

Synthesis of Well-Crystalline Lattice Carbon Nanotubes via Neutralized Cooling Method

A. TERMEHYOUSEFI¹, S. BAGHERI², N. A. KADRI³, F. MOHAMED ELFGHI¹, M. RUSOP⁴, AND S. IKEDA¹

¹*ChECA IKohza, Department of Environmental & Green Technology (EGT), Malaysia Japan International Institute of Technology (MJIT), University Technology Malaysia (UTM), Kuala Lumpur, Malaysia*

²*Nanotechnology & Catalysis Research Centre (NANOCAT), University Malaya, Kuala Lumpur, Malaysia*

³*Department of Biomedical Engineering, Faculty of Engineering, University Malaya, Kuala Lumpur, Malaysia*

⁴*NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia*

In this contribution, vertically aligned carbon nanotubes were synthesized by chemical vapor deposition (CVD). The effects of intrinsic disorders constructed by mobile surface contaminants on the structural perfection of carbon nanotubes (CNTs) were investigated. The results indicated a complete picture on the effect of the involved parameters on the lattice defects of modulated CNTs based on the cooling step. Raman scattering showed that the different cooling methods of the CVD preforms altered the bound complex defects of the structure of the CNTs. Moreover, an array of CNTs was removed from the silicon substrate by applying the neutralized cooling method on the CVD, while the vertical and parallel orientations were retained. The FESEM images, coupled with Raman spectroscopy results, confirm the morphological improvements of the growth CNTs based on the neutralized cooling method.

Keywords Carbon nanotubes; Crystalline; CVD; Defects; Nanostructures.

INTRODUCTION

Uniform and crystalline carbon nanotubes (CNTs) have great potential and are important for diverse bio-transducer applications such as for electrochemical, optical, and pyroelectric biosensors [1, 2]. Defects and disorders of CNTs play most significant roles, and they can dominate physical property measurements. Numerous studies have reported on the use of correlation between quantity and the defect types of the synthesized aligned CNTs on the basis of perpendicular growth mechanisms [3]. The flow rate and flow type, deposition, and annealing process, catalyst, and precursor are some of the important variables that have been optimized for the purpose of decreasing the disorders in crystalline CNTs for their proposed applications [4, 5].

Published reports on the observed correlations among different growth conditions suggest a unified theory on the relationship among aspect ratio, growth temperature, and synthesis periods of CNTs [6]. The proposed relationship suggests that carbon feeding rate and deposition times are the key parameters for optimizing the growth mechanism and mass production of CNTs [7, 8].

The presence of defects subtly alters the properties of CNTs [9]. Neutralized cooling method, which has a cooling rate that is higher than typical methods, increases the carrier gas diffusion and neutralizes the formation defects of CNTs. Herein, we describe the neutralized cooling method as a new method for improving the morphological properties of CNTs that directly affect the energy gap [10] of semiconducting approaches by removing physisorbed clusters of CNTs or amorphous carbon. According to this method, the carbon feeding rate was controlled by altering the carrier gas in the diffusion of nanotube feedstock to neutralize the formation of disorders in the cooling step of CVD. Among the candidate carrier, gases, argon, and oxygen have advantageously exhausted the feedstock into the quartz by invariable acceleration with a flow microcontroller [11]. Oxygen, as a carrier gas in the cooling process, prevents highly mobile carbons from forming small, physisorbed clusters of CNTs, or amorphous carbon [12]. The FESEM technique, coupled with Raman spectroscopy, has been used to confirm the morphological improvements of the growth of CNTs based on the neutralized cooling method.

MATERIALS AND METHODS

Approximately 0.05 g of ferrocene was used to produce Fe catalyst particles for seeding nanotube growth in the presence of 10 mL camphor oil in a horizontal electronic furnaces. The furnaces were equipped with a quartz tube (35 mm outer diameter) that acted as a reactor for CNT production. Several parameters, such as the

Received May 24, 2014; Accepted August 17, 2014

Address correspondence to A. Termehyousefi, ChECA IKohza, Department of Environmental & Green Technology (EGT), Malaysia Japan International Institute of Technology (MJIT), University Technology Malaysia (UTM), Kuala Lumpur, Malaysia; E-mail: at.tyousefi@gmail.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lmmp.

deposition temperature, feedstock acceleration, and total reaction time, were adjusted to refine the growth process of vertically aligned carbon nanotubes. The entire CVD was based on vaporization and deposition. In the first step, ferrocene was used to prepare the catalyst, which was performed by heating the internal surface of the first furnace up to the optimal temperature, followed by the feeding gas. In the second step, at 800°C, decomposed carbon sources were deposited onto the silicon substrate to produce perpendicular nanostructures of carbon.

Subsequently, the carrier gas was changed into oxygen, and the CVD was cooled down for 5 min, gas and exposed to oxygen gas. The neutralized cooling method is concluded by the removal of grown CNTs from the quartz tube at 400°C [13].

The CNTs were then characterized by FESEM (ZEISS Supra 40VP) operated at 5 kV to evaluate the structure and diameter of the sample. The Raman spectra were obtained using micro-Raman spectroscopy (Horiba Jobin Yvon-DU420A-OE-325) with Ar⁺ ion (wavelength 514.5 nm) to determine the adsorption, desorption, and surface area of the samples.

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of well-aligned CNTs optimized by the neutralized cooling method. Generally, peak intensities ranging from $\sim 1300\text{ cm}^{-1}$ to 1350 cm^{-1} and $\sim 1580\text{ cm}^{-1}$ to 1600 cm^{-1} represent the disordered D line and graphitic G line, respectively [14, 15]. The D peaks for CNT growth using neutralized and conventional cooling systems were ~ 1354.60 and $\sim 1346.35\text{ cm}^{-1}$, respectively, whereas the G peaks were at $\sim 1588.40\text{ cm}^{-1}$ and $\sim 1577.10\text{ cm}^{-1}$, respectively. The I_D/I_G ratio, which is calculated to estimate the variation in the CNT quality in the neutralized cooling method, was 1.28, where the I_D/I_G ratio of growth CNTs in the conventional cooling method was 1.19.

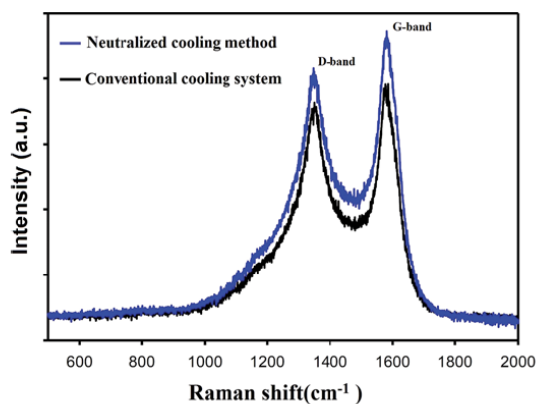


FIGURE 1.—Raman spectra of applying a different cooling system to the CVD.

Based on the absence of the radial breathing mode in the Raman shifts, the grown CNTs were likely to contain more than a single wall [16]. The results also showed that similar Raman shifts occur in both samples; however, the intensity of the G band of the CNTs grown by the naturalized cooling method is higher than that of the conventional cooling technique, which would result in higher I_D/I_G .

This observation suggests that the crystalline quality of the CNTs structure changes according to the variation in the cooling rate and the feeding gas [13]. Reproducibility of the experiments and accuracy of the Raman spectra was verified using replicates of the experiments employing similar growth mechanisms. The optimizations of the deposition process, annealing process, and cooling process of CVD can improve the crystallinity of the growth CNTs, as shown in Fig. 2. The degree of crystallinity of the growth CNTs were characterized by Raman spectrum which shows that the most crystalline CNT growth is at higher cooling rate. Modifying the conventional cooling system as a first critical parameter is a possible method to decrease the defects of the growth CNTs. In fact, diffusion of the hydrocarbon in the cooling process and the duration of the cooling system have a direct effect on the crystallinity of growth CNTs. The results also showed the effect of the high temperature annealing as a second critical parameter on the crystallinity of the growth CNTs. Some kinds of defects are initially present in nanotubes, which are then removed via annealing. According to the results, increasing the annealing temperature will increase the axial alignment, as well as increase the crystallite size, which indicates that developing the graphitic domains remains ongoing during annealing. Deposition time, as a third critical parameter, also plays an important role in the crystallinity of CNTs. The density of the growth

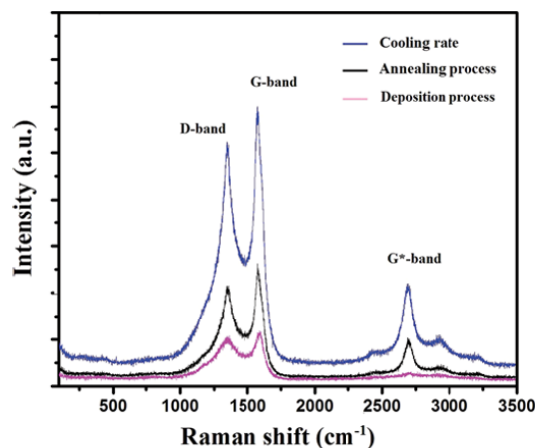


FIGURE 2.—Raman spectra involving parameters on crystallinity of the CNTs.

Link to Full-Text Articles:

<http://www.tandfonline.com/doi/abs/10.1080/10426914.2014.961475#.VRN2l47fv5k>