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Development of Sol-Gel Process for Synthesis of Single-Walled Carbon Nanotubes

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Support and catalyst materials have been proved to be critical to scalable chemical vapour deposition (CVD) synthesis of carbon nanotubes. In present study, we found that porous Al_2O_3, SiO_2 prepared by sol-gel process of its organosilane compound and salts was an eminent support for CVD growth of single-walled carbon nanotubes ($SWNT_S$). The quality of as-grown ($SWAT_S$) on Al_2O_3, SiO_2 support and Fe, Mo catalyst was stable; the effect of reaction condition such as furnace temperature, flow rate of the gas and type of catalysts and supports on the properties of as ($SWNT_S$). Products were thoroughly investigated and characterize by TEM, SEM, TG and other technologies. The results indicated that the yields of ($SWNT_S$) on Al_2O_3, SiO_2.With Fe and Mo could be up to about 100%. The obtained purify of the as growth product was higher than 85% after treatment with HCl, HNO_3 and HF. This advantage of support is efficient and stable growth of ($SWNT_S$).

Key Words: Catalyst synthesis, Sol-gel process, Chemical vapour deposition, Carbon nanotubes.

INTRODUCTION

Many advanced studies have been made in elucidating the mechanisms for single-walled nanotube formation under different conditions[1-5]. A detailed understanding of nanotubes growth is essential to the design of a rational synthesis in which control is gained over such parameters as defect frequency, number of layers, helicity, length and parity.

Our goal is to grow starting from a nanotube seed crystal, a single continuous, defect-free nanotube fiber to any desired length. Since the production method that currently produces the longest, most perfectly formed nanotubes is the TCVD methane. Carbon nanotubes might be usefully employed in nanometer-scale engineering and eletronics.

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Electrical conductivity measurment is also investigated on the bulk material and single-walled nanotubes.

EXPERIMENTAL

All the common chemicals were of analytical grade and were commercially available. The water used in all experiments was twice distilled with quartz heating tube. A model Cambridge stereoscan 360 scanning electron microscopy (SEM) was used to observe the surface of nanotubes. A model FEG CM 200 Philips transmission electron microscope (TEM) was used to take photo of the nanotubes fragments.

Synthesis

Chemical vapor deposition method involves thermal decomposition of hydrocarbons (usually CH_4) at temperatures ranging from 500 to 1000°C in the presence of a catalyst containing transition metals such as Fe and Mo. This process, which is more energy efficient than the electric arc-discharge and laser ablation methods, is ideal to generate well-defined structures of nanotube. The yield and structure of nanotubes are affected by the type, purity and porosity of the catalyst. It has been shown that methane CVD process can be used to obtain approximately 200 % yield (2 g of SWNTS per g of catalyst) of high quality nanotubes. The methane CVD process shows promises for large-scale production of defect free carbon nanotubes.

Carbon nanotubes produced in a typical process are close ended and are usually associated with other carbonaceous species such as nanoparticles, fullerenes and catalyst particles. Carbon nanotubes can be treated by acid leaching techniques (activation), which dissolve the graphitic and catalyst particles, to yield high purity materials. In addition heat treatment in air (< 400°C) followed by acid treatment opens the ends of carbon nanotubes.

Carbon nanotubes possess some peculiar properties. They can be metallic or semiconducting depending on the diameter and helicity of the nanotube and presence of structural defects on the carbon nanotube surface. Metallic SWNTs, that are several microns long, exhibit two-terminal resistances on the order of 10 to 100 kΩ. Semiconducting SWNTs of similar configuration have electrical resistance ranging from 100 kΩ to several mega-ohms. Carbon nanotubes also possess intriguing elastic properties. The average value of the Young's modulus (elastic modulus) of SWNTs is several times larger than that of diamond ,making them the strongest known structures.

RESULTS AND DISCUSSION

A series of silica plates, treated in this way, were coated with gold and examined by scanning electron microscopy. The black deposite on a second series of plates was removed by scraping, dispersed in acetone (Fig.1a) and analyzed by the following techniques: transmission electron microscope (Fig. 2) and energy depressive X-ray analysis.

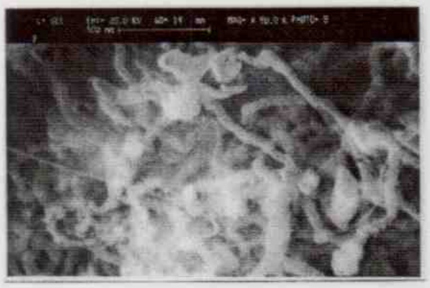

Fig.1a SEM photograph of carbon nanotubes before etching

Fig.1b SEM photograph of carbon nanotubes after etching

SEM studies of the gold-coated plates revealed the presence of nanotube bundles closely aligned with the nanotracks (length 1-5 mm) created by laser etching. The tubes within these bundles were of uniform length (≤ 50 μm) and external diameter (*ca.* 30-50 nm; Fig. 1b). The residual cobalt on the plate was removed, probably by the action of HCl and was collected in the exit bubblers as cobalt chloride. No traces of encapsulated or polyhedral particles were detected in present studies. Aligned-nanotube films were also observed in other etched regions.

TEM observations (Fig. 2) confirm the presence of multi-layered graphitic tubules (30-55 nm outer diameter, 60-80 layers). In most cases, cobalt (particles ≤ 50 nm diameter) was detected by EDX analysis within the nanotube growth, but they were absent from a significant number (5 %) of the closed end-caps. Occasionally, substantial sections of tubes were filled with cobalt. Analyses using electron energy-loss spectroscopy (EELS) show that the nanotubes consist of pure carbon accompanied by traces of nitrogen (< 2-5 %). Sharp ionization edges at 284 and 291 eV correspond to π^* and σ^* features associated with sp^2 hybridized carbon. A very broad weak feature at 400 eV may be due to nitrogen, generated during triazine decomposition and trapped inside the tubules. Both EELS and EDX measurements indicate that chlorine is entirely absent.

It is not clear at this stage why the particle alignment occurs. The nanotubes appear to grow preferentially through the aligned cobalt crystals. Overcrowding may be responsible for simultaneous tube growth from the surface. The experiment was conducted with the cobalt catalyst on the lower (inverted) silica surface. No aligned tube growth occurred when the cobalt-coated/etched surface was on the upper face, so that gravitational effects may well be significant.

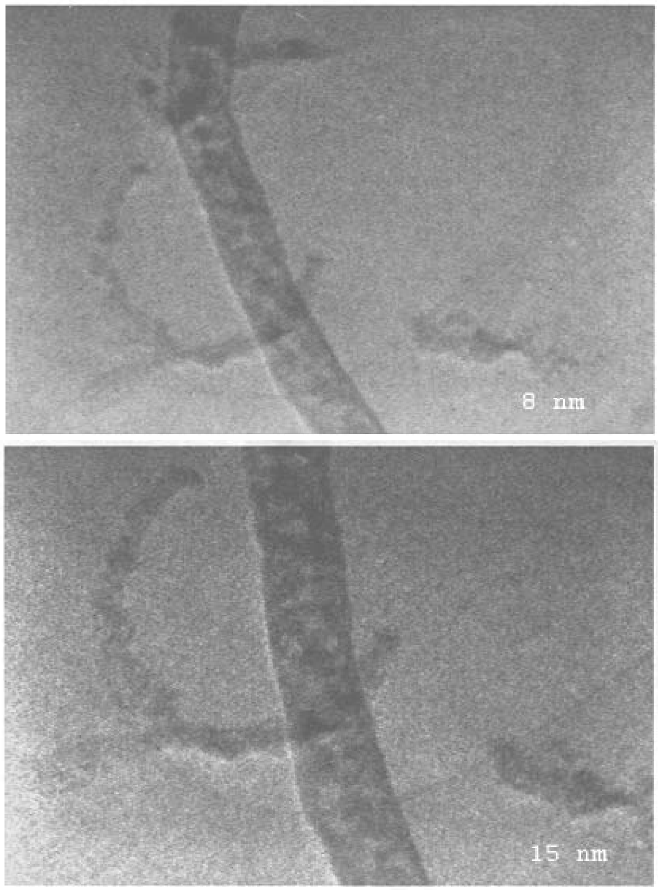

Fig. 2. TEM photograph of carbon nanotubes

An electron diffraction pattern recorded for a group of nanotubes reveals a highly ordered graphitic arrangement within the bundles, especially with respect to the (001) plane. In addition, the outer rings indicate the presence of hexagonal graphite, commensurate with a preferential direction for nanotube growth (related to a non-helical arrangement corresponding to an armchair configuration). These patterns are usually observed (20-30 %) within analyzed samples.

While this work was in progress a report appeared describing the large-scale synthesis of aligned carbon nanotubes by passage of acetylene over iron nanoparticles embedded in mesoporous silical. Pyrolytic formation of nanotubes in high yield that are substantially free from pyrolytic carbon over coatings have been reported by Hyper ion Inc, but full details of the methods and product characterization have not been published, and the nanotubes do not appear to be aligned[6,7].

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