KINETICS OF CARBON NANOTUBE GROWTH BY PYROLYSIS OF FERROCENE / XYLENE

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Introduction

Carbon nanotubes have many potential applications due to their unique electronic and mechanical properties and high aspect ratio \cite{1}. For most of these potential applications, massive production of aligned carbon nanotubes (NTs) is required \cite{2}. In this regard, the chemical vapor deposition (CVD) method is the most promising synthesis route for producing large quantities of carbon nanotubes at a low cost.

All CVD methods utilize a catalyst to grow carbon nanotubes, due to the low synthesis temperatures (<1200°C) as compared to arc-discharge or laser ablation methods. The carbon for nanotube growth is normally supplied as a hydrocarbons such as benzene, acetylene, methane, or xylene. The most effective catalysts are transition metals such as Fe, Co, Ni, and their alloys. The catalysts can be introduced to the CVD system by three methods: (1) prepared nano-scale catalytic particles sitting on support powders (alumina/or silica) \cite{3-5}; (2) catalyst thin films (<100nm) deposited on silica or Si flat substrates by magnetic sputtering \cite{6, 7}; and (3) floating catalyst \cite{8-14}. The floating catalyst CVD method avoids a separate catalyst preparation step; rather, the organo-metallic precursors (metallocenes) decompose in-situ to form nanoscale catalyst particles. This floating catalyst method can produce both MWNTs \cite{8-12} and SWNTs \cite{13, 14}.

In this work, a two-step pyrolysis process was developed to study the kinetics of multi-wall carbon nanotube (MWNT) growth.

Experimental Procedure

The two-step CVD reactor includes two heating furnaces similar to previous setup \cite{12}: (1) the ferrocene powders were evaporated in the preheater (~140°C) under the 25% H\textsubscript{2} -Ar carriage gas, and then ferrocene decomposes in the reactor at 500°C to form nanosized Fe catalyst particles on the quartz substrates and quartz reactor tube; (2) pure xylene C\textsubscript{8}H\textsubscript{10} was then fed via syringe pump at 1 ml/hour and decomposed at a higher temperature (650−750°C) for 30−120 minutes to grow the MWNTs.

Results and Discussion

Nano-scale catalyst Fe particles and a few short nanotubes with obvious Fe particles sitting at the tip ends were deposited on the flat quartz substrates after pyrolysis of ferrocene at 500°C, as shown in Figure 1a. Then after second step, or pyrolysis of pure xylene at 650−750°C under 10% H\textsubscript{2}-Ar carriage gas, well-aligned MWNTs grew normal to the quartz substrate surface and reactor wall (see Fig. 1b).

TEM observations show that the MWNTs deposited on quartz substrates are very pure and with uniform inner core diameters (see Fig.2). The influence of reaction temperature and time on MWNT length and outer-diameter was also studied. TEM measurements (Fig.3) show temperature is more critical to the average outer-diameter and inner-diameter of these MWNTs than reaction time. The temperature determines the Fe catalyst particle coarsening rate during MNWT nucleation and the carbon atom diffusion rate during MNWT growth (elongation and coarsening of NT wall). The nanotube elongation and wall coarsening are competitive, so higher pyrolysis temperatures of xylene result in larger outer-diameter and smaller inner-diameter MWNTs. Furthermore, compared with the continuous process (pyrolysis of ferrocene-xylyene mixture), under the same process parameters, the deposited MWNTs by the two-step process have a much smaller average outer-diameter with a larger mean inner-diameter, because the catalyst particles also coarsen due to the constant flux of Fe in the continuous process. For example, at 750°C for 2 hours, MWNTs have an average outer-diameter of 30 nm and inner-diameter of 10 nm by the two-step process, while MWNTs have average outer-diameter of 66 nm and
inner-diameter 4 nm by the continuous process in which a ferrocene-xylene mixture was fed at 1 ml/hour.

TEM images of the MWNT tip and root ends (Fig. 4) show that most MWNTs have closed root ends and have catalyst particles sitting at the tip ends, which suggests that those MWNTs grew by a tip-growth mode in this two-step process.

Conclusions

Well-aligned MWNT arrays can grow by a two-step CVD process. The average MWNT outer-diameter is more sensitive to the reaction temperature than reaction time. Compared with the continuous process, the two-step process can produce MWNTs with much smaller outer-diameters and larger inner-diameters, and the growth mechanism is tip growth.

Reference


Figure 1. SEM images of deposited materials on quartz substrate. (a) catalyst particles and short MWNTs after the first step, pyrolysis of ferrocene powder at 500 °C; (b) aligned MWNT arrays after second step, pyrolysis of pure xylene at 700°C for 2 hours.
Figure 2. Typical TEM image of MWNTs deposited on quartz substrate by the two-step process: first pyrolysis of ferrocene powder at 500 °C then pyrolysis of pure xylene at 700°C for 2 hours.

Figure 3. The average outer-diameter (a) and length (b) of MWNTs by two-step process at various pyrolysis temperatures of xylene and reaction times.

Figure 4. Typical TEM images of root ends (a) and tip ends (b) of MWNT arrays deposited on the quartz substrate.