Controllable preparation and properties of single-/double-walled carbon nanotubes

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Abstract

In this paper, we discussed recent studies done in our laboratories with a floating catalyst chemical vapor deposition (CVD) method. We can grow single- or double-walled carbon nanotubes (SWNTs/DWNTs) with different kinds of catalysts. Single-walled carbon nanotubes without amorphous carbon coating were prepared by thermally decomposing acetylene (C$_2$H$_2$) at the temperature range of 750–1200 °C with ferrocene as catalyst. While with sulfur promoted ferrocene catalyst, double-walled carbon nanotubes were mass-produced by pyrolyzing C$_2$H$_2$ at the temperature range of 900–1100 °C. Furthermore, tunable growth of DWNTs with different diameter was achieved in our experiment. It is found that DWNTs produced at lower carbon partial pressure have much smaller inner tubes, even DWNTs with the smallest inner diameter of 0.4 nm was found in here. As convenient and effective tool, radial breathing mode (RBM) of Raman scattering technique can be used to distinguish SWNTs from DWNTs. In further studies of Raman scattering with DWNTs, the possible match of the inner tubes and the outer tubes according to the RBM bands was assigned, and different chirality types were discussed according to the diameter and chirality dependence of resonant Raman vibration. We also investigated the temperature-dependent frequency shift of resonant Raman spectra of DWNTs in the range of 78–650 K. We found that different RBM peaks, which are relative to different tube diameters, have different temperature coefficient of frequency shift, and the larger diameter carbon nanotubes have more RBM frequency downshift with increasing temperature. It is ascribed to the RBM frequency variation to the temperature dependence of the stretching force constant of C–C bond. Besides, Polarized Raman spectra were preformed on well-aligned SWNTs structure fabricated through post-growth method and found that the angular dependence of Raman intensity is consistent well with the predictions of the resonance Raman theory.

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1. Introduction

Since the discovery, carbon nanotubes (CNTs) have attracted much attention because of their unique structural and physical properties and many potential applications [1–3]. During the process toward the practical application, it is a critical issue to be addressed that how to make CNTs optionally, especially with specific diameter and certain chirality. The controlled synthesis single-wall carbon nanotubes (SWNTs) and double-wall carbon nanotubes (DWNTs) have received much attention over the past decade including different methods, such as laser vaporization, DC arc discharge, and chemical vapor deposition (CVD) [4–27]. Among these, a continuous CVD synthetic method, in which SWNTs are grown in a flowing gaseous feedstock mixture, was developed to provide a mass-production method of SWNTs [4–12]. Compared with SWNTs, DWNTs were firstly produced as the dominant products by the arc discharge technique with a catalyst mixture of Ni, Co, Fe, and S [13]. Subsequently,
several works have been issued in recent years to discuss the synthesis of DWNTs [14–21]. Otherwise, Iijima and co-workers reported that SWNTs and DWNTs could be produced synchronously by the decomposition of methane on mesoporous silica, whereas the zeolite support material is reported to yield only SWNTs [22].

In this paper, we have selectively synthesized single- or double-walled carbon nanotubes by the floating catalyst CVD method during the past three years [23–27]. In our studies, we reported that C2H2 could be a very ideal carbon feedstock to produce clean and pure SWNTs by controlling the experimental parameters carefully. Experiments here may be helpful to grow SWNTs from other hydrocarbon by the floating catalyst process. We also found that double-wall carbon nanotubes can be synthesized as the dominant products by adding sulfur as a promoter in the same system. Our experiments indicated that the growth of DWNTs was strongly dependent on the sulfur addition, and without sulfur only SWNTs were produced. After developed the experimental set-up, tough texture of single-walled carbon nanotubes with area up to several tens square centimeters (called SWNTs nonwoven) was prepared by thermally decomposing methane (CH4) in a developed floating CVD method [28]. It is found that the SWNT nonwoven exhibited extremely high Young’s Modulus of ca. 0.4–0.7 TPa. Simple purification method, including oxidation in air and treatment with concentrated HCl, was performed to eliminate impurities in original samples.

On the other hand, Raman scattering spectroscopy was employed to identify SWNTs or DWNTs in our characterized methods [23,29]. Similar to that of SWNTs, Raman spectra of DWNTs has been experimentally shown to be resonant process and displayed two ‘fingerprint’ features of the radial breathing mode (RBM) at the lower frequency range and the splitting tangential mode (TM). However, we found that RBM frequencies of DWNTs take a wider range and display much richer peaks than those of SWNTs. It is shown that the peak position and line shape of Raman bands of DWNTs were strongly dependent on the laser energies due to the resonant Raman vibration [30]. With different excitations, we discussed the possible match of the inner tubes and the outer tubes according to the RBM bands and the different chirality types according to the diameter and chirality dependence of resonant Raman vibration. It is found that tubes (the inner or outer layers of DWNTs) with all kinds of chiralities could be synthesized, and a DWNT can have any combination of chiralities of the inner and outer tubes. Otherwise, the temperature-dependent Raman spectra of DWCNTs is also discussed [31]. We show here that different RBM peaks, which are relative to different tube diameters, have different Raman frequency shifts, and we attribute the RBM frequency variation to the temperature-dependent C–C bond stretching force constant. Besides, polarized Raman spectra were preformed on well-aligned SWNTs structure fabricated through post-growth method. It is found that the angular dependence of Raman intensity is consistent well with the predictions of the resonance Raman theory.

2. Experimental

Our experimental set-up is a two-stage furnace system fitted with a quartz tube (30 mm i.d.), which is shown in Fig. 1. Ferrocene (dicyclopentadienyl iron), acting as the source of catalyst, was sublimed in the first furnace at the temperature 60–90 °C. The sublimed ferrocene was carried by the flowing Argon (1200 sccm) and acetylene (3–10 sccm) mixture into the second furnace. The SWNTs growth temperature (the temperature of the second furnace) can vary from 750 to 1200 °C. The pressure inside the quartz tube was held constantly at 1 atm in all the following experiments. The as-grown SWNTs products were collected as piece of films at the outlet.

As to the growth of DWNTs, Ferrocene and sulfur powder were mixed uniformly and ground with mortar, and the catalyst mixture was sublimed in the first furnace. The other experimental parameters are same as those in the SWNTs production. For purification, the as-grown samples were heated in air at 400–500 °C for 48 h to oxidize Fe catalyst particles and other carbon impurity, and then immersed into concentrated HCl (38%) to dissolve the iron oxides. Finally, the samples were repeatedly washed with deionized water until the pH value of the filtrate almost equal to seven.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and micro-Raman spectroscopy (RM2000, JY64000) were performed to characterize the products. A special tensile machine was used to directly measure the mechanical properties of the samples.

![Fig. 1. Schematic of the floating catalyst CVD set-up.](image-url)
3. Results and discussions

3.1. General results

3.1.1. Morphology of the as-grown SWNTs

Single-wall carbon nanotubes (SWNTs) without amorphous carbon coating were prepared by thermally decomposing acetylene (C\textsubscript{2}H\textsubscript{2}) at the temperature range of 750–1200 °C in this floating iron catalyst system [23]. Fig. 2(a) shows a typical SEM image of the as-grown SWNTs product. It is clear that the products mainly consist of thousands of entangled filaments with very small diameter and small particles, and most of the small particles seem decorate on those filaments and are shown as bright color in the image. High resolution TEM image (Fig. 2(b)) shows that all of those filaments are SWNT bundles or individual SWNTs, and the particles are metal catalysts encapsulated by two or three graphite layers. Analysis of EDS indicates that the particles are iron. No amorphous carbon was found on the SWNTs.

In further investigation, we studied the effect of the experimental parameters, including reaction temperature and partial pressure of hydrocarbon. We found that the optimized temperatures for the growth of SWNTs are in the range of 900–1000 °C, which is different from other reports that the highest SWNTs' yield were often achieved at their highest available temperature up to 1200 °C [6 and 7]. The reason that we do not obtain highest yield at the higher temperature may be ascribed to the rate-limiting step for growth of SWNT is changed due to the much quicker thermal decomposition of C\textsubscript{2}H\textsubscript{2} at the higher temperature. We also found that the partial pressure of hydrocarbon is much crucial to synthesize SWNTs. When the C\textsubscript{2}H\textsubscript{2} partial pressure was higher than 12 Torr, almost no SWNTs could be obtained. At the controllable C\textsubscript{2}H\textsubscript{2} partial pressures blow 5.0 Torr, the product mass increased with the C\textsubscript{2}H\textsubscript{2} partial pressure increased. When the C\textsubscript{2}H\textsubscript{2} partial pressure excess 5.0 Torr, more thermal decomposed carbon was produced, which may make the catalyst particles inactive, and resulted in the decrease of SWNT production.

Illumed from the above investigation, we developed experimental set-up and then prepared the self-assembled two-dimensional random networks composed of isolated SWNTs, which is discussed in Ref. [24]. The remarkable advantage of the technique is that the random networks can be formed at relatively low temperature with a wide density range, which is distinct from the previous reports.

3.1.2. Morphology of the as-grown DWNTs

It is reported that the addition of sulfur to the starting materials could increase significantly the yield of SWCNTs in the arc discharge system [32] or in the floating catalyst CVD system [4]. Although our original intention by adding sulfur was to improve the production rate of SWNTs, most of the nanotubes in the products consist of two concentric graphene layers (DWNTs). We reported here that DWNTs were mass-produced by pyrolyzing C\textsubscript{2}H\textsubscript{2} at the temperature range of 900–1100 °C on the floating iron catalyst with sulfur added [25–27]. Morphology of as-grown DWNTs is shown in Fig. 3. Compared with above SWNTs, Fig. 3(a) revealed that the fraction of filaments in the as-grown sulfur promoted products is higher than that produced without sulfur addition.

Fig. 3(b) is an HRTEM image of discrete DWNTs. The outer diameter of the larger DWCNT (Labeled A) is 1.86 nm with an inner diameter of 1.13 nm, and the outer diameter of the smaller one (Labeled B) is 1.17 nm with an inner diameter of 0.40 nm. It was well known that nanotube with diameter 0.40 nm is the smallest carbon tube that is energetically stable, and they were produced by the arc discharge method [33] or by pyrolysis of tripropylamine molecules in the channels of porous zeoliteAlPO\textsubscript{4}–5 single crystals [34]. Here, we find that DWNTs with the smallest inner tube diameter can be synthesized in the floating catalyst CVD system, and the detail is given in Ref. [35]. Similar to SWNTs, DWNTs also form into bundles readily. Fig. 3(c) shows an HRTEM image of DWNTs bundles. It is difficult to identify the individual DWNT in the bundles due to the overlapping scattering of the tubes. However, the double-walled feature of these tubes is clearly visible on the periphery of the bundles or those discrete tubes.

The product of DWNTs has been systematically studied as a function of the reaction temperature, the partial pressure of hydrocarbon, the sublimed temperature of ferrocene,
and the relative molar value of ferrocene to sulfur. We found that the rational reaction temperature was at the range of 950–1150 °C and the partial pressure of C₂H₂ played a great role in producing the DWNTs at a given temperature. Through Hafner et al. [15] got a considerable amount of DWNTs with C₂H₄ at temperature of 850 °C, in our experiments with C₂H₂ as the carbon source in a floating iron catalyst system, it was more suitable to increase the temperature up to 950 °C. As the temperature increased above 950 °C, the yield of DWNTs as well as the quality was enhanced. However, when the temperature was above 1150 °C, the higher yield of the products was obtained, but most of them were amorphous carbon. The abnormality should be ascribed to the effect of temperature on the size of catalytic particles, due to the congregated tendency of the catalyst particles at the higher temperature. Compared with SWNTs, the appropriate reaction temperature in the experiment of DWNTs was higher than that of SWNTs in the similar method only without additive of sulfur. We ascribed that to the selective poisoning the surface of the iron catalyst particles by sulfur atoms. With the additive sulfur, the surface of the catalyst particles will reconstruct, which, coupling with the blocking action of sulfur atoms, will retard the formation of the graphitic overlayer outside the particles until the much higher temperature [36]. As to the partial pressure of C₂H₂, it is found the optimal pressure was 0.25 Torr. In further studies, we reported that tunable growth of DWNTs with different diameter was achieved by controlled the experimental parameters in this floating catalyst system [29]. It indicates that DWNTs produced at lower carbon partial pressure have much smaller inner tubes. We show that the production rate was highly sensitive to the amount of sublimed ferrocene. When the sublimed temperature was increased from 60 to 80 °C, the yield of the products were enhanced with the augment of ferrocene introduced into the reaction area, while the quality of the DWNTs was worsening synchronously. The optimal temperature of the sublimed catalyst was found at range of 65–70 °C. In our efforts to regulate the preparation conditions, we have tried to optimize the catalysts by adjusting its composition. But it was found that the catalyst composition by replacing the partial ferrocene with cobaltocene was inappropriate [26]. Although the functional mechanism of sulfur is complex, we believe that neither the selective poisoning of sulfur on the catalytic surface nor the Fe–S eutectic theory can give a certain explanation.

3.1.3. Morphology of the as-grown SWNTs nonwoven

We modified the experimental set-up by fitting a smaller, special quartz tube diameter of 10 mm into the outer quartz tube (35 mm i.d.). And methane was used as carbon resource in this experiment. After growing for 6–9 h, the products were peeled off as large pieces of nanotube texture from the wall of the quartz tube, which was defined as SWNTs nonwoven [28].

Fig. 4(a) shows the optical image of the as-grown nonwoven. The area of the SWNT nonwoven can reach several tens of cm², which is not previously reported. These large-piece SWNT nonwoven can be handled and manipulated easily, suggesting that these nonwoven is more attractive for practical applications in composite materials. SEM images of the nonwoven are shown in Fig. 4(b) and (c). It appears from Fig. 4(b) that the as-grown SWNT nonwoven is composed of the highly entangled carbon nanotubes bundles, decorated with very small diameter nanoparticles. The SWNT nonwoven is of compact structure, in which carbon nanotubes bundles range from several hundreds to thousands square micrometer. High Resolution TEM image (Fig. 4(d)) show that these entangled carbon nanotubes bundles are almost composed of SWNTs. The diameter of these carbon nanotubes among the bundles is about 1–2 nm. These carbon nanotubes are generally assembled into bundles with the diameter of ~30 nm, which firmly entangled among the nonwoven. The nanoparticles in nonwoven are iron catalysts encapsulated by several graphite layers. After purification, most of the iron particles are effectively removed (Fig. 4(c)). The compact structure of the nonwoven was maintained during
3.1.4. Morphology of well-aligned SWNTs structure

For obtained orientational SWNTs, we used post-growth method with SWNTs nonwoven as well as in situ growth method under electric field. In the latter method, we deposited well-aligned isolated SWNTs or bundles on the metal electrodes patterned on the SiO$_2$/Si surface through floating catalyst CVD method under ac electric fields at relatively low temperature (280 °C). And the patterned metal (Ta/Pt/Ta/) on SiO$_2$/Si wafer was prepared for applying electric field by photolithography and lift-off technique (shown in Fig. 5(a)). Fig. 5(b) shows that SWNTs grown under ac electric field (20 V, 300 KHz) for five minutes were well-aligned and perpendicular to the edges of two adjacent electrodes. In the mean time, we tried both ac and dc electric fields in the experiments and found only ac electric fields were effective for the alignment of SWNTs.

As to the post-growth method, well-aligned single-wall carbon nanotubes (SWNTs) structure with area of several tens of microns has been fabricated from SWNTs nonwoven by mechanical notching and heat treatment. The fabrication of well-aligned SWNTs structure included three processes. Firstly, the purified SWNTs nonwoven, which were easily attached to substrate were spread on a pre-cleaned glass slide or other smooth substrates. Secondly, the SWNTs films were nicked carefully using a sharp tip to generate some notches, which could be used as the local landmarks to find exact position. Finally, this pretreated SWNTs films on the glass slides were kept in an electric furnace at 200 °C under nitrogen atmosphere for about 24 h. A general view of the aligned SWNTs structure is shown in Fig. 5(c) and (d). It is observed that the SWNTs films near to the notch is pulled well aligned under the shrinking force between the both sides of the notch during the heat treatment process. Generation of the aligned SWNTs in this process can be likened to shear a nonwoven-cloth, in which process cloth fibers are tight and aligned in the tearing breach. The notch can be used as distinct local landmarks to position the laser spot on aligned SWNTs, as shown between two black lines in Fig. 5(c). The area of well-aligned SWNTs can be as large as 8×8 μm$^2$, which is easy to be found by an optical microscope. Fig. 5(d) shows the high magnification image of the well-aligned bundles with significantly straight and long nanotubes. These SWNTs bundles with diameter 20–30 nm are parallel to each other with about ~100 nm distance. The comparative high density aligned SWNTs can offer a very high efficiency to excite obvious Raman signal without employing previous surface-enhancement techniques.

3.2. Raman scattering measurements

3.2.1. Raman scattering characterization of SWNTs and DWNTs

Micro-Raman spectra, especially the radial breathing mode (RBM), can be effectively employed to study the properties of SWNTs and DWNTs. Fig. 6 shows micro-Raman spectra for an as-grown SWNTs film, measured with a laser excitation wavelength of 514.5 nm. The Raman spectra consist of two main groups of peaks. The first group includes the peaks at 137, 166, 187, 223, 266 cm$^{-1}$, which consists of the radial breathing modes whose frequencies
depend on the SWNT’s diameters (insert in Fig. 6(a)). According to the relation between diameter and frequency ($\omega_{\text{RBM}} = 223.75/d$ (nm)) [37], the SWNT’s diameter in the measured sample is at range of 0.84–1.63 nm, which agrees with the HRTEM observation. In the second peak group of high frequency, as seen in Fig. 6(a), the peaks at 1573 and 1594 cm$^{-1}$ are related to the $E_{2g}$ graphite mode. The D-line around 1344 cm$^{-1}$ is very lower compared with G-line

Fig. 5. (a) Schematic Diagram of Ta/Pt/Ta electrodes on the SiO$_2$/Si substrate and SEM image; (b) of very dilute well-aligned SWNTs prepared by in situ growth method under ac electric fields; (c) SEM image of the aligned SWNTs structure fabricated by post-growth technique including mechanical notching and heat treatment. The notch signed with black lines is regard as distinct local landmarks, which is benefit to easily find the position of well-aligned SWNTs (white lines square with 8×8 μm$^2$ scale); (d) The high magnification SEM image of well-aligned SWNTs bundles with diameter of less than 30 nm.

Fig. 6. Typical micro-Raman spectra of (a) as-grown SWNTs and (b) DWNTs. (c) high-resolution Raman spectra of RBM bands of DWNTs.
(1594 cm\(^{-1}\)), which indicates that the amount of amorphous carbon in the sample is very small.

On the other hand, micro-Raman scattering was performed on the as-grown samples of DWNTs measured with a laser excitation wavelength of 632.8 nm (Fig. 6(b) and (c)). Similar to that of SWNTs, the DWNTs Raman spectrum in the range of 100–2000 cm\(^{-1}\) also shows two ‘fingerprint’ modes, that is, the tangential mode (TM) with a splitting peak (1554 and 1594 cm\(^{-1}\)) and the radial breathing mode (RBM) in the low frequency range (insert in Fig. 6(b) and (c)). It is worth noting that the RBM frequencies of DWNTs take a wider Raman frequency range (100–400 cm\(^{-1}\)) and display much richer peaks than that of SWNTs (insert in Fig. 6(a)). A DWNT can be considered as two coaxial SWNTs coupled by Van der Waals interaction. The interaction may lead to some mixed Raman vibrational modes [38]. However, we consider that the weak van der Waals interaction may not significantly affect the basic vibration of the outer and inner tubes compared with that of their SWNT counterparts. Therefore, RBM Raman bands of DWNTs can be identified according to the basic rules of that of SWNTs [39]. Considering the thinnest inner diameter 0.4 nm and the interlayer spacing between the outer and the inner tube, we assume that the RBM peaks higher than 210 cm\(^{-1}\) might be originated from the inner tubes, while peaks at the lower frequency might be originated from the outer tubes or the larger inner tubes. Therefore, it is an interesting work to arrange a definite diameter value to the inner or outer tube. In reference [29 and 30], we assigned the possible match of the inner and outer tubes according to the diameter dependence of the RBM frequency of DWNTs. On the other hand, we determined the pair type of DWNTs from the diameter and chirality dependence of the interband energies and found that the inner and outer tube of DWNTs can be any chirality pairs, which validated the assumption of theories [40].

3.2.2. Temperature dependence of resonant Raman scattering in DWNTs and SWNTs

In further studies of Raman scattering, we investigated the temperature-dependent frequency shift of resonant Raman spectra of DWNTs [31]. In our experiment, Raman scattering was taken on the as-grown DWCNT film by a Renishaw microscopic confocal Raman spectrometer (RM2000). The 632.8 nm line of a He–Ne laser was used as the excitation. A 20× objective lens and a low laser power of ~1 mW were used to avoid laser heating. The spatial resolution of the Raman instrument is 1 cm\(^{-1}\). The DWCNT samples were kept in a hot/cold stage that was placed under the microscope of the Raman system. The sample temperature was tuned in the range of 78–650 K by liquid-nitrogen flowing or electric heating.

As expected, with increasing temperature, the frequency of the Raman peaks, including RBM and GM, downshift simultaneously (shown in Fig. 7(a) and (b)). We carried out the peak separations of the Raman bands

![Fig. 7. Raman spectra of RBM (a) and GM (b) the DWNTs at temperature of 150, 300, and 500 K, respectively. Temperature dependence of the RBM frequencies of the DWNTs (c) and GM (d) for the DWNTs. The relation between the normalized temperature coefficient of RBM frequencies and the diameter of DWNTs. The diameters (d, nm) were determined by the relation of d=224/\(\omega_{\text{RBM}}\), where \(\omega_{\text{RBM}}\) is each RBM frequency at 300 K using multilorentzian lines and investigated the Raman shift of several RBM peaks with temperature, which is shown in Fig. 7(c) and (d). It is found that RBM peak relative to carbon nanotube with the larger diameter has the larger frequency downshift. In here, we ascribed this downshift of the Raman shift to the temperature dependence of the C–C stretching force constant. It is indicated that the decreased force constant may be due to the softened C–C bond with increasing temperature and the temperature dependence of the force constants is smaller for the small diameter carbon nanotubes, which will have the smaller Raman frequency downshift with increasing temperature.

3.2.3. Polarized Raman scattering Characterization of isolated and Well-aligned SWNTs

Polarized Raman spectra of the well-aligned SWNTs were recorded at room temperature using a micro-Raman spectrometer (JY-T64000) fitted with a charge coupled device detector (CCD). A 100× microscope objective was used for focusing of the laser beam and collection of the scattered light. The 488 nm (\(E_{l}=2.54\) eV) laser excitation of Ar ion laser was provided and total power to the sample was filtered down to 40 \(\mu\)W over 1–2 \(\mu\)m laser spot. All Raman spectra were taken in backscattering configuration, with
the incident-light polarization parallel (VV) or perpendicular (VH) to the scattering-light polarization. To obtain the VH signal, the scattered light was rotated by $\lambda/2$ plate, keeping the same scattered-light polarization direction in the grating and in the CCD. A motorized x–y stage and a rotational stage were used to rotate the aligned SWNTs angle ($\theta_a$, between the SWNTs axis and the incident excitation polarized) in the horizontal plane with respect to the electric vector of the linearly polarized excitation from 0 to 90°.

Typical polarized Raman spectra of the well-aligned SWNTs are presented in Fig. 8. The Raman spectra with different angles $\theta_a$ between the polarization of the incident light and the nanotube axis were recorded with VV configuration (Fig. 8(a)). It is found that all Raman peaks exhibit a dramatically decrease in intensities as $\theta_a$ varies from 0 to 90°. Furthermore, all Raman modes with VV configuration reach maximum intensities when the polarization of the incident light is parallel to the nanotube axis ($\theta_a=0^\circ$), while nearly no signal can be detected when the polarization of the incident radiation is perpendicular to the nanotube axis ($\theta_a=90^\circ$). Fig. 8(b) shows the orientation-dependence of the polarized Raman spectra of the well-aligned SWNTs recorded with VH configuration. Obviously, with the increase of the $\theta_a$, the intensities of all Raman modes increase and go through a maximum at $\theta_a=45^\circ$ and then decrease symmetrically at $\theta_a=90^\circ$. Furthermore, it is worth noting that the Raman spectra for the two complementary angles show similar intensities.

The angular dependence of Raman intensity is ascribed to the resonance enhancement in the Raman spectra of SWNTs and an orientation dependence of the absorption response for the resonance, which can be explained in terms of the depolarization effect (‘antenna effect’) [41–43]. Due to the strong anisotropic geometry of the carbon nanotubes, the interband optical transitions from the valence band to the conducting band near the Fermi level can observed only for polarization parallel to the tube axis of SWNTs. It is predicated by the resonant Raman theory that a dramatic decrease in the Raman intensities of perfect SWNTs alignment for nanotubes oriented perpendicular to the excitation polarization. As for VV configuration in our experiment, when the polarization of the incident radiation is perpendicular to the nanotube axis ($\theta_a=90^\circ$), the Raman intensities of the well-aligned SWNTs are smaller than those of $\theta_a=0^\circ$ by a factor of $\sim 250$, which is about 50 times than previous report [44]. On the other hand, the comparatively weak RBM intensities with VH configuration in here are due to the degenerate vibrations of the $E$ modes (shown in insert of Fig. 8 (a) and (b)), which are reported previously [45 and 46].

For direct comparison to the theoretical intensity predictions and previous experimental results, relative Raman intensities in here are fitted with particular functions. Fig. 3(a) and (b) show the angular dependence of the relative Raman intensities of the peaks at 1592 cm$^{-1}$ (tangential stretching G-band mode) normalized to their

Fig. 8. Polarized Raman spectra of aligned SWNTs in the VV (a) and VH (b) configuration for various angles $\theta_a$ between the aligned SWNTs axis and the polarization of the incident laser beam. Angular dependence of the relative intensity of the peak 1592 cm$^{-1}$ for VV (c) and VH (d) scattering as a function of the measured angle $\theta_a$ between the polarized direction and the aligned nanotube axis. The dotted curves in (c) and (d) correspond to the function $\cos^4\Phi$ and $4(\cos^2\Phi)(\sin^2\Phi)$, respectively.
maximum intensities for VV and VH measurements, respectively. It is observed that the angular dependence can be fitted well with \( \cos^4(\theta_a) \) function (dashed line in Fig. 8(c)) for VV intensities, while \( \sin^2(\theta_a)\cos^2(\theta_a) \) function (dashed line in Fig. 8(d)) for VH intensities. These results are in excellent agreement with resonant theoretical assumption and previous experimental results [45]. It is confirmed that the angular dependence of Raman intensities for VV and VH validate well the predication of the resonant theory due to perfect SWNTs alignment used in our experiment [46].

3.3. Mechanical measurements of the samples

Due to the macroscopic area of SWNT nonwoven, we measured the values of \( E \) and failure strength of nonwoven by directly pulling the as-grown and purified nonwoven with a special tensile puller, which is discussed in reference [28]. The special stress–strain puller we used was once employed by Pan et al for measuring the Young’s modulus \( (E) \) and tensile strength \( (\sigma_b) \) of multi-walled carbon nanotubes (MWNT) by pulling very long aligned nanotube ropes [47].

Fig. 9(a) and (b) are typical stress–strain curves, which can determine the \( E \) value for the original and purified nonwoven, respectively. The apparent Young’s Modulus of the original nonwoven was \( \sim 0.188 \) TPa, while that of the purified nonwoven was \( \sim 0.139 \) TPa. With the free volume in the nonwoven considered, the real Young’s Modulus could reach up to \( 0.7 \pm 0.27 \) TPa, while that of the purified nonwoven was calculated as to be \( 0.5 \pm 0.19 \) TPa. We ascribed the high Young’s Modulus to these SWNT nonwoven’s special structure and good graphitization. Therefore, the Young’s modulus in our experiment is consistent with the theory prediction and the measurements results [48]. In our experiment, the special compact structure and firmly entangled connection is beneficial to the effective transfer of loading. As another reasons, these entangled nanotubes of nonwoven are grown in relatively high temperature (1100 °C), which result in well graphited and few defects.

On the other side, the failure strengths for the original and purified nonwoven are \( \sim 144 \) and \( \sim 107 \) Mpa, respectively (calculated from the maximum stress in Fig. 9(a) and (b). In our tensile experiment, we found two main processes, the elastic elongation of the entangled nanotubes bundles and the slippage between the aligned nanotubes bundles, occurred subsequently during loading force on the samples [49]. Therefore, the relatively low breakage values measured in our tests were mainly attributed to the slippage between the aligned nanotubes bundles, as opposed to real breakage of individual nanotubes.

4. Conclusions

In summary, we have reported that:

(i) Single-wall carbon nanotubes (SWNTs) without amorphous carbon coating were prepared by thermally decomposing acetylene \( (C_2H_2) \) at the temperature range of 750–1200 °C in a floating iron catalyst system. The \( C_2H_2 \) partial pressure was controlled to make a carbon supply-limiting growth of SWNTs. The higher reaction temperature above 1100 °C seemed not to favor the SWNT production due to the quick thermal decomposition of \( C_2H_2 \).

(ii) Double-wall carbon nanotubes (DWNTs) were mass-produced by pyrolyzing \( C_2H_2 \) at the temperature range of 900–1100 °C on a floating iron catalyst with sulfur promoted. It is indicated that the growth of DWNTs was strongly dependent on the sulfur addition, and without sulfur only SWNTs were produced. The effect mechanism of sulfur to the growth of DWNTs was discussed.

(iii) After developed the experimental set-up, tough SWNTs nonwoven with area up to several tens square centimeters was prepared directly by...
pyrolyzing CH$_4$ at the temperature \( \sim 1100 \) °C. The SWNT nonwoven exhibits extremely high Young’s Modulus of ca. 0.4–0.7 TPa, which has potential applications in mechanical reinforcement of composite materials.

(iv) Similar to that of SWNTs, Raman scattering by DWNTs has been experimentally shown to be a resonant process. The possible match of the inner tubes and the outer tubes according to the RBM bands was assigned, and different chirality types were discussed according to the diameter and chirality dependence of resonant Raman vibration. Otherwise, the temperature dependent frequency shift of resonant Raman spectra of DWNTs are investigated in the range of 78–650 K. We found that different radial breathing mode (RBM) peaks, which are relative to different tube diameters, have different temperature coefficient of frequency shift. The larger diameter carbon nanotubes have more RBM frequency downshift with increasing temperature. We attribute the RBM frequency variation to the temperature dependence of the stretching force constant of C–C bond.

(v) Polarized Raman spectra recorded with VV and VH geometry are performed on well-aligned SWNTs fabricated from SWNTs nonwoven to detect the polarization and nanotubes orientation dependence of the Raman intensity. The angular dependence of Raman intensity is consistent with the predictions of the theory (‘antenna effect’) and further confirms the resonance Raman model of the well-aligned SWNTs.

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