

## Research Letter

# Production of Carbon Nanofibers Using a CVD Method with Lithium Fluoride as a Supported Cobalt Catalyst

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Carbon nanofibers (CNFs) have been synthesized in high yield (>70%) by catalytic chemical vapor deposition (CCVD) on Co/LiF catalyst using acetylene as carbon source. A novel catalyst support (LiF) is reported for the first time as an alternative for large-scale production of carbon nanofibers while purification process of nanofibers is easier. In our experiment, the sealed furnace was heated at 700°C for 0.5 hour (the heating rate was 10°C/min) and then cooled to room temperature in the furnace naturally. Catalytic chemical vapor deposition is of interest for fundamental understanding and improvement of commercial synthesis of carbon nanofibers (CNFs). The obtained sample was sequentially washed with ethanol, dilutes acid, and distilled water to remove residual impurities, amorphous carbon materials, and remaining of catalyst, and then dried at 110°C for 24 hours. The combined physical characterization through several techniques, such as high-resolution transmission electron microscope (TEM), scanning electron microscope (SEM), thermogravimetric analysis (TGA), and zeta-sizer and Raman spectroscopy, allows determining the geometric characteristic and the microstructure of individual carbon nanofibers. Catalytic chemical vapor deposition is of interest for fundamental understanding and improvement of commercial synthesis of carbon nanofibers (CNFs). As a matter of fact, the method of CCVD guarantees the production of CNFs for different applications.

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## 1. INTRODUCTION

Carbon nanostructures have been intensively investigated due to their unique one-dimensional structure with adjustable electronic conductivity and unusual mechanical strength [1–3]. Since their discovery in 1991 [1], carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted a deal of interests due to their own unique characteristics and potential applications such as separation, gas sensing, catalyst support, energy storage, and environmental protection [4–6]. On the other hand, graphitic carbon nanofibers (GCNFs) represent a class of nanostructured carbon fibers with atomic structures uniquely different from that of carbon nanotubes. Herringbone GCNFs possess canted graphene sheets (also described as geodesic-like conical graphene sheets) stacked in a nested fashion along the long fiber axis. GCNFs of this type can be prepared with average diameters of 25 nm to 200 nm and lengths on the micrometer scale. The graphitic atomic structure of herringbone GCNFs gives a carbon nanofiber long-axis surface comprising C (sp<sup>2</sup>) edge sites, usually passivated by hydrogen atoms [7–9]. Several

studies have investigated various CNT or CNF products by using arc discharge, chemical vapor deposition (CVD), catalytic chemical vapor deposition (CCVD) approaches, and so on [10–12]. Among many published techniques for the fabrication of carbon nanotubes/nanofibers, catalytic chemical vapor deposition (CCVD), carried out with a small quartz/alumina tube under atmospheric pressure and high gas flow rate, has been found to be the only reliable method that can produce helical nanotubes with fine regular coils. However, the drawback with this approach is with the low yield of coiled CNFs on the basis of required high gas flow rate for the deposition. In the normal CCVD process, a high percentage of the gases used (such as C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and Ar) is discharged into the atmosphere without any participation in the chemical reaction [13–24].

In the work presented, curved carbon nanofibers (CNFs) are produced by CCVD acetylene on finely divided cobalt nanoparticles supported on alumina at reduced pressure and lower gas flow rates. The substantial reduction in the consumption of C<sub>2</sub>H<sub>2</sub> under the described reaction condition greatly alleviates environmental concern as well as safety

issues associated with traditional CCVD methods. The goal of this paper is the influence of a catalyst support (LiF) faster growth rate of carbon nanofibers (CNFs) using cobalt as the catalyst, and the yield of carbon nanofibers as a function of the amount of catalyst and catalyst support, so the concentration of  $\text{Ar}/\text{C}_2\text{H}_2/\text{H}_2$  and gas residence time were investigated.

## 2. EXPERIMENTAL PROCEDURES

An alumina tube (outer diameter = 30 mm, inner diameter = 25 mm, length = 1500 mm) was used as a reactor and installed in a horizontal electric furnace. The apparatus was equipped with a gas inlet and an evaporator to vaporize hydrocarbon and catalyst solution at the reaction region. The exhaust gas was removed out from the side of the alumina tube.

First, for preparation of catalyst, the catalyst precursor was dissolved in a solvent in which the LiF support was insoluble. Finally, the prepared catalyst/catalyst support was then dried in air overnight at  $110^\circ\text{C}$ . The dried catalyst was then ground to the form of a fine powder for subsequent deposition. The catalyst was placed in a cylindrical alumina boat positioned in the center of an alumina tube placed within a horizontal tubular electric furnace. The reactor was then evacuated to a suitable pressure with an Ar gas pump. After the reactor was heated to  $700^\circ\text{C}$  at a rate  $20^\circ\text{C}/\text{min}$ , acetylene ( $\text{C}_2\text{H}_2$ ) gas of 120 mL/min was flowed into the reactor for 30 minutes. The final product was then purified as follows: cobalt particles were removed by immersion into a 30%  $\text{HNO}_3$  solution under stirrer for 30 minutes and the solution was allowed to settle for 4 hours, followed by rinsing with bidistilled water using filtration; so, LiF salt was removed by bidistilled water, because catalyst support (LiF) is washable in water. The morphology of synthesized samples was taken by a Cambridge scanning electron microscope (SEM/EDS) operating at 25 kV. The size distribution and morphology of the samples were analyzed by transmission electron microscope (TEM) observation on a Philips CM200 transmission electron microscope operated at 200 kV. Particle size of catalyst/catalyst support has been monitored by a Malvern 3000 HSA Zetasizer operating at wavelength of 633.0 nm at ambient temperature. Thermogravimetric analysis (TGA) was also conducted on the catalyst precursors to understand their decomposition pathway (Shimadzu DTA-50 air atmosphere, dynamic heating). Raman spectra were taken at room temperature under ambient condition using an Almega Raman spectrometer with an  $\text{Ar}^+$  at an excitation wavelength of 514.5 nm.

## 3. RESULTS AND DISCUSSION

As previously discussed, the size of the catalyst particles is one of the important factors for the formation of carbon nanofibers. It is predicted that nanosized catalyst particles could catalyze the growth of carbon nanofibers. The nanoparticle size of catalyst/catalyst support product was analyzed using a zeta-sizer method. These measurements reveal the powders of two different particle size distributions (see Figure 1). The catalysts were particles with diameters

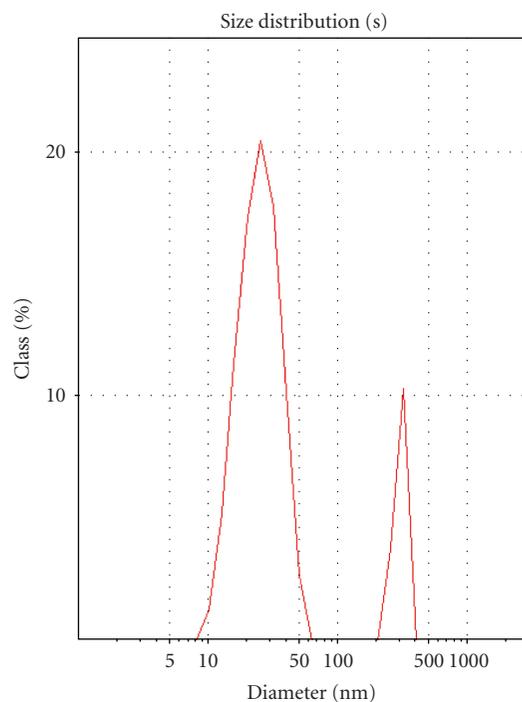
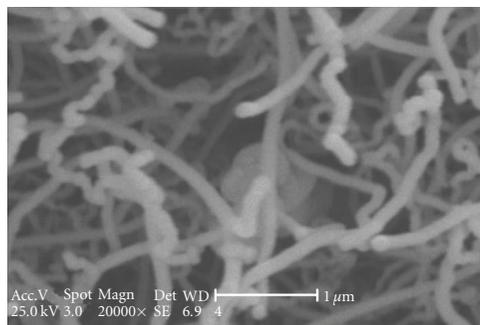


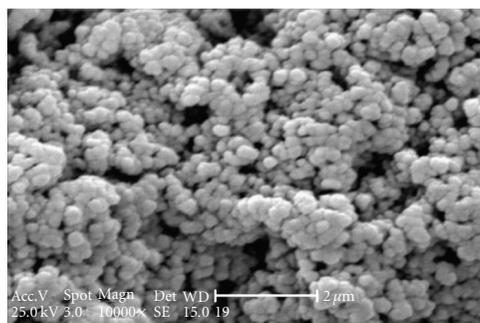
FIGURE 1: Dispersed particle size of catalyst in catalyst support measured by zeta-sizer.

two ranging from 10 nm to 70 nm and 200 nm to 350 nm. At the same time, these results are consistent with the SEM/EDS analysis. Based on this anticipation, we chose cobalt acetate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) as catalyst because it can be easily dissolved in acid. The vaporized cobalt atoms were carried into the reaction tube by the mixture of acetylene and hydrocarbon gas and reduced by the hydrogen gas into cobalt atoms that would aggregate into nanoscaled Co catalyst particles to grow carbon nanofibers. The relatively narrow size distribution is important for forming the ordered nanofibers in diameter. Figure 2(a) is a micrograph of the carbon nanofibers grow on catalyst particles deposited on an alumina substrate at  $700^\circ\text{C}$ , using LiF as a catalyst support. The curved-shaped carbon nanofibers with diameters distributed between 50 nm and 150 nm are grown on the catalyst. Without an LiF catalyst support, no formation of carbon nanofibers on the cobalt particles deposited on an alumina substrate at  $700^\circ\text{C}$  was observed (see Figure 2(b)). The result indicates that LiF plays an important role in synthesizing carbon nanofibers (CNFs). It is important to mention that the CNFs are grown at the temperature below the melting point of LiF (m.p. =  $848.2^\circ\text{C}$ ) by using thermal chemical vapor deposition (CVD). Another scanning electron micrograph (Figure 2(c)) also shows that the carbon nanofibers (CNFs) are approximately perpendicular to the catalyst particles. Most of the CNFs are extremely aligned, so many catalyst particles can be seen in the end of carbon nanofibers.

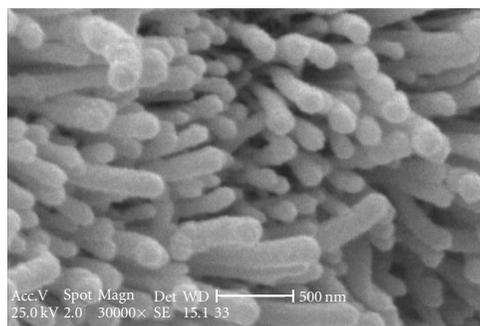
High-resolution transmission electron microscope (HRTEM) was employed to further characterize the structure of synthesizing powder via catalytic chemical vapor deposition (CCVD). TEM examinations (Figure 3(a)) of this



(a)



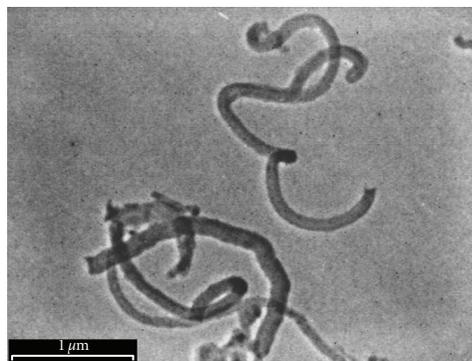
(b)



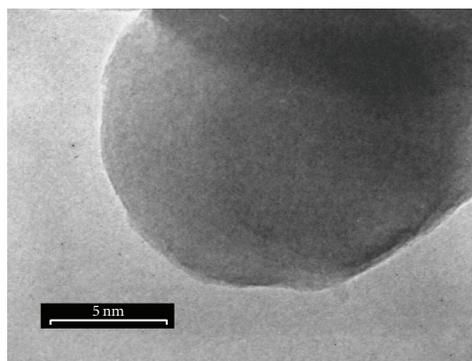
(c)

FIGURE 2: (a) SEM image of the nanofiber powders obtained after CCVD at 700°C; (b) catalyst nanoparticles without CNFs; (c) aligned CNFs on catalysts.

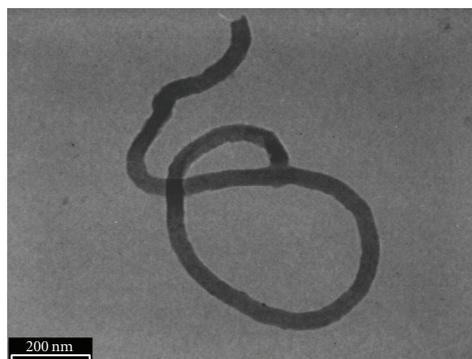
sample indicate that they are nanofibers in which the graphic layers are not clear and have small hollow cores. To prepare transmission electron microscope samples, the nanofibers were transferred to a carbon-coated copper grid. A drop alcohol was first added to the nanofiber film. Then, the film was scratched by a pair of tweezers to a carbon-coated copper grid. Most of the nanofibers are bent and have a uniform diameter along its entire length, indicating that the growth anisotropy in the one-dimensional is strictly maintained throughout the process. Furthermore, in most cases the catalyst particles are inside the ends of nanofibers and are smaller than the nanofiber diameters. Finally, the high-resolution transmission electron (HRTEM) micro-



(a)



(b)



(c)

FIGURE 3: (a) TEM image of Co catalyzed nanofibers with LiF catalyst support; (b) HRTEM of individual CNF image; (c) image of snake-like CNF grown on the Co catalyst.

scope image shows that individual graphitic carbon is carbon nanofiber with a highly uniform structure (Figure 3(b)). The TEM analyses have shown that a majority (i.e., about 70–75%) of the synthesized powder at 700°C correspond to snake-like carbon nanofibers (Figure 3(c)). This high yield suggests that the cobalt nanoparticles formed from thermal composition of  $(\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$  are very active catalyst.

It is necessary to evaluate the efficiency of the CCVD process. Figure 4(a) shows the result of TG analysis of the pristine carbon (as-synthesized) and purified samples. In Figure 4(a) (before purification), the TG analysis shows that a mixture of graphitic carbon (usually encapsulating metallic

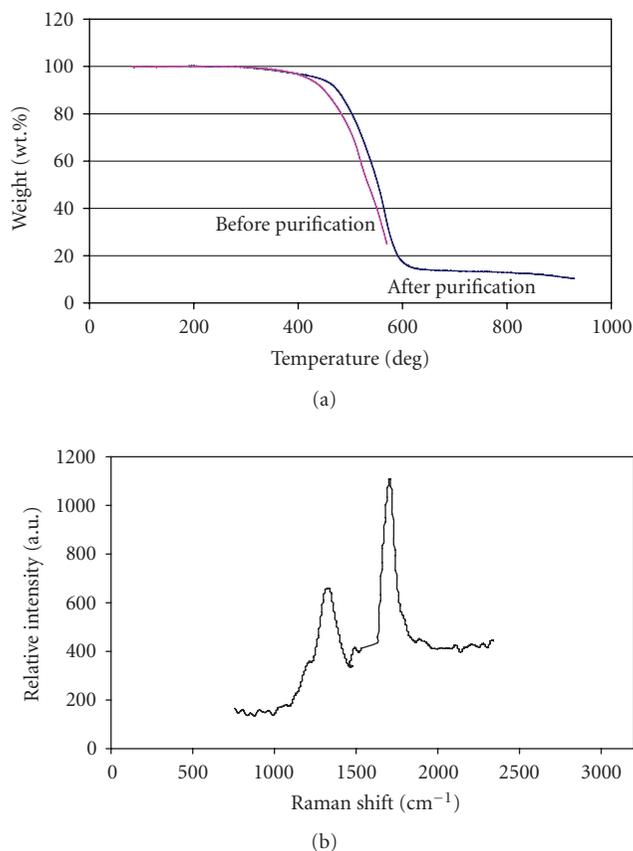


FIGURE 4: (a) TG analysis of the pristine carbon and purified samples by CCVD; (b) Raman spectrum of the CNF sample in the high frequency.

particle of Co), amorphous carbon, and carbon nanofiber bundles in the pristine sample was 23 wt.%. The early slight weight gain in the pristine sample can be taken due to the oxidation of metal catalyst. In the pristine sample, the weight starts to reduce near 425°C, CNFs completely evaporate above 575°C, while the weight loss of purified CNFs by burn-off starts from 470°C and completely burns out near 625°C, as shown in Figure 4(b) (after purification). The amount of residual catalyst dropped to 10 wt.% in purified sample for 60-minute purification. Thus, the high yield efficiency of this approach for the synthesis of CNFs can be concluded with a yield in the range of 95%.

The Raman spectrum shows the D- and G-bands at 1350 cm<sup>-1</sup> and 1690 cm<sup>-1</sup>, respectively. As shown before [25, 26], the D-band is representative for the disordered carbon structures and defects, meanwhile the G-band shows the graphitization and the crystalline properties of the nanofibers/nanotubes. The graphite-related tangential G-band [27] at 1690 cm<sup>-1</sup> was derived from Raman-allowed optical mode, which is related to vibration in all sp<sup>2</sup> carbon materials. The disorder-induced D-band [27] around 1350 cm<sup>-1</sup> from the Raman spectra of sp<sup>2</sup>-bonded carbon materials is strongly dispersive as a function of laser excitation energy ( $E_{\text{laser}}$ ). Generally, the ratio between the intensity of the G-band and D-band ( $I_G/I_D$ ) can be used to

show the structural defect and disordered carbon materials in a few micrometers scale. The  $I_G/I_D$  ratio obtained (see Figure 4(b)) was relatively high compared with that about 4, by the conventional catalytic chemical vapor deposition (CCVD) method. The  $I_G/I_D$  high ratio indicates the high purity of the present specimen.

#### 4. CONCLUSION

We have selectively synthesized (ca. 80% purity) carbon nanofibers (CNFs) by using catalytic decomposition of acetylene (C<sub>2</sub>H<sub>2</sub>) on well-dispersed Co single catalysts supported on a heat-resistant lithium fluoride (LiF) at temperature of 700°C. In the content of this preliminary paper, we report here a case of water washable catalyst support with a high yield. In addition to the case of using washable catalyst support, this synthesis route is easy, because lithium fluoride was easily washed in the purification stage. As a matter of fact, this special structure guarantees its usage in the world of nanocomposites (CNFs) as reinforcement material.

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#### REFERENCES

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] M. Ouyang, J.-L. Huang, and C. M. Lieber, "Fundamental electronic properties and applications of single-walled carbon nanotubes," *Accounts of Chemical Research*, vol. 35, no. 12, pp. 1018–1025, 2002.
- [3] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, "Exceptionally high Young's modulus observed for individual carbon nanotubes," *Nature*, vol. 381, no. 6584, pp. 678–680, 1996.
- [4] Y. F. Yin, T. Mays, and B. McEnaney, "Adsorption of nitrogen in carbon nanotube arrays," *Langmuir*, vol. 15, no. 25, pp. 8714–8718, 1999.
- [5] D. Li and Y. Xia, "Direct fabrication of composite and ceramic hollow nanofibers by electrospinning," *Nano Letters*, vol. 4, no. 5, pp. 933–938, 2004.
- [6] Y.-H. Li, J. Ding, Z. Luan, et al., "Competitive adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions from aqueous solutions by multi-walled carbon nanotubes," *Carbon*, vol. 41, no. 14, pp. 2787–2792, 2003.
- [7] W. H. Zhong, J. Li, C. M. Lukehart, and L. R. Xu, "Graphitic carbon nanofiber (GCNF)/polymer materials. II. GCNF/epoxy monoliths using reactive oxydianiline linker molecules and the effect of nanofiber reinforcement on curing conditions," *Polymer Composites*, vol. 26, no. 2, pp. 128–135, 2005.
- [8] J. Li and C. M. Lukehart, "Formation of graphitic carbon nanofiber (GCNF)/silica gel composites using surface-functionalized GCNFs and sol-gel processing," *Composite Interfaces*, vol. 11, no. 7, pp. 525–535, 2004.

- [9] L. R. Xu, V. Bhamidipati, W.-H. Zhong, et al., "Mechanical property characterization of a polymeric nanocomposite reinforced by graphitic nanofibers with reactive linkers," *Journal of Composite Materials*, vol. 38, no. 18, pp. 1563–1582, 2004.
- [10] Y.-M. Shyu and F. C.-N. Hong, "The effects of pre-treatment and catalyst composition on growth of carbon nanofibers at low temperature," *Diamond and Related Materials*, vol. 10, no. 3–7, pp. 1241–1245, 2001.
- [11] J.-M. Ting and N. Z. Huang, "Thickening of chemical vapor deposited carbon fiber," *Carbon*, vol. 39, no. 6, pp. 835–839, 2001.
- [12] M. Ritschel, M. Uhlemann, O. Gutfleisch, et al., "Hydrogen storage in different carbon nanostructures," *Applied Physics Letters*, vol. 80, no. 16, pp. 2985–2987, 2002.
- [13] V. Ivanov, J. B. Nagy, Ph. Lambin, et al., "The study of carbon nanotubes produced by catalytic method," *Chemical Physics Letters*, vol. 223, no. 4, pp. 329–335, 1994.
- [14] V. Vinciguerra, F. Buonocore, G. Panzera, and L. Occhipinti, "Growth mechanisms in chemical vapour deposited carbon nanotubes," *Nanotechnology*, vol. 14, no. 6, pp. 655–660, 2003.
- [15] S. J. Tauster, S. C. Fung, and R. L. Garten, "Strong metal-support interactions. Group 8 noble metals supported on TiO<sub>2</sub>," *Journal of the American Chemical Society*, vol. 100, no. 1, pp. 170–175, 1978.
- [16] T. Borowiecki, "Effect of the support on the coking of nickel catalysts in hydrocarbon steam reforming," *Reaction Kinetics and Catalysis Letters*, vol. 33, no. 2, pp. 429–434, 1987.
- [17] I. Yudanov, G. Pacchioni, K. Neyman, and N. Rösch, "Systematic density functional study of the adsorption of transition metal atoms on the MgO(001) surface," *Journal of Physical Chemistry B*, vol. 101, no. 15, pp. 2786–2792, 1997.
- [18] S. C. Davis and K. J. Klabunde, "Unsupported small metal particles: preparation, reactivity, and characterization," *Chemical Reviews*, vol. 82, no. 2, pp. 153–208, 1982.
- [19] S. J. Tauster, S. C. Fung, R. T. K. Baker, and J. A. Horsley, "Strong interactions in supported-metal catalysts," *Science*, vol. 211, no. 4487, pp. 1121–1125, 1981.
- [20] E. Couteau, K. Hernadi, J. W. Seo, et al., "CVD synthesis of high-purity multiwalled carbon nanotubes using CaCO<sub>3</sub> catalyst support for large-scale production," *Chemical Physics Letters*, vol. 378, no. 1-2, pp. 9–17, 2003.
- [21] D. Lupu, A. R. Biris, I. Misan, et al., "Growth of nanoscale carbon structures and their corresponding hydrogen uptake properties," *Particulate Science and Technology*, vol. 20, no. 3, pp. 225–234, 2002.
- [22] D. Lupu, A. R. Biris, A. Jianu, et al., "Carbon nanostructures produced by CCVD with induction heating," *Carbon*, vol. 42, no. 3, pp. 503–507, 2004.
- [23] A. Okamoto and H. Shinohara, "Control of diameter distribution of single-walled carbon nanotubes using the zeolite-CCVD method at atmospheric pressure," *Carbon*, vol. 43, no. 2, pp. 431–436, 2005.
- [24] L. Piao, Y. Li, J. Chen, L. Chang, and J. Y. Lin, "Methane decomposition to carbon nanotubes and hydrogen on an alumina supported nickel aerogel catalyst," *Catalysis Today*, vol. 74, no. 1-2, pp. 145–155, 2002.
- [25] C. J. Lee, J. Park, Y. Huh, and J. Y. Lee, "Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition," *Chemical Physics Letters*, vol. 343, no. 1-2, pp. 33–38, 2001.
- [26] R. D. Bach, G. J. Wolber, and H. B. Schlegel, "The origin of the barriers to thermally allowed, six-electron, pericyclic reactions: the effect of HOMO-HOMO interactions on the trimerization of acetylene," *Journal of the American Chemical Society*, vol. 107, no. 10, pp. 2837–2841, 1985.
- [27] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, and R. Saito, "Raman spectroscopy on isolated single wall carbon nanotubes," *Carbon*, vol. 40, no. 12, pp. 2043–2061, 2002.



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