

Effect of Experimental Factors in the Growth of Carbon Nanotubes from CO₂ by MPECVD Process

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The effects of experimental factors such as type of catalyst (nickel and cobalt) and substrate (iron and silicon wafer) in the growth of carbon nanotubes (CNT) from CO₂ by microwave plasma-enhanced chemical vapor deposition (MPECVD) was systematically studied. Catalyst size and CNT grown were examined using scanning electron microscope (SEM). Furthermore, gas chromatography (GC) was used to analyze the effluent gas. Moreover, suitable type of catalyst and substrate were determined in terms on the amount of CNT grown, purity, and carbon conversion.

Keywords : carbon nanotubes, chemical vapor deposition, nanotechnology

INTRODUCTION

Carbon nanotubes (CNTs) are one of the profoundly studied materials since its discovery in 1991 by Sumio Iijima. This is mainly due to its immense properties: many times stronger than steel, harder than diamond high electrical conductivity and thermal conductivity (Kumar et al. 2010). Consequently, researchers also find practical applications for CNTs, hence resulted to thousands of publications and patents about its production and application. CNTs have amazing range of applications but they have a limited success in the marketplace because of processing issues (Daenan et al. 2003). At this time, different methods were

developed. They were grouped into three which are laser ablation, arc discharge and chemical vapor deposition (CVD) (Daenan et al. 2003, Ebbesen et al. 1992, Iijima, 1991).

This study used microwave plasma-enhanced chemical vapor deposition process (MPECVD) to grow CNT from CO₂ with C₂H₂ as support carbon source gas. This is a type of a CVD process which uses microwave as a source of energy. In addition, plasma is formed during the process which excites and increases the collisions between the atoms within the gases resulting to higher decomposition of carbon sources. In spite of the fact that many researches sprouted since its discovery, still there is a need for

continuous study for modified methods in CNT growth, parameters and factors that may affect CNT structure and properties. Several studies using microwave and CVD process were already done by some researchers. Different factors and parameters were used in the aim that the best combination of these will be discovered to obtain high quality CNT as well as higher yield. This study focused on studying the effect of factors such as type of catalyst and substrate on the amount of CNT grown, purity, conversion of carbon source to carbon and CNT diameter.

MATERIALS AND METHODS

Different catalyst and substrates were used in this study. Nickel (Ni) and cobalt (Co) were used as catalysts, and iron plates (Fe) and silicon wafers (Si) as substrates. Catalyst solutions were prepared by dissolving separately nickel nitrate hexahydrate and Co powder to ethanol and PEG 400. Catalysts were deposited onto the substrates in different methods; dipping and spin coating. The goal is to evenly distribute a thin film catalyst onto the surface. From several preliminary runs, spin coating was found to be suitable for both substrates. After deposition, substrates with catalysts were calcined for 2 hours to convert catalysts to its metal oxide form. Reduction process was done to further reduce catalyst to its zero-valent form and to form islands in nanometer size. Substrates were then placed inside the reactor. Then, nitrogen gas was flown next. CO_2 and C_2H_2 were introduced into the system as carbon sources. When the system was stable, the oven was turned on

(power setting: 8 and temperature: 400 – 900°C). After the reaction, CNTs were formed on the substrate's surface. They were collected and analyzed through SEM to examine its morphology. They were also tested using X-ray Diffraction (XRD) to confirm its growth.

RESULTS AND DISCUSSION

After calcination and reduction, catalyst-substrates were analyzed using SEM analysis as shown in Figure 1. This figure shows that each catalyst was successfully deposited onto the substrate's surface. It reveals that nanosize catalyst islands were formed after reduction process which we need in the reaction to form nanosize carbon tubes.

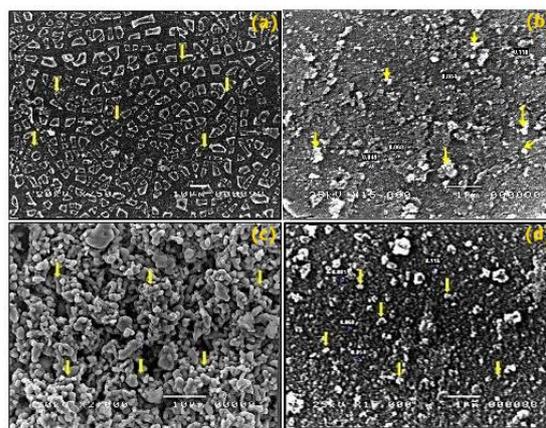


Fig. 1: Catalyst-Substrate SEM after Catalyst Deposition to Substrate (a) Ni-Fe (b) Ni-Si (c) Co-Fe (d) Co-Si

Though for Ni-Fe pair nanosize islands was not form which ranges from 1 – 5 um, still this will be reduce during the MPECVD process which involves higher temperature. Energy-dispersive x-ray (EDX) analysis also confirms deposition of

catalyst on the surface by showing the elemental composition of the surface. Results can be found in the work of Balean et al. (2012-2013). Figure 2 shows the SEM images from CNT grown from each catalyst-substrate pairs. It demonstrates that long small-diameter tubes were formed from MPECVD process.

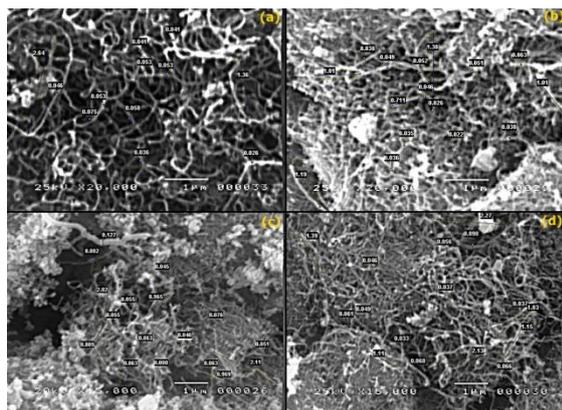


Fig. 2: CNT Images from SEM after MPECVD Process (a) Ni-Fe (b) Ni-Si (c) Co-Fe (d) Co-Si

Average diameters of CNTs are reported in Table 1. To support the claim that CNTs were indeed formed, XRD was conducted. Intensity peaks around 25 and 2 theta were observed in both chromatograms (Figure 3), where according to Cao et al. (2001), peaks around these values indicates CNT growth.

Table 1. Average Diameter of CNT Produced

Catalyst	Substrate	CNT Diameter (mm)
Ni	Fe	47.86
Ni	Si wafer	66.89
Co	Fe	72.50
Co	Si wafer	57.11

Experimental results are shown in Table 2. Note that the data presented in this table is not complete. Discussion of results was based from statistical analysis. For amount of CNT produced, Ni produced more CNT compared to Co. Amount of CNT is highly dependent on the catalytic activity of the catalyst used. This activity depends on electronic configuration specifically the number of electron vacancies in its d-orbitals as discussed in the study of Madix et al. (1978) and Esconjauregui et al. (2008).

When a transition metal is reacted with carbon it overlaps its d-orbitals with the p-orbitals of carbon (Sung et al. 1997). For carbon-metal interaction, fewer d-vacancies around two to four results to higher catalytic activity while larger d-vacancies. From the electron configuration

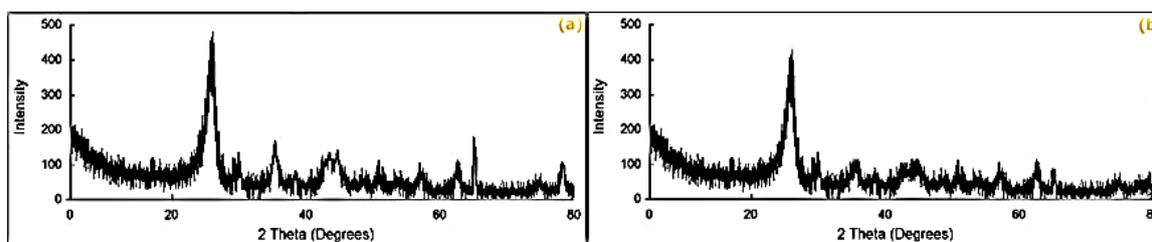


Fig. 3: XRD Analysis Chromatogram Results for (a) CNT Grown in Ni Catalyst (b) CNT Grown in Co Catalyst

Table 2. Experimental Results for CNT Grown using MPECVD Process

Catalyst	Substrate	CO ₂ /C ₂ H ₂ (% / %)	Wt. of CNT produced (mg)	CNT Purity (%)	Carbon conversion (%)
Ni	Fe	60/40	13.0	72.22	57.37
Ni	Fe	50/50	22.4	79.43	63.03
Ni	Fe	40/60	32.0	74.77	68.92
Ni	Si wafer	60/40	20.4	70.10	77.18
Ni	Si wafer	50/50	20.5	69.73	62.19
Ni	Si wafer	40/60	22.6	72.90	72.80
Co	Fe	60/40	11.8	70.24	41.16
Co	Fe	50/50	12.5	79.11	33.51
Co	Fe	40/60	12.9	78.66	29.45
Co	Si wafer	60/40	15.0	75.76	54.56
Co	Si wafer	50/50	17.2	73.50	55.81
Co	Si wafer	40/60	16.5	77.46	69.88

of both catalysts; Fe with 2 d-vacancies and Co with 3 d-vacancies; makes these catalysts highly reactive to carbon, thus producing high amount of product. In addition, the Gibbs energy of both catalysts were high: Ni higher than Co, signifying a more spontaneous reaction. These characteristics were also found in the study of Huang et al. (2002), Melechko et al. (2005), Awatashi et al. (2005), Esconjauregui et al. (2007) and Chesnokov et al. (2009). Furthermore, solubility and diffusion rate has something to do with the amount grown. The result was also affected by the increase in solubility and diffusion rate of carbon to both catalysts due to high temperature in MPECVD. This was also observed in the study of Kumar et al. (2010), solubility of carbon increases with high temperature. Another practical reason is the size of the catalyst island. Since formation of nano-sized catalyst island was successful, this resulted to high amount of product. In the study of Li et al. (2010), the CNT amount is highly

dependent in the size of catalyst-island. As noticed, after calcination and reduction, the size of catalyst in Ni-Fe pair is in microns, but still it formed CNTs. This catalyst island were further reduced during MPECVD process, wherein H₂ is present.

While for substrates, Si wafer produces more CNT. Appropriate catalyst deposition to the substrate is important because this will affect the CNT amount. Even distribution results to higher CNT amount. Comparison of each surface reveals that Si wafer is smoother than Fe. Hence, even distribution of catalyst solution was achieved in Si wafer compared to Fe where agglomeration and large catalyst island were formed. For purity, Co and Fe produced higher values compared to Ni and Si. However, from statistical analysis, these results show no significant difference, thus both catalysts and substrate gives the same effect. To compute for the carbon conversion values in Table 2, the influent and effluent gas were first analyzed using gas

chromatography (GC). From this, conversion is the gas composition that react divided by the input composition. Results show that Ni produced more carbon from carbon sources. This is due to the higher catalytic activity of Ni compared to Co. While for the substrate, Si wafer converted more carbon sources. This is because more catalyst was deposited onto the surface of Si, thus providing more active sites, resulting to more carbon source converted. From statistical analysis, these results showed significant difference. Examining the results for diameter in Table 1, Ni resulted to smaller CNT diameter. However from the statistical analysis, there is no significant difference between the results from Co. This implies that both catalysts have the same effect on the diameter. Both were reduced to its smallest size, which is important because CNT size is highly dependent on the catalyst size. The same statistical result was noticed from the substrates. Si wafer gave a smaller diameter. In fact, the effect of substrate is indirect. According to Ivanov et al. (1994) and Nagaraju et al. (2002), diameter is highly dependent on the catalyst dispersion on the substrate. Uniform distribution will prevent catalyst agglomeration. Catalyst agglomeration is not desirable because this will produce larger diameter. Due to the silicon surface, catalyst dispersion is more compared to Fe resulting to small and uniform catalyst islands.

CONCLUSIONS

CNTs were successfully grown by MPECVD process using nickel and cobalt catalysts from carbon dioxide and acetylene. This study focused on the effect of type of catalyst and substrate to amount of CNT grown, purity, carbon source conversion and diameter. Results were analyzed using statistical tools. From the results, it is seen that Ni is more suitable catalyst for growing CNT by MPECVD compared to Co in terms of amount. Ni presents a significant effect in the weight of CNT formed. On the other hand, Si wafer is better than Fe in terms of amount of CNT grown. Simultaneously, in terms of purity, there is no significant difference between the values resulting from both catalysts and substrates. Therefore, both catalysts and substrates are equally appropriate for CNT growth. Meanwhile, for the gas conversion, differences between the results were significant. From this, Ni allows more conversion of CO₂ and C₂H₂ to carbon compared to Co and Si wafer is better than Fe substrates. Lastly, Ni and Co, Fe and Si wafer are suitable catalysts and substrates respectively for CNT diameter. There is no significant difference from the analysis, hence both catalysts and substrates produces the same effect in diameter.

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