# CARBON NANOTUBES OVER NOVEL CATALYSTS

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## Introduction

Since their discovery by Iijima [1], the multi-wall carbon nanotubes (MWNTs) have attracted a great deal of interest due to their unique electrical and mechanical properties, and promising potential for technological applications [2-5]. The electrical and mechanical properties of the MWNTs [6-9] are largely dependent upon the physical properties such as the diameter, length, metal fillings, and chirality. Hence, there is a motivation to control the physical properties of the MWNTs by varying the growth conditions. In our previous work, continuous production of aligned MWNTs in massive scale using Chemical Vapor Deposition (CVD) on quartz substrates has been demonstrated [10]. In this work, we expand the investigation on silicon and alumina substrates, and control the physical properties of the MWNTs by varying the growth conditions.

The physical properties of the MWNTs are controlled by varying the catalysts, substrates, reaction temperature, and reaction time. The MWNTs were grown over silicon (Si) and alumina substrates coated with catalysts such as iron (Fe), terbium-iron (Tb:Fe), nickel (Ni), nickel-iron (Ni:Fe), and Copper (Cu). The physical morphologies of the MWNTs were investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Physical properties of the MWNTs such as the diameter, length, and density at different growing conditions were then determined from these micrographs and correlation were made.

## Experimental

In our work described here, the MWNTs were grown by CVD. We used xylene-ferrocene mixture for the growth of MWNTs over Cu-coated alumina substrate, and pure xylene for Fe- and Tb:Fe-coated Si substrate and Ni- and Ni:Fe-coated alumina substrates, respectively. The xylene-ferrocene mixture was first prepared by injecting 6.5 mol% of ferrocene in xylene, passing through a capillary tube at ~175$^0$C [10], and then vaporized under Argon/Hydrogen (Ar/$H_2$) atmosphere over Cu-coated alumina substrate in a two-stage reactor at 700 °C for 60-180 mins. The process for pure xylene is similar to the xylene-ferrocene, except the hydrocarbon gas is replaced with pure xylene. The metal coatings of about 30 nm thick were deposited using magnetron sputtering. The coating of catalyst with such thickness was found to be necessary as the catalyst particles of this size promote the initial nucleation and subsequent growth of MWNTs.

The morphology and chemical composition of the MWNTs were analyzed with SEM and TEM. The samples for TEM were sonicated in ethanol, and then deposited on copper grid for further studies. The details of experimental results with various reaction parameters are summarized in Tables 1 and 2.

## Results and Discussion

The growth of the MWNTs over Si and alumina substrates with various catalysts mainly depends on the following parameters: (1) the reaction temperature, (2) the reaction time, (3) the substrates, and (4) the nature of catalyst particles. In our work, we analyze the effect of these parameters on the physical properties (diameter and length) of the MWNTs by examining the SEM and TEM micrographs. The SEM studies revealed that at a reaction temperature of slightly lower than 700 °C, the density of MWNTs decreased considerably, and below 550 °C, the growth of these MWNTs did not occur (see Table 1). However, at substrate temperature higher than 700 °C, no significant increase in the density of these MWNTs was observed.

When the reaction time was maintained for 120 mins, an optimized high-yield MWNTs growth was observed over Tb:Fe-coated Si substrates (see Fig. 1). The outer diameter and length of the MWNTs are 40 nm and 1.5 μm. On reducing the reaction time to 60 mins, the yield of the MWNTs was substantially decreased (see Fig. 2), and the diameter and length of the MWNTs are reduced to 25 μm and 1 μm. On the other hand, we also found increasing the reaction time to 180 mins did not significantly increase the MWNT growth yield or change the MWNT physical properties (see Table 1). Hence, we conclude that the optimum reaction time for the maximum yield of the MWNTs is 120 mins in our experimental conditions.

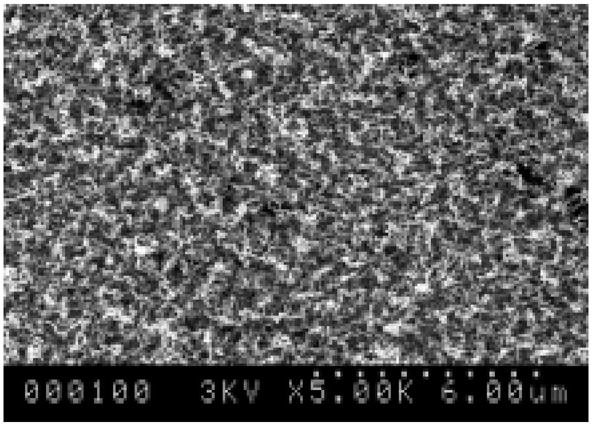


Fig. 1. SEM micrograph of MWNTs grown on Tb:Fe-coated Si substrate at 700 °C for 120 mins.

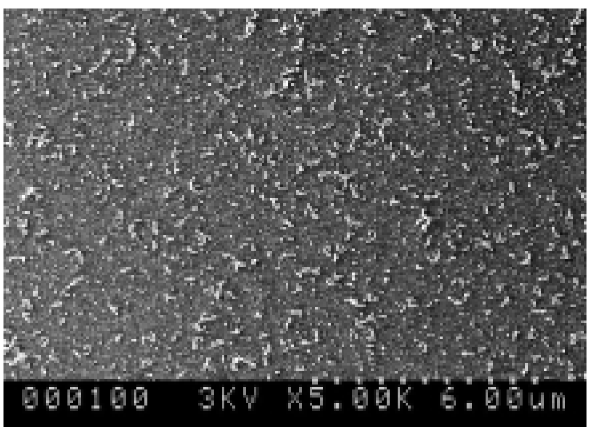


Fig. 2. SEM micrograph of MWNTs grown on Tb:Fe-coated Si substrate at 700 °C for 60 mins.

It is known that the catalyst plays an important role in the growth of MWNTs. In addition to the MWNTs diameter and lengths, we also examined the MWNTs density and the formation of graphitic particles as a function of various catalysts. Although the growth density of MWNTs on a Fe- and Tb:Fe-coated Si substrate is similar (see Table 2), some graphitic particles were observed for Fe as shown in Fig. 3. On the other hand, pure Tb did not yield into any MWNT growth (see Table 2). We have also grown MWNTs on alumina substrates coated with Ni:Fe, Ni, and Fe as catalysts, and we found that Ni:Fe has a higher MWNT density than Ni, while Fe has graphitic particles besides MWNTs (see Table 1). Our results clearly demonstrate that combination of Fe:Tb and Ni:Fe catalysts with pure xylene as hydrocarbon source improved the purity of the MWNTs.

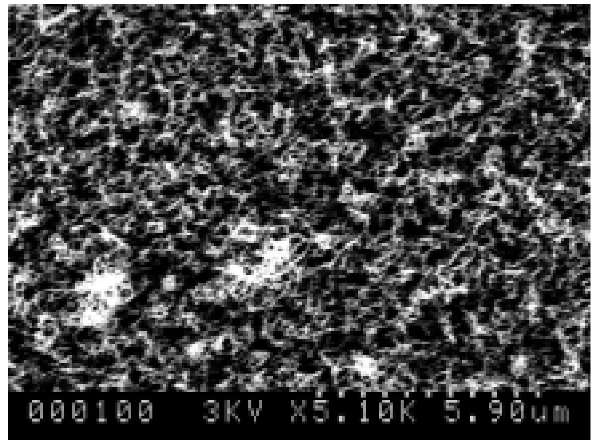


Fig. 3. SEM micrograph of MWNTs grown on Fe-coated Si substrate at 700 °C for 120 mins.

The flow rate and the composition of the carrier gases to the reactor also influenced the MWNT growth. In our experiment, a mixture of Ar and $H_2$ (Ar = 47.2%, $H_2$ = 36.4%) was introduced into the reactor simultaneously with the xylene to get good yield of MWNTs. According to our previous work [10], this percentage of Ar and $H_2$ provides optimal growth for MWNTs.

To reveal the structure of an individual MWNT, a small quantity of the MWNTs grown over Tb:Fe-coated Si was grind into fine powder, and dispersed on a copper mesh and investigated by TEM. The TEM image, shown in Fig. 4, illustrates the role of these metallic catalysts in the formation of MWNTs. The catalyst acts as a nucleating center for the hydrocarbon gas to condense and grow into tubular structure. Another interesting observation is the occurrence of catalyst particles at both ends of the tubes. Works are currently being done to understand the growth mechanism of the MWNTs, and to explain the appearance of catalyst particles at both ends of the MWNTs.

Table 1. The effects of catalysts and substrates on the growth of MWNTs. The temperature was 700 °C, and the reaction time was 120 mins. Xylene was used as a hydrocarbon source for all catalysts except Cu, which used ferrocene-xylene.

| Substrate | Catalyst | Diameter (nm) | Length (μm) | Remark |
|---|---|---|---|---|
| Si | Tb:Fe | 40 | 1.5 | High density MWNTs |
| Si | Fe | 15 | 4.0 | High density MWNTs with graphitic particles |
| Si | Tb | - | - | No growth |
| Alumina | Fe | 50 | 5.0 | High density MWNTs with graphitic particles |
| Alumina | Ni:Fe | 300 | 4.0 | High density MWNTs |
| Alumina | Ni | 70 | 3.0 | Low density MWNTs |
| Alumina | Cu | - | - | Only graphitic particles |

Table 2. The effects of temperature and reaction time on the growth of MWNTs on Tb:Fe-coated Si.

| Reaction time (min) | Temperature ($^{o}$C) | Diameter (nm) | Length (μm) | Remarks |
|---|---|---|---|---|
| 120 | 550 | - | - | No MWNT growth |
| 60 | 700 | 25 | 1.4 | Less density MWNTs |
| 120 | 700 | 40 | 1.5 | High density MWNTs |
| 180 | 700 | 50 | 1.5 | High density MWNTs |

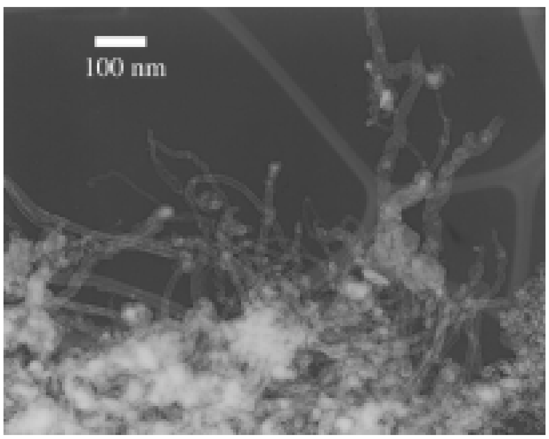


Fig. 4. TEM micrograph of MWNTs grown on Tb:Fe-coated Si substrate at 700 °C for 120 mins.


Fig. 5. SEM micrograph of graphitic particles formed on Cu-coated alumina substrate at 700 °C for 120 mins.

Decomposition of a ferrocene-xylene mixture at 700 °C over a Cu-coated alumina substrate produced cauliflower-like structures as depicted in Fig. 5. Our observation is consistent with Ivanov et al [11], where it is reported that acetylene decomposition on large Cu catalyst particles with about 200 nm in size produced amorphous carbon [11].

## Conclusion

We have analyzed the formations of MWNTs at various growth conditions including the reaction temperature, time, substrates, and catalysts. Our results show high density and purity MWNTs could be obtained at 700 °C, while there are no growth at 550 °C. The optimum reaction time was found to be 120 mins.

Our results clearly demonstrate that combination of Fe:Tb and Ni:Fe catalysts with pure xylene as hydrocarbon source improved the purity of the MWNTs. The size of the MWNTs varied from 15 nm to 300 nm in diameter and up to 5 μm in length. On the other hand, there is accumulation of carbon particle with Cu coating with ferrocene-xylene.

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