# 16 Template-directed Synthesis of Carbon Nanotube Array by Microwave Plasma Chemical Reaction at Low Temperature

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## 1.1 INTRODUCTION

Carbon nanotube (CNT) arrays have attracted particular interest in the recent few years because of their importance in developing novel functional devices for use as scanning probes and sensors (Keller, 1996; Kong *et al.*, 2000), as field emitters (de Heer *et al.*, 1995; Collins and Zettl, 1997), and in nanoelectronics (Tans *et al.* 1998; Frank *et al.*, 1998; Collins *et al.*, 1997). Ajayan *et al.* (1994) took the lead in producing aligned CNT arrays based on cutting thin slices of a nanotube-polymer composite. Subsequently, arrays of CNTs were prepared by using chemical vapor deposition (CVD) over catalysts embedded in mesoporous silica (Li *et al.*, 1996), anodic porous alumina template (APAT) (Kyotani *et al.*, 1999) or Fe-patterned porous silicon (Fan *et al.*, 1999) above 700 °C. In addition, Rao *et al.* (1998) directly synthesized CNT arrays on quartz tube by the pyrolysis of ferrocene or ferrocene-acetylene mixtures at 1100°C. However, these synthesis temperatures are too high and unsuitable in some cases where the deforming temperature of the substrate is lower than 700 °C. For example, it is desirable to directly take the aluminum substrate of APAT as electrode for field emission, which entails the temperature for synthesizing CNT arrays on APAT to be much lower than 660 °C i.e., the melting point of metal aluminum. Therefore, the low-temperature synthesis of CNT arrays is a challenging issue and is worth exploring.

Microwave plasma operated at low pressure is one kind of low-temperature plasma due to the non-equilibrium state between electrons and other heavy particles in plasma space which is full of active species. Consequently, the temperature for synthesizing CNTs by MW-PECVD could be greatly decreased. In this paper, a low-temperature approach, namely microwave plasma-enhanced chemical vapor deposition (MW-PECVD), has been reported to fabricate the well-aligned CNT array on APAT with a mixture of methane, argon and hydrogen as precursors in a rather simple procedure. Neither heating nor bias-voltage should be applied to the template, which makes the fabrication easily operated. This method has also been extended successfully to the synthesis of BN nanotube array.

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## 1.2 EXPERIMENTAL

The process started with the anodization of aluminum (99.5%) to obtain APAT. By anodizing an aluminum sheet in 0.3 mol/L oxalic acid at 0°C under 50V, APAT self-organized into a highly ordered hexagonal close-packed array of parallel vertically oriented pores. Figure 1a shows the scanning electron microscopic (SEM) image of our template with the channel diameters around 50 nm. The template was located in plasma zone and pre-treated by hydrogen-argon plasma for 30 min. Methane was then led into plasma system for growing CNT array for 60 min. The flux of hydrogen, argon and methane is 20, 45, and 10 sccm respectively. The system pressure was around $1.0\times10^4$ Pa measured by a Pirani vacuum gauge. The growth temperature was lower than 520 °C because no obvious change could be observed for the hard glass probe with the strain point of 520 °C which is put close to the alumina template. The resulting product was characterized by using scanning electron microscopy (SEM). Figure 1b shows the SEM micrograph of the as-grown template-containing sample without pre-treatment. It can be seen that those straight tubes are parallel to and isolated with each other.

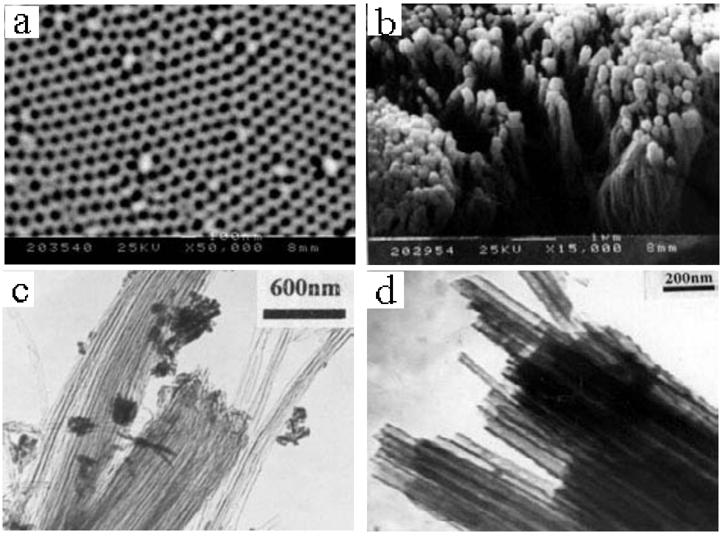

Figure 1. SEM/TEM images of anodic porous alumina template (APAT) and resulting products (a) SEM image of APAT; (b) SEM image of CNT array as-prepared; (c) TEM image of CNT bundles after the removal of APAT; (d) TEM image of BN nanotube bundles after the removal of APAT.

In order to learn more detailed information about the product, TEM image was obtained for the sample after dissolving the alumina template by using hydrochloric acid as a chemical etchant. The CNT bundles can still be seen clearly as shown in figure 1c due to the Van der waals interaction among the tubes. The nanotubes are straight with the lengths of ca. 4 μm and diameters of ca. 50 nm. The results from SEM and TEM observations indicate that the carbon nanotubes obtained in our experiments are well aligned and isolated.

Some striking features in this study are worth noting: Firstly, the synthesis temperature is rather low (<520 °C), which is crucial for growing CNT arrays on the substrate with low-deforming temperature. Secondly, it is feasible to control the parameters of the aligned carbon nanotubes such as diameter and density by regulating the character of APAT that in turn is easily adjustable through, e.g., the anodizing voltage, the type and concentration of electrolyte, the anodizing time and temperature. Thirdly, carbon nanotube array synthesized by this method is not inherently area limited and can be scaled up with the template size. Fourthly, neither heating nor bias-voltage should be applied to the template, which makes the fabrication easily operated. Finally, this method is also suitable for the synthesis of other nanotube arrays. Actually, BN nanotube array has also been successfully fabricated by using $B_2H_6$/Ar and $NH_3/N_2$ as the source of boron and nitrogen respectively as shown in figure 1d. Different from CNTs in figures 1b and 1c, it is observed that BN nanotubes have naturally open-ends, which is crucial for the subsequent electrochemical filling or the preparations of layered nanostructures for electronic devices. From above description, it is seen that the whole fabrication process is reliable, inexpensive and also universal to certain degree. These advantages are very important for both fundamental researches and future practical applications.

The growth mechanism of carbon nanotubes by chemical vapor deposition has been proposed as either base- or tip-growth on catalyst nanoparticles (Fan *et al.*, 1999; Lee *et al.*, 1999; Sinnott *et al.*, 1999) where the catalysts play a crucial role for the decomposition of hydrocarbon precursors. However, the growth mechanism within the nanochannels of alumina template still remains indistinct. In our cases, there is no catalyst particles inside the template nanochannels. In addition, it has not been found that alumina itself could catalyze the growth of CNTs. Based on above consideration, it is proposed that the synergism of “space limitation” and “plasma activation” is a key factor in our case. In other words, the nanochannels of APAT enforce the initial formation and subsequent epitaxial growth of the tubular nanostructure from the plasma activated species along the inner surface of the nanochannels where the density of the active species should be the largest due to adsorption. Accordingly, this preparation method should be applicable not only to CNTs but also to BN nanotubes as shown in figure 1d, and possibly to some other nanotubes such as BCN and CN when suitable precursors are used, which is of course very interesting for further exploration.

## 1.3 CONCLUSION

In summary, we have fabricated well-aligned carbon nanotube and boron nitride nanotube array by MW-PECVD within the nanochannels of anodic porous alumina template with $CH_4$, $B_2H_6$ and $NH_3/N_2$ as the source of carbon, boron and nitrogen respectively. The method presented in this paper offers a low-temperature, controllable and inexpensive technique route, and has the potential for synthesizing different kinds of well-aligned nanotube arrays, which is rather attractive for further scientific and technological studies.

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