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Synthesis of single-wall carbon nanotubes and long nanotube ribbons with Ho/Ni as catalyst by arc discharge

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Abstract

The effect of a new bimetallic catalyst Ho/Ni for synthesis of single-walled carbon nanotubes (SWNTs) by arc discharge has been studied. Long ribbons consisting of roughly-aligned SWNT bundles were obtained by a modified arc discharge apparatus. Ribbon lengths can reach as much as 20 cm. Both elements Ho and Ni play important roles in the synthesis of SWNTs with high yield and purity. Changes in the Ho and Ni concentration in the catalyst hardly affect the diameter distribution of SWNTs, but the yield and purity of SWNTs are very sensitive to the concentration. An optimal range of Ho/Ni compositions for synthesis of SWNTs with relatively high purity and yield is given.

Keywords: Carbon nanotubes; Catalyst; Arc discharge; Raman spectroscopy

1. Introduction

Single-walled carbon nanotubes (SWNTs) have various potential applications including their use in reinforcement of materials, nanoscale electronic devices and biomedical sensors, etc. [1–3]. Extensive attention is now focused on high yield synthesis of SWNTs in high purity and with desired nanostructures, such as diameter distribution and chirality. SWNTs have been produced by laser evaporation [4], arc discharge [5,6], and chemical vapor deposition (CVD) [7]. Large-scale synthesis of SWNTs can be achieved by using the arc discharge method [5,8], and SWNTs made by arc discharge have a high degree of crystallinity. One of the most important factors for the synthesis of SWNTs is the catalyst employed. Single transition metals, such as Ni, Co and Fe [9,10], were first used for this purpose. Later research shows that bimetallic components are more effective than single metals as catalysts, especially transition metals with some addition of rare-earth metals. So far, only a few mixtures of rare earths with the transition metal nickel have been studied, including Y/Ni, Ce/Ni, Tb/Ni, and La/Ni [5,6,11]. It has been found that different rare-earth elements have a strong influence on both the quantity and the nanostructure of the SWNTs produced. For example, Y/Ni has been proved to be one of the most effective catalysts among the rare-earth metal/Ni bimetals studied, even more effective than Co/Ni [12]. In a previous study, we also found that small diameter SWNTs can be obtained by using Ce/Ni as catalyst [6]. When Eu/Ni was used as catalyst, we usually obtained very few SWNTs with nanoparticles dominating the end product [13]. Recently, it has been suggested that Ni plays an essential role in producing SWNTs

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and that the rare-earth metal co-catalyst plays the role of a surfactant [14], but there is no clear mechanism to explain the huge difference between the rare-earth metals studied. Therefore, it is necessary to test whether other rare-earth metals have similar catalytic effects on the synthesis of SWNTs and whether they affect the nanostructure and yield of SWNTs. Such studies will provide valuable information to further understand the growth mechanism of SWNT. Here, we report on the properties of holmium, which has not previously been studied as a catalyst for the synthesis of SWNTs.

SWNTs and SWNT bundles can also form macroscopic assemblies, such as ribbons, fibers and ropes, etc., which have a relatively high degree of alignment. These are promising for a wide range of applications, such as composites, micromechanical actuators, and catalyst supports [3,15]. Some research has been done to obtain various macroscopic assemblies by using improved arc discharge methods. For example, Liu et al. [16] modified the arc discharge with a sloped cathode under H_2/Ar atmosphere and succeeded in synthesizing ordered SWNT ropes. Gu and co-workers [17] synthesized high purity SWNT fibers with Y/Ni as catalyst and a small quantity of sulfur as a promoter. In addition, Zhu et al. [18] and Cheng et al. [19] reported that long SWNT strands and SWNT ropes and ribbons, respectively, could be synthesized by catalytic decomposition of hydrocarbons using the CVD method. Very recently, Li and co-workers [20] used an improved apparatus to spin SWNT fibers directly by a CVD method.

In this work we also report that when Ho/Ni was used as catalyst for the synthesis of SWNTs for the first time, quasi-aligned SWNT ribbons were obtained by a slightly modified arc discharge method. The ratio of the catalysts Ho/Ni was also varied to find its influence on the yield and diameter distribution of SWNT, and an optimal range of Ho/Ni compositions for the synthesis of SWNTs is given.

2. Experimental section

In our experiments, the conventional arc apparatus [6] was slightly modified. In brief, a closed reaction chamber, in which a direct current arc can be generated between a cathode and a mobile anode, was fixed in a high-vacuum apparatus. A hole with 20 mm diameter was drilled on the top of the chamber and a netting was placed on top of the hole for collection. The cathode was a graphite rod with a diameter of 8 mm. The anode consisted of a 120×6 o.d. mm spectrally pure graphite rod, in which a hole (90×3 mm) was drilled and filled with a mixture of Ho_2O_3 (99.99%), Ni (99.99%) and graphite powder. The powder mixture ratio was $Ho/Ni/C = n{:}m{:}(100 - n - m)$ at.% ($n = 0.5$–4; $m = 1$–5). The arc discharge was created at a current of ~90 A and a voltage of 25 V with a constant distance maintained between the electrodes in helium atmosphere at a pressure of 600 Torr.

The arc process resulted in the production of web-like and collar-like assemblies of SWNTs, similar to those produced with Y/Ni as catalyst [5]. In addition, SWNT ribbons were also obtained. In general, semi-transparent ribbons with lengths up to 10–20 cm hung between the netting and chamber while relatively short ribbons were obtained on the netting. The ribbons are so thin and sticky that they wave in the flowing gas in the apparatus and strongly adhere to tweezers when collected. The diameters of the SWNT ribbons obtained vary from several microns to hundreds of microns. Another intriguing phenomenon is that much less chamber soot, which is thought to contain a low concentration of SWNTs, was produced.

The total as-grown SWNT product, including ribbons, collar, web-like soot (collectively named cathode soot) and chamber soot were collected and weighed. Usually, 0.6–1 g was obtained with a typical run time of 5–10 min, depending on the catalyst composition. The as-grown samples were characterized using scanning electron microscopy (SEM, JEOL, JSM-6700F), transmission electron microscopy (TEM, JEOL-2010), thermogravimetric analysis (TGA, Perkin–Elmer), Raman spectroscopy (Renishaw 1000) using excitation wavelengths of 488 nm (Argon ion laser), 514.5 nm (Argon ion laser), 632 nm (He–Ne laser) and 780 nm (diode laser), and UV–NIR spectroscopy (UV-3150 Shimadzu).

3. Results and discussion

SEM observations showed that SWNTs are abundant in web-like and collar-like assemblies within all the as-grown products collected. Figs. 1a and b shows SEM images of the as-grown web-like samples produced with 1:2 at.% Ho/Ni as catalyst. The highest content of SWNTs was found in the ribbons while the chamber soot contained the lowest concentration.

Fig. 1c shows an optical image of as-grown ribbons with about 10 cm length hung between the chamber and netting. Some ribbons, several centimeters long, slouched on the netting (see arrow). Most of these ribbons seem semi-transparent. A part of a long ribbon was cut and observed by SEM. Fig. 1d is a low magnification SEM image of this ribbon. It shows that the SWNT ribbon is made up of homogenous SWNT bundles. A high magnification SEM image (Fig. 1e) indicates that the product had a high purity and that most of the slender SWNT bundles were roughly aligned, with some less well aligned bundles entangled with the aligned ones. The SWNT bundle diameter is estimated to be in the range of 10–30 nm and it is hard to find