

Preparation and Characterization of Y-type Carbon Nanotubes by Using Anodized Alumina Oxide (AAO) Template

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Abstract: In this work, potential-modulation method was used in two-step anodization process to make an AAO template with Y-type nanochannels. Then Y-type carbon nanotubes with controlled length and branch angle were prepared in the template based on chemical vapor decomposition (CVD) method with Co particles as catalyst and C_2H_2 as carbon source. The Y-type nanotube branches exhibit the angle distribution ranging from 20° to 120° . The results demonstrated that the oxidation potential should be responsible for the angles and length of the branches. Short pulse and high oxidation potential will result in the short and dense nanotube branches.

Key words: AAO template, Y-type carbon nanotubes, Stepping oxidation potential

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1 Introductions

Carbon nanotube is one of the promising devices, such as Ballistic switch (BS) and Ballistic rectifier (BR)^[1,2] that are of great importance for the device miniaturization in the future semiconductor technology. Because silicon is expected to reach its limits due to the inherent quantum effects when it approaches smaller size. For such applications, it is necessary to design molecules and nanotubes of different diameters and chirality^[3~5] together to form a junction such as Y- or T-junctions considered as prototypes^[6,7].

Up to now, although it is reported that the Y-type carbon nanotubes were successfully prepared by using pyrolysis-based method^[7] on dispersed catalysts and by using Y-type nano-channel alumina templates^[6,8], the relationship between the synthesis conditions and formation process of the Y-type carbon nanotubes have not been well-understood. Apparently, it is significant to do more experiments to understand what is the most important factor to affect the formation of

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Y-type template and its micro-mechanism.

In this work, several experimental conditions, especially the effects of stepping oxidation potential on the formation of Y-type AAO template were studied. The relationship between the oxidation potential and the formation of the related Y-type nano-channel template was also primarily analyzed.

2 Experimental

2.1 Preparation of Y-type AAO Template and Y-type Carbon Nanotubes

The process of pretreatment and the first step of oxidation were the same as the paper before^[9]. Thereafter the anodized Al substrate was immersed in 5 % H_3PO_4 for about 2 hours to remove partial alumina template, and then anodized again at the oxidation potentials which were stepped periodically between the two suitable potentials to obtain a template with Y-type configurations, that should be different from the template with regular straight nanochannels formed at the steady oxidation potential.

Alternating current source was used to deposit Co metal in the pores to perform as reaction vessels and catalyst. Next, the alumina membrane was removed from the substrate by being immersed in the saturated HgCl_2 solution and then put into furnace. Thermally treated by programmed heating-process was firstly reduced in carbon monoxide about 5h at 600 °C, and then carbon nanotubes were produced in the template with a mixture of acetylene and N_2 . Since the length and density of the carbon nanotubes should relate to the pyrolysis time in the furnace, it was fixed at 1 hour for different kinds of templates in this work.

2.2 Structural Characterization of Carbon Nanotubes

SEM (LEO570, U. S.) and TEM (JEM-100CXII, Japan) technology were employed in this work to obtain nanostructural information about the branching distribution and the related rules of the carbon nanotubes in this work. HF solution (20 %, V/V) was used to dissolve the template and obtain the carbon nanotubes dispersed on the copper meshes.

3 Results and Discussion

3.1 Characterization of AAO Template with Y-type Configurations

Considering that the formation of the alumina membrane is tightly related to the potential in the oxidation process, we could expect the template with branched channels if the oxidation potential was kept varying. The different modes of potential conditions used in this study are shown in Tab. 1.

Tab. 1 Different oxidation potential stepping conditions for formation of Y-type AAO template at 25

Experimental condition	1	2	3
Potential stepping range/ V	40 ~ 80	40 ~ 80	40 ~ 120
Duration time at each potential/ h	1	1/ 6	1
Stepping cycles	1	3	1

A SEM image of the cross section of the template with carbon nanotubes grown in is shown in Fig. 1a, which can be regarded as the frame of reference in this work, indicating straight nanochannels were formed. Although no clear branches could be observed directly, it was shown in the SEM images (Fig. 1b to Fig. 1d) that the nano-channels in the template become more irregular, which implied in a sense that branches could have appeared in the template. While in Fig. 2a and Fig. 2b, different branches can be distinguished clearly from the templates with carbon nanotubes in. Moreover, the irregular channels intensified with the increase of steps. When the oxidation potential was increased to 40 ~ 120 V, the template appeared thoroughly irregular as shown in Fig. 1d.

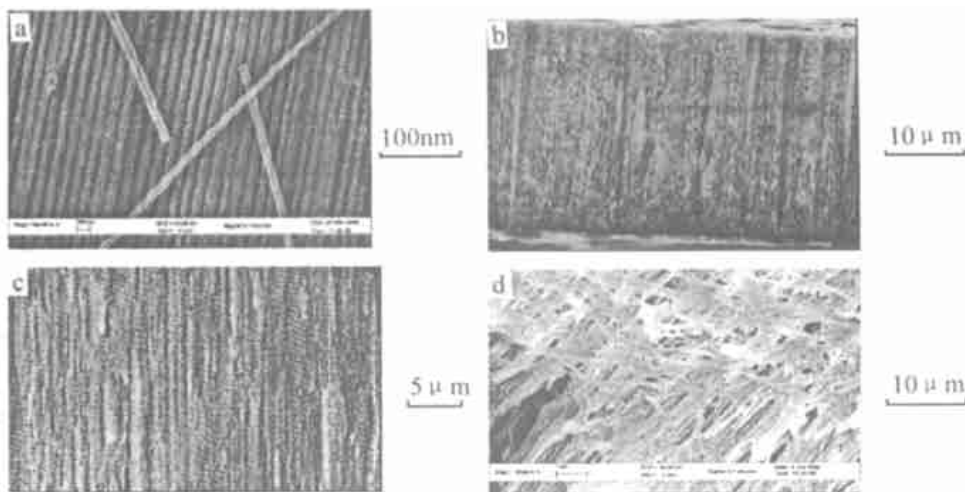


Fig. 1 SEM image of cross section of the alumina template with carbon nanotubes grown in (a) and of the membrane formed in the potential conditions as indicated in Tab. 1: condition 1 (b), condition 2 (c), condition 3 (d)

As indicated above, we concluded that the potential step from 40 V to 120 V would be too violent for the template to form regular nanochannels while the potential step from 40 V to 80 V was appropriate. In the following section, potential stepping condition 1 and 2 were separately used, and several cycles and different duration time at two potentials were performed to get the templates with different regular Y-type configurations.

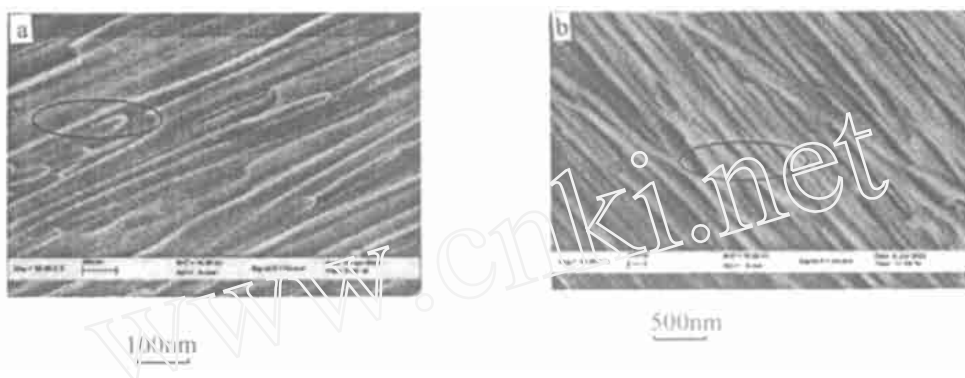


Fig. 2 SEM images of the cross section of Y-type AAO template with carbon nanotubes in potential condition 1 (a) and 2 (b) in Tab. 1

3.2 Characterization of Y-type Carbon Nanotubes

Compared with the SEM images of templates, the SEM and TEM images of carbon nanotubes could give more detailed and explicit informations. It can be seen that the TEM image in Fig. 3a showed the Y-type carbon nanotube with long and rare branches, which was from the template formed in the potential condition 1. On the contrary, the SEM image in Fig. 3b showed the short and dense branches, which was from oxidation potential condition 2. It can be seen that the branch angle between the two branches is about $20^{\circ} \sim 30^{\circ}$, which is different from the 120° of the theoretical model proposed by Scuseria. While the two branches are perfectly symmetrical at the beginning of the branching point, and that is of great importance for BR effect in application.

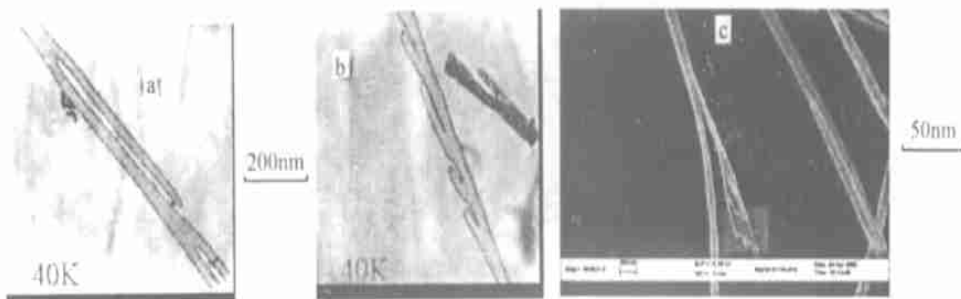


Fig. 3 TEM images of the Y-type carbon nanotubes growing from the alumina membrane oxidized at the square-wave potential ranging from 40 V to 80 V in different frequency and cycles: a) in potential condition 1 in Tab. 1, b) in potential condition 2 in Table 1, c) SEM image of Y-type carbon nanotube as Fig. 3. a

Based on the above results, it may be proposed that the Y-type configurations in the template were formed when oxidation potential was stepped from lower to higher oxidation potential. If the

duration is longer enough, the branch-structure in the template will grow to some extension. When carbon nanotubes grows along the nanochannels, the catalyst will split at the branch point, which was testified by the TEM images of the carbon nanotubes with catalysts in both end of braches and junctions^[10]. However, why AAO template develop different kinds of branches as different modes of potential step is not clear at this stage.

4 Conclusions

From the results and discussions, it can be seen that AAO template proved to be a good template to produce the Y-type carbon nanotubes because of the easy control and high efficiency.

With the periodical change of the oxidation potential, the Y-type nanochannels in the alumina template will give the corresponding change in branch angles and length in the configuration. The oxidation potential with short duration will produce the nanotubes with long and rare branches, while the oxidation potential with long duration will engender the short and dense branches. Further investigation will be concentrated on the mechanism of the formation and growing of Y-type carbon nanotubes in AAO template.

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Y 型分支的碳纳米管的氧化铝模板法 制备及其表征

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摘要: 利用两步氧化法,通过对氧化直流电压进行周期性调制可制备出带有 Y 型孔道的氧化铝模板;然后以金属钴为催化剂,乙炔为碳源,通过 CVD 法制取得到具有规则 Y 型分支的碳纳米管阵列.已制备出的碳管分支角度在 $20^{\circ}\sim 120^{\circ}$ 的范围内.实验表明,两段分支所成的角度以及分支的长度与合成氧化铝模板的脉冲电压调节规律有关,短脉冲,高氧化电压有利于生长出的短而密集的分支构型.

关键词: 氧化铝模板;Y 型分支;脉冲电压