

# C42\_EJSMT\_Effect\_of\_Catalyst\_Concentrations

*by* Wipsar Sunu Brams Dwandaru

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## 1 Effect of Catalyst Concentrations on the Growth of Carbon Nanotubes from Waste Engine Oil

S. Alfarisa<sup>1\*</sup>, R. N. Safitri<sup>2</sup>, W.S.B. Dwandaru<sup>3</sup>

<sup>1</sup> Department of Physics, Faculty of Mathematics and Natural Science,  
Universitas PGRI Palembang, 30251 Palembang, Indonesia

<sup>2</sup> Homeschooling Primagama Yogyakarta, 55221 Special Region of Yogyakarta, Indonesia

<sup>3</sup> Department of Physics, Faculty of Mathematics and Natural Science,  
Universitas Negeri Yogyakarta, 55281 Special Region of Yogyakarta, Indonesia  
\*e-mail: suhufaarfarisa@gmail.com

### 1 Abstract

Synthesis of carbon nanotubes with different concentrations of ferrocene (C<sub>10</sub>H<sub>10</sub>Fe) as catalyst (5.33, 10.66, 13.99-19.99 wt%) from waste engine oil precursor has been done to study its effects on the growth of carbon nanotubes. Thermal chemical vapor deposition method was used in this study. The synthesis process lasted for 30 minutes under argon gas ambient in constant precursor vaporization and synthesis temperature of 450°C and 750°C respectively. The characterization of prepared samples were done using field emission scanning electron microscopy, micro-Raman spectroscopy and thermogravimetric analysis. High density carbon nanotubes was produced at 17.99 wt% catalyst concentration with purity of 72%. The results show that the structure, diameter size and quality of carbon nanotubes are highly affected by the catalyst concentrations.

1 **Keywords** carbon nanotubes, waste engine oil, chemical vapor deposition, ferrocene

## INTRODUCTION

16 Carbon nanotubes (CNTs) are carbon material in the form of tubes and made of rolled up graphene layers [1, 2]. A single-walled CNTs consists of one layer of tube, meanwhile multi-walled CNTs are formed from more than a layer of tube. The tubes diameter is in nanometer range and a few micrometers in length. Due to their great properties, synthesis methods, carbon precursors, growth mechanisms, mass production and applications, CNTs are being intensively studied by researchers in the last 20 years. There are several methods to synthesis CNTs such as arc discharge, laser ablation, electrolysis, flame synthesis and chemical vapor deposition (CVD) [3, 4]. CVD method is the most widely used due to its ability to control the growth directions and scale up the production in large quantity [4].

The use of catalyst is crucial for the growth of CNTs using CVD technique because it takes a role in catalytic decomposition of carbon precursor and the graphitic structure formation of CNTs [5]. Several catalysts have been reported with different composition and preparation to produce CNTs such as iron (Fe), cobalt (Co), nickel (Ni), platinum (Pt), magnesium (Mg), molybdenum (Mo) and aurum (Au) [5-7]. Lee *et al.* reported that the CNTs growth with Fe catalyst have the highest crystallinity compared with Co and Ni catalysts [5].

15 On the other hand, carbon source also plays an important role for the growth of CNTs. Basically, any carbon containing compound can be used as the source or precursor for the production of CNTs. It is important to use carbon sources which are cheaper, easily accessible and available in large amount. This is related to the earning of large quantity CNTs as demanded by market and industry for their use in various applications. Moreover, global issue to preserve the environment should also be balanced with the development of technology. Waste materials containing carbon can be used as alternative sources for the production of CNTs. It only required the parameters optimization and experiment controlling for the production of the best and high quality carbon materials. For example, waste engine oil (WEO) is a high polycyclic aromatic hydrocarbons (PAHs) and contains metal contaminants [8]. Illegal disposal of WEO can pollute our environment. The use of WEO as carbon source to produce quasi aligned CNTs and their potential application in electron emission devices has been previously reported in [9]. It is a suitable source to produce CNTs since it contains high carbon content. However, the effect of catalyst concentrations on

the growth of CNTs from WEO has not yet reported. Hence, in this study, we report the effect of ferrocene ( $C_{10}H_{10}Fe$ ) catalyst on the growth of CNTs from WEO.

## MATERIALS AND METHOD

CNTs were grown on  $1 \times 1 \text{ cm}^2$  silicon substrates that have been ultrasonically cleaned using acetone, methanol and DI water before being used. Schematic thermal CVD (TCVD) is presented in Figure 1. Precursor and synthesis zone of double stage TCVD furnace were kept constant at  $450 \text{ }^\circ\text{C}$  and  $750 \text{ }^\circ\text{C}$ , respectively. Ferrocene was mixed with WEO at different concentrations (5.33, 10.66, 13.99-19.99 wt%) and then stirred for 30 minutes. 3 ml of the mixture was put in alumina boat and introduced into precursor furnace while the substrates were placed in the center of synthesis furnace. Argon (Ar) gas was flushed out for 10 minutes before the synthesis process starts. Synthesis zone was initially turned on followed by precursor zone. Precursor furnace was turned off after 30 minutes of synthesis time followed by synthesis furnace after annealing process.

The CNTs produced were then collected and characterized using field emission scanning electron microscopy (FESEM-Hitachi SU8020) with accelerating voltage of 5 kV at working distance of 4 mm using upper detector. The graphitization and purity of CNTs was also analyzed using micro-Raman spectroscopy (Renishaw InVia microRaman System) with 514 nm wavelength of  $Ar^+$  laser at power of 5% and thermogravimetric analysis (TGA-Pyris 1 Perkin Elmer) at constant heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under oxygen atmosphere.

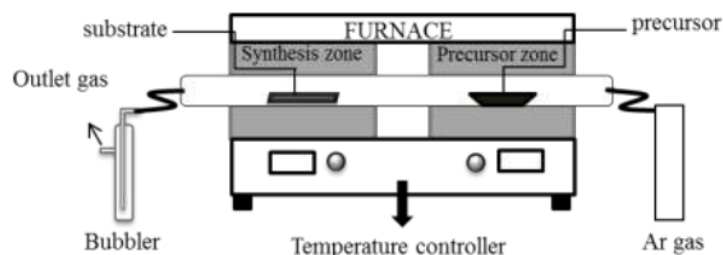
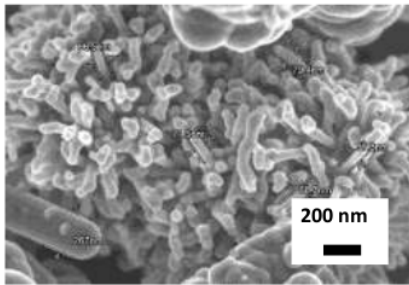


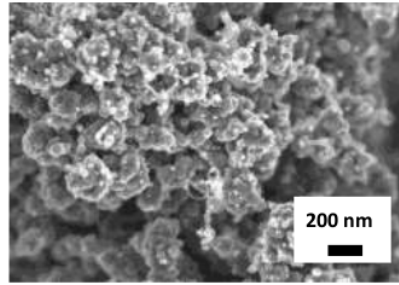
Figure 1 Schematic of TCVD method for the synthesis of CNTs from WEO precursor

## RESULTS AND DISCUSSION

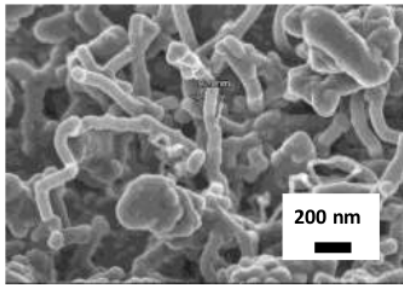
In this study, the initial catalyst concentration used was 5.33 wt%. It was then increased to be 10.66 and 15.99 wt%. The concentrations of ferrocene catalyst were varied around 15.99 wt% (13.99 - 19.99 wt %) since a better CNTs structure was obtained. Figure 2 shows the FESEM images of the synthesized CNTs at various catalyst concentrations. Generally, CNTs were observed at overall catalyst concentrations. Somehow, better morphology of CNTs was produced in the concentration range of 13.99 – 17.99 wt% catalyst concentrations. At catalyst concentrations lower than 13.99 wt%, only small amount of CNTs with short and agglomerated structures were observed. Low density and short CNTs were observed at the sample produced using catalyst concentration of 5.33 wt% (Figure 2(a)). The diameters of the tubes were range from 66.5 – 102.0 nm. Non-tubular agglomerated carbon structures were also observed along with the CNTs. For the sample synthesized at catalyst concentration of 10.66 wt% in Figure 2 (b), the carbon structure was elongated resembling a tube shape. Low dense CNTs were also observed attached to the structure.



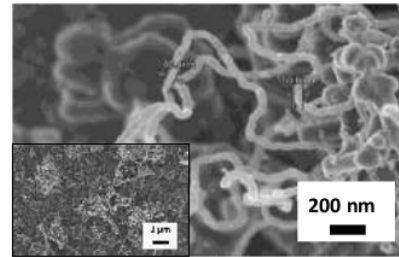
a. 5.33 wt% (50K X)



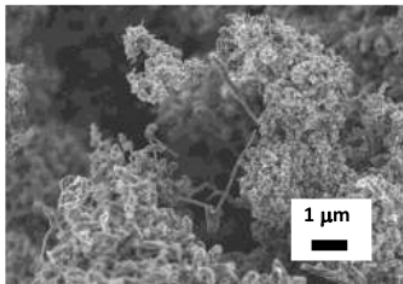
b. 10.66 wt% (50K X)



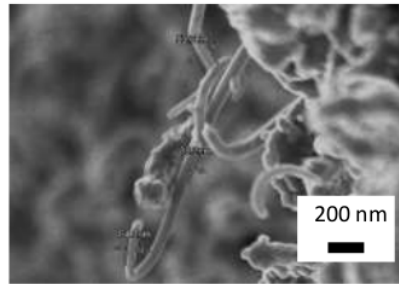
c. 13.99 wt% (50K X)



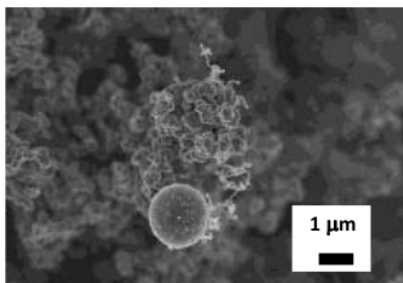
d. 14.99 wt% (50K X)



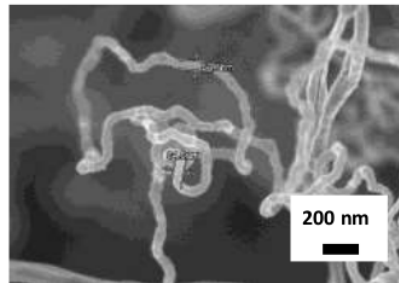
e. 15.99 wt% (10K X)



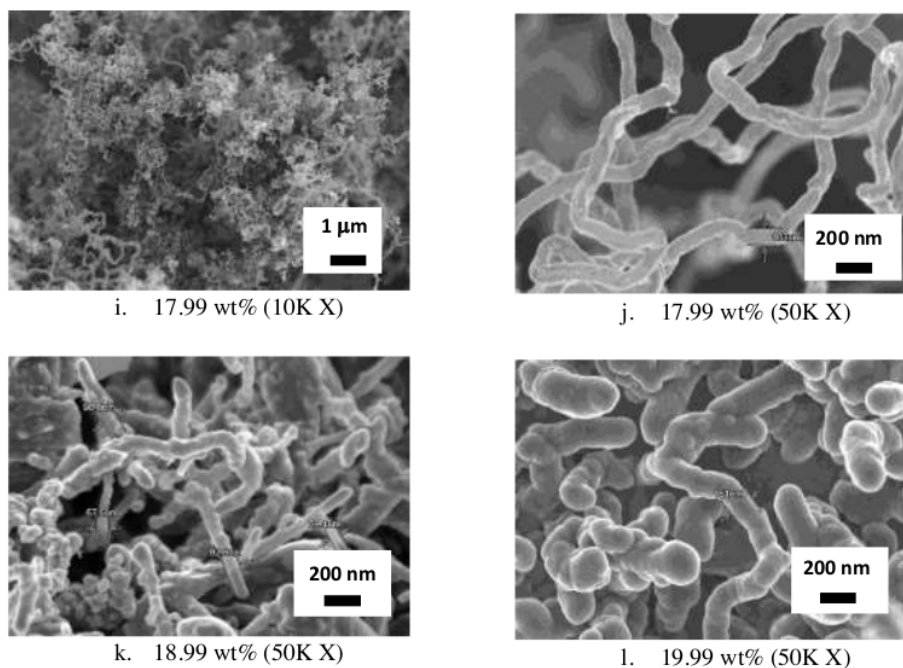
f. 15.99 wt% (50K X)



g. 16.99 wt% (10K X)



h. 16.99 wt% (50K X)



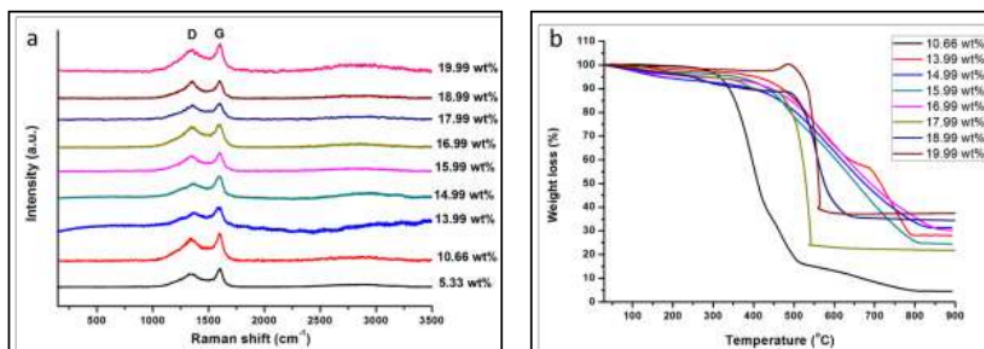
**Figure 2** FESEM images of CNTs synthesized at different catalyst concentrations (a) 5.33, (b) 10.66, (c) 13.99, (d) 14.99, (e)-(f) 15.99, (g)-(h) 16.99, (i)-(j) 17.99, (k) 18.99, (l) 19.99 wt%

When the catalyst was increased to 15.99 wt%, a little amount of better CNTs was observed along with the agglomerated carbon structure. Diameters of the tubes were ranged from 64.0 to 114.0 nm. The concentrations were then varied around this concentration in order to obtain a better growth of CNTs from WEO. Wide diameter ranges of CNTs were produced at catalyst concentrations below 15.99 wt%. CNTs synthesized at 13.99 wt% catalyst concentration were covered by higher agglomerated carbon structure. Longer and larger diameters of CNTs were seen at concentration of 14.99 wt% and the presence of other carbon impurities was observed from this sample. CNTs produced at 16.99 wt% gave the smallest diameter range (37.8 – 67.5 nm). However, FESEM observation revealed the low density of CNTs and the presence of carbon sphere with diameter of  $\sim 2 \mu\text{m}$  which obtained along with CNTs.

Much better growth of CNTs with higher density was produced at concentration of 17.99 wt% (Figure 2 (i)-(j)). A broad diameter range of the tubes were observed in the size of 21.8 – 103.0 nm. Increasing the concentration above 17.99 wt% did not give better results. Instead, the structure returned to agglomerate and the size got larger. Growth of uniformly large and short sausage-like carbon material was produced at the highest concentration of 19.99 wt%. Its diameter was up to 171.0 nm. Lower catalyst concentrations below 17.99 wt% gave smaller size carbon materials because of the smaller Fe particles formed while at higher concentration, catalyst decomposed more Fe particles which tend to agglomerate and formed larger Fe clusters.

Figure 3 (a) and Table 1 show the micro-Raman spectra and the summary of micro-Raman analysis of the carbon materials synthesized at different catalyst concentrations (5.33 – 19.99 wt%). The absence of radial breathing mode (RBM) around  $100 - 200 \text{ cm}^{-1}$  in overall sample indicated the non-existence of single-walled CNTs and hence confirmed that the CNTs produced from WEO in this study was dominated with multi-walled CNTs [10, 11]. Ratio between D and G bands ( $I_D/I_G$ ) from micro-Raman analysis can be used to measure the defect concentration of CNTs [12]. Overall samples exhibited high  $I_D/I_G$  ratio in the range of 0.85 to 0.96. However, the  $I_D/I_G$  ratio increased as higher catalyst concentrations were used. Only sample produced at catalyst concentration of 14.99 wt% has a moderate ratio of 0.65. This was in line with the resulting carbon structures which have different non-uniform structures at every catalyst concentration where most of them have agglomerated structures. Even though the FESEM images show that the best

CNTs were produced at 17.99 wt% catalyst concentration, further analysis using micro-Raman characterization showed that it has a high  $I_D/I_G$  ratio of 0.89. The high  $I_D/I_G$  ratio for the entire samples produced at different catalyst concentrations was believed due to the complex molecular structure of WEO with many contaminants and additives as revealed by FTIR, TGA, and GC-MS analyses. This affected the structure and properties including the graphitization degree of the CNTs. Moreover the presence of non-tubular carbon structure was also contributed to the high defect of the resulting CNTs.



**Figure 3** (a) Micro Raman spectra and (b) TGA curves of CNTs produced at various catalyst concentrations

TGA curves of the resulting carbon materials at different catalyst concentrations are given in Figure 3 (b). Initial weight loss was observed at most samples except CNT-17.99 and 18.99 wt% samples around 150 - 190°C which reduced about 1 - 5% of the total weight of the samples. This was due to the decomposition of hydrocarbon impurities and catalyst in WEO precursor. Poor quality of carbon material was presented by the sample at 10.66 wt% catalyst concentration due to the fast decrease of the weight loss. This sample started to decompose at temperature as low as 260 to 510°C which indicated the high a-C content in the sample. Weight loss by 12% from 510 - 800°C indicated the burning of small amount of CNTs in the sample. The remaining 5% of the total weight was from the catalyst and other volatile materials in the sample.

**Table 1** Size range and  $I_D/I_G$  ratios of carbon materials synthesized at different catalyst concentrations

Catalyst concentration (wt%)	Size (nm)	D peak ( $\text{cm}^{-1}$ )	G peak ( $\text{cm}^{-1}$ )	$I_D/I_G$ ratio
5.33	66.5 - 102.0	1354.07	1598.66	0.73
10.66	316.5 - 632.9	1357.38	1597.54	0.85
13.99	31.7 - 92.0	1366.52	1591.87	0.88
14.99	43.5 - 152.0	1362.78	1592.12	0.67
15.99	64.0 - 114.0	1356.90	1598.17	0.85
16.99	37.8 - 67.5	1362.42	1596.22	0.96
17.99	21.8 - 103.0	1362.07	1597.59	0.89
18.99	66.7 - 166	1350.60	1595.31	0.91
19.99	161.0 - 171.0	1362.89	1598.81	0.86

The samples produced at 13.99 – 16.99 wt% catalyst concentrations presented similar thermal stability. The samples were relatively thermally stable from 190 to 375°C. Above 375°C, significant weight loss occurred up to 800°C due to the burning of residual a-C content and CNTs. The oxidation of raw (more defective) CNTs started at 420 to 630°C and better graphitized CNTs were reported between 640 and 780°C [13, 14]. The weight loss by 6 – 12% was made up from the burning of a-C content and the remaining weights of the samples were in between 24 – 32%.

Weight loss by 6% of a-C content in CNTs-17.99 and 18.99 wt% occurred at temperature range of 350-435°C and 250-450°C, respectively. Small weight gain was observed in CNTs-17.99 wt% sample at 450°C due to the oxidation of metal particles exposed or adhered on the surface of CNTs [15]. In this case, it was from the Fe catalyst particles. This was also observed in the sample using 19.99 wt% catalyst concentration at 485°C. Weight loss of CNTs synthesized at 17.99 and 19.99 wt% occurred in the narrow temperature range of 455-540°C and 500-565°C. This indicated a better crystallinity degree of the nanotubes [16]. While, a broader range (490-650°C) was observed at the sample synthesized using 18.99 wt% catalyst. The remaining of 22, 35 and 37% of the total weights were measured from CNTs-17.99, 18.99 and 19.99 wt% samples, respectively. The optimum CNTs synthesized using 17.99 wt% catalyst concentration gave purity of 72%. This was consistent with FESEM analysis in Figure 2(i) and (j) which presented clear CNTs images with less impurity as compared with other samples. Moreover, micro-Raman analysis also supported this statement by the average  $I_D/I_G$  ratio obtained (0.89) from the CNTs produced using 17.99 wt% catalyst.

Catalyst played an important role for a better growth of CNTs from WEO. The use of low catalyst concentration led to the poor growth of CNTs due to the low energy to catalyze the growth process. As a result, lower density of CNTs was obtained [16]. However, too much increment of the catalyst concentration resulted in the enlargement of CNTs diameter as detected at the samples synthesized using 17.99 -19.99 wt% catalyst concentrations. This is reasonable since the higher use of catalyst concentration leads to the more abundant of catalyst particles which further agglomerate to form larger catalyst cluster. The use of 17.99 wt% catalyst concentration was the optimum parameter for the better growth of high density CNTs from WEO. In the meantime, more increment of the catalyst concentrations led to the production of short and large tubular carbon structure.

## CONCLUSION

The production of CNTs from WEO can be achieved using a relatively high catalyst concentration. Catalyst concentration will affect the size, density, crystallinity and purity of CNTs from WEO. At low concentrations, the formed CNTs tend to agglomerate with un-uniform structures and sizes. High density CNTs from WEO precursor was produced at 17.99 wt% ferrocene concentration with purity of 72%. Raising the catalyst concentration caused the larger tube diameter and agglomerated structure.

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