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# Growth of aligned single-walled carbon nanotubes under ac electric fields through floating catalyst chemical vapour deposition*

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Through floating catalyst chemical vapour deposition(CVD) method, well-aligned isolated single-walled carbon nanotubes (SWCNTs) and their bundles were deposited on the metal electrodes patterned on the $SiO_2$/Si surface under ac electric fields at relatively low temperature(280°C). It was indicated that SWCNTs were effectively aligned under ac electric fields after they had just grown in the furnace. The time for a SWCNT to be aligned in the electric field and the effect of gas flow were estimated. Polarized Raman scattering was performed to characterize the aligned structure of SWCNTs. This method would be very useful for the controlled fabrication and preparation of SWCNTs in practical applications.

**Keywords:** carbon nanotube, chemical vapour deposition
**PACC:** 6148, 8115H

## 1. Introduction

After more than ten years of extensive research of single-walled carbon nanotubes (SWCNTs) since they were discovered,[1,2] the growth of assembled SWCNTs has become an important challenge before SWCNTs can be used in practical devices. In the last few years people have developed many methods to align SWCNTs.[3−10] All of these methods can be divided mainly into two kinds: one is the *in situ* controlled approach[3−6] and the other is the post-growth assembly.[7−10] The key point of *in situ* growth of SWCNTs is that the catalyst is first predeposited onto the electrodes and then the substrate is placed at the centre of the reactor where the temperature is as high as 600–900°C. The post-growth assembly method can be carried out at a relatively lower temperature, for instance, in a solution or in the air at room temperature. Both of the methods are carried out under external forces such as electric fields,[4−6] magnetic fields[9] and gas flow.[10] However, the *in situ* method cannot avoid exposing the substrate to high temperatures. The post-growth method may destroy the structure of SWCNTs during the ultrasonic or some chemical process. In this paper, we develop a new technique to produce well-aligned isolated SWCNTs and bundles through floating catalyst chemical vapour deposition (CVD) method. An ac electric field is applied on the patterned Ta/Pt/Ta adjacent electrodes. The deposition of aligned SWCNTs is completed at a quite low temperature (about 280°C). We think this provides a new and simple way to assemble SWCNTs for applications.

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## 2. Experimental procedure

Before the growth of SWCNTs the patterned metal electrodes (Ta/Pt/Ta) on a $SiO_2$/Si wafer were first prepared by photolithography and liftoff technique. Ta(5nm)/Pt(15nm)/Ta(5nm) thin films were deposited by the vacuum deposition method. The width of the electrode was 30$\mu$m and the spacings between two adjacent electrodes varied from 10 to 50$\mu$m. The schematic diagrams of the top view and the side view of the electrodes are shown in Fig.1. The growth of SWCNTs was carried out through floating catalyst CVD which has been described elsewhere.[11,12] A three-section quartz tube mounted in a dual-furnace system was used to produce aligned SWCNTs. In Fig.2, "$A$" is the first furnace in which the catalyst was sublimated; "$B$" is the second furnace where the reaction undergoes; "$C$" is the low-temperature (about 280°C) deposition area where the patterned electrodes substrate is placed. The catalysts sublimated were then carried into the reaction area by gas flow which was a mixture of argon (500 sccm), methane $CH_4$(1.0 sccm) and acetylene $C_2H_2$(0.6 sccm). The patterned electrode substrate was adhered onto a quartz bracket upside down (position $C$ in Fig.2). We tried both ac and dc electric fields in the experiments and found only ac electric fields were always effective for the alignment of SWCNTs. The growth of SWCNTs lasted for 15min under atmospheric pressure. Scanning electron microscopy(SEM), transmission electron microscopy (TEM) and Raman scattering were used to study the structure and properties of aligned SWCNTs.

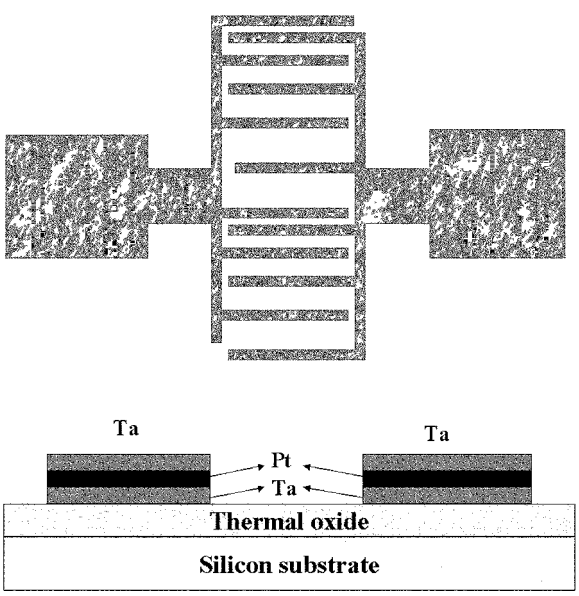


**Fig.1.** Schematic diagram of Ta/Pt/Ta electrodes on the $SiO_2$/Si substrate. (a) top view of the electrodes.(b) side view of the electrodes.

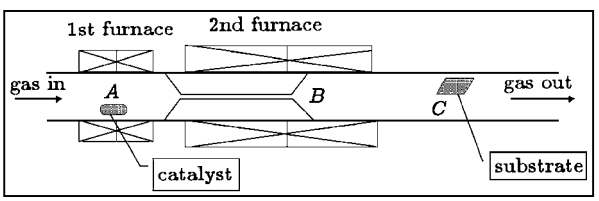


**Fig.2.** Schematic diagram of the floating catalyst CVD apparatus for preparing aligned SWCNTs.

## 3. Results and discussion

The morphology of aligned SWCNTs grown on the patterned electrode substrate was observed through a field-emission scanning electron microscope (FE-SEM S-5200) (Fig.3). Figure 3(a) shows that SWCNTs grown under ac electric fields (20V, 300kHz) are well aligned perpendicular to the edge of the electrodes. They are almost along the direction of electric fields. This could be confirmed from the SEM image of SWCNTs deposited at the tip of the electrodes (Fig.3(b)). But SWCNTs form random networks on the surface where the electric field is not present (Fig.3(c)), just as that described in Ref.[12]. In order to examine the product we also put a copper grid to collect SWCNTs in the furnace at the lower-temperature area (Fig.3(d)). On the copper grid the directions of SWCNTs are also distributed randomly. The inset of Fig.3(d) shows a typical HRTEM image of deposited SWCNTs. From the HRTEM image we can observe the isolated SWCNTs with diameters about 1–2nm. Besides, we also find that many SWCNTs are entangled into small bundles containing 2–5 pieces of SWCNTs. Perhaps this is due to Van der Waals interaction among the isolated SWCNTs during the growth.

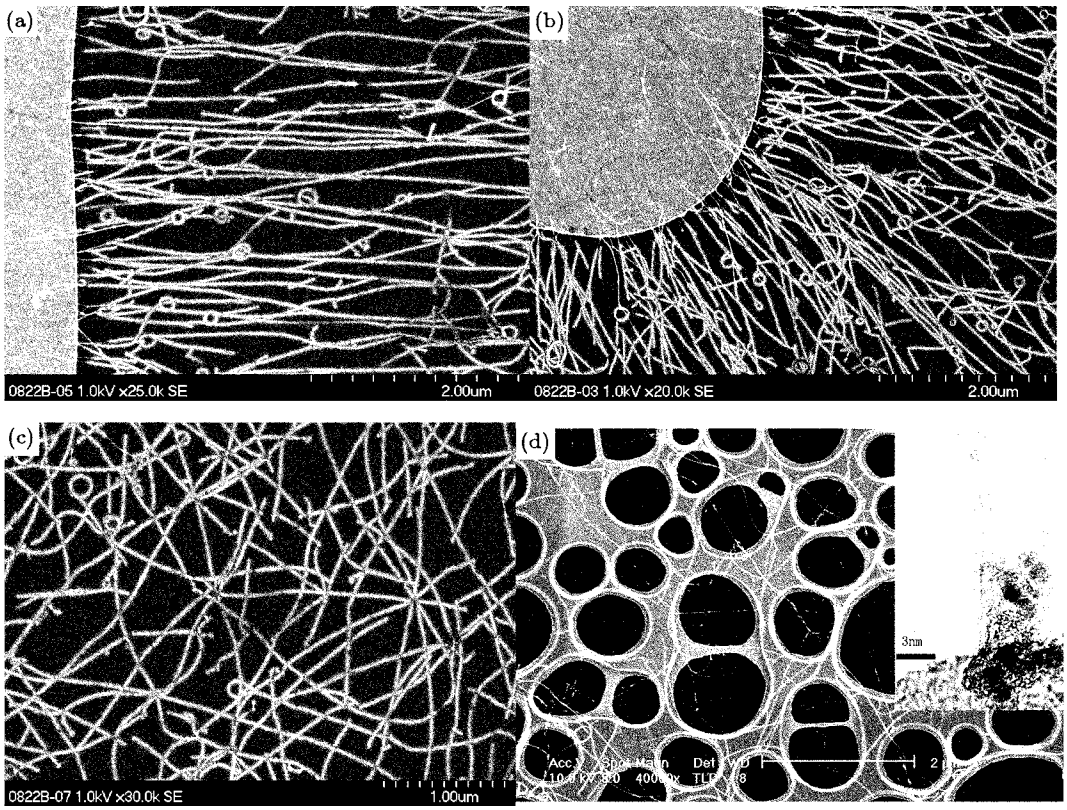


**Fig.3.** Typical SEM images of well-aligned SWCNTs deposited (a) between two adjacent metal electrodes grown under a voltage of 20V, a frequency of 300kHz (b) at the tip of the electrode. Random SWCNTs deposited (c) in the unelectric field area (d) on a copper grid (the inset is HRTEM image of a SWCNT).

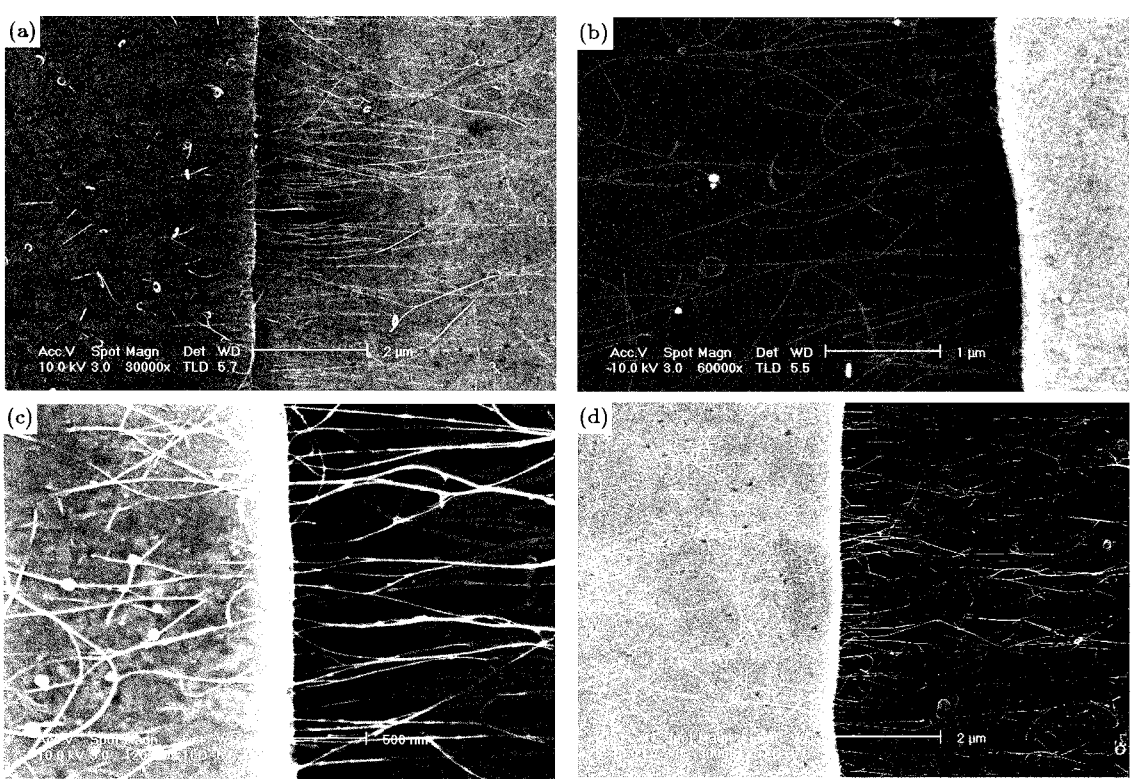


**Fig.4.** SEM images of aligned SWCNTs under different-frequency electric fields. (a)1kHz, (b)10kHz, (c)100kHz, (d)1MHz.

We have carried out several experiments at different frequencies of ac electric fields, as shown in Fig.4. We find that the frequency has very little effect on the alignment of SWCNTs. They are all aligned very well for frequencies from 1kHz to 1MHz at a voltage of 10V. However, the electric intensity has a relatively greater effect on the alignment of SWCNTs. In Fig.5 are shown SWCNTs deposited in different spacings on the electrodes from 10 to 50$\mu$m. It is found that their alignment degree decreases when the spacing increases. With a spacing of 10$\mu$m SWCNTs are aligned best. For a larger spacing, there are many unaligned SWCNTs in the middle area because the electric field is too weak to align SWCNTs in this case. But in the area near the edge of the electrodes, a few of SWCNTs aligned perpendicularly can be found. Moreover, it is also found that the density of the aligned SWCNTs could be controlled through adjusting the carbon source gas flow, the sublimation temperature and the deposition time. Figure 6(a) shows a typical image

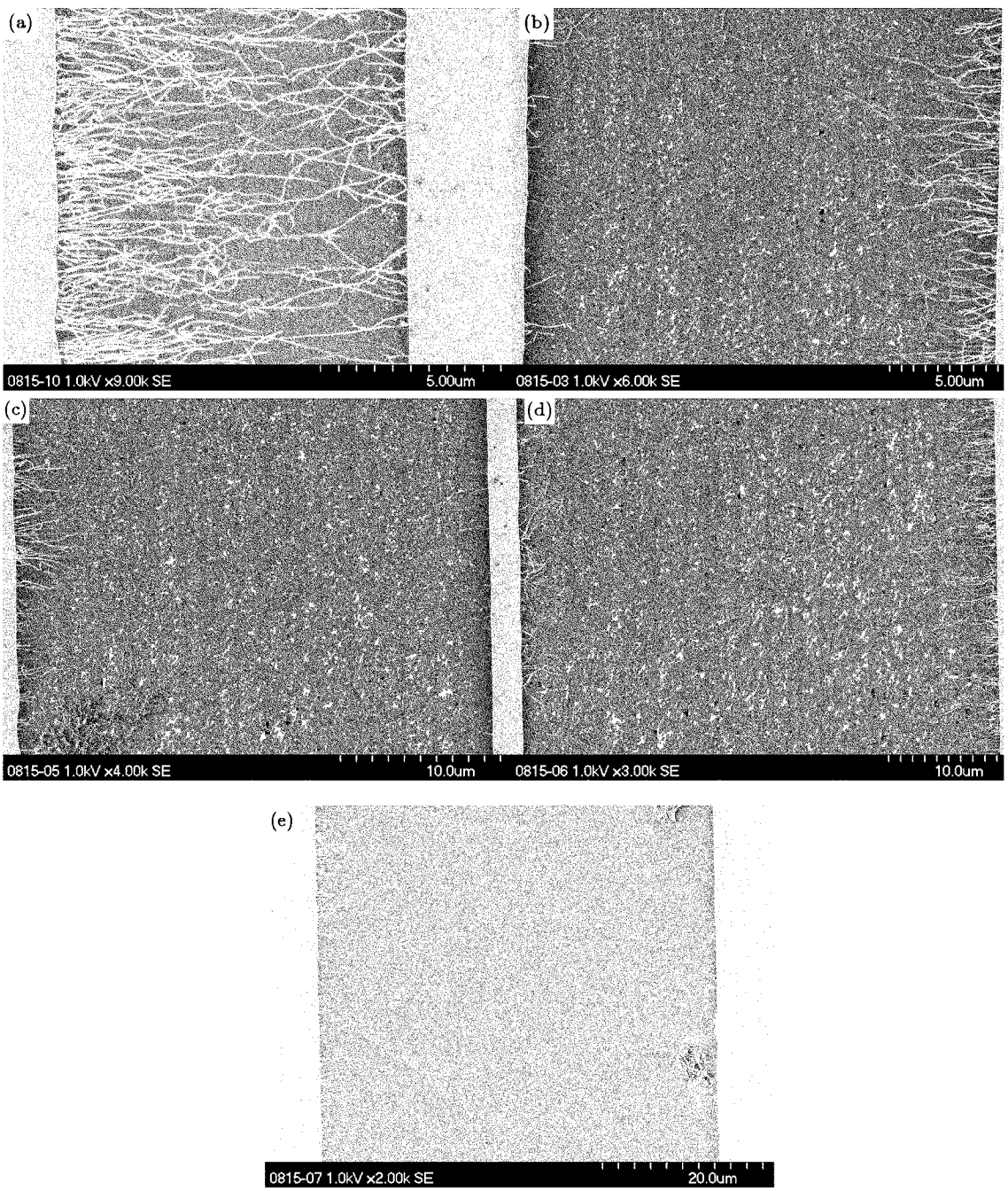


**Fig.5.** SEM images of aligned SWCNTs deposited at different spacings on the substrate. (a) 10$\mu$m, (b) 20$\mu$m, (c) 30$\mu$m, (d) 40$\mu$m, (e) 50$\mu$m.

of very dilute SWCNTs aligned only in a period of five minutes on the substrate. In the experiments we also found that dc electric field (about 1V/$\mu$m) usually causes arcing during the deposition, which leads to the breaking of most SWCNTs (Fig.6(b)). Actually dc electric fields usually cause arcing in a very short time when the field is switched on. The arcing intensity (1V/$\mu$m) of dc electric fields in our floating method is much lower than that (3V/$\mu$m) in some *in situ* methods.[4] But under ac electric fields very few SWCNTs are broken caused by the field intensity. Figure 6(c) shows that there are several aligned bundles in the electric field in which only one broken SWCNT bundle is found.

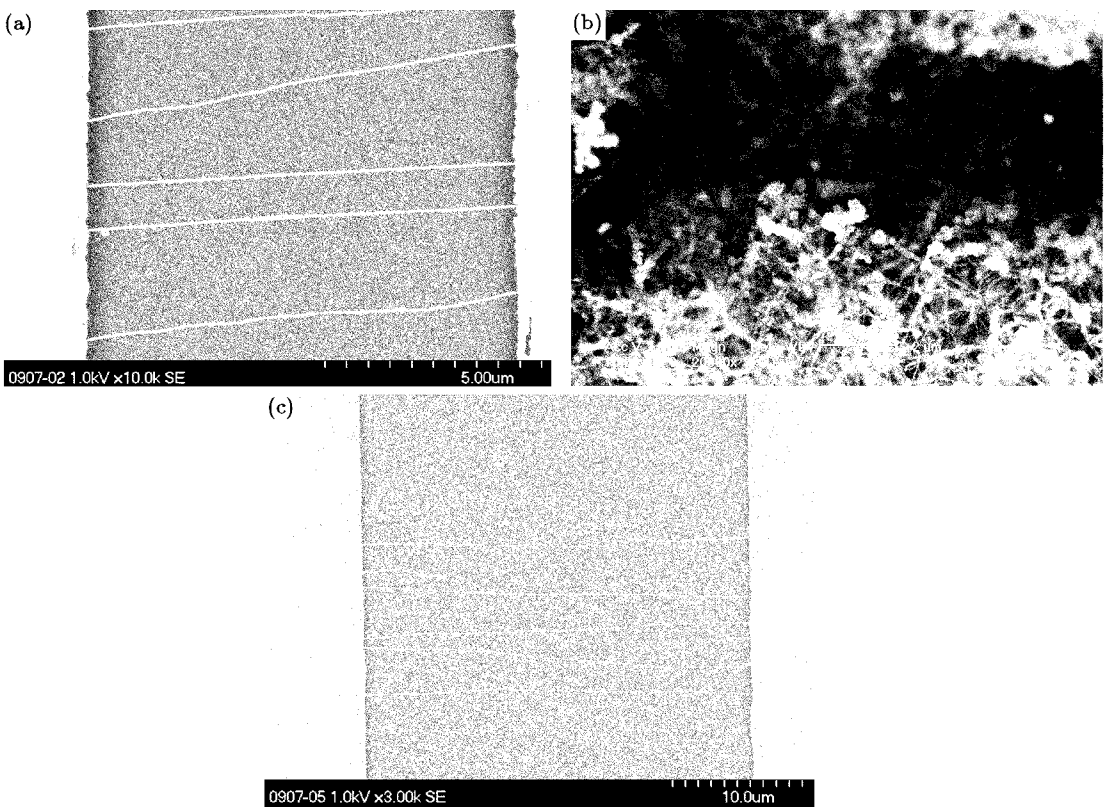


**Fig.6.** SEM images of (a)very dilute well-aligned SWCNTs under ac electric fields (5min deposition) (b) the SWCNTs under dc electric fields (1V/$\mu$m)with arcing (c) well-aligned SWCNTs under ac electric fields with only one SWCNT bundle broken.

Compared with the *in situ* and the normal post-growth assembly method, the deposition temperature (280°C) in our case is intermediate between that in the *in situ* method (600–900°C) and that in the post-growth assembly method (room temperature). During the growth, the catalyst in the first furnace is sublimated and carried by the argon flow into the second furnace (Fig.2 position $B$) where SWCNTs are fabricated at 1100°C. The grown SWCNTs are then carried to the end of the quartz tube where the electrode substrate is located (Fig.2 position $C$). When the electric field is switched on, SWCNTs in the field are polarized (Fig.7(a)), and the induced dipole moment is $\boldsymbol{P} = \alpha \boldsymbol{E}$, in which $\alpha$ is the polarization coefficient of the SWCNTs and $\boldsymbol{E}$ is the external electric field intensity. It should be pointed out that the polarization along the nanotubes ($\alpha_{\parallel}$) is much higher than that perpendicular to the nanotubes ($\alpha_{\perp}$).[13] From Ref.[4], the torque ($\tau$) of the electric field exerted on the carbon nanotubes is $\tau = |\boldsymbol{P} \times \boldsymbol{E}| = \alpha_{\parallel} E^2 \sin\theta \cos\theta$, where $\theta$ is the angle between the nanotube axis and the external electric field. For the semiconducting and metallic carbon nanotubes, Devel[14] showed $\alpha_{\parallel} = 4\pi\varepsilon_0(0.25R + 1.9)L^2$ ($R$ and $L$ are the radius and the length of the SWCNT, respectively, in units of 0.1nm). In our experiments SWCNTs grown in the quartz tube centre are suspended randomly in the gas flow. They could be aligned in a very short time because of the strong electric field and their small mass when they enter the field area

near the electrode edge (Fig.7(b)). Here we give a simplified model to estimate the alignment time for SWCNTs. We suppose a SWCNT is rigid during its rotation. $\theta_0$ is the initial angle between the electric field and the axis of the SWCNT. The alignment time $t_a$ is defined as the time that the SWCNT rotates from $\theta = \theta_0$ to $\theta$=0. The torque applied by the electric field is $\tau = 4\pi\varepsilon_0(0.25R + 1.9)L^2E^2 \sin\theta\cos\theta$. The angular acceleration is $d^2\theta/dt^2 = -12\tau/(mL^2)$. So the rotation time ($t$) satisfies the differential equation $d^2\theta/dt^2 = -\gamma\sin\theta\cos\theta$, here $\gamma$ is a constant we introduce to represent $48\pi\varepsilon_0(0.25R+1.9)E^2/m$. From this second-order equation we obtain the angular velocity $d\theta/dt = -(\gamma(\cos^2\theta - \cos^2\theta_0))^{1/2}$. The rotation time $t$ can be obtained as an Appell hypergeometric function ($F_1$) of cos$\theta$. The mass $m$ of a SWCNT could be estimated as a small rectangular layer of graphite. For a semiconducting SWCNT with diameter $D$=2$R$=1nm, length $L$=10$\mu$m, initial angle $\theta_0 = \pi/4$ and the electric field intensity $E$=1V/$\mu$m, the alignment time $t_a$ is about 4.6$\mu$s, calculated through numerical integration. When the frequency of the electric field is 10kHz, the period is 100$\mu$s. It is confirmed that a SWCNT can be aligned well within one electric period. If SWCNTs are much longer or if a higher frequency is used, the rotation time could be longer. Furthermore, because SWCNTs are not rigid but flexible and they are usually in the form of bundles, the situation could be much more complicated than our simplified model.

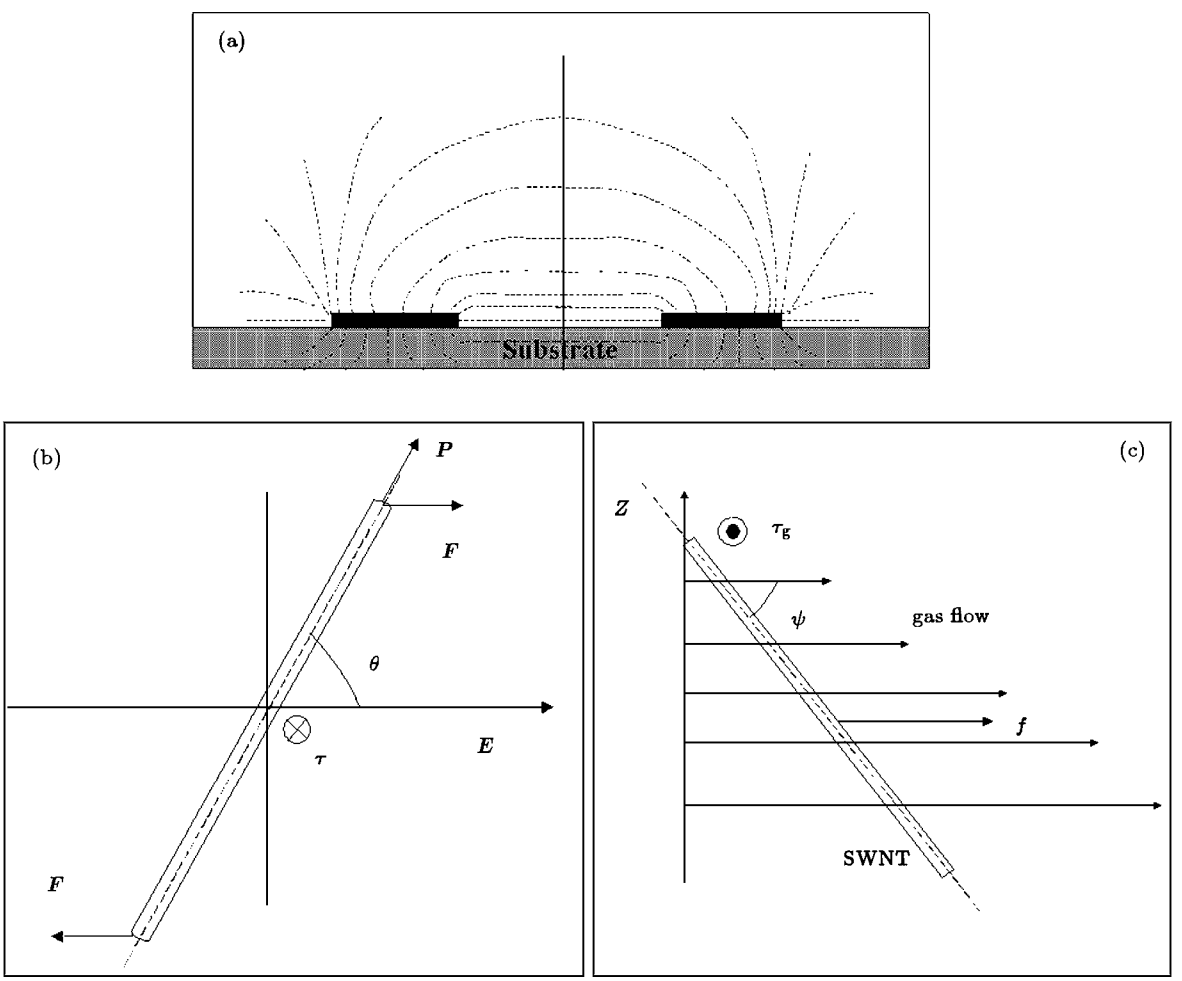


**Fig.7.** (a) Electric fields distribution. Schematic force diagram of one SWCNT (b) in the electric field and (c) in the gas flow.

In the experiments, we applied the electric fields parallel or perpendicular to the direction of gas flow. But we found that in the presence of electric fields the gas flow direction has very little effect on the alignment and deposition of SWCNTs. When the gas flow increases, it may have some effect although without electric fields, as that described in Ref.[10]. Here we have an estimation of the flow effect on SWCNTs. The flux of argon $\rho$ we used in the experiments is 500 sccm, and those of $CH_4$ and $C_2H_2$ are 1.0 sccm and 0.6 sccm respectively. So we can only take the argon flow into account and neglect the methane and acetylene in the estimation. The inner diameter $D_q$ of the quartz tube end is 3cm. Thus the velocity of argon flow can be calculated to be $v=4\rho/(\pi D_q^2)$=1.2cm/s. The friction force ($f$) on a SWCNT by the gas flow is given by $f=\eta\Delta S(\mathrm{d}v/\mathrm{d}r)$ (Fig.7(c)) according to the fluid mechanics, where $\eta$ is the coefficient of viscosity of the gas flow, $\Delta S$ is the surface area of the SWCNT and $\mathrm{d}v/\mathrm{d}r$ is the velocity gradient of the flow near the surface of the SWCNT. The torque by the gas friction is given through $\tau_g = fL\sin\theta = \eta L\Delta S(\mathrm{d}v/\mathrm{d}r)\sin\psi$, here $\psi$ is the included angle between the SWCNT axis and the gas flow. For a SWCNT with a diameter $D$=1nm, $L$=10$\mu$m, $\eta$=18$\times10^{-6}$Pa·s (according to the fluid mechanics), the velocity gradient estimated by $\mathrm{d}v/\mathrm{d}r = 2v/D_q$=0.8s$^{-1}$ and the angle $\psi=\pi/4$, the friction torque $\tau_g$ is about 3.3$\times10^{-25}$N·m. The torque exerted on the SWCNT in the electric field could be estimated by using the equation $\tau = 4\pi\varepsilon_0(0.25R+1.9)L^2E^2\cos\theta\sin\theta$. When $\theta=\pi/4$ it is about 1.8$\times10^{-18}$ N·m. So the effect of argon flow friction is several orders of magnitude less than that of the electric field. There are also many other factors, such as the gas pressure gradient near the SWCNT surface, the temperature and some catalyst particles that also affect the alignment of SWCNTs. But they are random and could not be compared with the role of the external field. This also can be confirmed through the SEM pictures of SWCNTs under zero electric field, where SWCNTs can be deposited in some direction without any relation to the argon flow, i.e. in a random arrangement (Fig.3(c)).

In order to explore the properties of SWCNTs aligned on the electrodes substrate, polarized Raman scattering has been performed using a He-Ne laser with an excitation wavelength of 632.8nm. The spectra were recorded by the Dilor Super Labram with a typical resolution of 1cm$^{-1}$ in a backscattering geometry at room temperature. The system consisted of a holographic notch filter for Rayleigh rejection and a microscope with 50× objective lens, allowing a spatial resolution of 2.0 micrometer. Before Raman experiments were carried out, we made on the electrode a small mark which could be seen under both SEM and microscope. Hence the laser point could be focused on the specific SWCNTs bundle near the mark, as shown in the inset in Fig.5(a). All the Raman scattering curves were obtained in backscattering configuration with the polarization of incident light parallel (VV) to that of scattering light (Fig.(8)). Because SWCNTs were almost perpendicular to the electrode edge in SEM, we used $\phi$ as the angle between the polarization of the incident light and the direction perpendicular to the electrode edge. Figure 5(a) shows the polarized Raman spectra of RBM-band and G-band of a very small bundle of SWCNTs. The Raman intensities, not only the G-band but also the RBM band, are dramatically decreased when $\phi$ increases from 0° to 90°. This phenomenon can be explained by the depolarization effect.[15] From the resonant RBM band of this small bundle we notice that only the 145cm$^{-1}$, which could be calculated at about 1.5nm diameter according to $d=\alpha/\omega_{\mathrm{RBM}}$($\alpha$=224cm$^{-1}$nm),[16] is resonant with the incident light and the other peaks are very small. It is due to the coincidence of $E_{33}$ of this semiconducting SWCNT with the photon energy $E_{\mathrm{laser}}$. The angular dependences of the Raman intensity of the peaks at 145cm$^{-1}$ and 1596cm$^{-1}$ are also shown in Figs.8(b) and (c), respectively. The Raman intensity does not completely decrease to zero when $\varphi$=90°. We suppose that it is because of a small angle deviation $\Delta\varphi$ of the SWCNTs from the direction perpendicular to the electrode edge. The angular dependence of the intensity of Raman scattering corresponds to the function $\cos^4(\varphi+\Delta\varphi)$. This deviation $\Delta\varphi$ could be estimated from the SEM pictures of SWCNTs to be 5–10° (inset in Fig.8(a)).

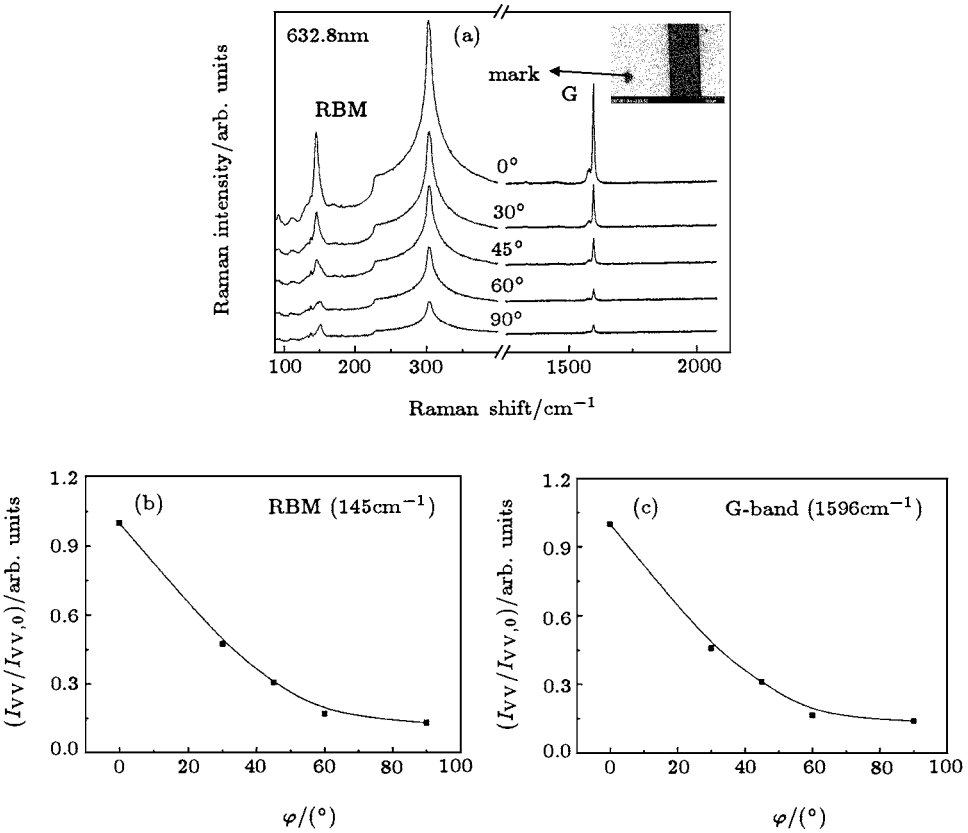


**Fig.8.** Polarized Raman scattering in VV configuration of a small aligned SWCNT bundle on the metal electrodes. (a) RBM and G-band for different angles $\theta$ (the inset indicates the SWCNT bundle on which polarized Raman scattering was performed). The angular dependence of (b) RBM and (c) G-band of the Raman intensity.

There are several important features in our growth method for the aligned SWCNTs on the electrodes. *Firstly*, SWCNTs are directly aligned and deposited onto the electrodes on the substrate without any chemical or ultrasonic process after they were grown in the quartz tube. This is the main difference between our method and some previously reported ones. In this way it can form highly qualified SWCNTs free of defects, just as the formerly reported SWCNTs in random networks.[12] *Secondly,* the catalysts are carried by the argon from the first furnace into the centre of the reactor, thus it is easy to control the growth of aligned SWCNTs by adjusting the gas flow or the catalyst sublimation temperature. In some *in situ* growth of aligned SWCNTs under electric fields, the catalyst is predeposited onto the electrodes before they are placed into the reactor.[3−6] It makes the controlling of the SWCNTs growth more difficult because the catalyst cannot be easily altered once it is formed. In addition, our electrodes can be re-used for further research after removing the deposited SWCNTs. *Thirdly*, the temperature in the location of the electrodes (about 280°C) is much lower than that of the reaction centre (1100°C), thus avoiding the electrodes to be exposed to high temperature. In fact, low temperature is a common character in the floating catalyst CVD method.[11,12] A range of temperature zones can be selected as the deposit position in the experiments. Most SWCNTs deposited in the quartz tube where the temperature varies from 200°C to 500°C (an area from position $C$ to the inside of the second furnace in Fig.2). In extremely low temperature area, such as below 100°C, few SWCNTs could be found in a certain grown time. This flexibility of selection for the temperature can be very useful for some substrates that are stable only at certain temperatures. We could choose the deposition zone in the furnace according to the intrinsic properties of the substrate. These features are not independent of each other in the experiments. They all together provide a complete means to align SWCNTs in their preparation.

## 4. Conclusion

In summary, we have provided a new way to achieve well-aligned isolated SWCNTs and some small

bundles on metal electrodes under ac electric fields through floating catalyst CVD method. SWCNTs could be aligned and deposited onto the substrate at a quite low temperature (about280°C) under ac electric fields. The effect of the electric field and some other important factors are described and compared with each other. We can conclude that ac electric field is very useful for controlling the preparation of SWCNTs in the CVD process.

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