Preparation of Isolated Single-walled Carbon Nanotubes with High Hydrogen Storage Capacity

ZHANG Ai-fei(张艾飞)[1,2], LIU Ji-ping(刘吉平)[1], LU Guang-shu(吕广庶)[1], LIU Hua(刘 华)[1]

(*1. School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*;
2. Chemistry Department, Luoyang Normal University, Luoyang, Henan 471022, China)

Abstract: Isolated single-walled carbon nanotubes with high proportion of opening tips were synthesized by using alcohol as carbon source. The mechanism of cutting action of oxygen was proposed to explain its growth. Compared with carbon nanotubes synthesized with benzene as carbon source, their specific surface area was heightened by approximately 2.2 times (from 200.5 to 648 m^2/g) and the hydrogen storage capacity was increased by approximately 6.5 times (from 0.95 to 7.17%, ω) which had exceeded DOE energy standard of vehicular hydrogen storage.

Key words: carbon nanotubes; synthesis; alcohol; benzene; mechanism
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1 INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention to scientists because of their great potential to adsorb hydrogen since their discovery in 1991 by Dr. Iijima[1]. There are mainly three methods for preparation of CNTs, including laser ablation, arc discharge and catalytic pyrolysis[2−4]. But CNTs prepared with hydrocarbon as carbon source have very serious agglomeration[5,6] and the two tips of a single CNT are usually closed by semi-spherical fullerenes, which is not suitable for the storage of a great amount of hydrogen[7,8]. It will also be a very complex and time-consuming task to separate, shorten and open closed tips of agglomerated CNT bundles in order to meet the requirements of hydrogen storage material. As a result, the application of carbon nanotubes as hydrogen storage media has been seriously retarded. Therefore, it is necessary to synthesize isolated carbon nanotubes with high proportion of opening tips directly. However, no related report has been found so far[9,10]. Isolated single-walled carbon nanotubes (SWNTs) with high hydrogen storage capacity were synthesized successfully here by using alcohol as carbon source.

2 EXPERIMENTAL

2.1 Materials

Alcohol, ferrocene, benzene and carbon bisulfide are all of analytic grade and provided by VAS Company. Helium (99.995%, φ) is supplied by Beifen Gas Corporation Ltd., Beijing. Hydrogen is provided by two Model GCD-300B hydrogen generators.

2.2 Synthesis

Carbon nanotubes were synthesized by floating catalytic pyrolysis method. Quartz tube (Length: 1500 mm, o.d.: 75 mm and i.d.: 65 mm) reactor is located vertically in electric furnace. Alcohol or benzene is chosen as carbon source, ferrocene is used as catalyst and carbon bisulfide as growth activator. The mixture of hydrogen and helium is employed as carrier gas. The specific procedure is as follows: The whole system is inspected carefully to know whether it is airproof before the reaction begins. Then nitrogen with the flow of 500 mL/min is introduced into the reaction system to remove air at room temperature for 2 h. And when the furnace is heated to growth temperature, nitrogen flow is switched off, and hydrogen, helium and liquid stuff are introduced. The flow of hydrogen and helium is 400 mL/min and 500 mL/min, respectively. The mass concentration of ferrocene in the solution of carbon source is 2.0 g/L and volumetric fraction of carbon bisulfide is 0.5%. The liquid stuff is first preheated at 573 K and then guided into the quartz tube with the flow rate of 1.0 mL/min. After the reaction has been conducted for 0.5 h, hydrogen and liquid stuff are turned off. The system is cooled down to room temperature under the protection of helium. The growth temperature is controlled at 973~1273 K. Only the growth temperature and the type of carbon feeders are changed during the growth of CNT while other

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parameters keeping constant.

2.3 Measurement

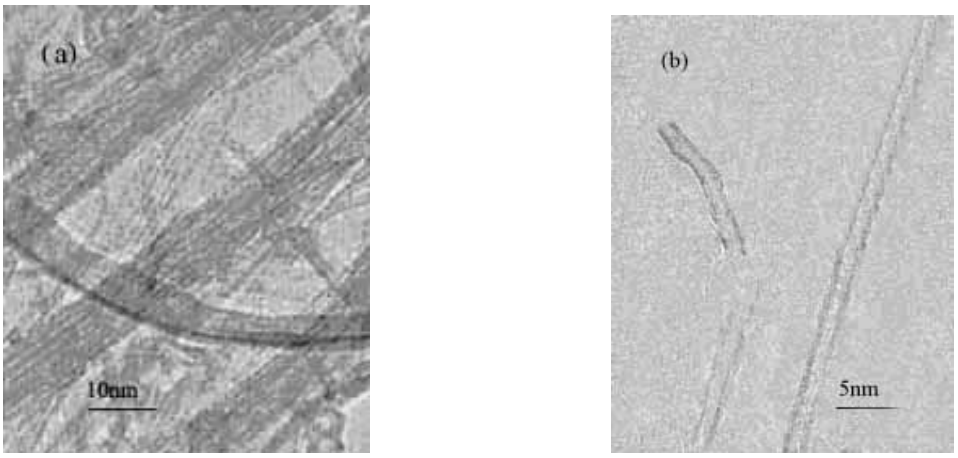
Raw CNTs were added into anhydrous alcohol followed by ultrasonic dispersion for 10 min. And then the sample was captured by micro-grid for subsequent HRTEM observation (JEM-2010, operated at 200 kV). RFS-100 Raman spectrograph (operated at laser excitation wavelength of 514.5 nm) was used to help identify the structure of CNTs. Hydrogen storage dynamics of isolated CNTs was measured according to the change of pressure in adsorption chamber before and after the adsorption.

3 RESULTS AND DISCUSSION

3.1 Characterization of Microstructure of SWNT Bundles and Isolated SWNT

Growth temperature has very significant effect on the type of carbon structure formed. The final products synthesized at different temperatures have different microscopic morphologies. If the growth temperature was lower than 1073 K, no solid products were formed. Bamboo-like carbon nano-fibers were produced when the reaction was implemented at 1173 K. But the fibers were solid, no hollow structure was observed. A large quantity of carbon nanotubes was synthesized at higher temperature of 1273 K. So the growth temperature was fixed at 1273 K for the preparation of carbon nanotubes in this work.

Figure 1(a) shows the HRTEM image of carbon nanotubes prepared with benzene as carbon source. SWNTs prepared mainly exist at the state of agglomerated bundle, consisting of 2~5 single tubes. The SWNT bundle is very long and it is very difficult to find its head and tail. The majority of the carbon nanotubes have the diameter of approximately 1.67 nm.



(a) SWNT bundles, benzene as carbon source (b) Isolated SWNTs, alcohol as carbon source

Fig.1 HRTEM images of SWNTs

Figures 2(a) and 2(b) are high frequency band and low frequency band of Raman scattering of SWNTs prepared with benzene as carbon source. G-band and D-band are located at the positions of 1595 and 1358 cm^{-1}, respectively. The area of D-band is much smaller than that of G-band, which is usually regarded as one of the evidences of the formation of single-walled carbon nanotubes. A small peak with the central position of 1579 cm^{-1} also appears at G-band. The line type of the split G-band shows that the SWNTs prepared are semi-conducting nanotubes. The spectrum in Fig.2(b) represents radial breathing mode (RBM) of SWNTs. There is only one peak at low frequency band, its centre locating at 201.8 cm^{-1}. As for SWNT bundles, inter-tube interactions usually induce an up-shift of about 10% of RBM frequency (ω)[11]. Therefore, the average diameter of SWNTs existing in a bundle ought to be calculated by the following equation: d (nm)=$238/\omega^{0.93}$. So the diameter of SWNTs prepared with benzene as carbon source is approximately 1.7 nm. It is very near to that observed by HRTEM.

HRTEM image of carbon nanotubes prepared with alcohol as carbon source is shown in Fig.1(b). The SWNTs with very uniform diameter of about 2.0 nm were synthesized. These SWNTs exist at isolated status, which is rarely discovered in carbon nanotubes synthesized by hydrocarbon as carbon source. The two ends of a single nanotube are often open, which will be very favorable to adsorb hydrogen, because the majority of the inner cavity of the tube becomes available. The length of isolated SWNTs varies from 30 nm to 200 nm. But isolated SWNTs are not stable in acid or atmosphere

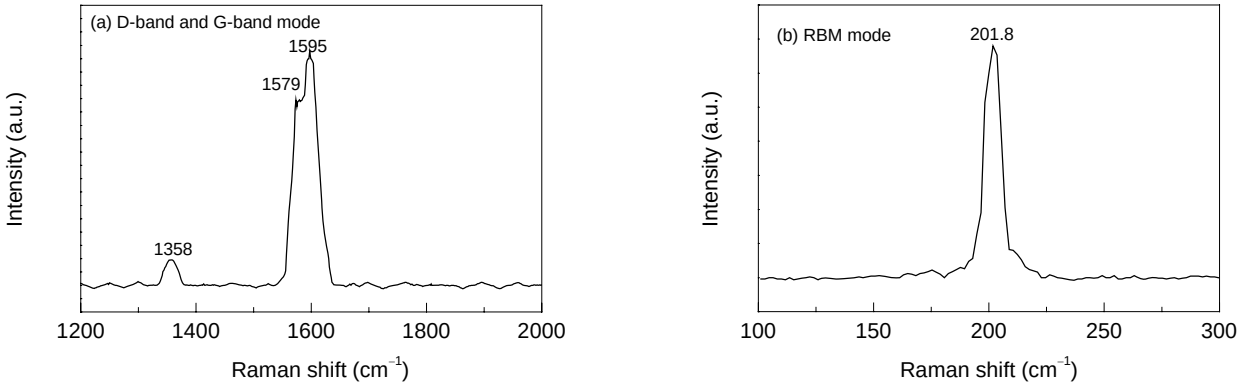


Fig.2 Raman spectra of SWNT bundles synthesized by using benzene as carbon source

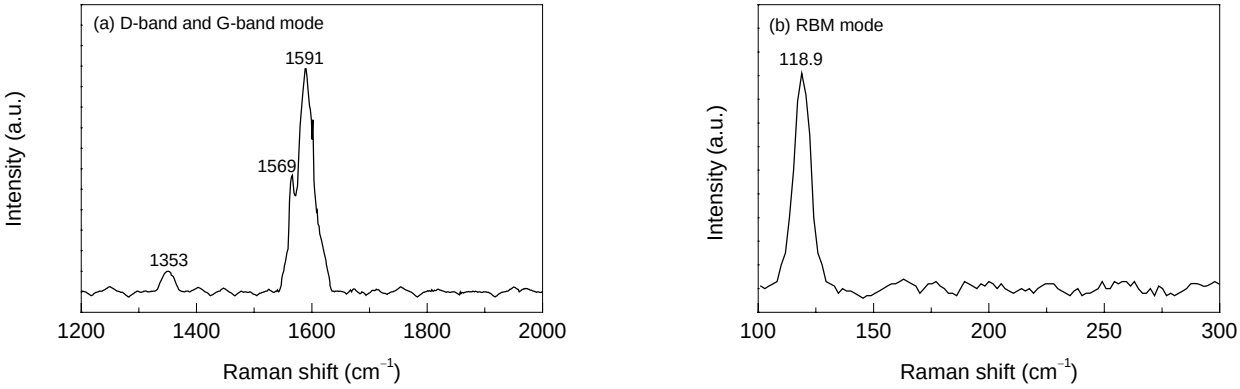


Fig.3 Raman spectra of isolated SWNTs synthesized by using alcohol as carbon source

with high humidity. So they should be packed and conserved in vacuum.

High frequency and low frequency bands of Raman scattering of SWNTs prepared by using alcohol as carbon feeder are shown in Figs.3(a) and 3(b). The peaks at 1591 and 1353 cm^{-1} represent G-band and D-band, respectively. The peak of G-band is much stronger than that of D-band, which suggests the existence of single-walled carbon nanotubes. A small peak at 1569 cm^{-1} usually appears for SWNTs sample, whose position has some kind of relation to the degree of the dispersion of SWNTs. Only one peak appears at low frequency band, locating at 118.9 cm^{-1}. According to the equation: d (nm)=238/ω, they have the diameter of about 2.0 nm. This also gives similar result to that acquired from HRTEM observations.

3.2 Growth Mechanism of Isolated Carbon Nanotubes

As shown by Fig.4, during the growth of a carbon nanotube, part of C–O bonds in alcohol molecule probably does not rupture completely and they may exist at two ends [position (a)] and at the side of SWNT [position (b)]. These oxygen atoms may impede adjacent tubes to assemble into bundle and form long carbon nanotubes with closed ends through the function of cutting. So isolated single-walled carbon nanotubes can grow on oxygen-containing condition. The present study shows that isolated nano-materials can be directly synthesized through the control of the atmosphere of reaction system. The problem of agglomeration of nano-materials can be resolved during their growth.

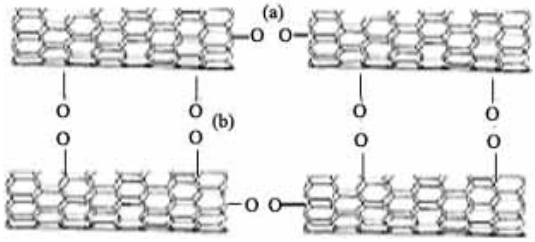


Fig.4 Growth mechanism of isolated SWNTs

3.3 Hydrogen Storage Dynamics of Isolated Carbon Nanotubes

The specific surface area of SWNTs prepared with benzene as carbon source (BCNTs) was 200.5 m^2/g, and that of isolated SWNTs prepared with alcohol as carbon source (ACNTs) was 648 m^2/g. The samples should be activated firstly in vacuum at 573 K for 6 h before their hydrogen storage properties are measured.

The dynamics of hydrogen adsorption in ACNTs and BCNTs at 273 K and 15 MPa is shown in Fig.5. The quantity of hydrogen adsorbed increases with adsorption time and finally reaches saturation. BCNTs get their saturation adsorption of 0.95% (ω) for adsorption time of 2.5 h and ACNTs, 7.17% (ω) for 4.5 h. The great difference between ACNTs and BCNTs probably lies in two reasons. Firstly, a great part of the ends of ACNTs is open, while almost all the ends of BCNTs are closed by semi-spherical fullerenes. As a result, inner cavity of BCNTs can not be used to adsorb hydrogen. Secondly, the average diameter (2.0 nm) of ACNTs is larger than that of BCNTs (1.67 nm). According to theoretical calculations, SWNTs with larger diameter own higher hydrogen storage capacity. So the difference between the diameters of two kinds of SWNTs may be related to their different adsorption abilities to some extent. It can be also seen from Fig.5 that it takes two more hours for ACNTs to reach adsorption equilibrium than BCNTs. Perhaps larger resistance needs to be overcome for hydrogen to enter inner cavity than to be adsorbed by the outside wall of SWNTs. We suppose that if the adsorption pressure continues to be enhanced, ACNTs may adsorb more hydrogen.

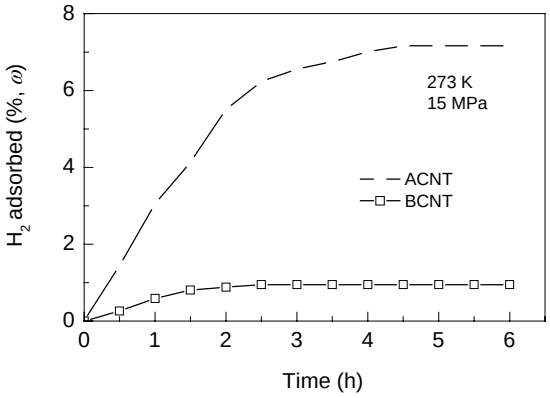


Fig.5 The dynamics of hydrogen adsorption in isolated SWNTs

4 CONCLUSIONS

In summary, isolated single-walled carbon nanotubes are prepared by using alcohol as carbon source. HRTEM and Raman analysis shows that isolated SWNTs prepared have an average diameter of approximately 2.0 nm and the length of approximately 30~200 nm. The cutting action of oxygen is probably primary reason for the formation of isolated SWNTs. They own excellent adsorption property with hydrogen storage capacity of 7.17% (ω) at 273 K and 15 MPa, which is much higher than that of SWNT bundles with closed tips. This study gives a new idea of directly synthesizing isolated carbon nanotubes by controlling the atmosphere of the reaction system. Thus, complex and time-consuming process of dispersing agglomerated SWNT bundles will become unnecessary. Moreover, it is possible to improve hydrogen storage capacity of SWNTs greatly by optimizing their microscopic textures.

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