*Jurnal Teknologi*, 49(F) Dis. 2008: 141–147


# EFFECT OF REACTION TEMPERATURE AND FLOW RATE OF PRECURSOR ON FORMATION OF MULTI-WALLED CARBON NANOTUBES

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**Abstract.** The effect of reaction temperature and flow rate of precursor on the quantity and quality of the multi-walled carbon nanotubes (MWNTs) produced by catalytic chemical vapour deposition (CCVD) was studied. The MWNTs were grown over molecular sieve supported catalyst at 700 and 850 °C with flow rate of acetylene at 15 and 30 sccm. The effect of an in-situ heat treatment on the as-grown MWNTs at 200 °C was investigated. Thermogravimetric analysis (TGA) results show that CNT purity decreases with increasing reaction temperature, from 63.31 wt% at 700 °C to 61.68 wt% at 850 °C. However, the increase of acetylene flow rate from 15 sccm to 30 sccm has improved the yield of MWNT from 63.31 wt% to 69.28 wt%. The MWNTs grown at 850 °C with 30 sccm of acetylene show 68.23 wt% of purity, attributed to the higher acetylene flow rate. Acetylene flow rate of 30sccm produced higher purity of MWNTs whereas reaction temperature of 700 °C is more effective in generating MWNTs. The in-situ heat treatment at 200 °C gave the highest purity of MWNTs at 87.52 wt%. TEM and HRTEM images suggest that the impurities on the wall layers of MWNT yield were burn off at 200 °C. The in-situ heat treatment is able to reduce the impurities and hence yielded higher purity MWNTs.

*Keywords:* Reaction temperature; flow rate of precursor; multi-walled carbon nanotubes; in-situ heat treatment; purity

**Abstrak.** Kesan suhu tindak balas dan kadar alir bahan pemula kepada kualiti dan kuantiti nanotiub karbon dinding berganda (MWNT) yang dihasilkan oleh pemendapan wasap kimia bermangkin (CCVD) telah dikaji. MWNT yang terhasil atas mangkin berpenyokongkan penapis molekul pada suhu 700 dan 850 °C dengan kadar alir asetilena pada 15 dan 30 sccm. Kesan rawatan haba *in-situ* pada suhu 200 °C kepada MWNT juga dikaji. Data daripada analisis termogravimetri (TGA) menunjukkan bahawa ketulenan nanotiub karbon menurun dengan kenaikan suhu tindak balas, iaitu daripada 63.31 wt% pada 700 °C ke 61.68 wt% pada 850 °C. Walau bagaimanapun, peningkatan kadar alir asetilena daripada 15 sccm ke 30 sccm telah meningkatkan hasil MWNT daripada 63.31 wt% ke 69.28 wt%. MWNT yang dihasilkan pada suhu 850 °C dengan kadar air asetilena 30 sccm nenunjukkan ketulenan setinggi 68.23 wt% yang disebabkan oleh kadar alir asetilena yang lebih tinggi. Kadar alir asetilena sebanyak 30 sccm menghasilkan MWNT yang lebih tulen, manakala suhu tindak balas pada 700 °C lebih berkesan dalam menghasilkan MWNT. Rawatan haba *in-situ* pada 200 °C menghasilkan MWNT dengan

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ketulenan tertinggi, iaitu sebanyak 87.52 wt%. TEM dan HR-TEM imej juga menunjukkan bahawa bahan asing pada lapisan dinding MWNT telah terbakar pada suhu 200 °C. Rawatan haba *in-situ* tersebut dapat mengurangkan bahan asing dan menghasilkan MWNT dengan ketulenan yang lebih tinggi.

*Kata kunci:* Suhu tindak balas; kadar alir bahan pemula; nanotiub karbon dinding berganda; rawatan haba *in-situ*; ketulenan.

## 1.0 INTRODUCTION

The discovery of carbon nanotubes by Iijima [1] continues to draw tremendous attention due to their myriad potential applications, deriving from their excellent mechanical, structural and electronic properties. There are three predominant methods for the synthesis of CNTs: electric arc discharge, laser ablation and catalytic chemical vapour deposition (CCVD) [2]. The CCVD involving simultaneous decomposition of a carbon source with a metal catalyst under a carrier gas atmosphere appears to be the most promising method for low cost large-scale production of CNTs, stemming from the relatively easy opportunity to upscale both the preparation and the purification methods. The growth mechanism of CNTs using CCVD involves the decomposition of carbon source, followed by the dissolution of carbon phase into metal catalytic nanoparticles and redeposition of carbon on the catalyst surface. Therefore, the synthesis of CNTs can be controlled by the variable parameters of catalyst, reaction temperature, flow rate of hydrocarbon precursor, etc. The quality and quantity of the as-grown CNTs can be controlled by manipulating the reaction parameters. Transition metals (Co, Fe or Ni) supported on oxides or zeolite are used as catalyst precursors in CCVD [2 – 4]. Both monometallic and bimetallic combinations of these metals are used for the synthesis of CNTs. It has been widely reported that an alloy phase is formed in the bimetallic catalyst [5], which the alloy phase has different properties compared to its individual component.

CNTs prepared under different experimental conditions of CCVD are different in their crystallinity and the thermal stability. Thermogravimetric analysis (TGA) is a useful technique to understand the purity and thermal stability of CNTs [6]. The impurities presents in the as-grown CNTs as amorphous carbon and defected outer layers are oxidized by thermal treatment in oxidizing atmosphere. The TGA curves showed that the thermal stability and yield of CNTs are vary due to the reaction temperature and flow rate of precursor. Thus, in this work, the TG curves of CNTs samples provide significant information to select the optimum experimental conditions for the synthesis of CNTs.

## 2.0 MATERIALS AND METHODS

The catalysts have been prepared by impregnation method. The transition metal salts of hydrated cobalt acetate and iron (II) acetate (Aldrich) are used to prepare the bimetallic combination of Co and Fe salt solution. The bimetallic solution was mixed with molecular sieves powder type 4A (Sigma-Aldrich) with constant stirring. After the complete mixing, the catalyst sludge is dried in oven at 90 °C followed by grinding it into a fine powder. The synthesis of CNTs was carried out in a tube furnace at atmospheric pressure. The prepared supported catalyst is spread on a ceramic boat. Acetylene ($C_2H_2$) with purity of 99.9999 % was used as the source of carbon for the production of carbon nanotubes (CNTs) and nitrogen ($N_2$) gas (99.9 %) acts as the carrier gas. After purging with nitrogen at 120 standard cubic centimetres per minute (sccm) for 15 minutes, $C_2H_2$ was allowed to flow at 15 or 30 sccm. The reaction was performed at 700 and 850 °C (5 °C/min) with reaction time of 30 minutes. After the reaction, an in-situ heat treatment was carried out at 200 °C for an hour to remove the impurities in the as-grown CNTs. The products were collected as black and fluffy powder. An in-situ heat treatment was carried out onto the CNTs synthesized at 850 °C ($C_2H_2$ 30 sccm) at the last part of the reaction. The $C_2H_2$ gas was switched off at 550 °C but the $N_2$ gas was kept flowing, the temperature of the furnace was maintained at 200 °C for 1 hour.

The quality, purity and yield of the CNT products were assessed using TGA, field emission-scanning electron microscope (FE-SEM) and high-resolution transmission electron microscope (HRTEM). TGA (SOTA 851$^e$ Metler Toledo) was used to determine the CNT purity and the quantity of residual catalyst support and metal catalyst, the analysis were carried out under oxygen atmosphere with heating rate of 10 °C/min from room temperature to 800 °C (isotherm 800 °C for 60 min). Meanwhile, FE-SEM (Zeiss Supra 35VP) and TEM (JEOL 2010) were used for qualitative analysis of the CNTs.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Reaction Temperature

The FE-SEM images of the MWNTs grown at different temperatures (700 and 850 °C) are shown in Figure 1, it can be observed that the morphologies of the MWNTs are greatly influenced by the reaction temperature. The MWNT yield obtained at 700 °C grew in bundles with high density (Figure 1(a)), the length of the CNTs are up to a few micron with diameter ranged from 12.3 to 20.9 nm. Whereas, the MWNTs grown at 850 °C were found to be compacted and less fluffy as shown in Figure 1(b), it can be observed obviously that the nanotubes are thicker than the nanotubes grown at 700 °C. Jacques *et al.* [7] reported that higher reaction temperature lead to the growth of larger catalyst particles and subsequently produce nanotubes with greater outer tube diameters.

The TGA curves of MWNTs are shown in Figure 2. All of the samples showed a similar oxidation behavior with single step degradation. Weight loss in the region corresponding to CNT oxidation is used to determine the CNT quantity in the

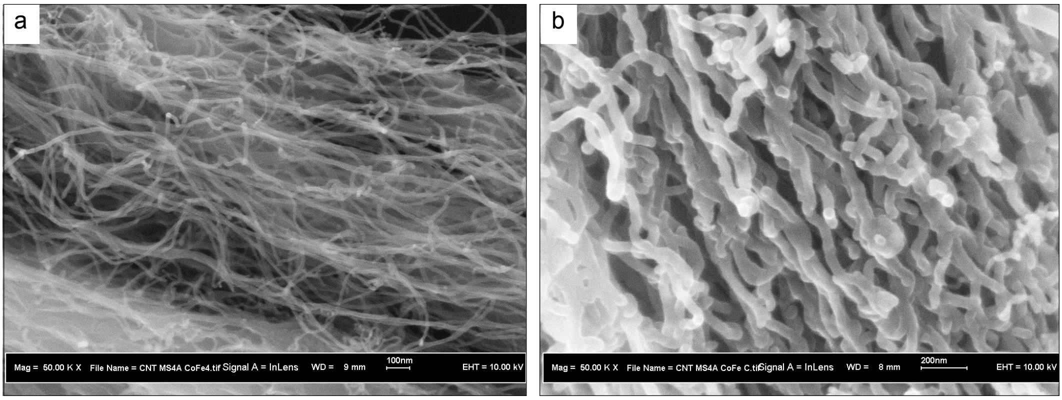


**Figure 1** FE-SEM images of MWNTs grown at reaction temperature (a) 700 °C and (b) 850 °C

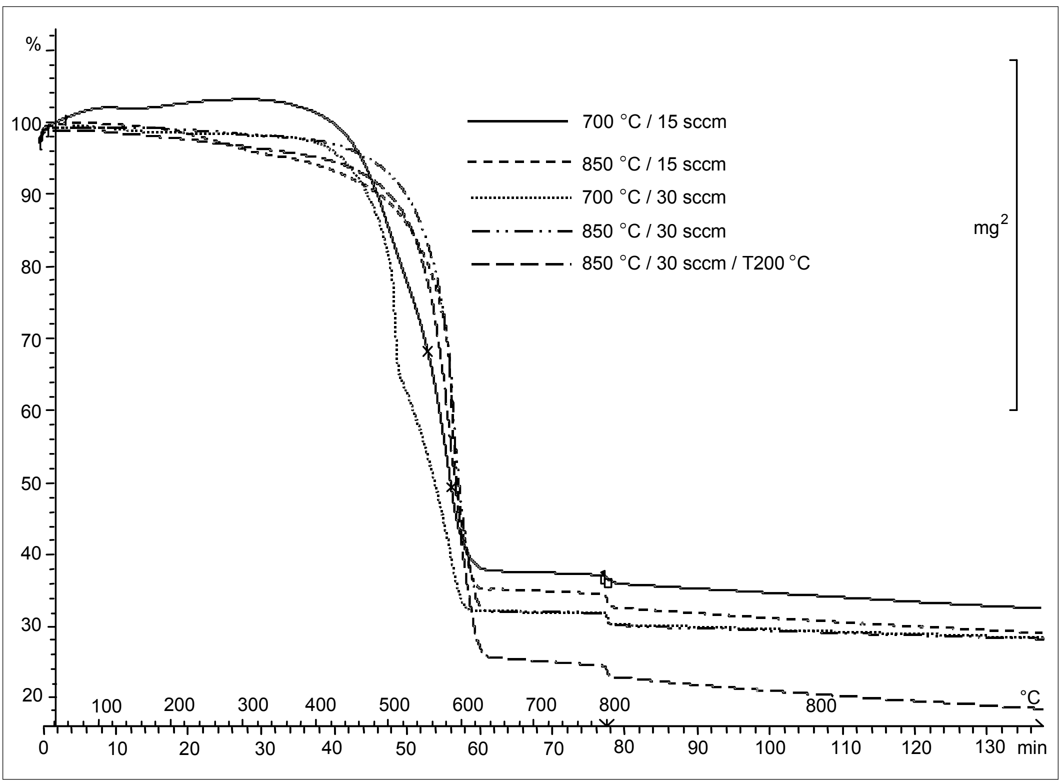


**Figure 2** TGA curves of MWNTs synthesized under different temperature and flow rate of $C_2H_2$

samples and hence infer the CNT purity and yield [6], literatures suggest [5, 8, 9] that the weight loss between 450 and 700 °C is specifically due to MWNT oxidation.

During the initial heat treatment, all samples showed a slight mass loss due to the presence of amorphous carbon on the MWNT walls [8]. The MWNTs produced at

700 °C showed 63.31 % weight lost, while the MWNTs obtained at 850 °C has lower weight loss at 61.68 %, this indicated that the purity of the latter sample is lower. Therefore, reaction temperature of 700 °C is more suitable to synthesis MWNTs using supported catalyst of Co/Fe.

## 3.2 Flow Rate of Acetylene

At reaction temperature of 700 °C and flow rate of nitrogen (carrier gas) was fixed at 120 sccm, we found that the MWNTs yield increases with increasing $C_2H_2$ flow rate. The MWNTs generated at $C_2H_2$ flow rate of 30 sccm possess clean and smooth graphite wall surfaces as showed in Figure 3(a). The purity of this MWNT can be verified by the TGA weight loss of 69.28 % (Figure 2) which is slightly higher than the MWNTs obtained at 15 sccm.

At higher reaction temperature of 850 °C, the purity of MWNTs also increased from 61.68 to 69.28 % by increasing the $C_2H_2$ flow rate, as depicted in the TGA curves (Figure 2) and FE-SEM image (Figure 3(b)). According to Chen *et al.* [10], higher flow rate of the precursor will prolong the resident time of the precursor on the catalyst surface which is beneficial for synthesizing well-graphitized CNTs. Higher $C_2H_2$ flow rate tend to increase the decomposition rate [10] and subsequently leads to higher yield of CNTs. Therefore, flow rate of acetylene of 30 sccm is effective in increasing the MWNTs yield in the CCVD process at 700 and 850 °C.

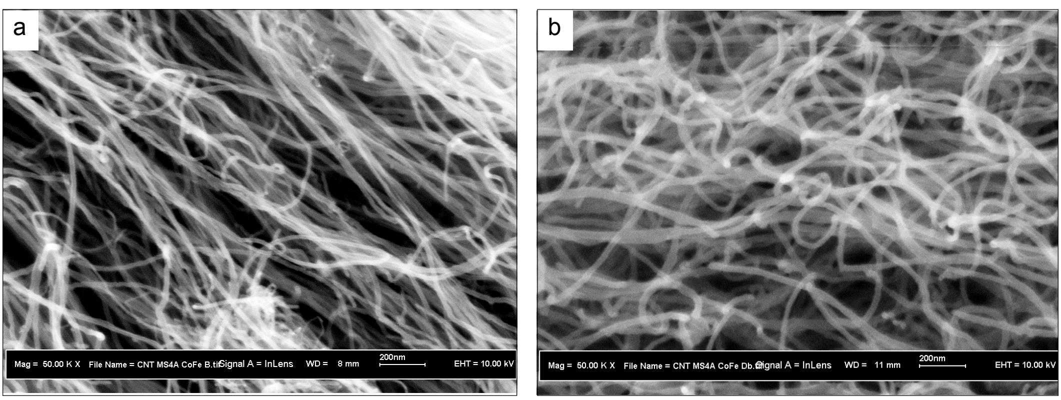


**Figure 3** FE-SEM images of MWNTs grown at different $C_2H_2$ flow rate (a) 15 sccm and (b) 30 sccm

## 3.3 In-situ Heat Treatment

The MWNTs grown at 850 °C with 30 sccm acetylene were heat treated in-situ at 200 °C during the last part of the reaction. The TGA curve of this sample in Figure 2 showed the highest weight loss amongst other MWNTs, *i.e.* 87.52 %, it is suggested

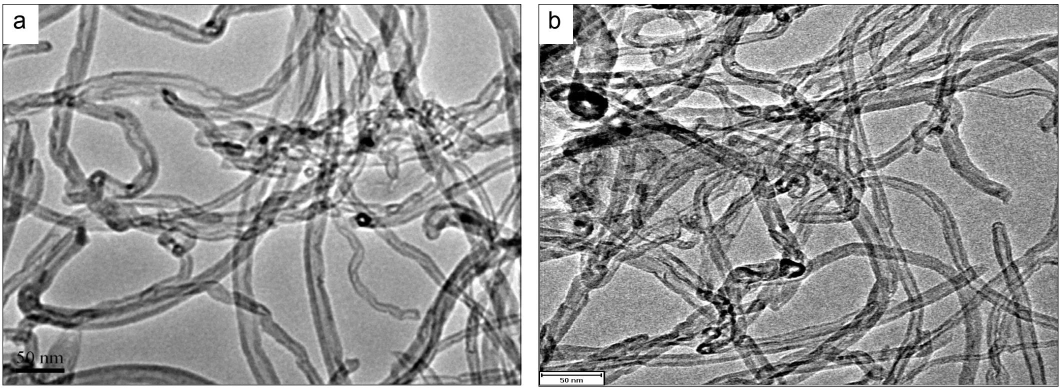


**Figure 4** TEM images of MWNTs synthesized at 850 °C with acetylene flow rate of 30 sccm (a) without heat treatment and (b) heat treatmented at 200 °C

that this MWNT has very high purity. Figure 4(a) showed the TEM image of the untreated MWNTs which the MWNTs were thicker with amorphous carbon deposition on the surface of the nanotubes.

In contrast, the MWNTs treated at 200 °C (Figure 4(b)) showed thinner wall layers and smoother surfaces which indicated that the impurities have been removed by the heat treatment. The heat treated sample was cleaner and fewer defect sites were detected. The in-situ heat treatment is able to reduce the impurities and amorphous carbon and hence yielded MWNTs with purity up to 88 %.

## 4.0 CONCLUSION

The experimental results showed that the reaction temperature of 700 °C is more suitable to produce higher MWNTs yield compared to reaction temperature of 850 °C. The reaction at 700 °C yielded MWNTs with 63 % purity. In addition, the flow rate of precursor also plays an important role in controlling the yield. At higher flow rate of $C_2H_2$ (30 sccm), the yield of MWNTs was successfully increased from 63.31 to 69.28 %. An effective and simple in-situ heat treatment at 200 °C is able to reduce the impurities and amorphous carbon on the surfaces of MWNT yield, hence enhancing the purity of the MWNT to 88 %.

## ACKNOWLEDGEMENT

The authors would like to thank Universiti Teknologi Malaysia (UTM) and the Ministry of Science, Technology and Innovation of Malaysia for sponsoring the research student under the National Science Fellowship (NSF).

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