CVD Growth of Carbon Nanotubes and Nanofibers: Big Length and Constant Diameter

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Summary: We report mass production of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) with relatively high length and aspect ratio. We synthesized carbon nanomaterials by chemical vapor deposition (CVD) of methane as the feeding gas on Fe/Mo nanoparticles that use alumina-aerogel support. Alumina-aerogel-supported Fe/Mo catalyst was prepared using sol-gel. Drying step performed using rotary evaporation and freeze-drying. CVD was performed using a quartz tube furnace. Samples were analyzed using scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Raman spectroscopy.

Keywords: carbon nanotube; CVD; nanofiber

Introduction

Since the discovery of carbon nanotubes in 1991,[1] carbon nanotubes have received lots of attention because of their unique physical, electrical and thermal properties. Single-walled carbon nanotubes (SWNTs) have many applications in nanoelectronic devices such as nanotransistors and molecular wires. But still lack of methods for mass production of carbon nanotubes is a major problem. The most popular methods that are currently used are arc discharge,[2] laser ablation,[3] and chemical vapor deposition (CVD).[4] Among these methods, catalytic chemical vapor deposition (CCVD) has the best chance for large-scale production. In this method important factors are catalyst, carbon-feeding gas and reaction conditions such as temperature and gas flow rates. Generally methane, ethylene, acetylene, hexane, alcohol and carbon monoxide are used as carbon feeding gases. Among the carbon-containing gases, methane is a suitable economical choice. Usually the catalysts used for CCVD contain metal particles such as Fe, Mo, Co and Ni or a mixture of them on MgO,[5] Al_2O_3 [6–8] or SiO_2.[9] Carbon nanofibers also can be provided using almost the same methods. CNFs can be used in different devices like scanning probe microscopy (SPM) tips or electron field emission sources and this make them interesting to synthesize and investigate.

Experimental Part

Catalyst Preparation

Materials used in our experiment were research-grade. Gases were obtained by national suppliers. Alumina-supported Fe/Mo catalyst was prepared using sol-gel process which was explained in detail somewhere else.[7,8] It was followed by a simple drying step. The entire sol-gel process was performed under reflux condition and stirring. Drying of the resulting gel was conducted in several easy steps: most of the solvent was removed using rotary evaporator. Then it was freeze-dried and ground in mortar to break the chunks.

SWNT growth and characterization

Synthesis of nanomaterials was performed in a CVD tube furnace which consists of a quartz tube (80 mm i.d., and 600 mm long) and gas flow controllers. About 50 mg Fe/Mo/Al_2O_3 catalyst was put in a quartz or alumina boat and the boat was placed in the

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center of a quartz tube. The sample was heated to reaction temperature ranging from 850 to 1000 °C in argon atmosphere. Then argon flow was switched to methane. Methane flow was maintained for 30 min before the sample was cooled to room temperature in argon flow. It was weighed and then characterized by scanning electron microscopy (SEM) utilizing a Philips XL30, transmission electron microscopy (TEM) with a PHILIPS CM 200 TEM/STEM (200 kV) and Raman spectroscopy using Nd-YAG laser ($\lambda = 532$ nm).

Results

The first thing that one can notice is a high nanomaterial yield. As it is shown in Figures 1–3 SEM images of aerogel-supported catalyst demonstrate that the entire catalyst surface is covered by web-like filaments. Although no specific purification was carried out, we can see a clean network of carbon fibers. For a typical CVD growth for 30 minutes at 850 °C and 950 °C, weight gain of the catalyst is about 120%. Although growth in reaction temperature of 1000 °C results in weight gain of about 200%, the impurities mixed with nanomaterials (such as amorphous carbon etc) increase. In our experiment, the complicated supercritical drying step in previous works,[7,8] was replaced by evaporating the solvent using a rotary evaporator followed by freeze-drying. This simple drying step did not make the gel shrink and therefore resulted in high surface area of the catalyst.

Diameter and length range of the filaments change substantially with variation of CVD synthesis temperature. In reaction temperatures lower than ~1000 °C filament diameter range is 15-40 nm and its length rarely exceeds 2 μm. But CVD growth at 1000 °C mostly yields filaments with relatively constant diameter of ~150 nm and up to 10 μm in length. Transmission electron microscopy indicates that as it is expected, the filaments with diameters in the range of 15–40 nm are actually bundles of SWNTs (Figure 4). CNTs are shaped in rope-like bundles due to Van der Waals force like the structure provided by other methods.

On the other hand, the nanomaterials grown at 1000 °C are mostly carbon nanofibers with a fairly big length and constant diameter.

Raman spectroscopy was also performed to study the yielded material. As it can be observed in Figure 5, G-band frequency that is related to vibrations in all sp^2 carbon materials is picked at around 1600 cm^{-1}. The other frequency around 1350 cm^{-1} refers to the disorder-induced D-band. The small ratio between the D-band and G-band intensities (I_D/I_G) has been usually used as a measure of graphitized structure and in consequence lack of defects in synthesized carbon nanomaterials. It can be derived that carbon nanomaterials grown at 950 °C have the most perfect graphitized structure. This result can also be verified by SEM images as less amorphous carbon is observed in Figure 2.

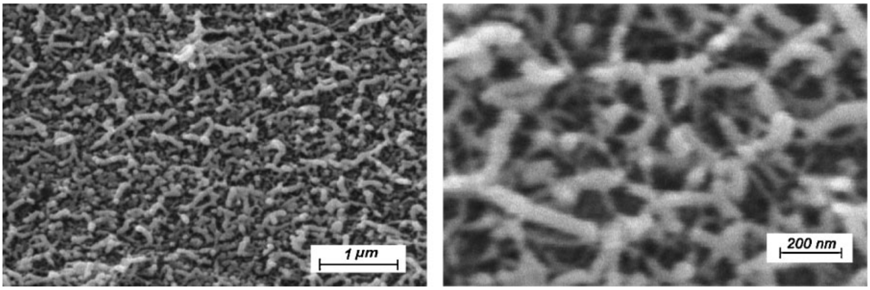

Figure 1.
SEM images showing nanomaterials synthesized at 850 °C.

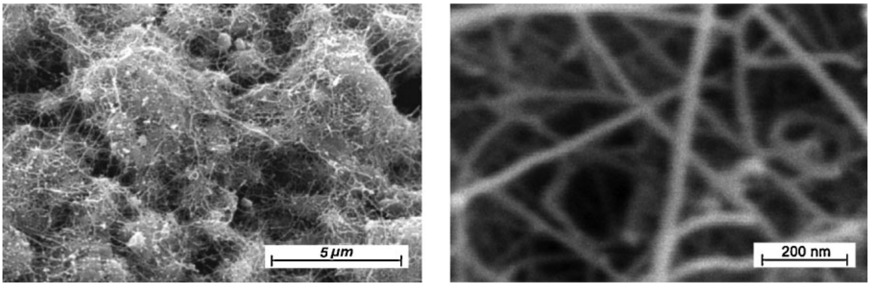

Figure 2.
SEM images showing nanomaterials synthesized at 950 °C.

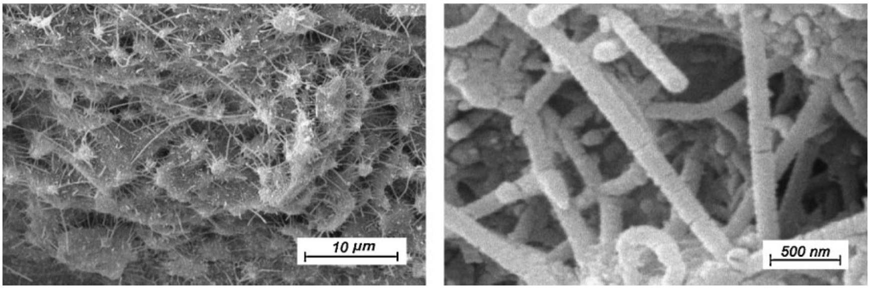

Figure 3.
SEM images showing nanomaterials synthesized at 1000 °C.

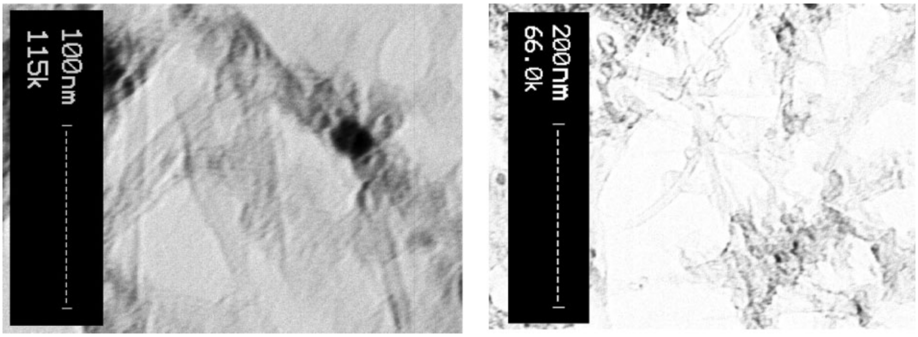

Figure 4.
TEM images showing nanomaterials synthesized at 1000 °C.

Raman spectroscopy also confirms the synthesis of SWNTs. In Figure 6, we can see the radial breathing mode (RBM) frequencies at 176.5, 184.6, 250.5 and 262.1 cm^{-1}. It is known that RBM frequency, ω_{RBM}, is inversely proportional to CNT diameter, d_t. If we make use of the estimation ω_{RBM} $(\text{cm}^{-1}) = 248/d_t\ (\text{nm})$,[10] the RBM frequencies 176.5, 184.6, 250.5 and 262.1 cm^{-1} correspond to nanotube diameters 1.40, 1.34, 0.99 and 0.94 cm^{-1} respectively. Comparison of the intensities indicate that most nanotube diameters are in the range of 0.9–1 nm.

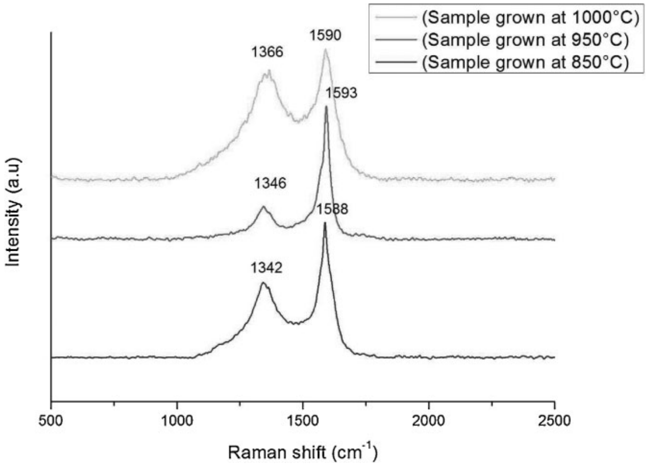

Figure 5.
Raman spectra of the synthesized carbon nanomaterials.

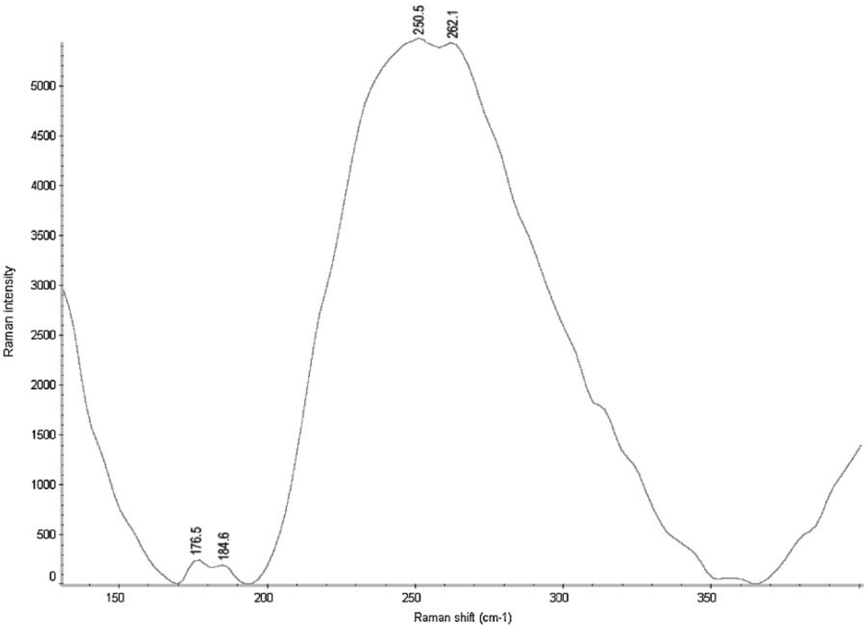

Figure 6.
Raman spectra (RBM frequencies) of SWNTs.

Conclusion

We investigated the effect of growth temperature on carbon nanomaterials synthesized by CVD of methane on alumina-supported Fe/Mo catalyst. A simple and effective drying step was conducted to prepare the catalyst and it has been shown that synthesis of carbon nanotubes and nanofibers are heavily dependent on CVD growth temperature. At reaction temperature of 1000 °C we find the nanofibers up to 10 μm long with a relatively constant diameter. In lower temperatures, the synthesized materials are mainly bundle of single-walled carbon nanotubes.

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