (c) and (d) reveal one of the nanotube bundles. These images show the morphology of as-prepared samples which clearly reveal the high purity and homogeneity of the sample.



Fig. 3. Low-resolution TEM image. It clearly shows that the bundles are quasi-aligned.



Fig. 4. An HREM image of a typical carbon nanotube. The tube has 10 layers on both the sides and is highly graphitized.

The TEM and SEM studies have revealed that at slightly lower temperatures than the optimized (700°C), i.e. between 500 and 600°C, the number of nanotubes formed was fewer, and below 500°C no nanotubes were formed at all. At temperatures higher than the optimized temperature, the amount of amorphous carbon increased. However, we have noted that this optimized temperature may vary with the different metal catalysts used in the synthesis process. For example, with Zeolite Y plus Co and V, the optimum temperature was 700°C, whereas the optimum temperature was found to be 600°C for Zeolite Y plus Co and Fe (cf. Table 1).

Acetvlene and nitrogen gases were used in this synthetic procedure. The rates at which they were passed through the reaction chamber during the experiment were 15 and 120 ml/min for acetylene and nitrogen gases, respectively. It should be noted that while doing the deposition, nitrogen and acetylene gases flow at the same time. We have concluded that these flow rates should be maintained during the reaction to obtain the maximum yield. Any variation of these flow rates, viz.: (1) acetylene (25 ml/min) and nitrogen (85 ml/min); (2) acetylene (25 ml/min) and nitrogen (200 ml/min); and (3) acetylene (15 ml/min) and nitrogen (85 ml/min), has shown that the yield of the nanotube decreased and the quality of the tubes also affected. It should be mentioned here that the optimized flow rates were irrespective of the catalyst used.

In our synthetic process, the reaction time was maintained at 60 min. Any change of this reaction time resulted in lower yields of the nanotubes, as revealed by SEM and TEM observations. For example, on reducing the reaction time to 30 or 45 min, the yield was decreased. In addition, on increasing the time, for instance to 90 min, amorphous carbon was concomitantly produced. Hence, we think that the optimum reaction time for the maximum production of the tubes is ~ 60 min in the current experimental arrangements.

It is known that a zeolite/silica support containing Co particles could produce non-aligned carbon nanotubes [4]. Therefore, we have examined the yield of the tubes on binary metallic particles (zeolite plus Co–M where M is transition metal atoms). Almost all the transition metals were used. Of all the combinations, Co–V and Co–Fe gave the best yield and were able to produce almost same kind of quasi-aligned carbon nanotube bundles. Right now, we are studying the activity of these two catalyst supports by SEM and TEM and hence a comparative report on the activity of these two catalysts will be reported elsewhere.

3.3. The nature of the support and a probable growth mechanism of the nanotubes

The support obviously plays a pivotal role in the synthesis of the present carbon nanotubes. The pore size of the support is a key factor in shaping the inner diameter of the tubes. We have used zeolites with a definite pore size. We are currently using various types of zeolites having smaller pore size, in an attempt to obtain single-walled nanotubes. Silica and alumina may also be used as a support, to obtain the same kind of quasi-aligned carbon nanotube bundles but they have their own drawbacks. We have observed that in the case of silica, the removal of amorphous carbon from the sample is extremely difficult (since Si and C are in the same group, so the resemblance of their reactivity might play a role in this case). The removal of alumina from the nanotube sample is almost impossible because under the experimental temperature the structure of alumina changes. It becomes sparingly soluble in acid and alkali solutions and hence it is quite difficult to isolate pure nanotubes from the solutions.

The formation mechanism, as well as such an alignment of the present carbon nanotubes, is most interesting. The HREM image (Fig. 4) shows that there are 10 concentric graphitic layers with the regular circular shaped inner pore. The central questions to be answered are: (1) why are the tubes so selective about the outer and inner diameter, in particular? and (2) what is the driving force behind the formation of 10-12 graphitic layers? In an effort to elucidate the growth mechanism of these nanotubes, we have noticed that to get the maximum activity of the catalyst, during the synthesis of aligned carbon nanotubes, the metal particles should be on the surface of zeolite and not inside the pore of zeolite [4]. This largely depends on the mixing time of metal/metals salts with the zeolite powder at the preparatory phase of the catalyst itself. The optimum

mixing time should thus be maintained to obtain the most activated catalyst. Experimentally we have confirmed that the diameter of the nanotubes becomes larger as the reaction time increases. The pore size of the zeolite also plays a significant role for the determination of the inner diameter of the aligned carbon nanotubes. For example, the zeolite we used has the pore size of 2.5 nm and the inner diameter of aligned carbon nanotubes is almost of the same size.

The inner diameter of carbon nanotubes, therefore, varies with the size of metal particles, mixing time and the pore size of the zeolite used. As the gases (here acetylene and nitrogen) are allowed to pass through the reaction chamber, the reaction proceeds from the reaction center towards the periphery. This leads to the formation of graphitic layers of generally 8-10 fold, depending on the extent of the reaction from the center to the periphery. In this regard, we think a hypothesis on capillary action and a rolling effect of the metal particles [2,15,16], which tries to explain the formation of these graphitic rings as well as the formation of nanotubes, seem to be somewhat clumsy. As already mentioned above, the circumstantial evidence from TEM images as well as the EDX analysis does not clarify that the metal particles, which, according to the hypothesis, should have been present at the tip or at the base of the tubes, are absent or rarely present. We therefore believe that the building up process of these carbon nanotubes has a different formation mechanism.

The zeolite used here, acting as a support in this reaction process, has regular pores. The metal particles are embedded within these pores and position themselves in a regular array, similar to the case of regular arrays of Co particles as reported elsewhere [11]. The metal salts used in the present case have extremely low melting points, and hence at the reaction temperature (700°C) they are in a highly reactive vapour phase. As the gases (nitrogen and acetylene) are passed through the reaction chamber, carbon nanotubes align themselves in the direction of the gas flow. Presumably, the highly reactive metal salts in the gaseous state flow down along with the gases, leaving almost empty tipped nanotubes.

Here, we have presented a simple and novel way to synthesize aligned nanotube bundles at lower temperatures, in bulk quantities and at the same time we have also tried to develop the idea of obtaining smaller diameter nanotube in the near future by using much smaller pore sized catalyst and metal particles. The different parameters guiding the reaction process have also been discussed with regard to optimizing the quality and quantity of the sample. Detailed studies of the electrical conductivity, magnetic properties, elastic character, electron energy loss spectroscopy (EELS) as well as field emission studies of these bundles and the atomic resolution of these nanotube bundles using STM are underway in our group and hence will be reported in subsequent publications.

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