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Effect of hydrogen on the growth and morphology of single wall carbon nanotubes synthesized on a Fe–Mo/MgO catalytic system

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Abstract

Single wall carbon nanotubes were synthesized from thermal pyrolysis of methane on a Fe–Mo/MgO catalyst by radio frequency catalytic chemical vapor deposition (RF-CVD) using argon as a carrier gas. Controlled amounts of hydrogen ($H_2/CH_4 = 0$–1 v/v) were introduced in separate experiments along with the carbon source. The properties and morphology of the synthesized single wall carbon nanotubes were monitored by transmission electron microscopy, Raman scattering, and thermogravimetric analysis. The nanotubes with the highest crystallinity were obtained with $H_2/CH_4 = 0.6$. By monitoring the Radial Breathing Modes present in the Raman spectra of the single-wall carbon nanotube samples, the variation of the structural and morphological properties of the carbon nanotubes with the flow level of hydrogen, reflect changes of the catalyst systems induced by the presence of hydrogen.

Keywords: Single wall carbon nanotubes; Chemical vapor deposition; Catalysis

1. Introduction

High quality carbon nanotube materials are desired for both fundamental and technological applications. The term "high quality" refers to the absence of structural and chemical defects over a significant length scale along the tube axes. So far, arc-discharge [1,2], laser-ablation [3], and chemical vapor deposition (CVD) [4,5] have been developed as the principal methods for obtaining high quality carbon nanotube materials. However, the outcome for most of these processes, especially for CCVD, could be improved by the introduction of additional hydrogen gas that reduces the catalytic systems used in the synthesis process. Generally the CNTs synthesized by catalytic decomposition of hydrocarbons are found to be covered by thick layers of amorphous carbon, which need to be removed prior to any application that the nanotubes are used for [6]. Furthermore, due to the deposition of non-crystalline carbon around the catalyst particles, the overall synthesis process could be highly hindered. Therefore, the purpose of introducing the additional hydrogen gas source was proposed for etching off amorphous carbon produced during the synthesis process in order to minimize the catalyst from being poisoned and it is generally believed that the addition of hydrogen or other gases are required and desirable to synthesize CNTs [7,8].

It is generally understood that high quality CNTs cannot be grown from pure hydrocarbon gases without any additional non-hydrocarbon (carrier) gases by CVD mainly due to the formation of amorphous or other types of carbonaceous structures. Fine and long multiwalled carbon nanotubes (MWNTs) with small amounts of amorphous carbon were prepared by d.c. arc discharge plasma of graphite electrodes in hydrogen gas [9].

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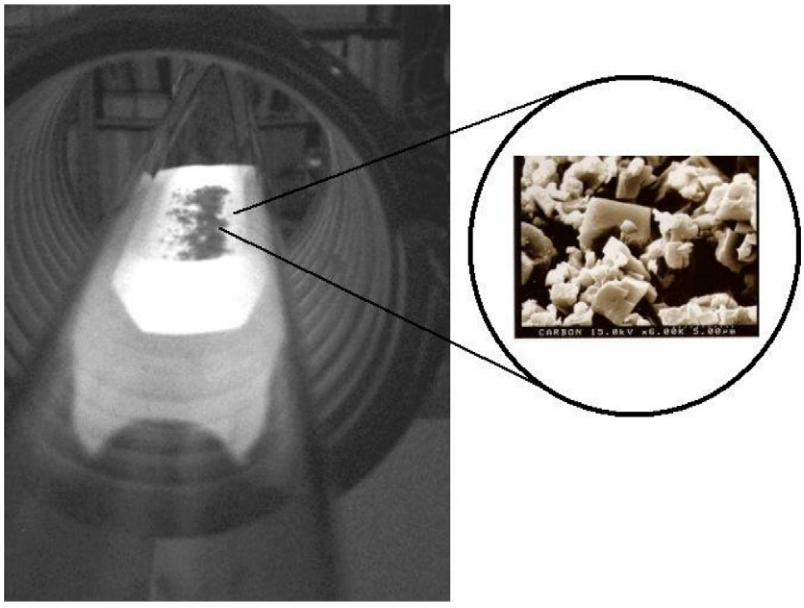

Fig. 1. The RF-cCVD furnace used to grow the carbon nanotubes. It can be observed the graphite susceptor that contains the catalyst powder placed inside a quartz tube, which was positioned in the middle of a water-cooled coil, connected to the RF generator.

Hydrogen can be used as a carrier gas in conjunction with other gases such as Ar, N_2, He, etc. As previously shown, the interaction of the H_2 with the substrate (Si) could be responsible for various effects that affect the growth of high quality vertically aligned nanotubes [10]. By using CH_4/H_2 source gases, vertically aligned carbon nanotubes were grown on a Cr film by bias-enhanced hydrogen microwave plasma CVD [11].

This work reports the experimental findings of the hydrogen influence on the quality and morphology of single wall carbon nanotubes grown on a Fe–Mo/MgO catalyst by Radio Frequency (RF)-CVD with methane as the carbon source. Such a study can facilitate the understanding of the growth mechanism of carbon nanotubes and the role that gaseous hydrogen plays in reducing the catalyst nanoparticles and the kinetics of the carbon nanotubes growth.

2. Experimental details

Single wall carbon nanotubes were catalytically synthesized from the thermal pyrolysis of methane on a bi-metallic catalyst system Fe–Mo supported on MgO. The Fe–Mo/MgO catalyst with the chemical weight ratio composition of Fe : Mo : MgO = 1 : 0.1 : 12 was produced by the impregnation method [12]. The metal salts $Fe(NO_3)_3{\cdot}9H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were first dissolved into distilled water and the resulting solution was introduced over a suspension of powdered MgO in distilled water, followed by sonication for an hour. The solvent was evaporated inside a rotoevaporator at 90 °C. The mixture was dried over night under vacuum at 150 °C and further calcinated in air at 700 °C for seven hours.

The carbon nanotubes were synthesized at 850 °C by RF-CVD [13,14]. For the synthesis, approximately 100 mg of catalyst was placed onto a graphite susceptor and then introduced into a quartz tube inside of a copper coil connected to a radio frequency generator with a frequency of 350 kHz, as shown in Fig. 1, and as previously described [13,14]. The quartz reactor was purged with argon for 10 minutes followed by rapid heating (330 °C/min) to the reaction temperature of 850 °C. Once the temperature was stabilized, a mixture of CH_4 (90 ml/min) and controlled amount of hydrogen (H_2/CH_4 = 0; 0.166; 0.333; 0.5; 0.666; 1) was introduced for 30 minutes. At the end of the reaction, the system cooled down naturally in Ar. To determine the intrinsic weight loss of the catalyst, a "blank" experiment with only Ar and without the carbon source was performed. The carbon deposits (CD) for each synthesis were calculated by the following formula [15] $\mathrm{CD}(\%) = [\frac{m_{\mathrm{ar}}-m_{\mathrm{b}}}{m_{\mathrm{br}}}] \times 100$, where m_{ar} is the sample mass after reaction, m_{br} is the sample mass before the reaction, and m_{b} is the catalyst mass after the blank experiment.

The purification of the carbon nanotubes was performed by treating the samples with HCl (1 : 1) under sonication for 30 minutes. Next, the product was washed with distilled water until a neutral pH was obtained and finally it was dried at 120 °C. The nanotubes were oxidized at 450 °C for 15 minutes (at a heating rate of 10 °C/min) in order to burn out the amorphous carbon covering on the metallic nanoparticles, and then a second HCl washing was applied to remove the metal particles. Distilled water washing and drying done as previously described, completed the purification process.

To understand the complex effects of the reaction conditions on the carbon nanotube morphology and quality, they were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman scattering spectroscopy. Raman scattering studies were done at room temperature with two laser excitations: 514 nm (2.41 eV) and 633 nm (1.96 eV) with a Horiba Jobin Yvon LabRam HR800 spectrometer equipped with a charge-coupled detector, and two grating systems: 600 and 1800 lines/mm. The laser beam intensity