CONTROLLABLE SYNTHESIS, GROWTH MECHANISM AND RAMAN SPECTROSCOPY OF DOUBLE-WALLED CARBON NANOTUBES

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Abstract

Double-walled carbon nanotubes (DWNTs) provide an ideal model to study the effect of interlayer interaction on the phonon and electronic structures of carbon nanotubes (CNTs), and have some unique properties and potential applications as nanodevices. In this paper, we present a review of our research works on the controllable synthesis of DWNTs and understanding of their growth mechanism and Raman spectroscopy. Firstly, we will demonstrate the controllable synthesis of DWNTs using a floating catalytic chemical vapor deposition method (FCCVD). It is worth noting that aligned DWNT long ropes with a narrow diameter distribution and high purity can be directly obtained by the above method in the optimized conditions. In the second part, we will discuss the effect of sulfur, a growth promoter usually used in the FCCVD method, on the structure of CNTs. Single-walled CNTs (SWNTs) and DWNTs with different diameters are selectively obtained only through changing the concentration of sulfur in the same reaction system. Based on HRTEM observations, thermodynamic and kinetic considerations, a localized liquid zone nucleation model at low temperatures is proposed for the growth of SWNTs and DWNTs prepared by the FCCVD method. Finally, we will present the Raman features of DWNTs and discuss the effect of interlayer interaction on their phonon and electronic structures. A double-peak profile is found in their radial breathing mode (RBM) feature, which can be associated with the outer and inner tubes, respectively. By polarized Raman studies and symmetry assignments of the *G* band, we find that the two constituent tubes remain their original mode symmetries and vibrations along axial and circumferential directions. The analysis on the unique features of *D* band and *G*′ band of DWNTs constitutes the first Raman evidence for atomic correlation and the resulting electronic structure change of the two constituent tubes in DWNTs.

Introduction

Controllable synthesis of carbon nanotubes (CNTs) is the basis for their further theoretical studies and potential applications. In particular, single-walled CNTs (SWNTs) and double-walled CNTs (DWNTs) are employed as model systems for nanoscience, for investigating a variety of new phenomena, and for exploring potential applications [Dresselhaus MS]. For example, single-walled carbon nantoubes (SWNTs) can be expected to be used as the building blocks of nano-scale electronic devices, since they can be either semiconducting or metallic depending on their diameters and chiralities.[Saito R, Dresselhaus MS] Although some interesting applications can be explored only in multi-walled carbon nanotubes (MWNTs), the fundamental studies and engineering applications have been still relatively limited, because of the difficulty in the synthesis of MWNTs with homogeneity in diameter and shell number. DWNT is a special MWNT only consisting of two coaxial SWNTs, which provide an ideal model to study the effect of interlayer interaction on the phonon and electronic structures of CNTs. Theoretical calculations for energy bands of DWNTs have concluded that their electronic structures can be modified by the interlayer interaction.[Saito R] Moreover, they are expected to have some potential applications directly as nano-scale devices, [Saito R, Saiito R, Zhang SL] due to its special double wall structure, such as molecular conductive wire or molecular capacitor in a memory device, depending on the electronic properties of the two constituent tubes.[Saito R] Therefore, it is very important to realize the selective synthesis of DWNTs, and to obtain their detailed structural information, such as diameters and electronic properties of the two constituent tubes, and to identify the effect of interlayer interaction on their electronic structures, for their promising applications as nano-scale devices. In this paper, we present a review of our research works on the controllable synthesis of DWNTs and understanding of their growth mechanism and Raman spectroscopy.

Experimental

The synthesis equipment was described in detail in our previous paper.[Cheng HM] In general, methane was used as the carbon source, hydrogen as the carrier gas, ferrocene as the catalyst precursor, and thiophene was carried into the reactor by methane to enhance the growth of CNTs. For the growth of DWNTs[Ren WC], the reaction tube was first heated to reach 1373 K in a hydrogen atmosphere. Then, methane and hydrogen, accompanying with the catalyst precursor and thiophene, were introduced into the reaction tube for 5 min, followed by cooling the CVD system in hydrogen to room

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temperature.

The morphology and microstructure of the products were characterized using high-resolution transmission electron microscopy (HRTEM, 200kV) and Raman spectroscopy (excited by 632.8 nm laser). All Raman spectra were taken in backscattering configuration, with the incident and scattered light propagating perpendicular to the rope axis. In the polarized Raman studies of DWNT ropes, [Ren WC] the axis of the DWNT rope was carefully rotated manually to ensure the laser signals from almost the same spot of a thin DWNT rope (~10 μm), and the angles (θ) between the axis of the rope and the polarization direction of the incident laser were calculated from the optical micro-images obtained from a digital camera, with an accuracy of ± 2º.

Results and Discussion

Controllable synthesis of DWNTs

In 2002, we demonstrated for the first time that floating catalyst chemical vapor deposition (FCCVD) method can be used for the synthesis of DWNTs with high quality. [Ren WC] This technique has many advantages: cheap raw materials, low reaction temperature, simple equipment, semi-continuous or continuous production, high purity, as well as high DWNT content (Fig. 1). Therefore, it is possible to synthesize high quality DWNTs on a large scale and at a low cost. Moreover, the DWNTs prepared by this method possess smaller diameters and a narrower diameter distribution compared to those from arc discharge.

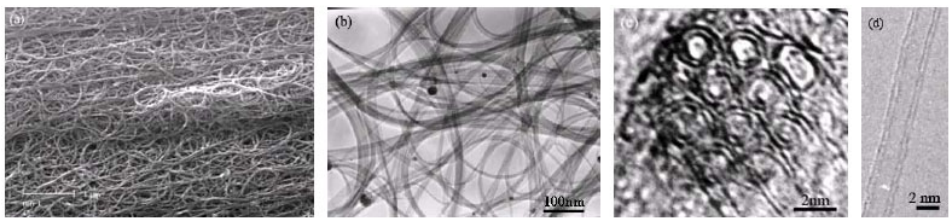

Figure 1. SEM, TEM and HRTEM images of the as-prepared DWNTs. (Ren WC, Chem. Phys. Lett. 2002)

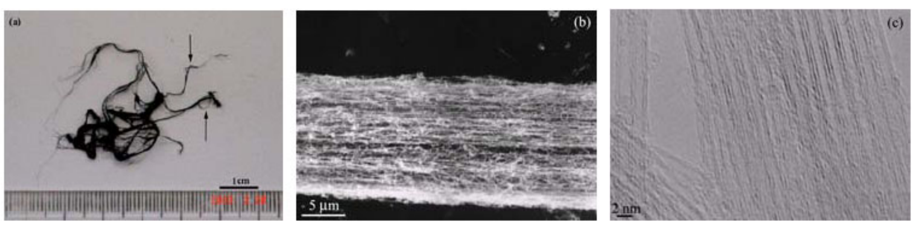

Figure 2. Optical photo, SEM and HRTEM images of aligned DWNT ropes. (Ren WC, J. Phys. Chem. B 2005)

To further improve the mechanical and electronic properties of DWNTs and to push their applications as electronic nanodevices, we successfully produced well-aligned DWNT long ropes up to several centimeters (Fig. 2) with a narrow diameter distribution using the FCCVD method, [Ren WC] with precise control of preparation parameters. It is worth noting that more than 90% of the CNTs are DWNTs, and the outer and inner tube diameters of the DWNTs in the ropes are in the range of 1.7-2.0 nm and 1.0-1.3 nm, respectively, which is the narrowest diameter distribution for directly synthesized DWNTs with the exception of the coalescence of C_{60} in preexisting SWNTs. Furthermore, based on the resonant Raman measurements, the electronic properties of the two constituent tubes were identified and metallic-semiconducting pared DWNTs were found to dominate in the product. The successful synthesis of those DWNTs opens up the possibility of further fundamental studies and applications as mechanical, optical and electronic nanodevices.

Growth mechanism of CNTs produced by FCCVD method

To understand the growth mechanism of CNTs, the effect of sulfur, a promoter usually used in the FCCVD method to enhance the growth of CNTs, on the structures (shell number and diameter distribution) of CNTs obtained was investigated in detail. [Ren WC] It is interesting to find that (1) the addition of sulfur is necessary to enhance the growth of SWNTs and DWNTs, due to the formation of large catalyst particles during the growth process; and (2) in a certain range, the diameter and shell number are increased only by increasing the addition amount of sulfur. Based on this rule, SWNTs, DWNTs and MWNTs with different diameter distributions were efficiently and selectively obtained only by changing the sulfur addition amount. Moreover, it is also demonstrated that very short herringbone-type carbon nanofibers with a narrow diameter distribution can be selectively obtained using this FCCVD method. [Ren WC]

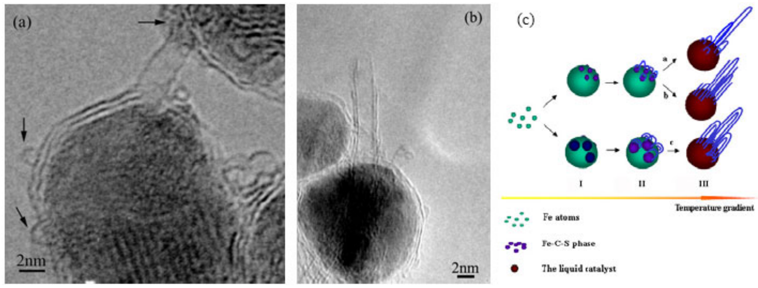

Figure 3. (a), (b) HRTEM images of the correlation between SWNTs, DWNTs and the attached catalyst particles, and (c) The diagram of the *localized liquid zone growth model at low temperature* for SWNTs and DWNTs produced by FCCVD method. (Ren WC, J. Nanosci. Nanotechnol. & J. Phys. Chem. B 2006)

On the basis of the above experimental results, HRTEM observations, energy and kinetic considerations, a *localized liquid zone nucleation model at low temperature* (Fig. 3) for SWNT and DWNTs was proposed and several viewpoints are addressed as follows [Ren WC]: (1) the nucleation of SWNTs and DWNTs starts at a low temperature zone in front of the reaction zone, and a temperature gradient is necessary to realize the role of sulfur in the formation of CNTs; (2) the addition of sulfur results in a localized liquid zone on the surfaces of catalyst particles as initial nucleation sites; (3) the growth of cap-closed SWNTs starts from the formation of the cap-like structures, and the addition of sulfur leads to the change of surface tension and introduces some defects in the graphite island on the surface of catalyst particles, consequently enhances the nucleation of SWNTs and DWNTs with closed tips; and (4) the shell number of CNTs is closely related to carbon supply and CNT diameter. These results open up a possibility for guiding the structure-controlled growth of CNTs.

Raman spectroscopy of DWNTs

To probe the detailed structural characteristics and to identify the interlayer interaction effect, the resonant Raman spectra of DWNTs were studied systematically (Fig. 4). Firstly, we found that the RBM feature exhibits a double-peak structure. [Ren WC] Based on HRTEM observations and theoretical calculations, the low and high frequency RBM features of DWNTs are assigned to be associated with their outer and inner tubes, respectively. This result provides the possibility of determining the diameter and chirality of DWNTs using resonant Raman spectroscopy. Moreover, the indices of DWNTs are identified reasonably from the observed RBM peaks according to the interlayer spacing of 0.34-0.41 nm obtained from HRTEM observations. It is worth noting that it is not a one-to-one relationship between outer diameter and inner diameter, which provides a direct evidence for different chirality combinations of DWNTs.

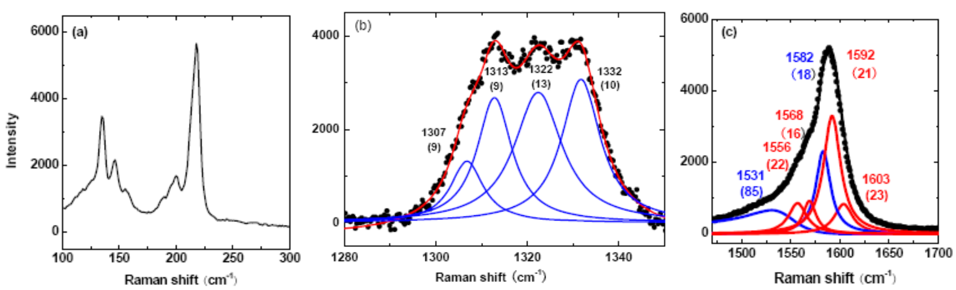

Figure 4. (a) RBM, (b) *D*-band, and (c) *G*-band features of DWNTs. (Ren WC, Phys. Rev. B 2005 & 2006)

Secondly, we performed polarized Raman studies on the *G* band of well-aligned DWNT ropes and experimentally found that the depolarization effect is weakened with increasing the shell number of CNTs. [Ren WC] Based on group theory analysis and related theoretical predictions, the mode symmetry was identified and consequently we found that the *G*-band profile consists of two groups of well-resolved modes related to the two constituent tubes of DWNTs. Moreover, it is worth noting that the two constituent tubes generally retain their original mode symmetries and vibrations, suggestive of a weak interlayer interaction on the axial and circumferential vibrations.

Thirdly, we have assigned the four peaks firstly found in the *D* band and *G′* band of DWNT bundles. [Ren WC] The two outer peaks are deduced to originate from a strong coupling between the two constituent tubes of commensurate DWNTs and the two inner peaks are curvature-related and can be assigned to originate from the two tubes with a weak coupling. This finding experimentally verifies that: (1) the atomic correlation between the two constituent tubes of DWNTs has a very important influence on their electronic structures, and (2) additional van Hove singularities occur in the joint density of states of commensurate DWNTs compared to those of independent SWNTs. This observation and elucidation constitute the first Raman evidence for atomic correlation and the resulting electronic structure change of the two constituent tubes in DWNTs, which opens the possibility of predicting and modifying the electronic properties of DWNTs for their electronic applications.

Conclusions

The efficiency of floating catalyst chemical vapor deposition method for the selective synthesis of DWNTs with high quality was demonstrated in this review paper. It is found that sulfur plays an important role in structural control of CNTs in the FCCVD method, and SWNTs, DWNTs and MWNTs with different diameters can be synthesized by only changing the concentration of sulfur in the reaction system. Based on the experimental facts and related theoretical considerations, a localized nucleation model on the surface of catalyst particle at low temperature was proposed for the synthesis of CNTs by FCCVD method. Moreover, the Raman spectroscopy of DWNTs was studied systematically. These observations and findings provide some useful information on enhancing structural control of CNTs, probing their detailed structural characteristics and understanding their growth mechanism.

Acknowledgement

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