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Growth of Carbon Nanotubes on Quartz Plates by Chemical Vapor Deposition Using (Ni, Fe)- Phthalocyanines

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Carbon multiwall nanotubes were formed on quartz plates by vacuum chemical vapor deposition at 700°C using (Ni, Fe)-phthalocyanines (Pcs) as source materials. From FePc, two types of nanotubes were obtained. The first were the usual tubes whose tips were coiled, as obtained from NiPc, and the second were straight bundles of tubes of equal length shaped like winter mushrooms. Most of the mushroom shaped tubes strongly adhered to the substrate in contrast to the usual tubes. This adhesion was inferred to be induced by the contents (Fe metal) inside the base of the tube.

KEYWORDS: chemical vapor deposition, carbon nanotube, catalysis, phthalocyanine

1. Introduction

Carbon nanotubes have attracted much attention since their discovery[1)] and synthesis,[2)] because of their remarkable electronic[3)] and mechanical[4)] properties. Nanotubes are now commonly prepared by carbon-arc discharge,[1,2,5)] carbon-laser ablation[6)] and catalytic pyrolysis of hydrocarbons.[7–11)] Among these methods, chemical vapor deposition (CVD) utilizing metal-phthalocyanines (Pcs) as source materials is interesting, because of its simplicity.[11)] That is, it is exciting that carbon multiwall nanotubes (MWNTs) grew in high density on quartz plate over a temperature range of 700–800°C by vacuum CVD, using NiPc as a vapor source. The growth of the tubes was found not only from NiPc but also from FePc and CoPc, while it was not found from CuPc. This dependence on the metal element indicates that Ni, Fe and Co metals should play the role of catalyst in carbon nanotube formation. However, there were no detailed descriptions of nanotubes obtained from FePc and CoPc. Another study on the vacuum CVD of carbonaceous material on quartz plate, in which round Ni particles were deposited, revealed that carbon nanotubes could grow only when the diameter of the metal particle was 20–30 nm.[12,13)]

In this paper we report on deposits grown on various sites of a quartz plate as well as on carbonaceous material torn off a quartz tube using FePc as a source material; observed the samples using a scanning electron microscope (SEM). In nanotubes obtained from FePc, a new type of nanotube in the form of straight bundles of tubes of equal length was included, in addition to the usual type of nanotube prepared from NiPc, and it was found to grow at the rough sites of the quartz plate. In order to determine if the shape and the growth rate of the nanotubes depend on the starting materials or not, a study of NiPc is also presented.

2. Experimental

The vapor source material, metal Pc, was purified by preliminary sublimation at 460°C in a high-vacuum system. Temperature control of the vacuum CVD was performed by double electric furnaces, which were closely placed in series so as to keep the section between them at a high temperature; one furnaces was for vaporizing source material and the other was for the growth of nanotubes. A small quartz tube (8 mm in outer diameter and 50 cm long) was inserted into a large quartz tube (16 mm in inner diameter and 100 cm long). The outer tube was connected to a hig-vacuum oil diffusion pumping system with a background pressure of 8×10^{-7} Torr, and the inner tube was used for CVD. The source material, 4–6 mg in weight and a quartz plate were placed at the closed end and the middle of the inner tube, respectively. The vaporization and deposition temperatures were set at 340–370°C and 700°C, respectively. The CVD period was several hours in most cases.

X-ray diffraction measurements using CuKα radiation were performed using a powder X-ray diffractometer (RINT 1100, Rigaku). Images of the morphology of the deposits were obtained utilizing a scanning electron microscope (S-2100A, Hitachi). The saturation magnetization (Ms) of the samples was evaluated by a Quantum Design SQUID, model MPMS, by scanning a magnetic field of up to 0.5 T.

3. Results and Discussion

X-ray powder diffraction patterns of the deposits obtained by vacuum CVD, using NiPc and FePc as source materials, are shown in Fig. 1. The as-grown material deposited on a quartz plate from NiPc (Fig. 1(a)) exhibits three peaks corresponding to MWNT, Ni (111) and Ni (200). The peaks of Ni were significantly reduced by refluxing of the as-grown material in nitric acid for two days (Fig. 1(b)). The Ms value of the purified sample measured by SQUID was 0.50 emu/g. The residual content of Ni metal estimated from the above value using the Ms value of Ni metal (54.5 emu/g) was 8.4×10^{20} atoms/cm^3. The yield of carbonaceous material deposited on the quartz wall was 45–50 weight % of the NiPc source material. The final yield after purification was about 40 weight %, since a small fraction of the product was lost during the refluxing process in acid. Taking the content of carbon (67.28 weight %) in a NiPc molecule from a raw material into consideration, the yields of carbon contributing to the as-grown carbonaceous material and the purified nanotube are estimated to be 67–74 weight % and 59 weight %, respectively. That is, carbon nanotubes can be formed at a very high efficiency by the present method using NiPc.

Most of the deposits prepared from CVD of FePc were found to adhere strongly to the surface of the quartz tube and had to be torn off by ultrasonication in nitric acid. However, they exhibited a similar X-ray pattern to that of Fig. 1(b), with a large peak of MWNT and a small peak of Fe (111)

(Fig. 1(c)).

SEM images of the deposits formed on the quartz plates from NiPc and FePc are shown in Fig. 2. The general features of the nanotubes grown on quartz plate resemble ones shown in ref. 11. That is, the outer diameter of a tube is several times larger at the base than at the tip of the tube, and a thin part bends and coils around the tip. In both deposits, the outer diameter of the tube is 20–40 nm in the thin part, giving much the same value. However, the tube length is 20–30 μm for the deposits from NiPc, while about 10 μm for that from FePc, suggesting a higher nanotube growth rate by a Ni metal catalyst.

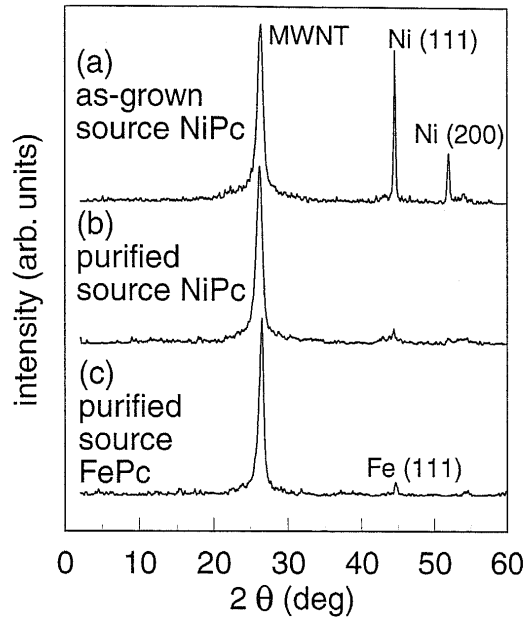

Fig. 1. X-ray diffraction patterns of (a) as-grown deposits, (b) deposits after refluxing in nitric acid for two days, obtained by vacuum CVD using NiPc source, and (c) deposits after refluxing in nitric acid, obtained by CVD using FePc source.

A small fraction of the products prepared from FePc could be easily torn off the quartz tube without washing in acid. This material exhibits a distinctive feature. That is, it takes the form of straight bundles of tubes of equal length and is shaped like winter mushrooms (Enokidake in Japanese), as shown in Fig. 3(a). The inner tube of each Enokidake-shaped nanotube at the base was closely packed with Fe metals and gave the appearance of a knife-cut edge, as shown in Figs. 3(b) and 3(c). In contrast, the bases of the mushroom-shaped tubes which were torn off by ultrasonication in nitric acid were etched and the sides of the tubes were exposed, as shown in Figs. 3(d) and 3(e).

The mushroom-shaped tubes did not coil at the thin part. However, the outer diameter of the tubes is large at the base and small at the tip. The outer tube diameter, judging from the magnified photographs of those tubes, is 210–250 nm at the base, 100–130 nm at the middle part and about 40 nm at around the tip, and the tube length is about 15 μm.

In order to clarify the sites on which the mushroom-shaped tubes grew, the deposits formed at various sites on the quartz plate were examined by SEM. The mushroom-shaped tubes were found not on the flat surface of the quartz plate but at a part of the vertical section of the plate edge, as shown in Fig. 4. This vertical section was obtained by breaking the quartz plate with a diamond cutter and had a number of rough sites. Thus, we believe that these tubes prefer to grow on the rough sites of the quartz plate.

It should be mentioned that in products prepared from NiPc, we did not find the mushroom-shaped nanotubes. Most of the mushroom-shaped nanotube prepared from FePc adhered strongly to the quartz plate. This adhesion is inferred to

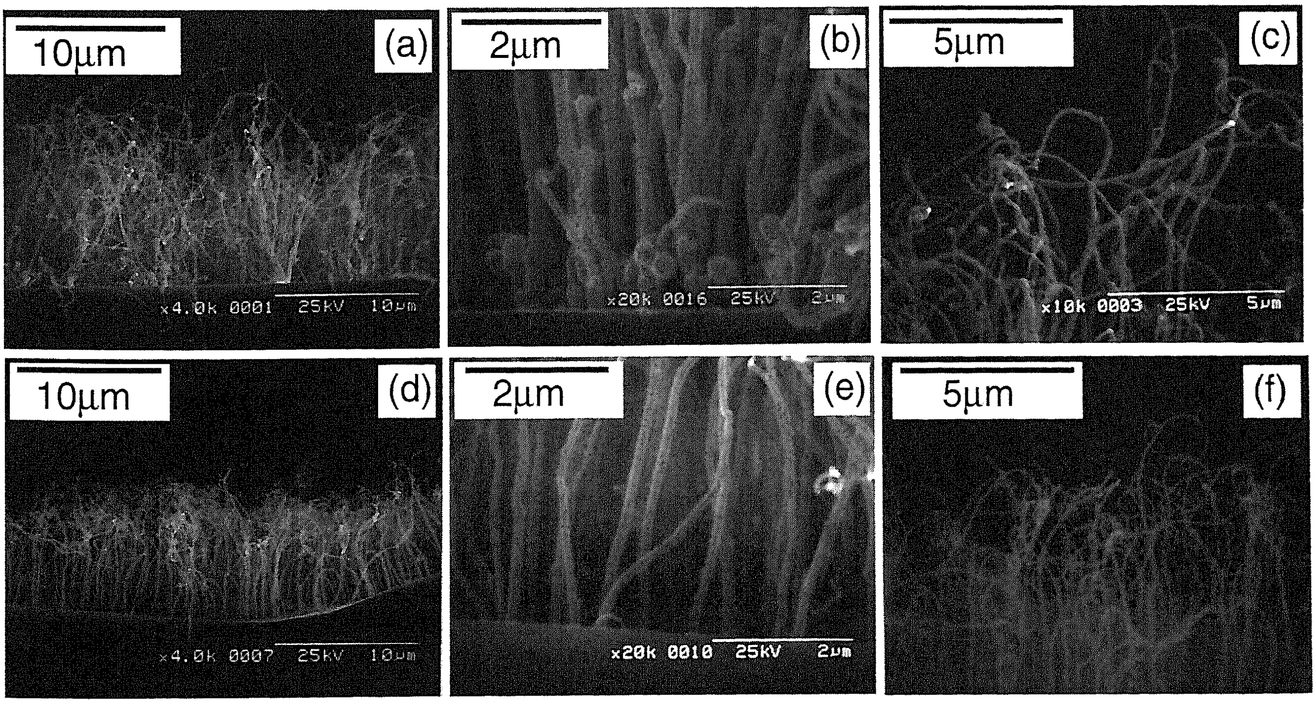

Fig. 2. SEM images of (a) side view, (b) side view around the base, (c) side view around the tips of nanotubes obtained by vacuum CVD on a quartz plate using NiPc source, (d), (e) and (f) nanotubes obtained from FePc correspond to (a), (b) and (c) from NiPc, respectively.

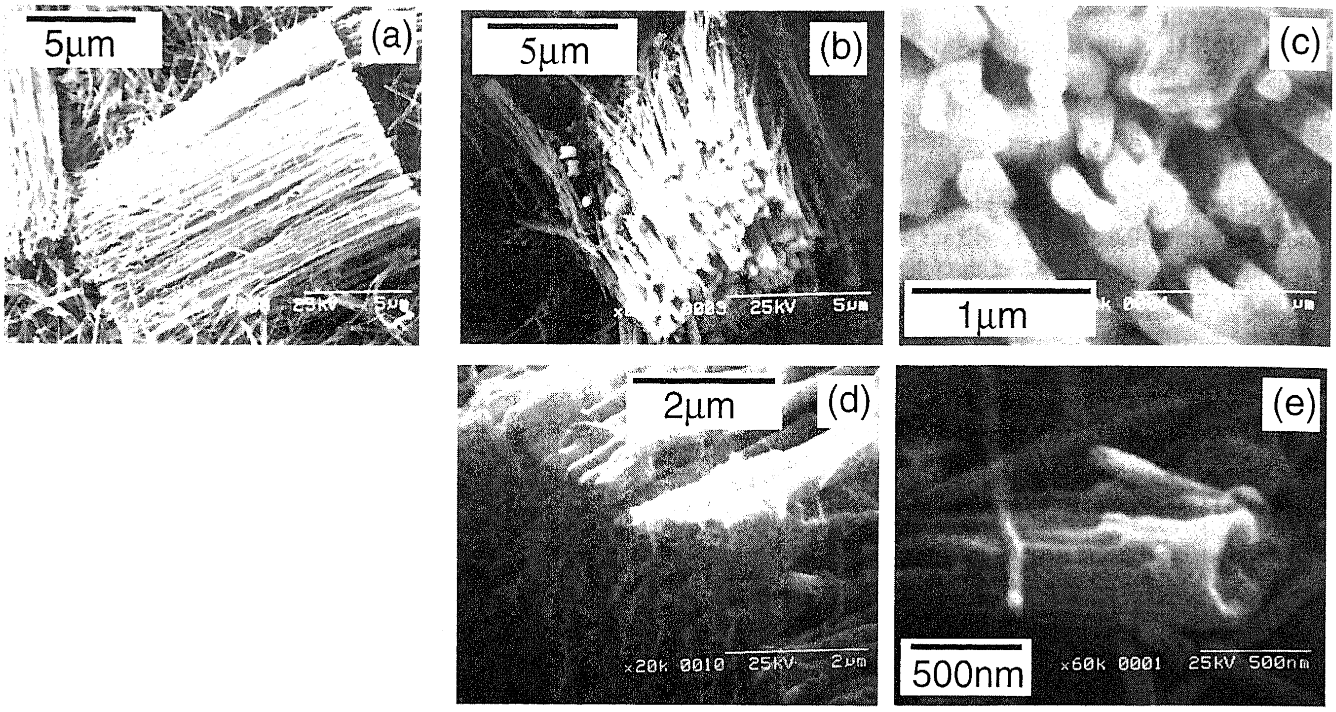

Fig. 3. SEM images of deposits obtained by vacuum CVD using FePc source: (a) as-grown deposits torn off from the quartz tube, (b) bases of as-grown deposits, (c) magnification of the base (b), (d) bases of deposits etched in nitric acid, and (e) magnification of base (d).

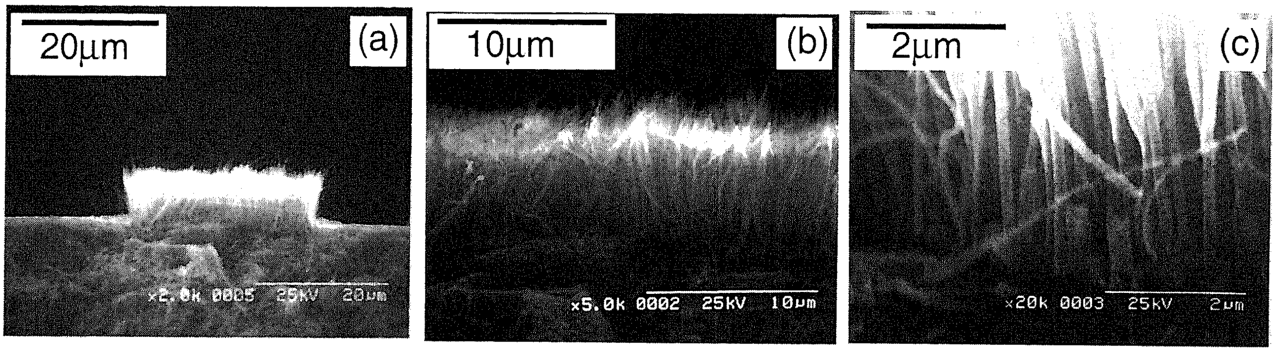

Fig. 4. SEM images of (a) mushroom-shaped tubes grown at a part of the vertical section of a quartz plate, (b) magnification of (a), and (c) magnification of the base.

be induced by the contents (Fe metal) inside the base of the tube. This feature of carbon nanotubes prepared from FePc contrasts with the characteristics of the usual nanotubes prepared from NiPc, and may be more suitable for applications of carbon nanotubes in devices such as electron emitters.

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