論 文 の 内 容 の 要 旨

Thesis Summary

論文題目　Development of production methods of submillimeter-long carbon nanotubes
(サブミリメータ長カーボンナノチューブの合成法の開発)

氏　　名　　陳　忠明

Chapter 1. Introduction

Carbon nanotubes (CNTs) have attracted lots of attentions owing to their unique one dimensional nanostructure and outstanding properties. Because CNTs have the ability of forming self-organized conductive network, in addition to their high electric conductivity, flexibility, large specific surface area (SSA), high chemical/ mechanical stability, and light weight, they are an attractive candidate for various applications. Some focuses are put on their use in electric storage devices, such for mobile electronics, electric vehicles, and storage of renewable energies. However, the high cost of the high quality single wall CNTs (SWCNTs, ~1,000 USD/g) and the low quality of the low-cost multi-wall CNTs (MWCNTs, ~100 USD/kg) are the main obstacles to put them in practical applications. Thus, low-cost mass production of high quality CNTs is highly required.

Chemical vapor deposition (CVD) is now considered to be most promising, in which gaseous carbon sources are continuously fed, decomposed by catalyst nanoparticles, and yield CNTs of a similar diameter with the nanoparticles. Millimeter-scale growth of SWCNTs is now possible via on-substrate growth in several groups including ours, however such SWCNTs proved to have diameters increasing with their lengths. How to keep small nanoparticles active and stable is a key issue in order to achieve longer CNTs with smaller diameters. I have carefully studied the formation of catalyst nanoparticles, their structural change at high temperature, the resulting CNT structures, and found an effective means to obtain longer SWCNTs with smaller diameters. Mass production of MWCNTs has already been realized by fluidized bed CVD (FBCVD) at a capacity of several hundred tons annually per plant, however such MWCNTs are heavily entangled with the powder catalysts and have inferior conductivity. Our group has recently developed an original FBCVD process, which yields submillimeter-long few-wall CNTs (FWCNTs) semi-continuously. I have applied the careful control over the catalyst and carbon feeds and a new type of reactor, and achieved the production of submillimeter-long CNTs with smaller diameters using a bigger reactor.

Chapter 2. Methane-assisted CVD yielding millimeter-tall SWCNTs of smaller diameter

When we consider the production of CNTs at a low cost below 100 USD/kg, high-purity experimental-grade feed gases need be replaced with cheaper ones. Especially, H_2 is a common feed gas in most CVD processes for CNT production, and hence, there is a practical motivation for replacing the high purity H_2 with the low purity H_2 that is available at a low cost and/or a byproduct in chemical factories. We examined the use of low purity H_2 (96 vol% H_2 with 4 vol% CH_4) in CVD using a C_2H_2 feedstock, and obtained SWCNTs with unexpectedly smaller diameters, larger height, and higher quality compared with those grown using pure H_2.

We used the low purity H_2 in the millimeter-scale growth of SWCNTs from 0.3 vol% C_2H_2 on flat substrates with an Fe/AlO_x catalyst, and unexpectedly found that SWCNTs grew taller with the low purity H_2. Raman scattering spectroscopy showed that the taller SWCNTs grown with low purity H_2 had an improved quality. Atomic force microscopy (AFM) showed that Fe particles were smaller and denser and transmission electron microscopy (TEM) showed that SWCNTs had smaller diameters with the low purity H_2. X-ray electron spectroscopy revealed that a small amount of carbon is deposited on/in Fe particles with the low purity H_2. The 1 vol% CH_4 in 25 vol% H_2/ 74 vol% Ar was found responsible for that carbon, which presumably kept Fe particles small and dense by reducing their surface energy. These effects were observed only for CH_4; CNTs with lower quality grew when C_2H_4 or C_2H_2 were fed with H_2. The low reactivity of CH_4 is considered to be essential to just stabilize the Fe particles but not to grow CNTs itself. This CH_4-assisted CVD is an efficient and practical method that uses H_2 containing CH_4 that is available as a byproduct in chemical factories.

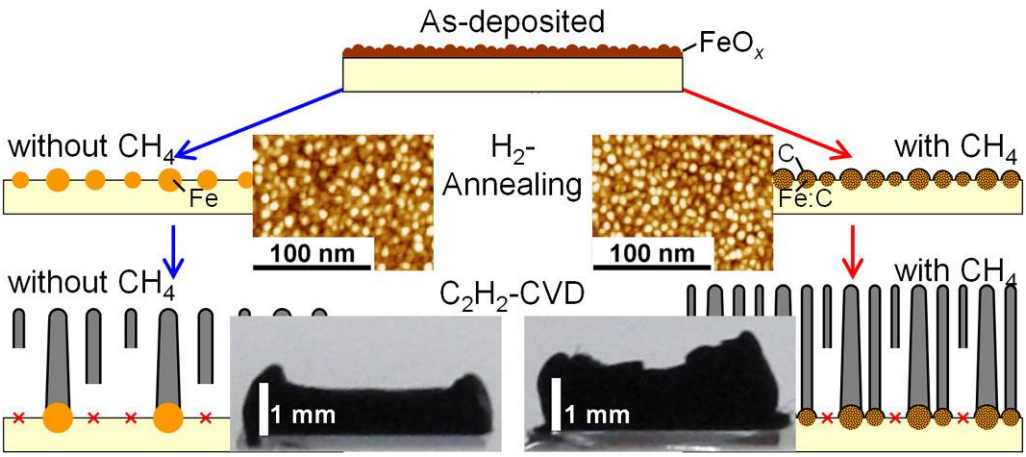

Fig. 1. Millimeter-tall SWCNTs synthesized on a flat substrate using a high-purity H_2 (left) and a low-purity H_2 (right). The contaminant CH_4 unexpectedly yielded and kept Fe catalyst particles smaller and denser, resulted in taller SWCNTs with smaller diameter.

Chapter 3. FBCVD of submillimeter-long CNTs using an internal heat-exchange reactor

We previously developed an original FBCVD and realized semi-continuous production of submillimeter-long FWCNTs from C_2H_2 in a subsecond residence time at a high carbon yield ≥ 70%. But the high gas feed causes insufficient heating of the bead bed when scaled up. In this work, we designed and developed a new FBCVD reactor having internal heat-exchange and preheating zones and examined its performance in producing submillimter-long CNTs at improved productivity. All experiments for catalyst (re-)deposition, CNT growth, separation of synthesized CNTs, and removal of residual carbons were performed in the single reactor.

After confirming the significant improvement in the temperature uniformity of the fluidized bed, we performed the semicontinuous production of CNTs. Snapshot of the bed was taken without gas flow at each step by interrupting the semi-continuous operation. The pristine Al_2O_3 beads had a static bed height of 3 cm (Fig. 2a) and kept that height after the deposition of Fe/AlO_x catalyst from ferrocene and aluminium isopropoxide vapors. After the CNT growth by CVD using 1.1 vol% C_2H_2, the bead bed expanded remarkably to 13 cm in height (Fig. 2b). Then the CNT arrays were separated from the beads by vigorously fluidizing the beads with an increased Ar flow, and collected in a 500 mL bottle by gravitational and filter separation (Fig. 2d). The bead bed decreased its height from 13 to ~3 cm (Fig. 2c), indicating the almost perfect separation of CNTs from the beads. Then, the residual carbon on the beads was removed by flowing O_2/Ar. The amount of CNTs was increased from 0.25 to 0.82 g/cycle with a carbon yield of ~60%, while the submillimeter-long CNT structure was retained (Fig. 2e). But FWCNTs had an increased average diameter of 11 nm and a reduced carbon purity of 97.2 wt% and reduced SSA of 367 m^2/g. Careful control over the catalyst and CVD conditions are needed for improvements both in quantity and quality of CNTs, which is made in the next chapter.

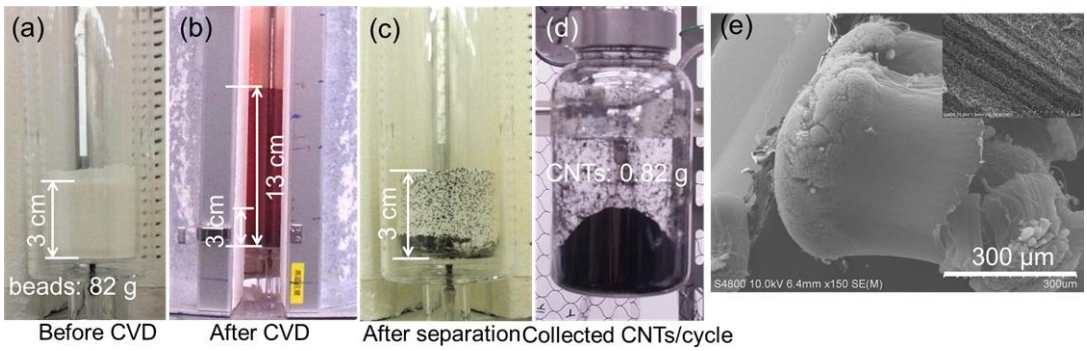

Fig. 2. Snapshots of the static bed at each step of the semi-continuous FBCVD process (a-d) and an SEM image of the as-collected submillimeter-long CNTs.

Chapter 4. Semi-continuous production of CNTs with smaller diameter using an internal heat-exchange reactor

CNTs with smaller diameter and thinner walls are more flexible and conductive. Here, we examined to reduce the diameter of CNTs by FBCVD by preparing smaller Fe catalyst particles and activating such small Fe particles.

The size of Fe particles were made smaller by reducing the Ar carrier gas for ferrocene vapor to 1/5. CNTs were produced at a similar weight for 10 min CVD using 1.1 vol% C_2H_2 for both catalyst conditions, whereas their amount increased with CVD time only for the standard catalyst condition (Fig. 3a). Smaller Fe particles proved to have smaller lifetime with 1.1 vol% C_2H_2. With the reduced C_2H_2 of 0.37 and 0.73 vol%, on the other hand, the amount of CNTs were almost the same for both catalyst conditions (Fig. 3b). Moreover, the amounts of CNTs increased with CVD time for both catalyst conditions, suggesting the retained activity of small Fe particles for 20 min. The average CNT diameter decreased from 11 to 6.5 nm with the reduced ferrocene feed. Moderate C_2H_2 feed of 0.73 vol% was optimum, which realized both fair CNT growth rate and fair catalyst lifetime. Resulting CNTs had a reduced average diameter of 6.5 nm, an increased SSA of 440 m^2/g, and carbon purity of 99.6−99.8 wt% at a similar CNT amount of 0.61 g/cycle.

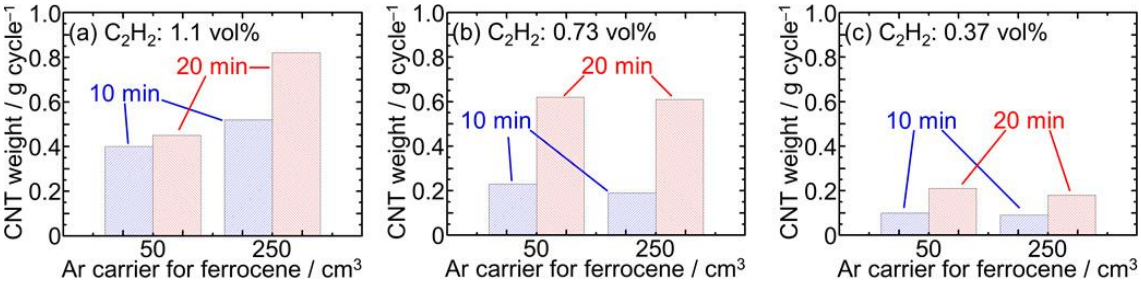

Fig. 3. Dependence of the amount of CNTs produced on the catalyst and carbon feeds. Moderate Fe feed with moderate C_2H_2 feed yielded CNTs with improved quality and a fair quantity.

Chapter 5. Conclusions

To realize the low-cost production of high-quality CNTs, control over the catalyst from the nanometer-scale catalyst size to the meter-scale reactor size is essential. For the catalyst scale, I have developed the CH_4-assisted CVD method for on-substrate CVD, in which the Fe catalyst particles were kept small and stable by using a low purity H_2 containing CH_4. Reduction of catalyst particle size and thus the CNT diameter at the nanometer-scale was realized by reducing the catalyst feed, and the activation of such catalyst particles was realized by moderating the carbon feed, at a scale of FBCVD apparatus. Efficient heating of the gas and bed was realized by the FBCVD reactor with internal heat-exchange and preheating zones, which will lead our semi-continuous FBCVD process to the meter-scale practical reactors. These production methods will contribute to realize the practical use of submillimeter-long CNTs.