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Effect of Parameters on Carbon Nanotubes Grown by Floating Catalyst Chemical Vapor Deposition

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Abstract. There is a critical need to understand the effect of the growth parameters on the characteristics of carbon nanotubes (CNTs) in order to optimize the process for the production of CNTs with specific characteristics that will exhibit enhanced functionality for the application. Floating Catalytic Chemical Vapor Deposition (FCCVD) is a promising method to produce high yield bulk CNTs. Effects of parameters namely flow rate of ethylene and argon, reaction temperature and weight of ferrocene on CNTs grown by FCCVD were investigated. The growth of CNTs began with the vaporization of an amount of ferrocene at 150 °C under argon ambient followed by exposure to ethylene at different temperatures. Properties of CNTs such as crystallinity and diameter were determined using Scanning Electron Microscopy and Transmission Electron Microscopy and Raman Spectroscopy. Temperature of 800 °C and 850 °C are found to be suitable for CNTs growth with the temperature of 850 °C producing bigger diameter CNTs. Low flow rate of ethylene (20 sccm) produced CNTs with higher degree of crystallinity.

Keywords: Floating catalytic chemical vapor deposition, carbon nanotubes, crystallinity.
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INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attraction among researchers because of its unique mechanical and electrical properties [1-4]. Multiwalled nanotubes (MWCNTs) are widely used as composite materials and field-emission devices while single-walled nanotubes (SWCNTs) is considered to be the building blocks for electronic applications [2]. Study on the characteristic of carbon nanotubes is crucial in order to establish the nanoscale attributes that can deliver unique and enhanced functionality of the target applications of materials. [2]. Among the synthesis techniques of CNTs, Chemical Vapor Deposition (CVD) is the most suitable method for industrial-scale production due to its simplicity, low cost and low deposition temperature [1, 4-5]. Floating Catalytic Chemical Vapor Deposition (FCCVD) is a CVD method that allows CNTs to be grown in the reactive gaseous phase by directly introducing carbon feedstock gas and catalytic gas in the furnace without the supporting substrate [6-8]. Understanding the role of each growth parameters will provide the ability to control the synthesis of CNTs and facilitate its use for various applications [3, 6, 9-14].

From the literature review, high temperature will produce larger diameter of CNTs with high percentage of yield up to a certain limit [5, 15]. Normally, CNTs can be synthesized in the temperature range of 600 to 1100 ºC. Kim and his friends suggested that CNTs growth can be carried out under the temperature of 600 to 800 ºC [3]. Fan *et al*. reported the growth of SWCNTs and MWCNTs in the reaction temperature range between 900 to 1100 ºC by using FCCVD method [16]. On the other hand, Kunadian *et al.* used different reaction temperature (650 to 900 ºC) to synthesize CNTs by FCCVD method [11]. Liu *et al.* had reported the absence of CNTs when grown at 750 ºC, few

MWCNTs, and carbon impurities at 800 ºC, mixture of single and multi-walled CNTs at 850 ºC and SWCNTs only at above 900 ºC using Fe-Mo/MgO catalyst with ethanol as the carbon source [14]. Yu *et al*. [5] reported the increase of carbon yield with increase in temperature. However, the morphology of CNTs produced is different when changing the catalyst to Mo-Co/MgO. These findings indicate the importance of catalyst in determining the characteristics of CNTs produced.

Thiele *et al*. [15] reported a linear diameter-temperature relationship between 600 to 800 ºC with C_2H_2 over Fe. Yu *et al.* reported similar trend for the growth of CNTs between 700 and 850 ºC with CH_4 on Fe-Mg/MgO [5, 15]. In contrast, Son and his co-workers reported a decreasing CNT diameter with an increase of temperature from 800 to 950 ºC using CH_4 [17]. Liu *et al*.[14] and Philippe *et al*. [18] indicated that there is no relationship at all by consistently produced SWCNT at 750 to 950 ºC using ethanol with Fe-Mo/MgO as the catalyst and MWCNTs at 500 to 700 ºC using C_2H_2 on Fe/Al_2O_3 catalyst. Thus reports from other researchers seems to indicate that the effect of temperature on the diameter size of CNTs produced has not been properly established and still debatable [15].

Here, the objective of the work is to study the effect of growth parameters on CNTs properties namely diameter size and crystallinity by using FCCVD method. This study emphasizes the need to establish an optimized method by understanding the effect of growth parameters such as reaction temperature, amount of catalyst (ferrocene) used and flow rate on the characteristics of carbon nanotubes produced.

MATERIALS AND METHOD

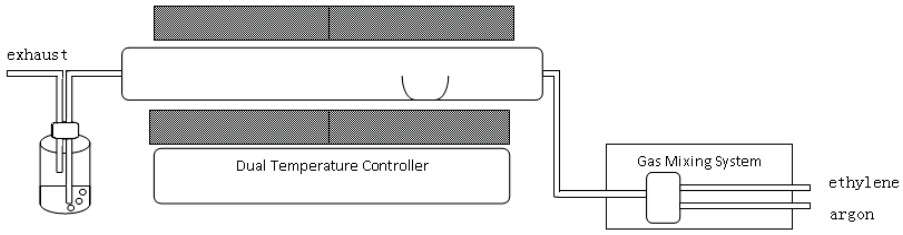

FIGURE 1. Schematic diagram of the FCCVD system

The experimental setup comprises a horizontal quartz tube reactor with dual heating zones in which ferrocene is placed at the low temperature zone as the catalyst. Figure 1 represents the schematic diagram of FCCVD system. Argon was purged in when ramping up the temperature of the furnace at 15 °C per min. Ferrocene (0.1 and 0.2 g) was vaporized at 150 °C and carried by argon flow into the second zone where the temperature was set at 750 °C. Ethylene was purged into the furnace with the flow rate of 10, 20 and 50 sccm for one hour. After 1 hour, the reactor was cooled down to room temperature under argon ambient. These steps were repeated by changing the temperature to 800 and 850 °C. The raw product was collected from the walls of the quartz tube leaving some that might be difficult to extract. The morphology, diameter distribution and crystallinity of the samples were characterized using Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 55 VP), Transmission Electron Microscope (TEM, Zeiss Libra 200FE), and Raman spectroscopy (Horiba Jobin Yvon HR800). Yield of CNTs was calculated using the formula below:

$$Yield\ of\ CNTs\ produced = \frac{Amount\ of\ CNTs\ produced\ (g)}{Amount\ of\ ferrocene\ used\ (g)} \times 100\%$$

RESULTS AND DISCUSSION

In order to confirm the formation of CNTs, TEM analysis was carried out. Close inspection of TEM images shows the presence of Multi-Walled Carbon Nanotubes (MWCNTs) in samples. Figure 2(a) shows the typical MWCNT while Figure 2(b) shows the presence of defective CNTs presence which has a rough tube walls. Some of Fe particles encapsulated inside the wall tube can be seen in Figure 2(c). Based on Figure 2(d), CNTs produced consists of 18-20 layers of wall. Few straight nanotubes can be seen in Figure 2(e). Besides that, MWCNTs grown with various sizes of long tubes or coiled shapes tubes are shown in Figure 2(e). Table 1 summarizes the yield of CNT sample produced.

As shown in Figure 3, there is no product gain when the reaction temperature was set at 750 ºC except for sample C_1 (0.01 g). This implied that there is an effect of temperature on the growth of CNTs. Lower temperatures do not encourage the growth of CNTs as catalyst favors degradation and agglomeration, resulting in low yield and producing non-CNTs product.[19]. Agglomeration increases the size of catalyst Fe which does not encourage CNTs growth [20]. With bigger sized catalyst, the surface area is lesser leading to a decrease in the frequency of effective reaction for CNTs growth. The requirement of higher temperature for the growth of CNTs is evident by the yield recorded for the temperature of 800 ºC and 850 ºC even though the flow rate of ethylene and the amount of ferrocene used are changed.

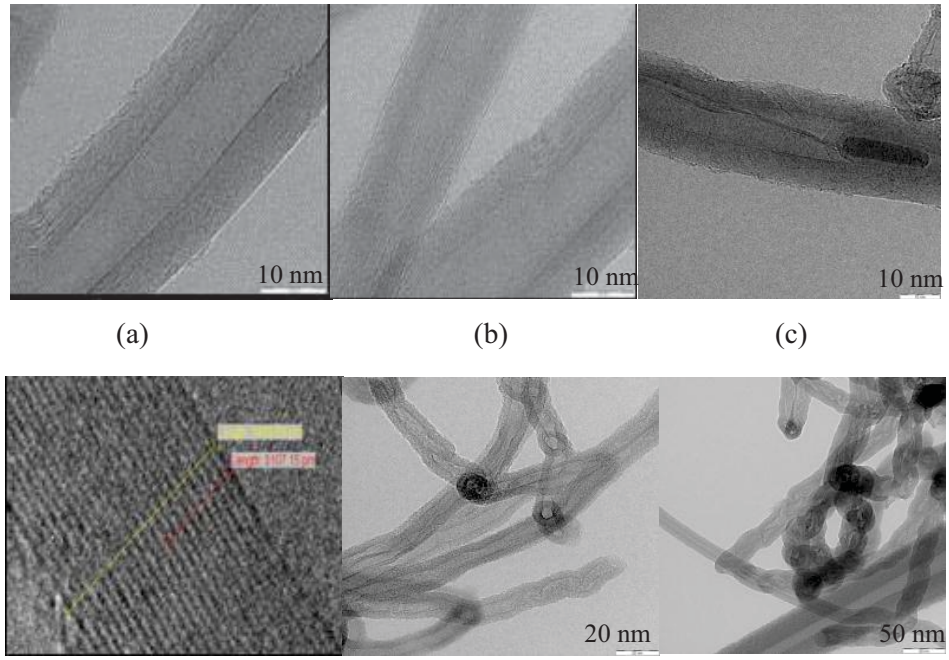

FIGURE 2. TEM images of CNTs

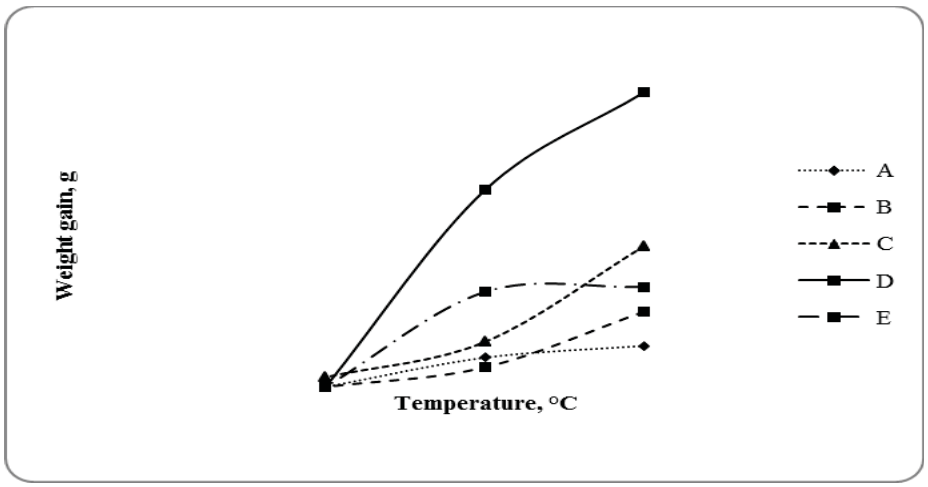

FIGURE 3. Weight gain of unpurified samples A, B, C, D and E

TABLE 1. Summary of the weight of each sample

Ethylene: Ar/sccm	Model	Weight of Catalyst/g	T/ ºC	Weight/g
10:90 A	A_1	0.1	750	No product
	A_2	0.1	800	0.030
	A_3	0.1	850	0.042
20:80 B	B_1	0.1	750	No product
	B_2	0.1	800	0.02
	B_3	0.1	850	0.077
50:50 C	C_1	0.1	750	0.010
	C_2	0.1	800	0.046
	C_3	0.1	850	0.144
10:90 D	D_1	0.2	750	No product
	D_2	0.2	800	0.201
	D_3	0.2	850	0.301
20:80 E	E_1	0.2	750	No product
	E_2	0.2	800	0.097
	E_3	0.2	850	0.102

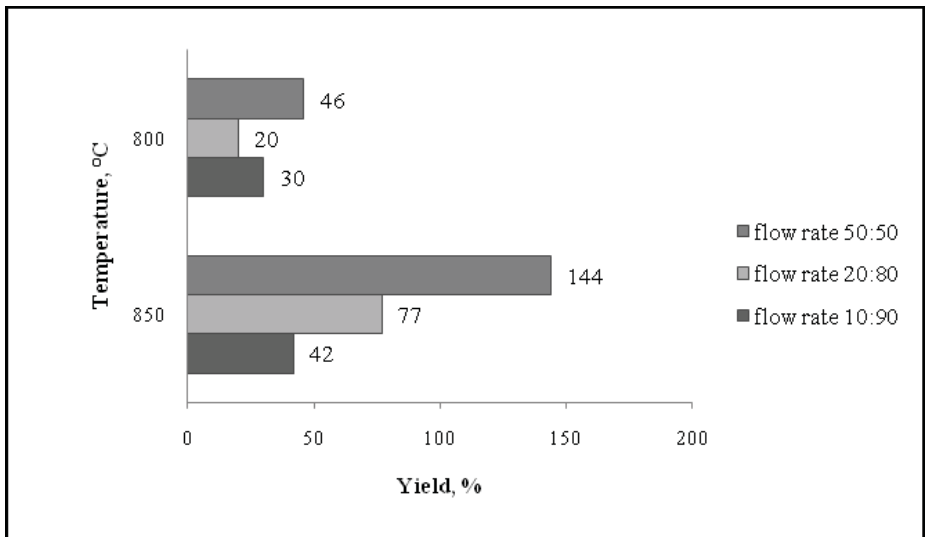

FIGURE 4. A comparison of yield gain at different flow rate versus temperature with 0.1 g ferrocene

Figure 4 shows the effect of flow rate on the yield of CNTs produced. With 0.1 g of ferrocene used, the highest yield is obtained for the flow rate of 50 sccm ethylene. This

is to be expected as the introduction of more carbon into the furnace will accelerate the production of CNTs. However, the optimum flow rate cannot be determined by the yield of CNTs only but also its quality. Crystallinity is one of the criteria to investigate the 'quality' of CNTs in the way of the degree of graphitization. Some studies show the evidence of trade-off between yield and quality. For example, Liu *et al.* reported a yield of 0.005 g of CNTs per gram of metal catalyst used with good quality. However, with the yield of more than 20 g of CNTs the quality is lower [14]. These studies suggest that yield and quality might not be simultaneously maximized. The degree of crystallinity of CNTs can be derived from the intensity ratio of I_D / I_G. The lower the ratio of I_D /I_G, the higher would be the degree of crystallinity. As we can see from Figure 6, even though Sample D_3 has the highest amount of crude CNTs (0.301 g), the degree of crystallinity is considered quite low (0.74). Also, the weight of Sample C_3 (0.144 g) is considered higher but its crystallinity level is the second lowest (0.979). Besides that, the crystallinity of Sample B_3 (0.54) and Sample C_2 (0.48) are good as compared to other samples. It should be highlighted that at 850 ºC, high yield of CNTs (C_3) with lowest quality can be produced using 50 sccm ethylene whereas good yield and crystallinity can be obtained for the sample using 20 sccm flow rate of ethylene (Sample B_3).

Based on Figure 6, the diameter range decreases as temperature decreased with various flow rate of ethylene from 10 sccm (Sample A), 20 sccm (Sample B) and 50 sccm (Sample C). The difference diameter range does not change much if compared to both Sample A and Sample B, as the flow rate of ethylene is just in 10 sccm difference. However, when the flow rate of ethylene is increased to 50 sccm, there is a significant change of diameter range i.e. C_2 (43-96 nm) and C_3 (82-340 nm), meaning that, at 850 °C with 50 sccm encourages non-CNT nanoscale product

formation and not CNTs. The results seem to agree with Thiele *et al*. works [15]. The diameter of CNTs is increased with increase in temperature and this might be due to the addition of wall layers of CNTs which was grown from the carbon atoms available during the process. It is also possible that the rate of CNTs formation become higher and thus increasing the yield gain. The diameters of the CNTs are controlled by the formation of the carbon layers, which in turn depends on the amount of carbon atoms presents in the chamber. On the other hand, Samples D_2 to

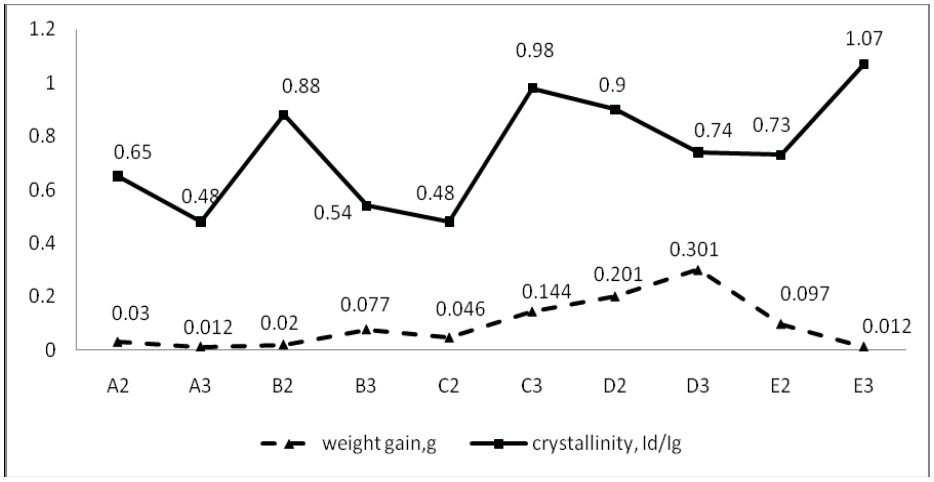

FIGURE 5. Comparison of weight and crystallinity of each sample

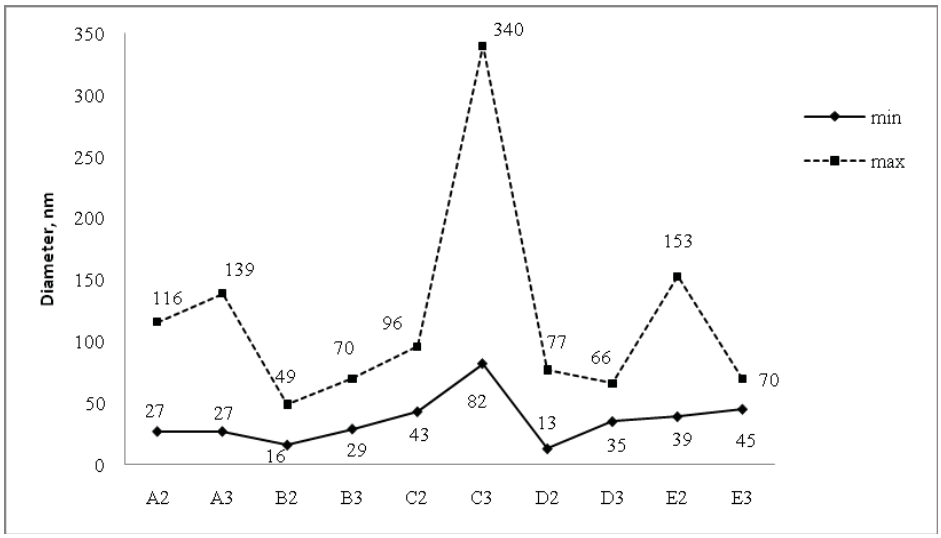

FIGURE 6. Diameter range of each sample

E_3 have the same weight of ferrocene (0.2 g). There is an inverse relationship between temperatures towards diameter range with addition of ferrocene. D_2 (13-77 nm) has wider size distribution compared to D_3 (35-66 nm). Similar situation goes to Sample E_2 (39-153 nm) and Sample E_3 (45-70 nm). McKee [6] reported that higher catalyst concentration will lead to more and larger nanocatalyst particles than a comparatively lower catalyst concentration. Larger particles size will create bigger size of CNTs. Figure 7 shows the SEM images of each sample produced. As shown in SEM images, sample A_3, sample B_3 and sample C_2 have smooth and less defective tubes with crystallinity of 0.48, 0.54 and 0.48 respectively. The images of sample E_3 shows the tubes are short and not in cylindrical shape. Short tubes indicates that the reaction has just started and resulted in low yield of CNT production.

CONCLUSION

By using the method of FCCVD, the yield of MWCNTs is promising. Temperature of 800 and 850 °C are found to be suitable for CNTs growth, producing diameter range of 13-340 nm with different flow rate of ethylene (10, 20 and 50 sccm) and ferrocene (0.1 g and 0.2 g). Yield is directly proportional to the temperature. However, higher yield does not mean good quality of CNTs. Despite of their weight gain, Sample B_3 (0.54) and Sample C_2 (0.48) have the highest degree of crystallinity. The diameter increases proportionally with the temperature increase when 0.1 g ferrocene. However an inverse relationship was found when the weight of ferrocene was 0.2 g. It can be suggested that the temperature of 850 °C under 20 sccm of ethylene with 0.1 g forrecene is the optimum condition for CNT growth.

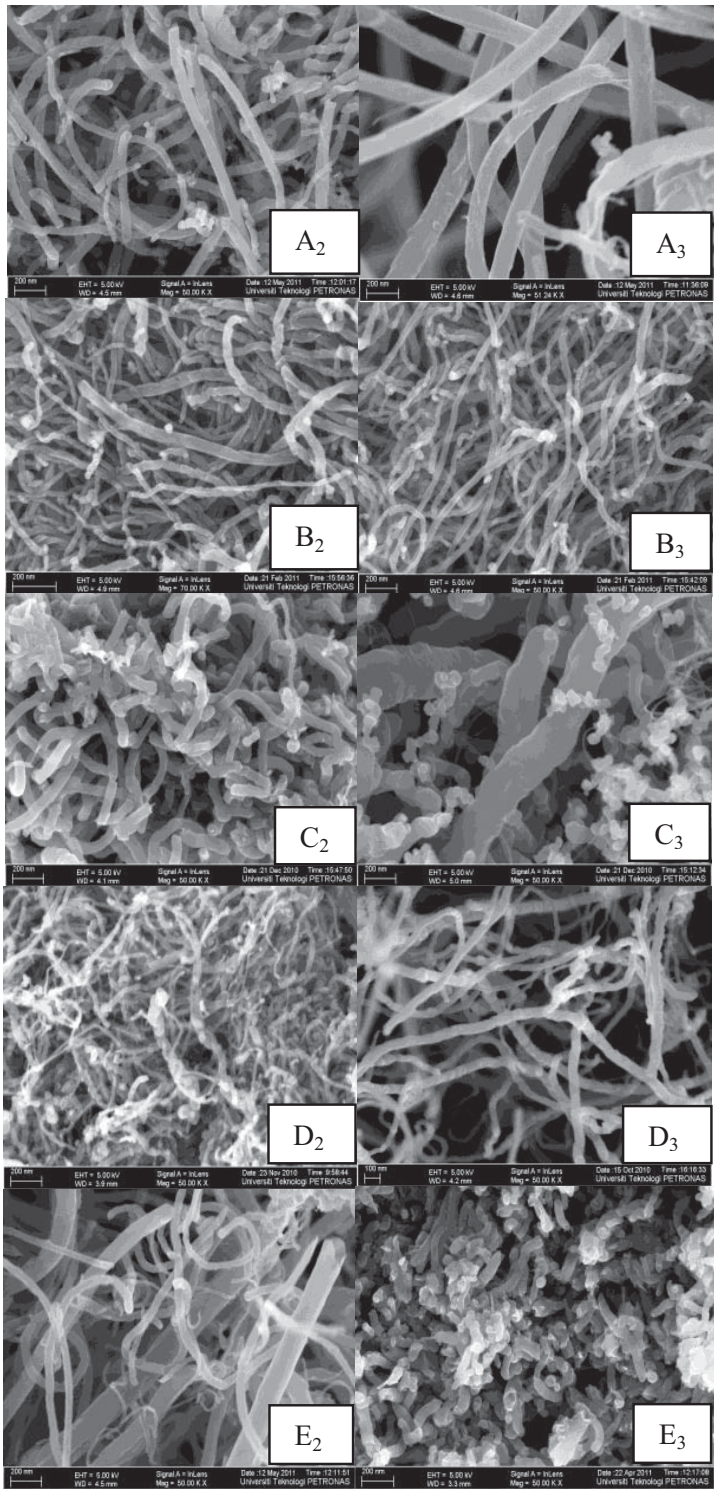

FIGURE 7. SEM images of each sample at 50K magnification except B_2 at 70K

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