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# Carbon nanotube arrays

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**Abstract.** Carbon nanotube arrays were prepared by chemical vapor deposition (CVD) of hydrocarbon gas on various substrates. The effect of substrates on the growth, morphology and structure of carbon nanotubes were investigated. Aligned carbon nanotubes with high density and purity were achieved by CVD on bulk silica substrate. On the film-like substrates, very long carbon nanotubes of length $\sim 2$ mm were produced, which is an order of magnitude longer (1 mm vs. 100 $\mu$m) than that described in most previous reports. High-resolution transmission electron microscopy (HRTEM) investigation illustrates that these carbon nanotubes are well graphitized and very pure. The tubes are typically consist of several to tens of concentric shells of carbon sheets with spacing about 0.34 nm. Micro-Raman spectroscopy has been carried out to detect the microstructures of CNT. The observed ratio of the integrated intensity of D and G band was found different from that of carbon nanotubes produced by arc-discharge method and pyrolytic graphite (PG). The resonance properties and higher order Raman bands are also different from other forms of carbon. With the help of the results of SEM and HRTEM the origination of the broader band structure were discussed.

**PACS.** 68.65.+g Low dimensional structures (superlattices, quantum well structures, multilayers): structure, and nanoelectronic properties – 81.15.Gh Chemical vapor deposition (including plasma-enhanced CVD, MOCVD etc.) – 81.20.Fw Sol-gel processing, precipitation – 61.16.Bg Transmission, reflection and scanning electron microscopy (including EBIC)

## 1 Introduction

The discovery of carbon nanotubes (CNT) [1] has stimulated great interest among scientific communities [2, 3]. Large quantities of CNT can now be produced by either arc discharge [4] or thermal decomposition of hydrocarbon [5]. Controlled growth of the carbon nanotubes, with regard to their length and diameter as well as their alignment, is important both for potential applications and for detailed characterization of their properties. The direct production of aligned isolated CNT by thermal decomposition of hydrocarbon gas is a new idea. Because a substrate containing a catalyst will affect the growth of CNT, many works have focused on the improvement of the substrate [6–8]. In principle, mesoscopic pores distributed in mesoporous substrate have a special effect on the formation and property of low-dimension materials formed on the substrate. Li *et al.* [9–11] have studied the impact of various substrates, especially the mesoporous substrates, on the growth and morphology of the CNT. On the basis of systematic studies of the effect of various mesoporous substrates on the carbon nanotube growth, they developed a new method for preparing substrates with aligned pores in which catalyst particles were embedded, and produced the aligned, isolated, and dense CNT on these mesoporous substrates by chemical vapor deposition (CVD) [9]. At the same time, Terrones *et al.* [12] have produced the aligned nanotubes using laser-etched cobalt thin film as a substrate, in which the tubes grow perpendicularly to the catalytic substrate only in the etched regions. Recent reports describe the production of very long ($\sim 2$ mm in length) aligned nanotubes by pyrolysis of acetylene over iron/silica nanoparticles on the surface of the film-like mesoporous silica [13]. Here, we will discuss the morphology and structure of CNT grown on different substrates and the facts that determine the growth of CNT. We also discuss Raman scattering, performed directly on the as-formed aligned carbon nanotubes, to elucidate the dependence of Raman peak positions and intensities on the microstructures. It is possible that matrices consisting of aligned nanotubes may be useful as novel, mechanically strong composite materials and as field emission sources.

## 2 Experimental procedure

The experimental procedures employed in the growth of the aligned CNT can be divided into two main types, which are described below.

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### 2.1 Aligned carbon nanotube growth on the bulk silica substrates

The mesoporous silica substrates with aligned pores were prepared by a sol-gel process from tetraethoxysilane hydrolysis in iron nitrate aqueous solution [14]. Analytically pure tetraethoxysilane, ethyl alcohol and iron nitrate aqueous solution (0.1–1.5 M) were mixed with mole ratio 1:4:$(10-14)$ by magnetic stirring for $\sim 30$ min. Then 0.2 ml concentrated hydrogen fluoride or hydrochloric acid was added to 30 ml of the mixture, and the mixture was stirred for another 15 min. After gelation of the mixture, the gel was dried for one week at 60 °C for the elimination of excess water and other solvents. Then the gel was calcined at 450 °C for 10 h in vacuum. In this process the relative uniform pores were formed and embedded with iron oxide nanoparticles. Subsequently, the iron oxide nanoparticles contained in the gel were reduced to iron particles at 550 °C in 180 torr of flowing 9% $H_2/N_2$ (110 cm$^3$/min) for 5 h. Afterwards, a mixture of acetylene and nitrogen was introduced into the reaction chamber at a flow rate of 110 cm$^3$/min and with a volume ratio of 1:10. During the reaction, the gas pressure in the chamber was 180 torr, and CNT were formed on the substrate by the decomposition of acetylene at 700 °C.

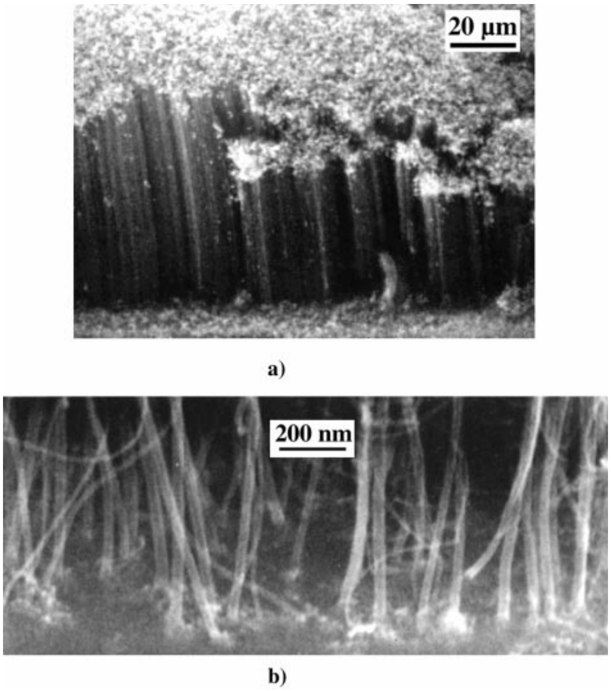

**Fig. 1.** (a) Low-magnification SEM image of a nanotube array composed of aligned carbon nanotubes. This array with a thickness of $\sim 50\,\mu$m was obtained by growing for 2 h. (b) High-magnification SEM image of carbon nanotubes growing outwards perpendicularly and separately from the mesoporous silica substrate and forming an array. These carbon nanotubes have diameters of $\sim 30$ nm and the spacing between the tubes is $\sim 100$ nm.

### 2.2 Very long aligned carbon nanotube production on the film-like silica substrates

The method used here is similar to that reported by Li *et al.* [9], but some improvements have been made in substrate preparation so that a substrate film of thickness 30–50 mm could be obtained [13]. After gelation, the film-like substrates were calcined at 450 °C for 10 h under vacuum and then reduced at 500 °C for 5 h in a flow of 9% $H_2/N_2$ under 180 torr. At this stage, large quantities of iron/silica nanoparticles, which acted as a catalyst for nanotube growth, formed evenly on all surfaces of the substrates. Afterwards, this gel was used as a substrate for production of CNT under the conditions described above.

### 2.3 Characterization of the aligned nanotubes

A scanning electron microscope (SEM), S-4200, attached by an energy-dispersive X-ray (EDX) system, and a high-resolution transmission electron microscope (HRTEM), JEM 200-cx, were employed to characterize the morphologies, distributions, and microstructures of the CNT formed on the different substrates. Raman characterization was carried out directly on the as-formed aligned CNT using a Renishaw Raman microscope system.

## 3 Results and discussion

### 3.1 SEM and TEM investigations on aligned carbon nanotubes formed on the bulk silica substrates

Silica substrates prepared by the sol-gel method have many aligned mesoscopic pores in which catalyst particles are embedded during the substrate formation, and CNT formed on the silica have distinctive morphology and structure. Figure 1a is an SEM image of the CNT layer, which has a thickness of about 50 $\mu$m. Generally, the thickness of the CNT depends on the growth time, pressure, and density of the reaction gases. Under the conditions described above, the growth rate of CNT is about 20 $\mu$m/h. However, increasing growth time leads to the CNT becoming slightly curved and ceasing to grow further. A high-magnification SEM image (Fig. 1b) clearly shows that the CNT formed on the silica substrate are aligned and approximately perpendicular to the surface of the substrate. One can see that CNT with diameter of about 30 nm are isolated, with spacing at about 100 nm. Basically, the diameters of CNT are determined by the catalyst particles embedded in the substrate, so we can reproduce a specific substrate and obtain CNT of the same diameter by applying the same conditions. On the other hand, the growth direction of the CNT is determined by that of pores, because of their template effect. Mesoporous silica was ground into powder in micrometers to verify the template effect of the nanometer pores on the growth direction of the nanotubes. Then the powder was pressed into a pallet which was used as substrate to produce CNT under the same conditions described above. As a result, a thick layer of CNT formed

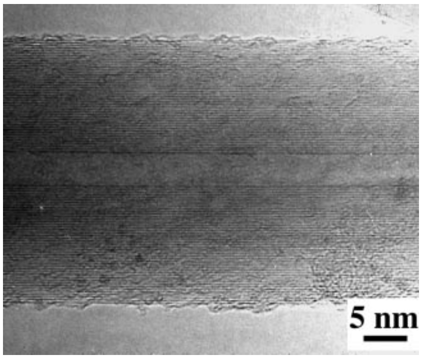

**Fig. 2.** HRTEM image of a carbon nanotube. The spacing between the graphite sheets is 0.34 nm.

on the pallet which contained randomly grown tubes. This indicates that the broken alignment of the pores caused by grinding make CNT grow on the pallet randomly. In addition, whether the pores have a template effect is also determined by their sizes. Pores with large diameters can not take template effect for the tube growth. For example, CNT with diameter of 30 nm can be formed on the silica substrate with pores 200 nm in diameter, but these tubes grow randomly. EDX spectra taken from the tips of the aligned tubes show that the tips are composed mainly of carbon and a small amount of iron (98.76 and 1.09 wt. %, respectively). Some areas of the tube tips contain trace amounts of silicon and oxygen, both less than 0.2 wt. %, which may be attributed to small silica fragments. EDX spectra taken from central parts of the tubes show only carbon peaks.

By using large-area mesoporous silica substrates, aligned carbon nanotubes with several square millimeters have been prepared. The substrate has been successfully removed to retain aligned tubes. EDX spectra collected from the tube roots of the nanotubes demonstrate the presence of carbon alone; neither silicon nor iron could be detected, which indicates that no impurity was attached on the tube roots.

HRTEM images show that the aligned CNT are well graphitized and typically consist of $\sim 40$ concentric shells of carbon sheets, with a spacing of about 0.34 nm (Fig. 2). Only a small amount of carbonaceous materials is at the periphery of the carbon nanotubes because of the low growth temperature (700 °C).

## 3.2 SEM and TEM investigations on very long aligned carbon nanotubes

By using the film-like silica substrates, we have prepared carbon nanotubes with very high yield. Every surface of the substrate was covered with a nanotube array composed of large quantities of highly aligned nanotubes (Fig. 3a). The length of the nanotube arrays increased with the growth time, and reached about 2 mm after 48 h of growth (Fig. 3b), which is an order of magnitude longer (1 mm vs. 100 $\mu$m) than that described in most previous reports. We believe that the length of the nanotubes formed on the film-like silica substrate could be even longer if the growth time was further increased, which is very different from the case of bulk substrate described in Sect. 3.1 probably because of the different growth model.

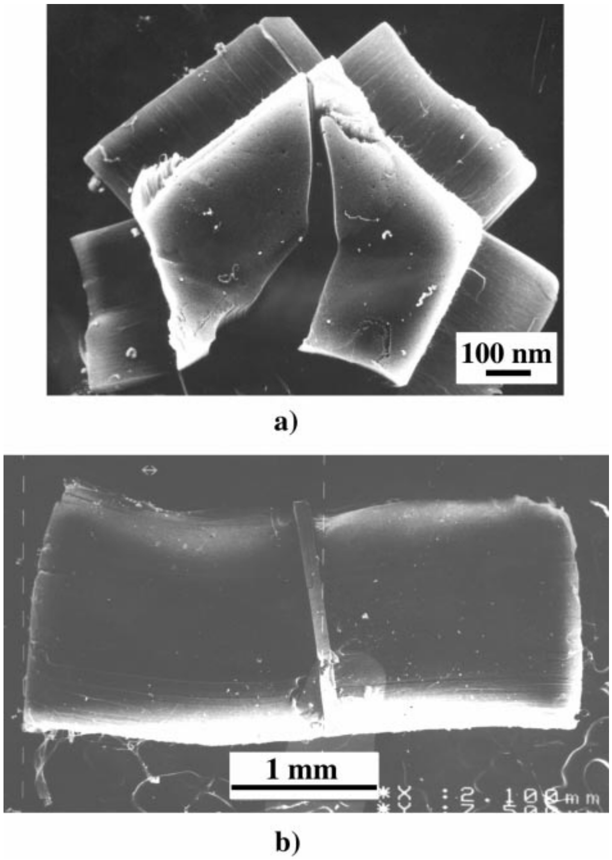

**Fig. 3.** Low-magnification SEM images of aligned carbon nanotube arrays. (a) Top view of a sample after 5 h of growth. All the surfaces of the substrate are covered with nanotube arrays grown outwards perpendicularly from the surfaces of the substrate. (b) A sample after 48 h of growth showing the very long ($\sim 2$ mm in length) nanotube array.

High-magnification SEM images (Fig. 4a) on the very long nanotube array show that carbon nanotubes grow outwards separately and perpendicularly from the substrate to form an array. The nanotubes within these arrays are of uniform external diameter (20–40 nm), with a spacing of about 100 nm between the tubes. Most of the nanotubes in the arrays are highly aligned, although a few of them appear to slightly tangle or curve. The arrays can be easily stripped off from the substrates, and the SEM image (Fig. 4b) taken from the root part of the array shows that the nanotubes are separated and aligned. We note that no traces of polyhedral particles or other graphitic nanostructures are detected in both the root part and the central part of the array.

HRTEM observations (Fig. 5) reveal that the multilayered graphitic tubes (10–30 layers) are coated with a small amount of amorphous carbon on their periphery, because of the low growth temperature and long growth time.

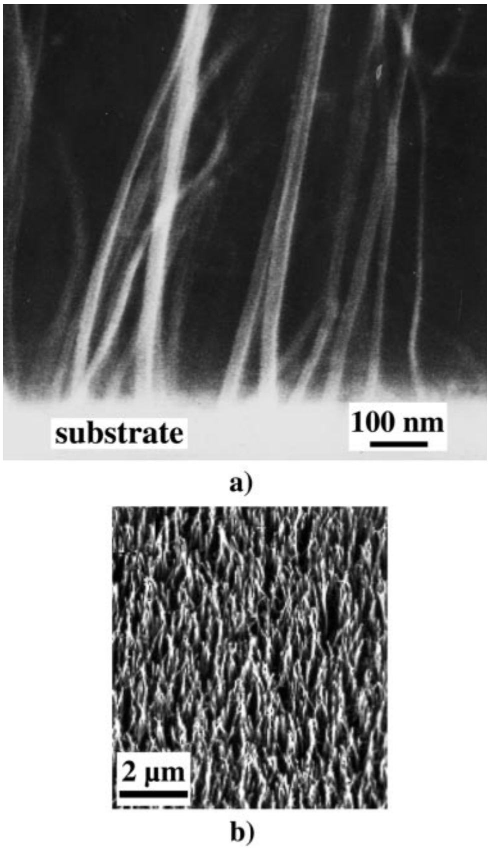

**Fig. 4.** (a) High-magnification SEM image of an aligned carbon nanotube array after 48 h of growth, showing aligned nanotubes have uniform external diameters (20–40 nm) and spacing ($\sim$ 100 nm) between the tubes. (b) SEM image of the root part of the nanotube array showing isolated and aligned nanotubes.

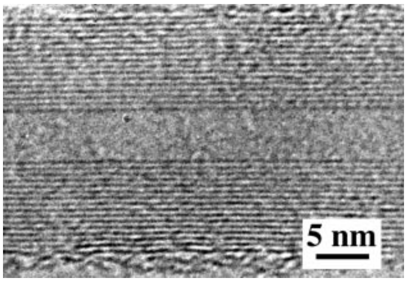

**Fig. 5.** HRTEM image of a carbon nanotube after 48 h of growth.

To determine whether the very long nanotubes grow unbrokenly from the bottom to the top within the nanotube arrays, we cleaved some thinner nanotube bundles from the arrays and measured their resistivity ($\varrho$) at temperatures from room temperature to 10 K by a four-probe method. The temperature dependence was semiconductor-like for most samples, but metallic behavior was also seen ($\varrho \approx 10^{-2}$–$10^{-3}\,\Omega\,\mathrm{cm}$ and $|\Omega\,\mathrm{d}\varrho/\mathrm{d}T\Omega| \approx 10^{-5}$–$10^{-6}\,\Omega\,\mathrm{cm\,K^{-1}}$ at room temperature). These results indicate that these very long nanotubes indeed grow continuously, without any interruption within the nanotube arrays.

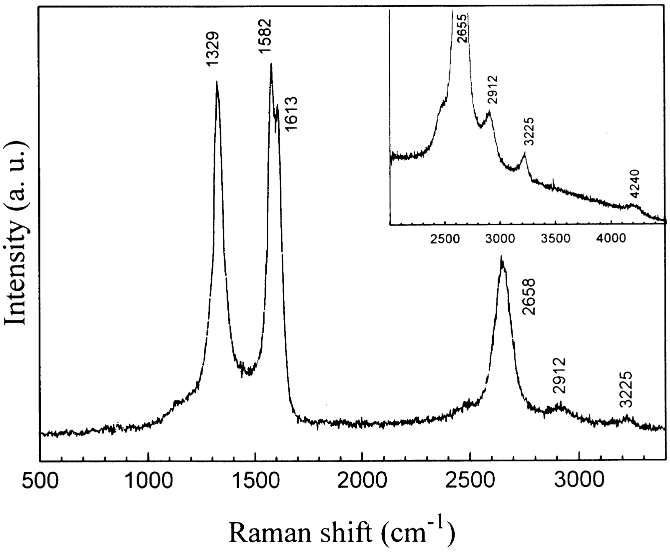

**Fig. 6.** Raman spectrum of the aligned carbon nanotube array showing the first- and second-order Raman peaks. The insert shows the higher order Raman peaks of the nanotube array.

### 3.3 Raman scattering on aligned carbon nanotubes

A Raman spectrum (Fig. 6) of the aligned CNT shows a very strong peak at $1582\,\mathrm{cm}^{-1}$ (G band) with a shoulder at $1613\,\mathrm{cm}^{-1}$ (D$'$ band) and a strong peak at $1329\,\mathrm{cm}^{-1}$ (D band). One of the significant differences of Raman spectra between the CNT produced by the CVD method and the CNT produced by the arc method is the intensity of Raman band at $1329\,\mathrm{cm}^{-1}$. With the SEM and TEM studies of the present aligned CNT taken into account, the appearance of the strong D band can be interpreted as being caused by (1) the lower graphitization degree of the CNT or turbostratic structures formed in some carbon sheets in the tubes (2) the highly compacted aligned tubes. In a word, the large amount of crystalline domains on the nanometer scale and the surface of the tubes must account for the enhancement of the D band. The details on Raman scattering of aligned carbon nanotubes has been described in detail elsewhere [11].

## 4 Conclusions

The growth of CNT produced by CVD is affected by both the catalyst particles and the structures of the substrates. The pores in the bulk substrates take a template effect during the tube growth. In the case of the film-like substrates, the tip growth mechanism is dominated and leads to the production of very long aligned carbon nanotubes. TEM and Raman studies show that the tubes are well graphitized, and the appearance of a strong D band indicates that nanometer-scale turbostratic structure may be formed in carbon tubes. Large-area aligned, pure, and dense CNT grown by these methods may be useful for the applications of these nanotubes.

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