



Growth of carbon nanotubes and nanofibres in porous anodic alumina film

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Abstract

By acetylene pyrolysis at 650 and 550°C, carbon nanotubes were synthesized successfully in porous alumina templates anodized in sulfuric and/or oxalic acid solution. For templates anodized in oxalic acid followed by boiling in distilled water, thermal decomposition of acetylene at 650°C in the pores results in the formation of carbon nanofibres. For templates anodized in sulfuric acid, only carbon nanotubes were formed, even if boiling in water was adopted to process it. This indicates that the modifications of the catalytic effects in acetylene pyrolysis by boiling in water are different for these two types of templates. All the carbon nanotubes and nanofibres have similar lattice structures under HRTEM examination. No carbon nanotubes or nanofibres can be formed when the chemical vapour deposition temperature decreases to 500°C. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Extensive investigations have been made on carbon nanotubes (CNTs) motivated by their exciting electric, chemical and mechanical applications [1–4]. Recent studies show that the production of aligned arrays of carbon nanotubes in a porous anodic alumina template (AAT) is very promising. The morphology of the obtained tubes can be Y-junctions, multi-branched or straight with highly ordered distribution, depending on the channel structure of the template [5–8]. Coulomb blockades in a

single tunnel junction directly connected to multi-walled carbon nanotubes grown in porous anodic alumina was detected [9]. Recent works show that multi-branched CNTs can be obtained in templates oxidized in oxalic acid solution at high anodic voltages without transition metal deposition [7]. In order to test if the ramification phenomenon also holds true for other acid solution, 1.2 M sulfuric acid solution was adopted for the preparation of porous templates in this paper.

On the other hand, in the catalytic test reaction of the decomposition of HCOOH at 330–390°C using anodic alumina made in sulfuric acid as the catalyst, the final promotion of the total catalytic activity was 13.7 times that of the non-treated oxide after repeated boiling in water [10]. So, in this study, the templates anodized in both oxalic and sulfuric acid were boiled in distilled water for 15 min, and then acetylene pyrolysis in the presence of treated and non-treated templates was carried out. The corresponding morphology and wall structures of the attained nanotubes and/or nanofibres were studied in detail.

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2. Experimental

Pure Al (99.99%) plates were annealed at 500°C and electrochemically polished in (5:1, v/v, solution of EtOH–HClO₄) for 3 min at 20 V. Porous anodic alumina templates were produced by anodizing the polished aluminum plate at different anodic voltages in 0.16 M oxalic acid solution or 1.2 M sulfuric acid solution for 25 min. The solution was rigorously stirred and kept at 15°C.

The anodic films were cleaned carefully after anodization. Boiling in water was carried out for 15 min. Pairs of alumina templates with or without boiling in water were put into a tubular stove with a gas-flow mixture of N₂–C₂H₂ (90:10) at a rate of 100 ml/min at a specified temperature for 2 h, finally they were cooled to room temperature. The nanotubes and nanofibres were released by dissolving alumina in 10% NaOH solution. The nanotubes or nanofibres were thoroughly washed and dispersed in pure EtOH by sonication. A drop of the suspension of the nanotubes or nanofibres was placed on a copper grid for structure observation. Conventional transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) (TEM; JEM–

1200EXII and HRTEM: JEOL 2000EX) were adopted for structure examination.

3. Results and discussion

3.1. Carbon nanotubes grown in the templates without boiling in water

Fig. 1 shows two transmission electron microscopy (TEM) images of the multi-wall CNTs grown by chemical vapour deposition (CVD) at 650°C in templates anodized at 18 V in 1.2 M sulfuric acid solution (Fig. 1a) and at 60 V in 0.16 M oxalic acid aqueous solution (Fig. 1b). A few small, short and irregular branches, besides the straight ones, were observed in some of the CNTs in Fig. 1a. There were also a few bamboo-like knots in these kinds of nanotubes. When the anodic voltage was increased to 22 V in the sulfuric acid solution, the obtained CNTs had more branches than when obtained at 18 V. When the anodic voltage was increased further to 24 V, anodic dissolution became predominant and anodic oxidation became negligible, little anodic alumina was formed, and then no

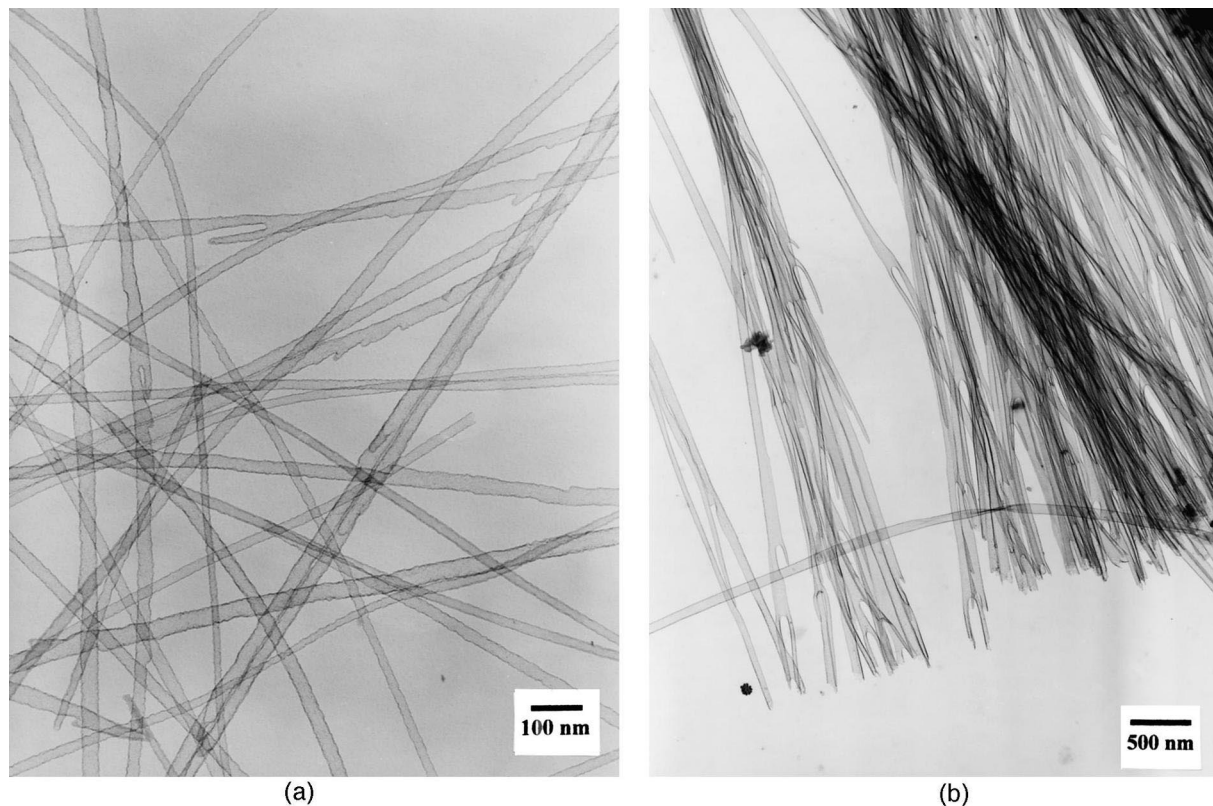


Fig. 1. TEM image of the CNTs grown by CVD at 650°C in templates anodized at 18 V in 1.2 M sulfuric acid solution (a) and CNTs in templates anodized at 60 V in 0.16 M oxalic acid aqueous solution (b).

carbon nanotubes were formed after the CVD process. Comparing with the CNTs prepared in sulfuric acid, those grown by CVD at 650°C in the template anodized at 60 V in 0.16 M oxalic acid aqueous solution were smooth without any bamboo-like knots. However, there were more and longer irregular branches in these kinds of CNTs (as shown in Fig. 1b). The structure and number of the branches depended mainly on the electrolyte and the anodic voltage. The number of the branches increased as the anodic voltage increased [6,7]. Apart from the branch conformation difference, the two types of CNTs had different diameters. The diameter of CNTs from templates anodized at 18 V in the sulfuric acid solution was 24 ± 8 nm (mean \pm standard deviation), while that of CNTs from templates anodized at 60 V in the oxalic acid solution was 86 ± 10 nm. The templates anodized at 18 V in the 1.2 M sulfuric acid solution had a pore density of about 56×10^9

cm^{-2} , while those anodized at 60 V in the 0.16 M oxalic acid solution had a pore density of about $69 \times 10^8 \text{ cm}^{-2}$ [11,12]. As the pore density was identical to that of the CNTs grown in the templates, aligned CNTs with a higher density were obtained using templates anodized in the sulfuric acid solution in this experiment.

Fig. 2a and b show the lattice images of the walls of CNTs grown by CVD at 650°C in templates anodized at 18 V in 1.2 M sulfuric acid solution and at 60 V in 0.16 M $(\text{COOH})_2$ solution, respectively. The walls of both types of CNTs consist of numerous stacked flakes or chips of carbon atomic layers, which is different from that of multi-wall carbon nanotubes made by arc-discharging and other CVD methods. The wall thickness ranges from 3 to 5 nm. All the above results indicate that multi-branched CNTs can be obtained not only in the template anodized in oxalic acid [6], but also in that anodized in sulfuric acid.

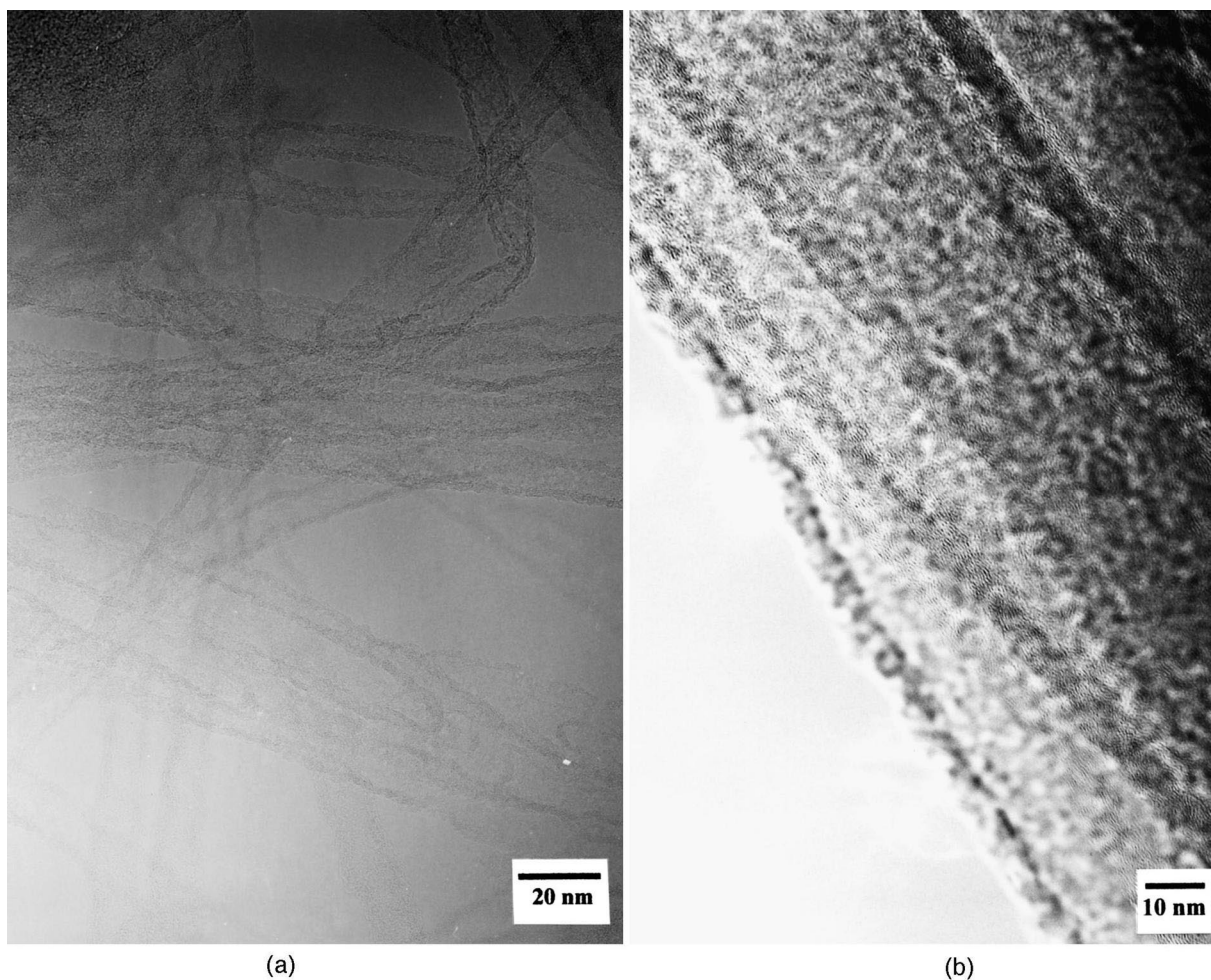


Fig. 2. The lattice images of the nanotube walls of CNTs grown by CVD at 650°C in templates anodized at 18 V in 1.2 M sulfuric acid solution (a) and at 60 V in 0.16 M oxalic acid aqueous solution (b) for 25 min.

Both kinds of CNTs have the same wall structures, regardless of the anodic voltage and the electrolyte adopted for anodization.

3.2. Carbon nanotubes or nanofibres grown in templates after boiling in water

Porous anodic alumina film acts as both a catalyst and template in the formation of carbon nanotubes by thermal decomposition of acetylene. Since boiling in water can increase the catalytic activity of porous anodic alumina greatly in the thermal decomposition of HCOOH at 330–390°C [10], in this experiment, boiling in water was adopted to process a porous template, in order to find a possible modification of catalytic decomposition of acetylene and possible modification of the conformations of CNTs. Two types of anodic alumina templates, anodized at 60 V in 0.16 M oxalic acid aqueous solution (AAT1) and at 18 V in 1.2 M sulfuric acid solution (AAT2), respectively, were treated in boiling distilled water for 15 min. Then they were used as templates for the growth of carbon nanotubes. Fig. 3a and b shows the

carbon nanotubes and nanofibres grown at 650°C by CVD in the above-mentioned two templates after boiling in water, respectively. The carbon nanotubes with the bamboo-like appearances grow from the template anodized in sulfuric acid. However, it should be especially noted that solid carbon nanofibres rather than carbon nanotubes are obtained in the template anodized in oxalic acid by growing at 650°C by CVD. Both the nanotubes and the nanofibres have a relatively rough surface, compared with the nanotubes obtained from the templates without boiling in water. Especially for the CNTs obtained in the template anodized in sulfuric acid, the number of the bamboo-like knots increases greatly after boiling in water (as shown in Figs. 1a and 3a). Our recent work shows that subtle topographic modification of internal pores can be copied by the growth of carbon nanotubes [13], so that the above-mentioned results may suggest boiling in water resulted in corrosion of the internal pore surface.

From the results obtained in Section 3.1, it can be realized that without boiling in water both AAT1 and AAT2 show similar catalytic effects on the decomposition of C₂H₂ and the formation of carbon nanotubes. However,

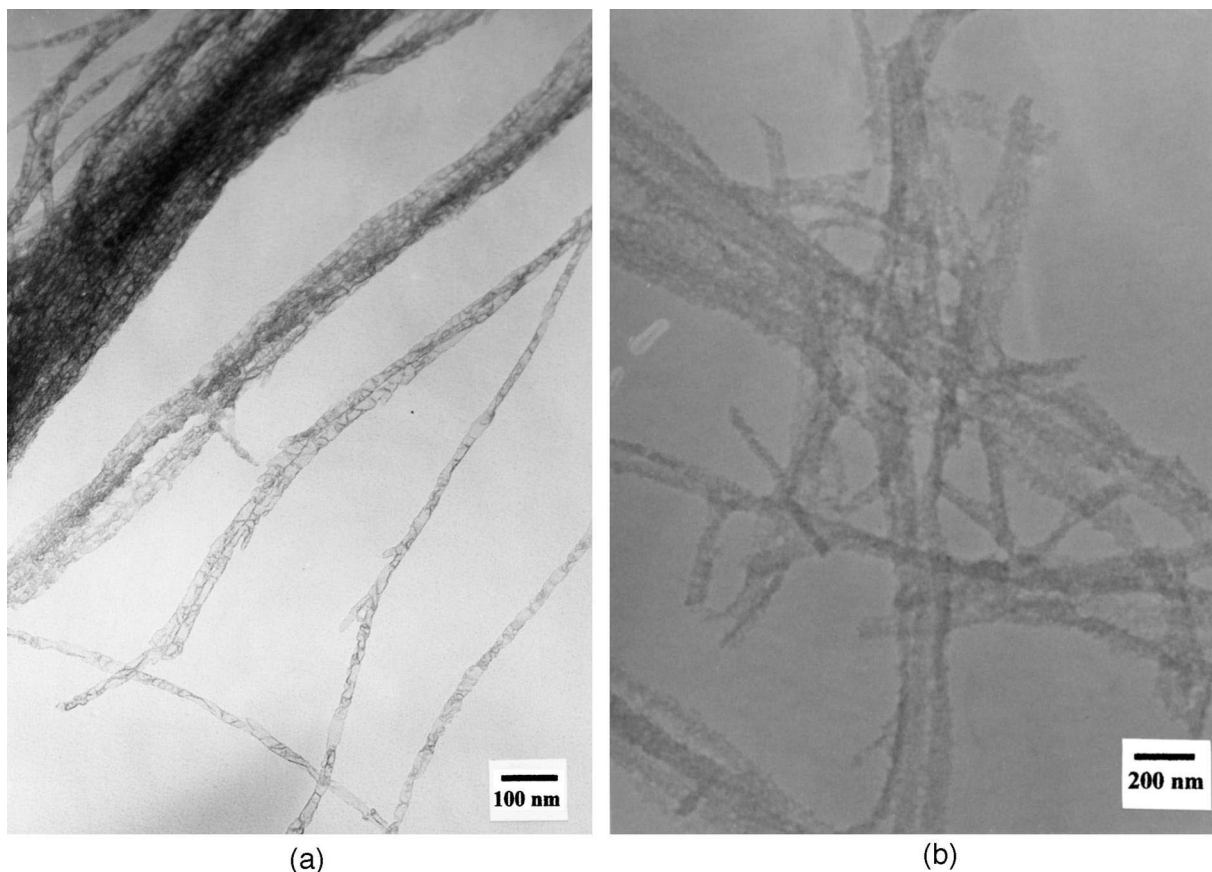


Fig. 3. TEM images of the carbon nanotubes (a) and nanofibres (b) grown by CVD at 650°C in templates corresponding to those of Fig. 2a and b after boiling in water.

after boiling in water, carbon nanofibres are formed in the templates anodized in oxalic acid, which provides clear evidence that boiling in water increases the catalytic activity of AAT1 in the decomposition reaction of C_2H_2 . As for the templates anodized in sulfuric acid and then boiling in water, only carbon nanotubes are obtained. Meanwhile, for the templates anodized in sulfuric acid solution, the carbon nanotubes grown by CVD at 650°C before and after boiling in water have the same tube wall structures, which suggests that boiling in water improved neither the rate of the decomposition of C_2H_2 nor the crystallinity of the tube wall. The above results obviously indicate that the effects of boiling in water are different for these two types of templates. It was reported that the anions of the electrolyte used for the oxide preparation are always incorporated inside the templates [10]. In fact, the walls of the anodic alumina cells consist of two layers: an outer layer of homogeneous, anion-contaminated alumina, containing most of the impurities and an inner layer of relatively pure alumina. In the cases of the sulfuric and oxalic acid electrolytes, the number of anions of the electrolyte incorporated in the templates reaches about 11% of the oxide mass [12,14]. The compositions of the outer layers of anion-contaminated alumina in AAT1 and AAT2 are obviously different. Typical levels of anion species incorporated into AAT1 and AAT2 are 2.4 wt.% oxalate and 12–14 wt.% sulphate, respectively [15]. The difference in the catalytic activities modified by boiling in water may be just related to the different anions incorporated into the templates. The effects of the incorporated anions and the boiling in water on the catalytic role are complex and this issue needs further investigation.

Fig. 4 shows the lattice images of the carbon nanofibres formed in the templates anodized in oxalic acid followed by boiling in water. The lattice images of the nanofibres and nanotubes are equivalent to each other in their crystallinity. It may be concluded that boiling in water only increases the decomposition rate of C_2H_2 and the carbon deposition rate, but it does not improve the crystallinity of the obtained carbon fibres. Therefore, the catalytic activity of the porous alumina template boiling in water is still much lower than that of a transition metal [16]. Generally speaking, all the walls of the carbon nanotubes and nanofibres have a similar lattice structure, regardless of the electrolytes adopted for anodizing.

3.3. Carbon nanotubes grown at lower temperatures

In the view of energy consumption and the future application of the carbon nanotubes in anodic alumina, it is desirable to lower the CVD temperature for the growth of CNTs. Therefore, carbon nanotube formation by CVD in templates with or without boiling in water was studied at relatively low temperatures.

The thermal decomposition of acetylene at 550°C in AAT1 and AAT2 with or without boiling in water was

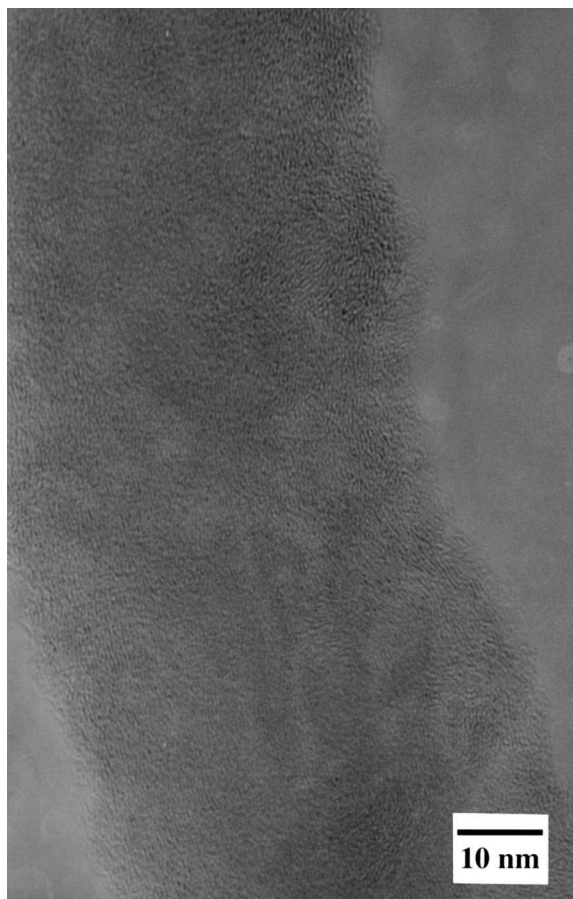


Fig. 4. The lattice images of the carbon nanofibres formed in templates anodized in oxalic acid and followed by boiling in water.

carried out. It was found that carbon nanotubes can be successfully formed in all the templates, but no carbon nanofibres are formed. On the other hand, for the carbon nanotubes produced at 550°C, there is no evident effect of boiling in water. When the CVD temperature is decreased further to 500°C, no carbon nanotubes or nanofibres are formed. It can be concluded that acetylene pyrolysis in porous anodic alumina depends on temperature as well as on boiling in water. After TEM and HRTEM examination, it was found that the carbon nanotubes formed at 550 and 650°C had similar wall structures and appearance. Fig. 5 shows a typical TEM image of CNTs grown at 550°C by CVD in the templates anodized at 18 V in the 1.2 M sulfuric acid solution for 25 min.

4. Conclusions

As an alternative method for the common use of oxalic acid, acetylene pyrolysis in porous template obtained by



Fig. 5. TEM images of CNTs grown at 550°C by CVD in templates anodized at 18 V in 1.2 M sulfuric acid solution.

anodic oxidation in sulfuric acid solution can produce aligned carbon nanotubes with a higher density ($\sim 56 \times 10^9 \text{ cm}^{-2}$) and with branches. Both 650 and 550°C are suitable temperatures for the growth of nanotubes. After boiling in water, carbon nanofibres, rather than nanotubes, can be obtained in the templates anodized in oxalic acid solution by growing at 650°C through the CVD method, which indicates an obvious promotion of the catalytic activity for anodic alumina. However, boiling in water has little effect on the catalytic activity for acetylene pyrolysis on the anodic oxide films formed in sulfuric acid solution. All the carbon nanotubes and nanofibres have similar tube wall structures under HRTEM examination. No tubes can be formed if the CVD temperature decreases to 500°C.

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