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The influence of boundary layer on the growth kinetics of carbon nanotube forests

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ABSTRACT

The growth of carbon nanotube (CNT) forests has been limited to the centimeter scale due to insufficient understanding of their growth kinetics. To investigate the growth kinetics of CNT forests, we characterized the mass transport phenomena arising during CNT forest. We formulated the hypothesis that such growth is mass transport limited and proposed a model describing this mass transport. According to our model, the effects of diffusion boundary layers on the growth rate are significant. The initial growth rate is expected to increase with the velocity of the bulk gas flow as the boundary layer thickness decreases. To test this prediction, CNT forests were grown at various total gas flow rates in the range 170–1700 sccm, which correspond to flow velocities in the range 0.79–to 7.9 cm/s. The initial growth rate was found to increase from 1.4 mm/h to 3.5 mm/h as the total flow rate increases from 170 sccm to 1700 sccm. Thus there is a clear inverse proportionality between the initial growth rate and the thickness of the diffusion boundary layer, which confirms that the growth of CNT forests is mass transport limited. These results provide new insight into the growth kinetics of CNT forests.

1. Introduction

The chemical vapor deposition (CVD) method for the growth of carbon nanotubes (CNTs) on a substrate is now a familiar technique in the field of CNT research. Particularly, when CNTs are grown with high areal number density, they stand on the substrate forming a vertically aligned structure known as a CNT forest. The CNTs in a CNT forest have a high degree of alignment with few impurities and their growth is more controllable than with other growth techniques. Thus, CNT forests have a variety of potential applications such as field emitters [1], super-capacitor electrodes [2], membranes [3] and strong fibers [4,5], and are of particular interest as model systems.

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There have been steady needs to grow tall CNT forests because many applications of CNT forest require long CNTs; for example, in fiber applications the tensile strength increases as the component CNTs become longer [6]. The height of CNT forest have shown a gradual advance from the millimeter scale to the centimeter scale [7–10], up to about 2 cm [11]. In principle, however, CNTs can grow much longer. To date, the longest CNTs ever reported are 55 cm in length (without forming a forest structure) [12]. In this case, the CNTs grew according to the so called "kite mechanism" in which the catalysts float like kites while producing the CNTs [13]; remarkably, their growth rate is as high as 5000 μm/min. Looking back at the history of carbon research, the growth of vapor grown carbon fibers (VGCFs), which contain a CNT-like structure along their axes, is particularly noteworthy. Such fibers were produced on a centimeter scale within a few minutes with growth rates as high as 2100 μm/min [14], 30000 μm/min [15], and even 150000 μm/min [16] from metal catalysts floating in the vapor phase. In contrast, the growth rates of CNT forests are less than 100 μm/min. The marked difference between the growth rates of the two systems is illustrated in Fig. 1. Why is the growth of CNTs in forest structures so slow even though individual CNTs can grow much faster?

Previous research into the growth of CNT forests has mostly focused on increasing the growth lifetime. As a result, catalyst lifetimes have been extended to as long as 10 hours, but the reported growth rates are so low that several tens of hours would be required to grow a centimeter-scale CNT forest with the reported growth rates, as shown in Table S1. Significant increases in the heights of CNT forests are not likely to be achieved by merely extending the growth lifetimes. Nevertheless, the growth rates of CNT forests have not received much research attention. The understanding of the growth kinetics of CNT forests is so undeveloped that even the rate limiting step of their growth remains unclear.

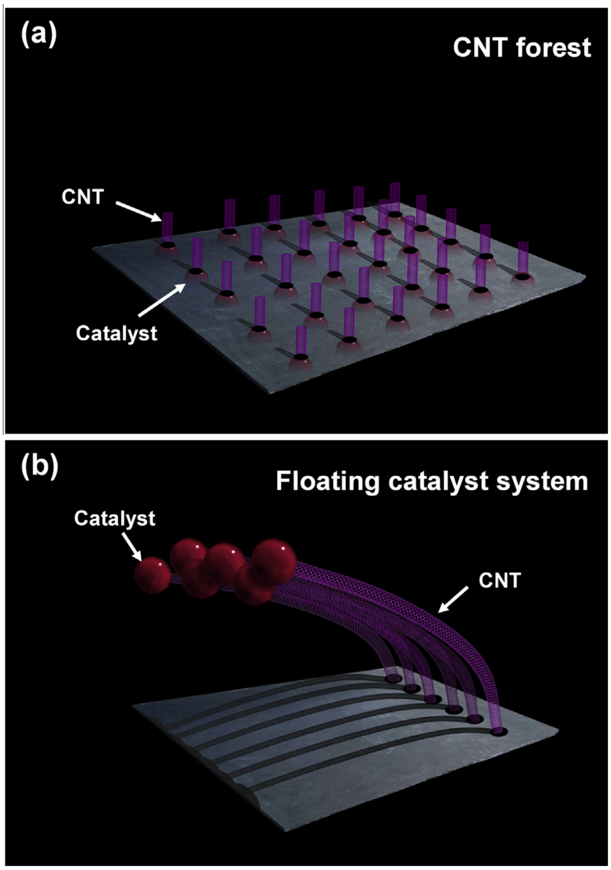

Fig. 1 – Comparison of the growth of CNTs in the forest and floating catalyst system. (A color version of this figure can be viewed online.)

The purpose of this study was to investigate the growth kinetics of CNT forests and to identify the rate limiting step of their growth. Here, we made a hypothesis that the growth is mass transport limited, because the reactant molecules travel a considerable distance to the catalysts at the bottom of CNT forests, so the growth of CNTs in CNT forests is much slower than in a floating catalyst system. A model describing this mass transport was developed and tested experimentally. According to this model, the effects of the diffusion boundary layer on the growth rate are significant; the importance of this factor has not previously been recognized. By correlating the initial growth rate and boundary layer thickness, we verified that the growth of CNT forests is mass transport limited. An as-grown 1.8 cm tall CNT forest was characterized with SEM, TEM, and Raman analysis, and its component CNTs were found to be uniform and of fine quality despite the long growth time.

2. Experimental

A silicon wafer was used as the substrate for the growth of the centimeter-tall CNT forests. The substrate was first coated with a 10 nm thick aluminum oxide film by performing atomic layer deposition, and then coated with a 1 nm thick Fe thin film by using e-beam evaporation. The substrate was cut into small pieces with dimensions of about 0.2 cm × 1 cm. CNT forests were synthesized on each piece by using conventional thermal CVD (Lindberg/Blue M) with a quartz tube reactor. The inner diameter of the tube was 21.4 mm and its length was 50 cm.

The catalyst-coated substrate was loaded into the tube reactor. The substrate was located 12 cm downstream from the middle of the tube reactor. Then the reactor was heated to 820 °C over 15 min with flowing Ar gas. During the ramping process, H_2 gas was supplied together with Ar when the temperature passed through 725 °C. When the temperature reached 820 °C, a gaseous mixture of Ar, H_2, C_2H_4, and ethanol vapor with Ar carrier gas was introduced and the synthesis was carried out. C_2H_4 was used as the carbon source and ethanol was used to enhance the growth and prolongs the catalyst lifetime since it decomposes into active carbon species and H_2O [8]. The volumetric ratio was $Ar{:}H_2{:}C_2H_4 = 5{:}10{:}2$. The heater was turned off after the reaction and the substrate was removed after it had cooled to below 200 °C under an Ar gas flow.

The morphologies of the vertically aligned CNT forests were examined by performing field-emission scanning electron microscopy (FE-SEM, JEOL JMS-7400F) and scanning transmission electron microscopy (STEM, JEOL JEM-2200FS with an energy-dispersive X-ray spectrometer).