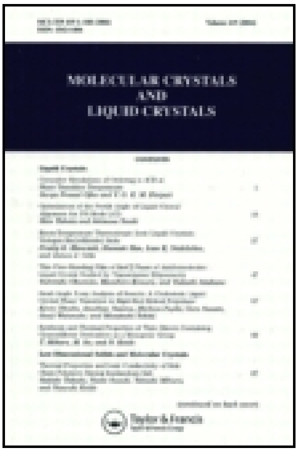

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Synthesis, Purification and Properties of Carbon Nanotubes

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SYNTHESIS, PURIFICATION AND PROPERTIES OF CARBON NANOTUBES

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Abstract The synthesis, purification and properties of the carbon nanotubes are described. The synthesized and purified nanotubes were analyzed by XPS (ESCA) and found to be chemically modified in the oxidation process. The possibilities of filling nanotubes with metals are discussed based on the high pressure experiment with mercury.

INTRODUCTION

A carbon nanotubes is a cylindrical graphitic micro-crystal with nanometers in diameter and micrometer in length [1], and illustrated graphically in Figure 1. The nanotubes synthesized by the carbon arc discharge method [2] are composed of multi-layer graphite shells, the interlayer spacing being about 3.4 Å, which is close to that of graphite. Each graphite shell contains an array of carbon hexagons often arranged in a helical pattern. Both ends of the nanotube are closed by the presence of pentagons, so the nanotubes have a seamless structure unless the opening technique is applied to the nanotubes [3]. The inner hollow cavity is such a narrow and restricted space that only a few molecules would be found. If there is no adsorption and no condensation, they may exist as a completely free gas under standard conditions.

Due to the unique structural features, such as the one dimensionality and the inner hollow cavity, the nanotube is expected to be a carbon material having unusual properties. Raman spectroscopy revealed that the nanotubes posses a high degree of crystallinity. This suggests that other physical properties such as mechanical strength and conductivity should reflect features of pure single crystals [4]. Theoretical calculations have predicted that the electric properties of nanotubes change, from metallic to semi-conducting, depending on the diameter and the helicity [5-7]. One of the most striking aspect of this prediction is that there is a possibility that one could make a metal or a semi-conductor using only carbon as an element if one could control the structure. ESR study of the purified nanotubes implies that metallic and /or narrow gap semiconducting nanotubes are actually present as predicted by theory [8].

In this paper the synthesis and purification of nanotubes are mentioned briefly and some properties of the purified nanotubes are described. Moreover, the utilization of the inner cavity of nanotubes as nanosize straw are discussed.

SYNTHESIS OF CARBON NANOTUBES

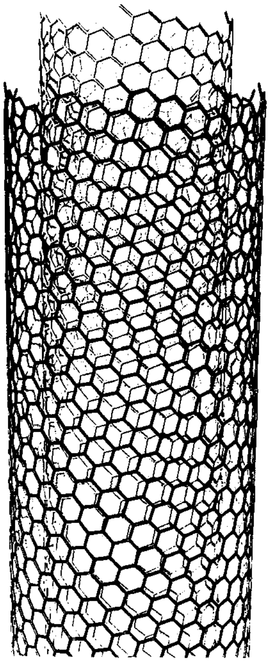

FIGURE 1. Carbon nanotube.

Multishell carbon nanotubes are synthesized by the carbon discharge method described in detail elsewhere [2]. When ca. 18 V of voltage (either d.c. and a.c.) is applied between two cylindrical carbon electrodes under inert gas atmosphere in a reaction vessel and two electrodes set close together, a carbon arc plasma is formed. The electric current is about 50 A, when carbon electrodes, 6 mm and 9 mm in diameter, are used. Immediately after the formation of arc plasma, a cylindrical deposit is formed on the larger electrode, while the smaller rod is consumed. It takes 30 to 40 minutes to obtain a 4 or 5 cm long deposit. The deposit is composed of two parts: an outer hard metallic shell and an inner soft fibrous black core. The TEM [2] and Raman [4] measurements revealed that the inner core was filled with carbon nanotubes and carbon nanoparticles with a ratio of 2 : 1. Carbon nanoparticles are graphitic polyhedrals, whose size are a few to several tens nanometers. Figure 2 (a) shows a TEM picture of the crude product in the core. The yield of the nanotubes and nanoparticles was more than 30 % in the best cases. The stabilization of the arc plasma brings about the high yields. Observations by AFM and SEM revealed that the nanotubes deposits exhibit a fractal-like pattern of growth and that the micro-bundle composed of neatly packed and aligned nanotubes is one of a key units of growth [9].

PURIFICATION OF CARBON NANOTUBES

As described above, the crude product by carbon discharge method contains not only nanotubes but also nanoparticles. Therefore, the nanoparticles must be removed from the product in order to investigate the precise properties of the nanotubes. The purification method by air oxidation at high temperatures (750° C) was recently reported [10]. In this process the nanoparticles are consumed more rapidly than the nanotubes because of their structural and geometrical differences. However, the yield of the purified nanotubes is lower than 1 % probably due to the local inhomogenious oxidation. To overcome this problem, we tried to perform the liquid phase oxidation and found that yields of more than 40 % of purified nanotubes can be obtained under suitable conditions. The detail procedure will be described elsewhere [11]. Among several strong oxidants, potassium permanganate in acidic solution was found to give by far the best result for the purification of the nanotubes. As is shown in Figure 2 (a) (before purification) and (b) (after purification), the nanoparticles are removed from the crude products and the nanotubes are purified.

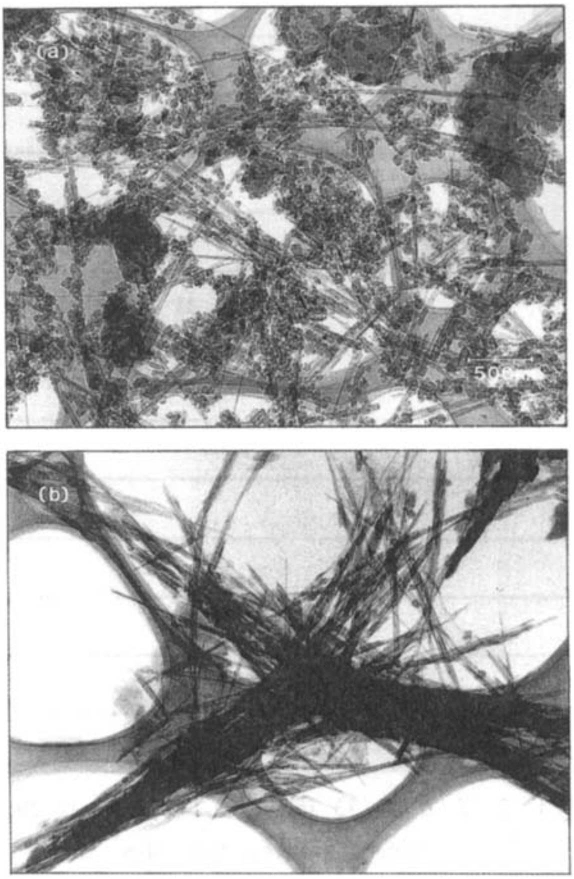

FIGURE 2. Carbon nanotubes before (a) and after (b) liquid phase oxidation.

Comparison with the crude nanotubes, the purified nanotubes easily aggregate when dried, however, they disperse well in liquids such as water and alcohol. The change of the wetting property of the nanotubes is due to the chemical modification of the surface as described later. The nanotubes purified by the liquid phase oxidation, as well as by the air oxidation, lose their caps on both ends to become opened. The opened nanotubes can be used for doing nanoscale experiments in the hollow inner cavity.

PROPERTIES OF PURIFIED NANOTUBES

Before measurement of the purified nanotubes properties was carried out, their size distributions were directly measured through TEM observations. Figure 3 (a) and (b)

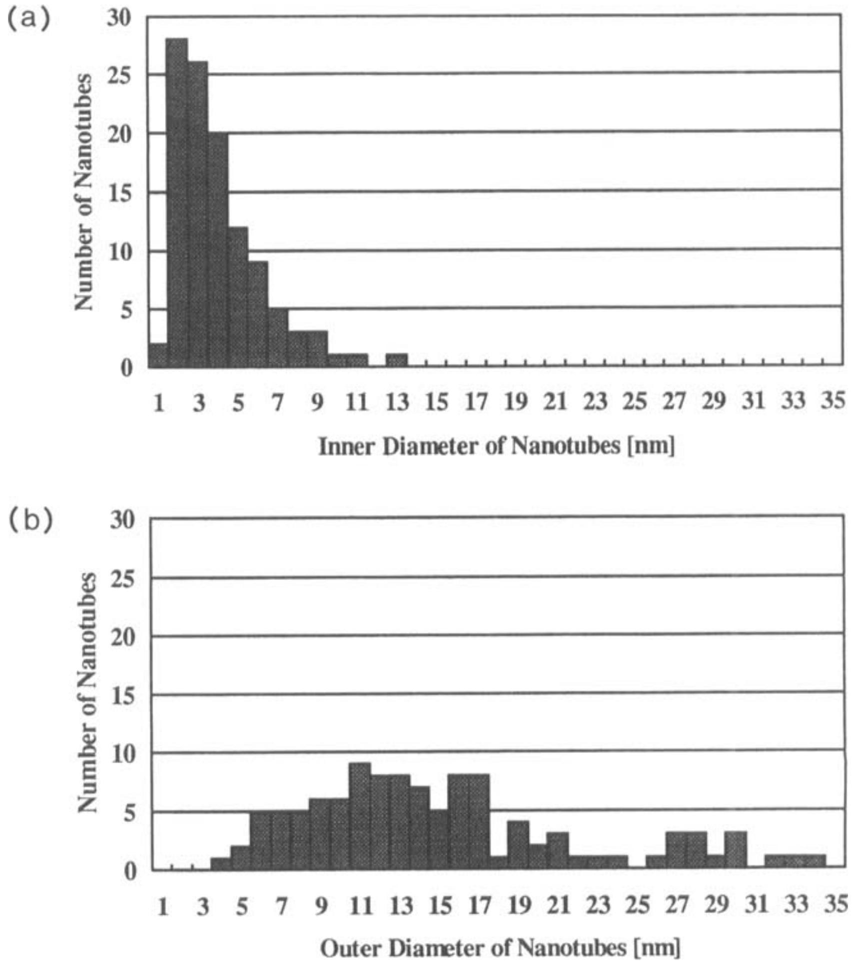

FIGURE 3. The histograms showing the frequency of the observed nanotubes versus the different inner diameter (a), and the outer diameter (b).

illustrate the histograms of the inner and the outer diameter distributions for the nanotubes purified by the liquid phase oxidation described in Reference [11]. The inner diameter has a narrow distribution around 3 nm, while the outer diameter has a broad distribution from 4 to 34 nm with a ca. 12.5 nm of maximum. Comparing with the crude nanotubes, the purified nanotubes are relatively wider. This is because the thinner nanotubes in the crude product are completely oxidized and disappear in the course of the purification process.

It is natural to think that the some property changes will occur in the purified nanotubes due to oxidation. A simple demonstration is that the purified nanotubes are easy to disperse in liquids as described above. The sonicated water solution of the purified nanotubes keeps turbid for several days, while the crude nanotubes begin to precipitate in water immediately after stopping the sonication. Moreover, a pH change of the suspension is observed. An aqueous solution of the crude nanotubes keeps the pH value around neutrality, while that of the purified nanotubes exhibits an acidity of ca. pH 4.6. These observations mean that the oxidation process changes the chemical make-up of the tips and even the outer (and the inner) layer of the nanotubes.

In order to investigate any significant chemical modification precisely, the purified nanotubes were analyzed by XPS (ESCA). Figure 4 shows the XPS (ESCA) spectra of the unpurified (crude) nanotubes (a) and the purified nanotubes (b) in a wide scan range. The main peak around 285 eV, appearing both in spectrum (a) and (b), is clearly assigned to C1s. No other significant peaks are observed in the spectrum of the purified nanotubes (a). However, in the spectrum of the purified nanotubes (b), the peak at 533 eV, which is unambiguously assigned to O1s, is clearly observed. These observations mean that the unpurified nanotubes contains no oxygen within the resolution, while the purified nanotubes contain significant amounts of oxygen (from peak area analysis, the ratio of oxygen atom to carbon atom is ca. 0.08 as summarized in Table I). Furthermore, the narrow scan analysis of the C1s peak of the purified nanotubes revealed that this peak has a shoulder on the higher energy side. Peak separation analysis indicates that ca. ten percent of the carbon constituting the purified nanotubes are bound to oxygen and form carboxyl, hydroxyl and carbonyl groups. From these results it is concluded that the acidic property of the purified nanotubes suspension originates from the presence of these acidic groups.

According to the XPS data, it is safe to say that no less than 10 % of the carbon in the hexagonal carbon network of the nanotubes is chemically modified to form the oxygen-containing functional groups in the oxidation process. This value is fairly large, considering that the outer layer of a typical anotube represents only ca. 15 % of the total carbon (this is estimated using the size distribution data shown in Figure 3).

Therefore, there is a possibility that a few outer layers of the nanotubes is completely modified due to oxidation.

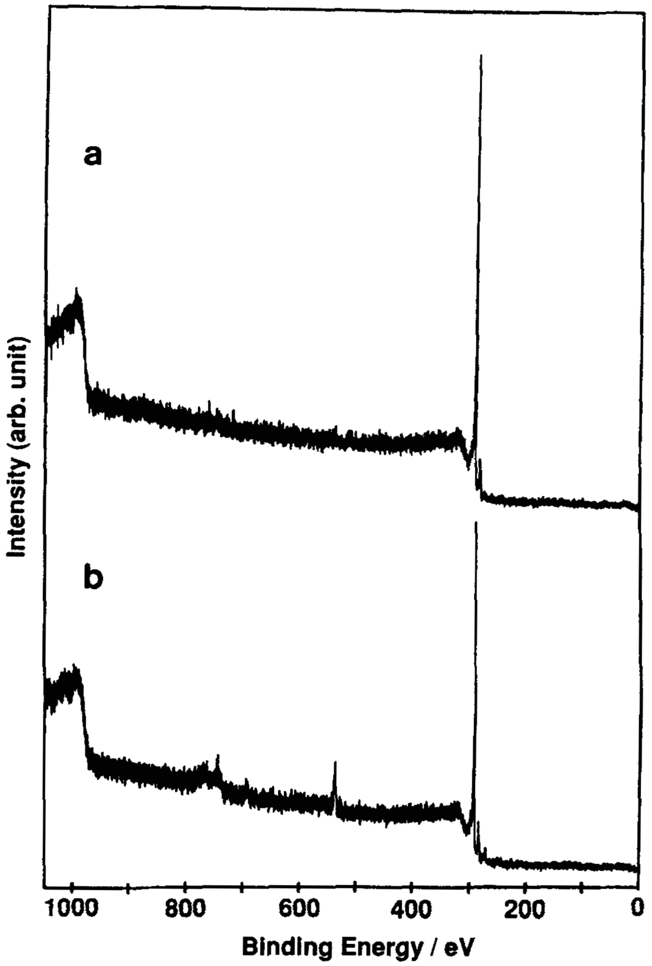

FIGURE 4. XPS (ESCA) spectra of the crude nanotubes (a) and the purified nanotubes (b) in a wide scan range.

The surface modification is advantageous for further chemical decoration and modification of the nanotubes. However, it is a problem if one wishes to measure the properties of the nanotubes as uniform quasi-one dimensional crystals. Further experiments revealed that the surface hydrophilic groups can be eliminated by simply annealing the purified nanotubes. The annealing was done at around 2800 ° C. The XPS analysis of the annealed nanotubes showed that very little oxygen was left and the abundance of the functional groups is less than 1 %. The data for the O1s peaks analysis of the crude, the purified and the purified and annealed nanotubes are summarized in Table I.

TABLE I The area ratio of the O1s to C1s (O1s/C1s) and the ratio of the number of oxygen to that of carbon (O/C) on the crude, the purified and the purified and annealed nanotubes

	crude nanotubes	purified nanotubes	purified and annealed nanotubes
O1s / C1s	0.00_9	0.23_7	0.02_8
O / C	0.00_3	0.08_3	0.00_8

UTILIZATION OF NANOTUBES AS NANOSIZE STRAWS

The nanotube has a narrow and hollow cavity. The average inner diameter of the purified nanotubes is less than 3 nm according the data in Figure 3. This small size means that only several tens atoms could be aligned radially, if the inner cavity was filled with atoms. If a desired material can be introduced into the nanotube, the nanotube would act as a mold and a quasi-one dimensional structure composed of the desired material would be produced inside the nanotube.

Theoretical calculations first predicted that the open nanotubes should act as nano-straw and draw in molecules from vapor or fluid phases [12]. The experimental filling of the nanotubes was first achieved by Ajayan et al. [13]. They opened the closed nanotubes using the reaction with lead and oxygen to fill the nanotubes with a lead compound. However, further experiments revealed that the nanotubes opened before filling could not draw in molten lead by capillarity [2]. The reason why the filling did not succeed has been discussed elsewhere [14]. Recently Dujardin et al. reported the wetting and capillary of the nanotubes in detail [15]. According to their report, the nanotubes will only be wet and filled by substances having low surface tension such as S, Se and Cs, the upper limit being less than 200 mN/m. They pointed out that the limit of the surface tension implies that pure metals will not be drawn into the inner cavity of nanotubes due to their high surface tension, and that it is necessary to apply very high pressure to the molten metal in order to introduce it into the nanotubes.

The author attempted to fill the nanotubes with mercury because mercury, which is a liquid metal at room temperature, should be easy to handle in the high pressure experiment. Now let's estimate the necessary pressure to fill the nanotubes with the molten metal. If the surface tension of the metal is balanced by the pressure difference due to the external force pushing the metal into the nanotube, the following equation applies:

$$-2\pi r\gamma\cos\theta = \pi r^2\Delta P$$
$$\therefore r\Delta P = -2\gamma\cos\theta \qquad (1)$$

where r is the inside radius of a nanotube, γ is the surface tension, θ is the liquid-solid contact angle as shown in Figure 5 and ΔP is the difference between the inside pressure, P_0 and outside pressure P. If the inside pressure is negligible comparing with the outside pressure, ΔP equals P. In the case of mercury, the surface tension, $\gamma = 480$ mN/m, the contact angle, $\theta = 140°$ (these values are generally used for the interface between mercury and carbonaceous compounds [16]). On the assumption that these values are valid for the interface between mercury and nanotubes, substituting these values in equation (1) yields the following equation:

$$r P = 7.5 \times 10^3 \qquad (2)$$

where the unit of r and P are expressed in nm, kg/cm^2, respectively. According to the data shown in Figure 3, the inside radii of the opened nanotubes are typically between 1 and 5 nm, therefore, the necessary pressures are predicted to range from 1500 to 7500 kg/cm^2 according to equation (2).

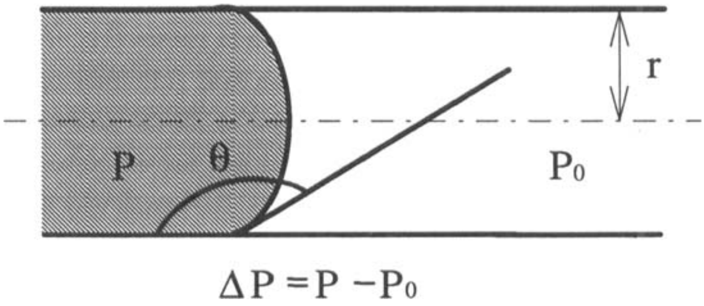

FIGURE 5. The contact angle in the tube.

The high pressure experiment to fill the opened nanotubes with mercury was carried out using pressures up to ca. 2100 kg/cm^2. Figure 6 shows the inverse of the applied pressure vs. the intrusion volume of mercury. The circles indicate the dada plots in the forward process and the squares those in the backward. The first intrusion of mercury began at just above 1 kg/cm^2 and continued up to 10 kg/cm^2. This intrusion appears to be due to the impregnation of the mercury in the space between nanotubes. The long plateau from 10 kg/cm^2 on means that there is no intrusion of mercury in this range. The second intrusion occurred from 1750 kg/cm^2. This would be due to the filling of the nanotubes with mercury. These pressures correspond to the radii of nanotubes from ca. 3.6 to 4.3 nm according to equation (2). However, this intrusion is reversible as shown in the backward process. These observations suggest that filling nanotubes with mercury is possible, but as expected the pressure is always needed in order to keep the mercury inside. The Absence of mercury in the inner cavity of the nanotubes was confirmed by TEM observations. Surprisingly, the first intrusion of mercury remained. This would be because the mercury changes into fine particles and is trapped in the small space between nanotubes. In order to obtain the further information on the filling of nanotubes with mercury, higher pressure experiments will be needed.

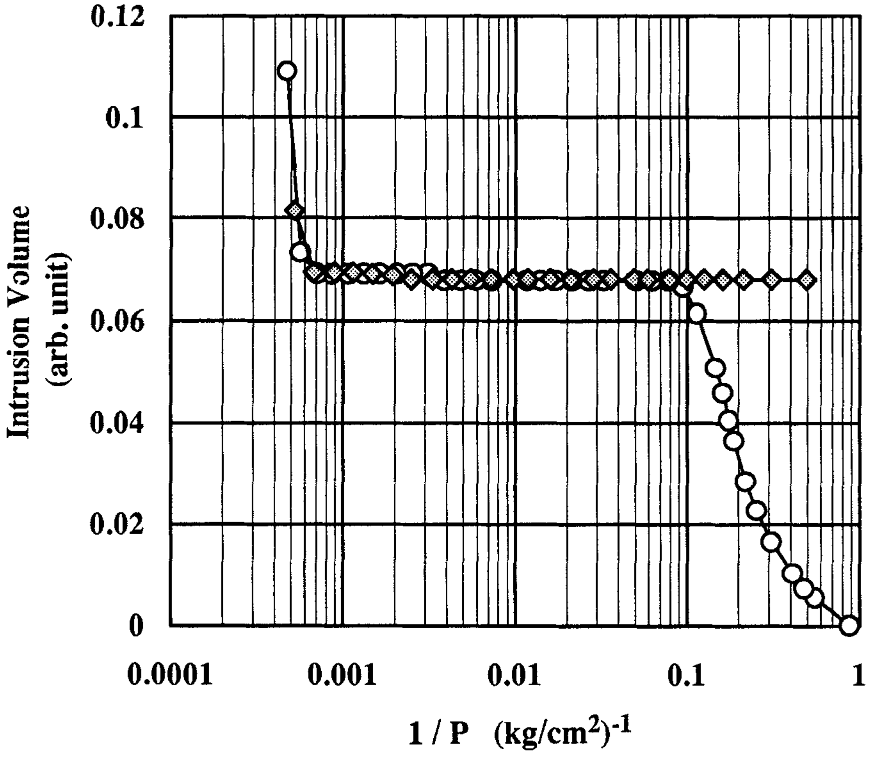

FIGURE 6. The inverse of the pressure versus the intrusion volume of mercury.

CONCLUSION

A series of the procedures for the synthesis and purification of the nanotubes were outlined. The XPS analysis revealed that the surface of the purified nanotubes were chemically modified to form hydrophilic groups such as carboxyl, hydroxyl and carbonyl groups. However, further annealing was found to eliminate these groups. These functional groups can be advantageous in considering further chemical decoration and modification of carbon nanotubes. The high pressure experiments indicated that the filling of nanotubes with mercury is possible, but the filling is not maintained without high pressure.

REFERENCES

[1] S. Iijima, Nature 354, 56-58 (1991)

[2] T.W. Ebbesen and P.M. Ajayan, Nature 358, 220-222 (1992)

[3] P.M. Ajayan, T.W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, Nature 362, 522-525 (1993)

[4] H. Hiura, T.W. Ebbesen and K. Tanigaki, Chem. Phys. Letters 202, 509-512 (1993)

[5] J.W. Mintmire, B.I. Dunlap and T. White, Phys. Rev. Letters 68, 631-634 (1992)

[6] N. Hamada, S. Swada and A. Oshiyama, Phys. Rev. Letters 68, 1579 -1581(1992)

[7] R. Saito, M. Fujita, G. Dresselhaus and M.S. Dresselhaus, Appl. Phys Letters 60(18), 2204-2206 (1992)

[8] M. Kosaka, T.W. Ebbesen, H. Hiura and K. Tanigaki, Chem. Phys. Letters 225, 161-164 (1994)

[9] T.W. Ebbesen, H. Hiura, J. Fujita, Y. Ochiai, S. Mastui and K. Tanigaki, Chem. Phys. Letters 209, 83-90 (1993)

[10] T.W. Ebbesen, P.M. Ajayan, H. Hiura and K. Tanigaki, Nature 367, 519 (1994)

[11] H. Hiura and T.W. Ebbesen, submitted.

[12] M.R. Pederson and J.Q. Broughton, Phys. Rev. Letters 69, 2689 (1992)

[13] P.M. Ajayan and S. Iijima, Nature 361, 333-334 (1993)

[14] T.W. Ebbesen, Annu. Rev. Mater. Sci. 24, 235-264 (1994)

[15] E. Dujardin, T.W. Ebbesen, H. Hiura and K. Tanigaki, Science (in the press)

[16] H.L. Ritter and L.C. Drake, Ind. Eng. Chem. Anal. Ed., 17, 782,787 (1945)