Centimetre-Long Carbon Nanotubes from Ethanol Decomposition

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ABSTRACT

Centimetre long carbon nanotubes were successfully grown from ethanol decomposition in chemical vapor deposition by using iron as the catalyst and silicon as the substrates. Ethanol is found to be a good carbon source to produce clean and long carbon nanotubes. Scanning electronic microscopy images show that the carbon nanotubes are up to 4 cm long. Atomic force microscopy and Raman spectrum were performed. The surface morphology was also studied using scanning electronic microscopy, and possible growth mechanism is discussed.

Keywords: Carbon nanotubes, CVD, Catalyst, Ethanol.

1. INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention due to their unique structure and electronic properties [1-2], but many of their advantages can not be realized in applications because of their short length and other handling issues. Intensive research on their synthesis has been done via arc-discharge, laser ablation, and catalytic chemical vapour deposition (CVD), and it is found that early encapsulation of catalyst by graphite is the a reason of the growth termination [3-5].

Long carbon nanotubes will revolutionize many advanced technologies. For example, they can be used to make fibres more than an order of magnitude stronger than any current engineering fibres, scaffolding for neuronal growth, neuronal and other medical implants, conducting coils in micro electric motors, and nano optical and electronic cables.

Recently we report a simple CVD method (CVD) to grow long carbon nanotubes [6]. 4 cm long carbon nanotubes were successfully grown from ethanol decomposition. Atomic force microscopy and Raman spectrum were performed, indicating that resulted carbon nanotubes are single walled with diameter range of 1nm~2.25nm. The details of long CNT growth are reported in this study.

2. EXPERIMENTAL PROCEDURE

Silicon wafer covered with a layer of 100 nano-meter silicon oxide was used as the substrate, and iron was used as the catalyst. 0.3 g ferric chloride hexahydrate (FeCl3.6H2O) was dissolved into 10 cc ethanol to form a catalyst solution, and this solution was applied on one edge of a substrate through a dip-pen. Then the substrate was put into a one-inch quartz tube inside a furnace, which was then heated to 900°C in 94% argon + 6% hydrogen gas mixture and held at 900°C for 5 to 30 minutes to decompose and reduce the catalyst. After that, ethanol vapor was introduced into the furnace by flowing a carrier gas, argon hydrogen mixture, through an ethanol bubbler at room temperature. 10 sccm ethanol-carrying gas was mixed with 20 sccm diluting gas before being introduced into the tube furnace. The furnace was kept at the synthesis temperature for 15 minutes to 5 hours, and then sample was cooled down to room temperature for measurements.

3. RESULTS AND DISCUSSION

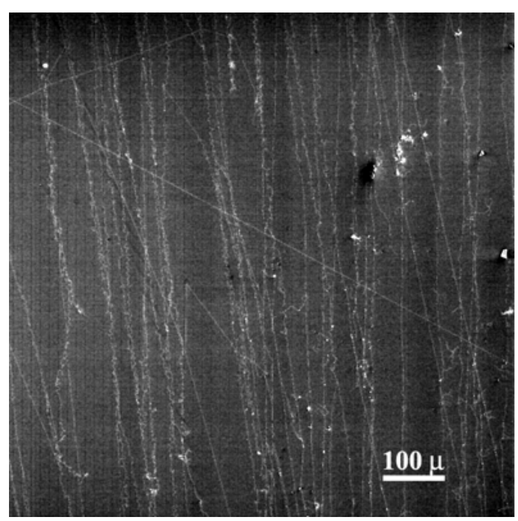

Figure 1: SEM image for long CNTs.

A typical scanning electronic microscopy (SEM) image of our samples is shown in Figure 1. Most of CNTs are centimeter long, and the longest is 4cm long, which is shown in Figure 2 by superimposing 230 SEM images on a photograph of silicon substrate.

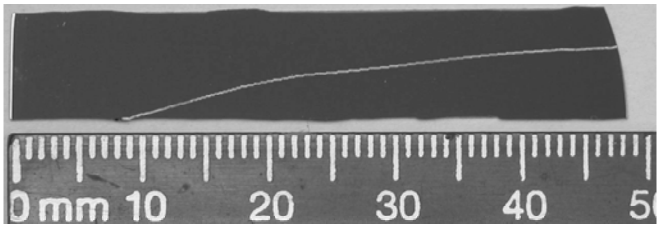

Figure 2: The photograph of a 4.8-cm-long Si substrate and a curve formed by superimposing on it 230 scanning electron microscopy images taken along an individual 4-cm-long single-walled nanotube (SWNT).

The CNT density was affected by several synthesis parameters including the concentration of catalyst solution and growth temperature. The oxide layer on the Si substrate was found to promote CNT growth. CNTs longer than 2.5 cm were consistently obtained over a wide synthesis-parameter window. The initial heating rate and gas flow rate had only minor effects on the CNT length and density.

The 4cm long CNT was measured by atomic force microscopy (AFM), and has a 1.4nm diameter from its height profile scan. Raman spectra and images of CNTs were also obtained with a Kaiser Optical confocal imaging Raman microscope. The sample excitation was performed with 6 mW of 514.5 nm light. From a sampling of 20 different CNTs, we observed the G-peak splitting profiles and radial breathing mode (RBM) frequencies that are consistent with those of single-wall CNTs. Both metallic and semiconducting types are present. Frequencies observed in the RBM region ranged from 110 cm^{-1} to 190 cm^{-1}, corresponding to nanotube diameters of 2.25 nm to 1.31 nm.

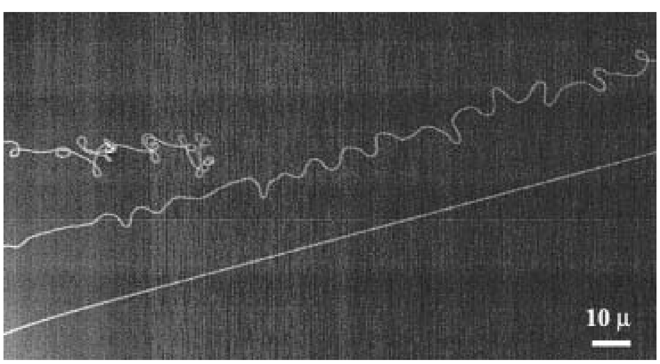

Figure 3: Different morphology of CNTs.

The long CNTs appeared to grow by the tip growth mechanism, i.e. the catalytic Fe particles moved with the growing CNT tips. Otherwise, a base growth with a stationary catalyst particle would have required the whole CNT to overcome the van der Waals forces with the substrate and slide on the substrate, which is clearly impossible. From morphology study, it is also found that the long CNTs are straight while shorter CNTs look wavy, and most CNTs become wavy and tangled with themselves at their ending part, although their other segments are straight. As shown in figure 3, the CNT on the top is wavy and tangled before it ends on the substrate, the CNT in the middle is starting to become wavy and will terminate on the substrate after growing several hundred micrometers longer, and the CNT at the bottom is straight and continues to grow to longer length. It strongly suggests that once a CNT develops undulations, its growth soon stops. Note that the undulating growth was not caused by a local disturbance of the flowing gas, because straight CNTs also grew near undulating CNTs (see Figure 3). Possible causes for the undulating CNT growth and the eventual inactivation of the catalyst particle include the deterioration of the catalyst particle properties and the change in the interaction of the catalyst particle or CNT with the Si substrate surface.

4. CONCLUSIONS

We developed a simple CVD method to grow centimetre long CNTs by using ethanol as carbon source and iron as catalyst. The resulted CNTs have a diameter range of 1nm to 2.25nm. Their Raman results are consistent with those of single-wall CNTs. Long CNTs were grown in tip-growth mode, and their termination possibly related to the interaction of the catalyst particles with silicon substrate.

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