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MICROWAVE INDUCED PLASMA CHEMICAL VAPOR DEPOSITION SYNTHESIS OF CARBON NANOTUBES FROM CARBON DIOXIDE AND ACETYLENE AS CARBON SOURCE CATALYZED BY NICKEL, COBALT AND MOLYBDENUM*

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Abstract: Microwave Chemical Vapor Deposition (MCVD) process using domestic microwave oven was successfully used to grow carbon nanotubes (CNT) from carbon dioxide and acetylene. Nickel, cobalt and molybdenum were used as catalyst supported by iron, silicon wafer and alumina substrates. Different combination of this substrate and metallic catalyst were formulated and used to produce CNT with varying condition to determine the substrate-catalyst-reacting environment combination that will produce the best quality CNTs. It was found that Ni is the most appropriate catalyst compared to Co and Mo and Fe is the most suitable substrate compared to Si wafer and alumina. CNTs produced were analyzed using Scanning Electron Microscope, X-ray Diffraction (XRD) analysis and Energy-dispersive X-ray Spectroscopy (EDX). Effluent gas was analyzed using Gas Chromatography (GC).

Key Words: carbon nanotubes; microwave induced plasma; CNT metallic catalysts

1. INTRODUCTION

Since the discovery of carbon nanotubes (CNT) in 1991 by Sumio Iijima, it became the most intensively studied material because of its excellent mechanical and electrical and thermal properties (Ortega-Cervantez et al., 2005). There are three major methods for growing CNT and these are laser ablation, arc discharge and chemical vapor deposition (CVD) (Daenan et al., 2003; Ebbesen et al., 1992; Iijima et al., 1991). In this study Microwave Chemical Vapor Deposition (MCVD) method was used to synthesize CNT.

Generally, anything that has carbon can be used as carbon source for the production of CNT. In this study CO_2 and C_2H_2 were used as carbon sources. In the study of Khedr et al. (2008), Huh et al. (2005) and Policicchhio et al. (2006), acetylene was used to produce CNT. CO_2 was one of the newest carbon sources for the production of CNT and was already used by Xu et al. (2007).

* Some of the data, equations and method were presented in another paper by Fritzie Hannah Balean and Dr. Joseph Auresenia in 9th World Congress of Chmical Engineering, Korea

Combination of this substrate and metallic catalyst were formulated and used to

produce CNT with varying condition to determine the substrate-catalyst-reacting environment combination that will produce the best quality CNTs. The experiment was performed based from general factorial design of experiments. From this, input parameters such as ratio of carbon nanotubes and acetylene gas, catalyst (Ni, Co, Mo) and substrate (iron, alumina, silicon wafer) were investigated to determine the effects on the output variables such as amount of carbon nanotubes produced, diameter and length of CNTs, purity, and percent conversion of carbon source to carbon deposited. From the results of these experiments, the best combinations of factors that will result to highest carbon nanotubes deposited, highest aspect ratio, highest purity of CNTs produced and highest conversion of carbon source to carbon deposited was determined.

2. METHODOLOGY

Growth of CNT will be accomplished using MCVD process from carbon dioxide and acetylene. First step was the deposition of catalyst to the surface of the substrates. Irons plates and silicon wafer were cut to 1.3cm x 1.3 cm while alumina powders were formed into tablets. Catalyst was prepared by dissolving soluble salts in an appropriate solvent and spin coated in iron and silicon wafer substrates and spray-coated in alumina substrates. After deposition, substrates will be calcined in air-environment for 2 hours at 550^0C and reduced in a hydrogen-nitrogen environment for 1 hour at 450^0C. Figure 1 shows the catalyst-substrates after calcination and reduction.

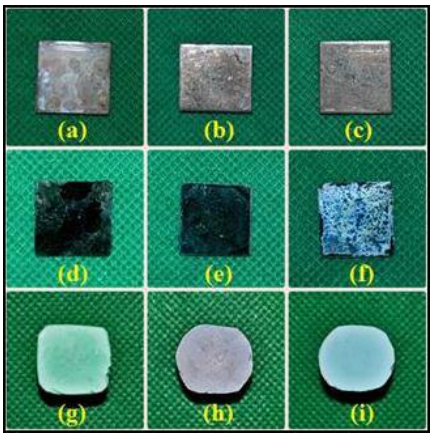

Figure 1. Catalyst and substrates after calcination and reduction

Substrates were stored in an air-tight container prior MCVD process. In MCVD process substrate was placed inside a quartz glass reactor. After that the system was made into vacuum up to 21 inHg gauge. Once vacuum condition is attained, the microwave oven was turned on at power setting of 8. Nitrogen gas which is the carrier gas will be flowed

inside the reactor. After a few minutes, controlled flowrates of CO_2 and C_2H_2 are introduced inside the reactor. Microwave induced plasma condition was attained and was observed as bright colorful glow inside the quartz reactor. The gases achieved the reactive plasma state and reacted forming CNTs on the substarte which contained the catalyst. After production, product was purified by oxidation process wherein samples are heated at 800^0C for 4 hours.

3. RESULTS AND DISCUSSION

Results of the productions are tabulated and summarized in Table 1. This includes weight of CNT produced, CNT Purity and carbon conversion. This was computed using equations 1 and 2. Weight of CNT produced is the weight of product after purification step.

$$\%\ pure\ (by\ weight) = \frac{W_{AP} - W_{BP}}{W_{BP}} x\ 100 \qquad \textbf{(Eq.1)*}$$

$$conversion\ (\%) = \left(\frac{V_{CO_2 \rightarrow C} + V_{C_2H_2 \rightarrow C}}{V_{CO_2,inlet} + V_{C_2H_2,inlet}}\right) * 100 \qquad \textbf{(Eq.2)*}$$

where:

W_{AP} = weight of the product after purification step
W_{BP} = weight of the product before purification step
$V_{CO_2 \rightarrow C}$ = volume of carbon dioxide converted to carbon
$V_{C_2H_2 \rightarrow C}$ = volume of acetylene converted to carbon
$V_{CO_2,inlet}$ = volume of carbon dioxide in inlet
$V_{C_2H_2,inlet}$ = volume of acetylene in inlet

Table 1. CNT production results

Run	Factor 1 Catalyst	Factor 2 Substrate	Factor 3 CO2/C2H2	Response 1 Wt. of CNT Produced	Response 2 CNT Purity	Response 3 Carbon Conversion
1	Nickel	Iron	60/40	13.0*	72.22*	67.71*
2	Nickel	Iron	50/50	22.4*	79.43*	76.93*
3	Nickel	Iron	40/60	32.0*	74.77*	84.09*
4	Nickel	Si wafer	60/40	20.4*	70.10*	74.61*
5	Nickel	Si wafer	50/50	20.5*	69.73*	77.57*
6	Nickel	Si wafer	40/60	22.6*	72.90*	69.19*
7	Nickel	Alumina	60/40	7.0	73.68	61.06
8	Nickel	Alumina	50/50	8.5	65.89	69.41
9	Nickel	Alumina	40/60	20.6	76.58	77.08
10	Cobalt	Iron	60/40	11.8	70.24	71.15
11	Cobalt	Iron	50/50	12.5	79.11	74.93
12	Cobalt	Iron	40/60	12.9	78.66	75.30
13	Cobalt	Si wafer	60/40	15.0	75.76	71.29
14	Cobalt	Si wafer	50/50	17.2	73.50	76.45
15	Cobalt	Si wafer	40/60	16.5	77.46	73.40
16	Cobalt	Alumina	60/40	14.0	75.68	77.35
17	Cobalt	Alumina	50/50	7.0	76.92	64.96
18	Cobalt	Alumina	40/60	13.1	71.58	75.49
19	Molybdenum	Iron	60/40	8.9	71.77	70.71
20	Molybdenum	Iron	50/50	13.5	68.18	73.64
21	Molybdenum	Iron	40/60	14.2	64.55	75.83
22	Molybdenum	Si wafer	60/40	14.8	67.58	75.55
23	Molybdenum	Si wafer	50/50	18.5	71.98	79.74
24	Molybdenum	Si wafer	40/60	17.8	73.55	77.12
25	Molybdenum	Alumina	60/40	3.8	71.70	42.32
26	Molybdenum	Alumina	50/50	10.9	71.71	74.84
27	Molybdenum	Alumina	40/60	2.5	73.53	62.02

Presence of CNT in the product was verified by XRD analysis shown in Figure 2. This figure shows peaks around 25 at 2 theta.

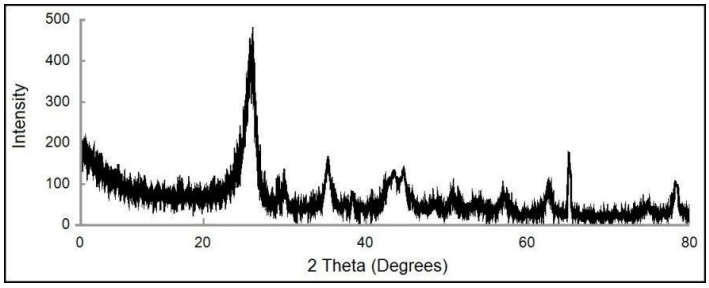

Figure 2. XRD Analysis for CNT produced*

Morphology of CNT produced was also studied using SEM analysis. SEM micrographs of products are shown in Figure 3 to 5. From these figure CNT grown were slightly curly and entangled and varied diameter and length. Average diameter is tabulated in Table 2.

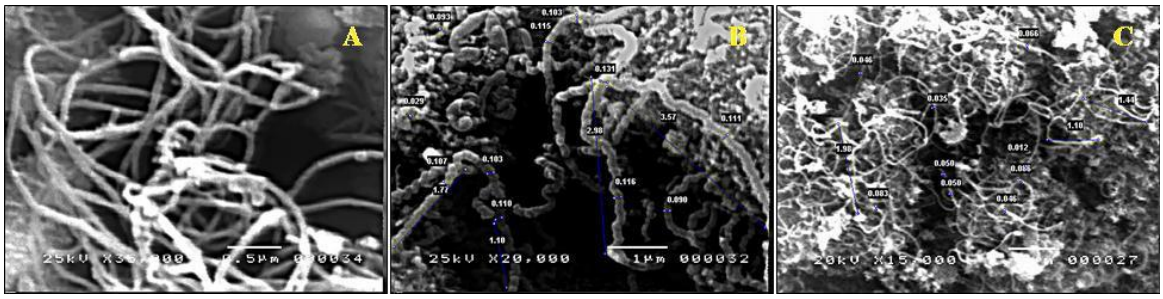

Figure 3. SEM Micrographs for CNT produced from (a) Ni-Fe *(b) Ni-Si *(c) Ni-Al_2O_3

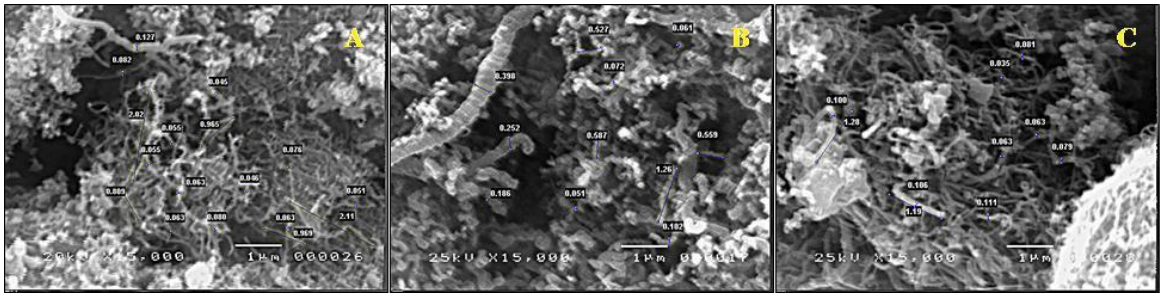

Figure 4. SEM Micrographs for CNT produced from (a) Co-Fe (b) Co-Si (c) Co- Al_2O_3

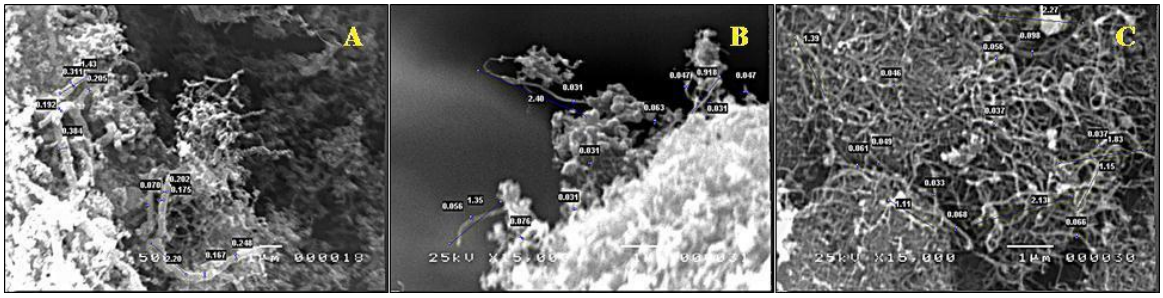

Figure 5. SEM Micrographs for CNT produced from (a) Mo-Fe (b) Mo-Si (c) Mo-Al_2O_3

Table 2. Average diameter of CNT grown

Sample	Factor 1 Catalyst	Factor 2 Substrate	Average Diameter (nm)
1	Nickel	Iron	46.43*
2	Nickel	Si wafer	65.75*
3	Nickel	Alumina	48.67
4	Cobalt	Iron	50.67
5	Cobalt	Si wafer	60.13
6	Cobalt	Alumina	82.14
7	Molybdenum	Iron	137.34
8	Molybdenum	Si wafer	98.75
9	Molybdenum	Alumina	170

Based from the experiment, highest weight of CNT produced was from combination of Ni-Fe-40/60 which was equal to 32 mg. Highest purity was from Ni-Fe50/50 producing 79.42% pure CNT. Highest carbon conversion was achieved from Ni-Fe40/60 which was equal to 84.09 %. Smallest diameter of CNT was grown from Ni-Fe combination.

Results were analyzed using statistical analysis. From the analysis, only catalyst and substrate has a significant effect on weight of CNT. Only catalyst has a significant effect on CNT purity and CNT diameter. And carbon ratios have no significant effect on 3 responses. Furthermore, there was no significant interactions between factors.

Analysis of gases was done using GC analysis and results are summarized in Figure 6. From the results, C_2H_2 conversion is always higher than the CO_2 to carbon conversion. Effluent gas was composed of unreacted N_2, CO_2, C_2H_2 and traces of CO in some runs.

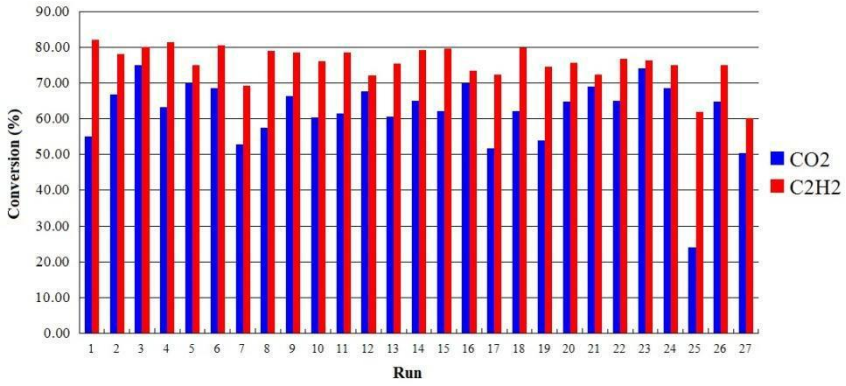

Figure 6. Summary of acetylene and carbon dioxide conversion

4. CONCLUSIONS

Curly and entangled CNT were formed from MCVD process using domestic microwave oven from carbon dioxide and acetylene. Nickel, cobalt and molybdenum actively act in catalyzing CNT growth. Average diameter of CNT ranges from 46.43 nm to 170 nm.

Based from the experiment highest weight of CNT produced was from combination of Ni-Fe-40/60. Highest purity was from Ni-Fe50/50. Highest carbon conversion was achieved from Ni-Fe40/60. Smallest diameter of CNT was grown from Ni-Fe combination. From these results, Ni is the most appropriate catalyst compared to Co and Mo and Fe is the most suitable substrate compared to Si wafer and alumina substrates.

5. ACKNOWLEDGEMENTS

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