Diamond & Related Materials 60 (2015) 81–86

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

The effects of catalyst pretreatment, growth atmosphere and temperature on carbon nanotube synthesis using Co–Mo/MgO catalyst

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ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 20 October 2015
Accepted 24 October 2015
Available online 28 October 2015

Keywords:
Carbon nanotube (CNT)
Chemical vapor deposition (CVD)
Co–Mo/MgO catalyst
Catalyst pretreatment atmosphere
CNT growth atmosphere
CNT growth yield

ABSTRACT

The growth of high quality and high yield carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CVD) of CH_4 over Co–Mo/MgO catalyst was investigated for different growth temperatures and H_2 flow rates. It was observed that CNT yield decreased with the H_2 flow rate, however, quality increased with increasing H_2 flow rate. CNT yield increased for the temperatures 850–950 °C but dropped significantly above 950 °C. In this study, the highest yield of 1526% was obtained at the growth temperature of 950 °C. The optimum H_2 flow rate was 200 sccm; this rate gave both high graphitization and high yield of product. Various CNT growth atmospheres including Ar, H_2 and the mixture of both gases were also analyzed and it was observed that the highest quality CNTs were obtained for both pretreatment and growth carried out with H_2. This gave a high yield of 292%. On the other hand, CNT growth carried out under Ar atmosphere gave higher CNT yield of 368%, however, the CNTs grown with Ar were more defective and had larger diameters.

Prime novelty statement: We demonstrate a sorbitol added catalysis synthesis method and importance of the ideal growth conditions to improve high quality single walled carbon nanotube yield up to 1500%.

1. Introduction

Catalytic chemical vapor deposition (CVD) is the dominant method to produce CNTs because of its high efficiency [1,2]. The main challenge is to obtain high yield of product with high crystalline structure. The scaled-up and reliable production of CNTs offers a wide range of possibilities to synthesize CNT for various applications such as memory devices [3], MEMs/NEMs [4], hydrogen storage [5], electrochemical actuators [6], and sensor applications [7–11].

The key parameters in CNT growth by CVD are the catalyst material [12], growth temperature [13,14], growth time [15], composition and the flow rate of the carrier and hydrocarbon gases [16].

The gas environment in CVD growth of CNT is an important parameter for final quality and yield [17–19]. In general, CNTs grown by the CVD method are found to be covered by amorphous carbon, therefore a diluting gas is needed to etch away amorphous carbon formation and prevent the catalyst from being poisoned. These gases are also used to control the decomposition rate while providing a suitable environment for the growth process. The gas composition also affects the CNT size, structure, morphology, and areal nanotube density [20–25]. Commonly used ambient gases are N_2 [24], H_2 [26] and Ar [27–29].

H_2 treatment affects the CNT synthesis [30]. A low areal density of CNTs was obtained when there was no H_2 pretreatment, whereas, the catalyst particles agglomerated with very long H_2 pretreatment leading to very low quality CNT growth. H_2 is also essential for CNT growth [31], and it provides the activity of catalyst particles and optimization of CNT growth by adjusting reaction rate. The role of H_2 in determining the final CNT quality through its effect on the catalyst crystal structure and morphology was also confirmed [32]. By increasing H_2 amount CNT mean diameter can be dramatically decreased at high growth temperatures [33]. The growth mechanism of CNTs was studied in terms of the moderate etching of carbon deposited by hydrogen species and it was confirmed that hydrogen species etched the amorphous carbon deposited on the catalyst nanoparticles [34–35].

Appropriate growth temperature also is a key parameter in high quality CNT growth [13,36–40]. The growth rate, diameter, areal density, and crystallinity of CNT can be optimized with the growth temperature. The effects of growth temperature on the microstructure of CNTs grown at 600–750 °C by using the $Fe(CO)_5$–C_2H_2–H_2 system was studied [41]. It was found that the CNT length increased with the growth temperature up to 700 °C, and then quickly decreased at 750 °C. At higher temperatures, the formation of defect-free graphitic layers increases while at lower temperatures the graphitization degree decreases and amorphous carbon formation occurs [42].

In this study, the effect of H_2 flow rate and temperature on CNT yield and quality was examined on Co–Mo/MgO catalyst using CH_4 as

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http://dx.doi.org/10.1016/j.diamond.2015.10.025
0925-9635/

a carbon precursor. Various catalyst pretreatment and CNT growth atmospheres were studied and best environment for both pretreatment and growth processes was searched.

2. Materials and methods

In the present study, CNTs were synthesized over Co–Mo/MgO nanocatalyst particles which were prepared by the gel-combustion method [43]. The molar ratio of Co:Mo:MgO was 0.5:0.25:10 which corresponds to 1.06 wt.% Co and 0.86 wt.% Mo in the initial gel. For the preparation of the catalyst, $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_5Mo_7O_{24} \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ salts and $C_6H_{14}O_6$ (sorbitol) were dissolved in deionized water. Then, the solution was dried at 100 °C for 3 h to produce a uniform gel. This step was followed by a flash calcination of the gel in an oven at 550 °C for 30 min. Then, the material was grounded into a powder in a mortar. The powder was sieved with meshes of sizes between 75–250 μm. The catalyst particles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

CNTs were synthesized by the thermal CVD method at atmospheric pressure in a quartz tube of 1 in. diameter. A catalyst amount weighing 15.0 mg was used in each run for CNT growth. Carbon source was CH_4 and it was diluted with H_2 and/or Ar at different flow rates. The temperature during the catalyst pretreatment step was ramped to 850 °C with a rate of 5 °C/min and kept at this temperature for 1 h. Then, the temperature was set to the CNT growth temperature with the same rate. Carbon source was CH_4 and Ar, H_2 or Ar–H_2 mixture was sent to the system to dilute CH_4 during the CNT growth. For all sets of experiments CNT growth time was kept for 40 min and to terminate the growth, CH_4 flow was stopped and the system was left to cool under the same flow of gases sent for the pretreatment process. Obtained product was weighed for yield calculation. Yield of CNTs was calculated using the formula of $[(W_{out}-W_{in})/W_{in}]\cdot 100\%$, where W_{in} was the weight of the catalyst before reaction and W_{out} was the weight of the CNT product after subtracting the weight of amorphous carbon calculated using TGA data.

Catalyst was pretreated under H_2 atmosphere and after this reduction process, temperature was increased to CNT growth temperature for growth temperatures higher than 850 °C. The studied growth temperatures were 850, 900, 950, 1000 °C. At the growth stage, 50 sccm CH_4 and H_2 with different flow rates were sent into the system for 40 min. The investigated H_2 flow rates were 50,100,150 and 200 sccm.

After CNT growth temperature and H_2 ratio, CNT growth atmosphere was investigated. At catalyst pretreatment process Ar, H_2 and Ar–H_2 mixture were examined using total gas flow of 200 sccm. Then, temperature was raised to the CNT growth temperature of 1000 °C. The CNT growth was investigated under Ar, H_2 and Ar–H_2 mixture, possibly different from the pretreatment, keeping the total gas flow at 250 sccm for 40 min, and including a CH_4 flow with different flow rates. CNT growth temperature was kept at 1000 °C.

CNT growths were analyzed with SEM, thermo-gravimetric analysis (TGA), Raman spectroscopy, and transmission electron microscopy (TEM).

3. Results and discussion

A SEM image of the Co–Mo/MgO catalyst is given (Fig. 1a). The catalyst consisted of flake-like particles with sizes ranging between 75–250 μm. The XRD scan of catalyst particles (Fig. 1b) gave peaks associated with the MgO support particles. There was no observable peak for Co or Mo. This could be due to their nanometer size and high dispersion of Co and Mo throughout MgO.

3.1. The effects of growth temperature and hydrogen flow rate

Fig. 2 displays SEM images of CNTs synthesized under different growth temperatures and H_2 flow rates of 200 sccm. Under the growth conditions studied here, all samples had a high CNT population. SEM analysis pointed that growth temperature was a significant parameter on CNT structural quality. The effect of temperature on the morphology of CNTs was that at low temperatures as-grown CNTs were often found in a tangled form which was an indication of larger number of structural defects compared to that of straight CNTs. Therefore, the critical challenge was to improve the quality of CNTs. With increasing growth temperature, the amount of tangled CNTs decreased and at a temperature of 1000 °C CNTs were much more ordered and untangled for all H_2 flow rates.

Increasing H_2 flow rate also effected CNT morphology for all temperatures studied in this work. The quality of the tubes was improved when H_2 flow was increased from 50 sccm to 200 sccm for all four growth temperatures. The highest crystal quality nanotubes were grown at a growth temperature of 1000 °C and under H_2 flow rate of 200 sccm (Table 1).

Fig. 3 shows the Raman spectra of CNTs at different growth temperatures at H_2 flow of 200 sccm. The quality of the as-grown CNTs was studied by Raman spectroscopy. The low intensity of the D-band (1340 cm^{-1}) relative to the G-band (1580 cm^{-1}) indicated a very low defect density and high crystallinity of the sample grown at 1000 °C. At lower growth temperatures disorder level increased. For all four growth temperatures RBM peaks were observed at 150 and 200 sccm H_2 flow rate. Different RBM peaks appeared in the wavenumber range of 100–300 cm^{-1} with different excitation wavelengths as they came to resonance with different phonon modes of various chiralities [44]. Generally samples grown under low H_2 flow rates did not have RBM peaks. This indicated that higher H_2 flow rates were more appropriate for SWCNT growth.

The ratios of I_G/I_D of the CNTs are given in Table 1. At 850 °C the lowest I_G/I_D ratios were observed indicating the highly disordered tubes,

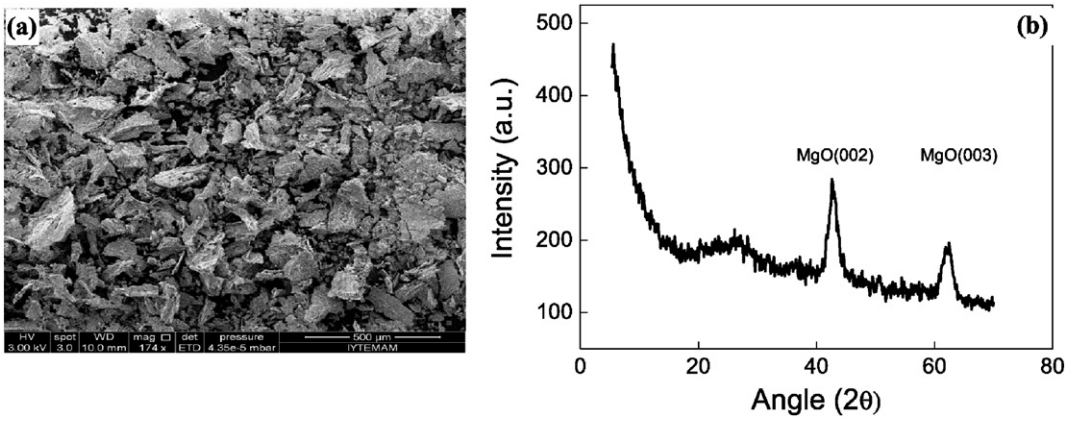

Fig. 1. (a) SEM image and (b) XRD scan of Co–Mo/MgO catalyst.

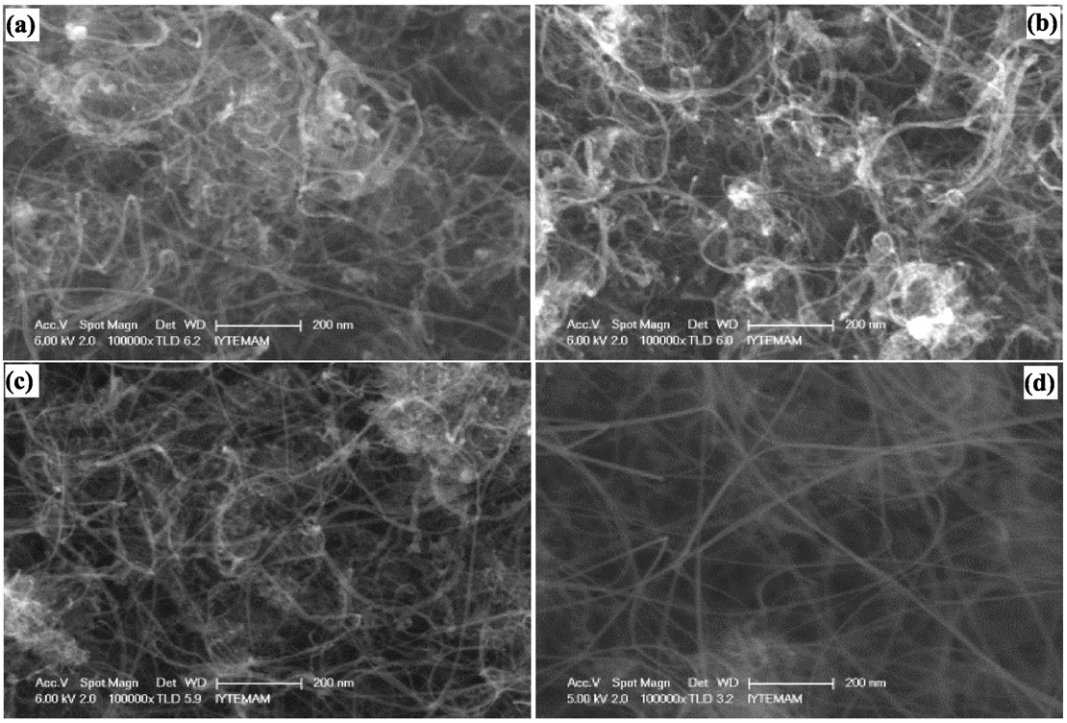

Fig. 2. SEM pictures of CNTs grown at (a) 850, (b) 900, (c) 950, and (d) 1000 °C under 200 sccm hydrogen flow; all scale bars are 200 nm.

high amorphous carbon content and hence, lower quality CNTs with respect to other growth temperatures. At 900 °C I_G/I_D ratios increased relative to 850 °C and with increasing H_2 flow rate less defective and hence, higher quality CNTs were observed. At 950 °C, all H_2 flow rates yielded I_G/I_D ratios relatively higher compared to other growth temperatures. When the results of 1000 °C growth were analyzed, it was noted that for this temperature and for all H_2 flow rates used at this temperature CNT quality was quite high. The highest I_G/I_D ratio of 13.63 for this study was obtained at 1000 °C and 200 sccm H_2 flow rate.

TGA analysis was carried out in order to obtain the deposited carbon content of the product. Amorphous carbon amounts are given in Table 1. Amorphous carbon content monotonically decreased with increasing growth temperature. CNTs grown under 850 °C gave larger amount of amorphous carbon compared to the other temperatures. The lowest amorphous contents were observed at growth temperature of 1000 °C.

Table 1
Raman I_G/I_D, amorphous carbon ratios and yields of CNTs.

Catalyst pretreatment conditions	CNT growth conditions		Amorphous carbon %	Raman I_G/I_D ratio	Yield %
H_2 (sccm)	H_2 (sccm)	Temperature (°C)			
50	50	850	16.4	1.85	825
100	100		16.2	1.57	816
150	150		27.5	3.53	678
200	200		7.8	2.63	795
50	50	900	8.6	1.56	1501
100	100		7.6	3.18	1094
150	150		8.4	5.89	1024
200	200		5.8	6.11	1093
50	50	950	8.2	5.64	722
100	100		6.7	4.64	635
150	150		8.2	5.70	489
200	200		2.3	7.01	1526
50	50	1000	3.5	3.25	779
100	100		3.9	5.57	397
150	150		–	5.87	339
200	200		3.1	13.63	292

When the amount of amorphous carbon formed under different H_2 flow rates was compared, it was observed that at high H_2 flow CNT amount increased. The highest quality CNT amount was synthesized under 200 sccm H_2 flow for all CNT growth temperatures.

Raman spectra, TGA and SEM data were in good agreement assessing the quality of CNTs; the disorder level decreased with increasing temperature and increasing H_2 flow rate.

The yields of growths also are given in Table 1. The highest CNT yield was obtained at 950 °C under 200 sccm H_2 and the obtained yield was very high: 1526%. It was observed that 950 °C was an optimum temperature to obtain the highest yield. On the other hand, the low yield obtained at 1000 °C might be due to the possible changes in the character of the catalyst material with the temperature. Highly reactive

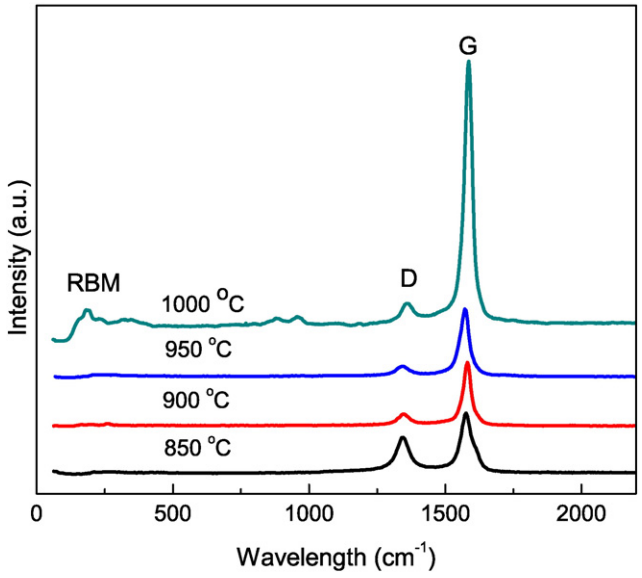

Fig. 3. Raman spectra of as-grown CNTs grown at (a) 850, (b) 900, (c) 950, and (d) 1000 °C at H_2 flow of 200 sccm.

Table 2
Amorphous carbon amounts and yields of CNTs grown under different pretreatment and growth atmospheres.

Catalyst pretreatment atmosphere		CNT growth atmosphere			Amorphous carbon %	Yield %
H_2 (sccm)	Ar (sccm)	CH_4 (sccm)	H_2 (sccm)	Ar (sccm)		
200	–	50	200	–	2.8	292
–	200				7.9	93
10	190				3.2	243
200 (at pretreatment)[a]	200 (at heating)				6.7	67
200	–	20	20	210	4.4	140
–	200				6.9	41
10	190				5.9	174
200 (at pretreatment)[a]	200 (at heating)				6.3	68
200	–	40	–	210	3.1	349
–	200				2.0	172
10	190				2.1	237
200 (at pretreatment)[a]	200 (at heating)				1.9	368

[a] Pretreated differently: Heated up to 850 °C under Ar and kept at 850 °C under H_2 for 1 h, then switched to Ar.

conditions at very high temperature (above 950 °C) might deactivate the catalyst before all metal particles were completely reduced. Below 1000 °C the number of reduced catalyst particles increased with increasing temperature, which might increase yield with increasing temperature. In this study, very high yield of CNT was obtained and it is very important for CNT commercial applications.

3.2. CNT growth under different pretreatment and growth atmospheres

Three different CNT growth conditions were investigated in this study. In the growth stage Ar, H_2 and the mixture of both gases were added in turn to CH_4. Four different catalyst pretreatment conditions were examined for all three growths (Table 2).

Fig. 4a displays a SEM image of the sample synthesized under H_2 pretreatment and H_2 growth. It shows that CNTs were straight and nontangled. The TEM observation of CNTs (Fig. 4b) indicated high structural quality (less defective tubes). The growths consisted of both SWCNTs and MWCNTs. There was no catalyst particles observed inside the CNTs.

Raman spectrum of the same sample is given in Fig. 5. The low intensity of the D-band relative to the G-band showed a very low defect density and high crystallinity of this sample. Raman spectra collected at several points on this sample resulted in RBM peaks which indicated that the CNT growth mainly consists of SWCNTs.

The TGA curve of the sample gave highest I_G/I_D ratio in Raman spectroscopy taken under an O_2 atmosphere is given in Fig. 6. The significant weight loss between 500 and 600 °C is due to the carbon nanotubes; both SWCNTs and MWCNTs are oxidized between 500 °C and 600 °C [45]. The oxidation temperature of amorphous carbon is between 200 °C and 450 °C. A very small decrease in weight in TGA curves within this temperature range indicates extremely low level of amorphous carbon formation, 2.8%.

Obtaining a large amount of product for a given amount of catalyst is very important for many applications. Yields and amorphous carbon amounts for each sample are given (Table 2). The yields were 292% for the H_2 pretreatment, 243% for the Ar + H_2 mixture pretreatment and below 100% for both the Ar-only and the Ar followed by H_2 pretreatment conditions. In terms of CNT yield and structural quality, for the H_2 growth condition, pretreatment in pure H_2 atmosphere had the highest yield and least amount of impurities. This could be due to reduction of metal oxide to metal catalyst during the pretreatment process as metal nanoparticles are more suitable for CNT growth.

In terms of both yield and quality, Ar + H_2 atmosphere growth condition yielded CNTs with characteristics generally inferior to those of CNTs grown under H_2 atmosphere. The highest product yield of all growth conditions was observed in growths carried under Ar atmosphere. However, SEM images showed that the mean diameters were larger than the previous two growth conditions containing H_2.

Amorphous carbon amount of the samples was calculated from TGA graphs and given in Table 2. The results indicated that catalyst particle reduction by H_2 during pretreatment provided samples with lower amorphous carbon content. However, if H_2 flow continued during growth stage after H_2 pretreatment, H_2 prevented amorphous carbon formation during growth process, but if Ar taken place at growth after H_2 pretreatment, then amorphous carbon amount increased. Another analyzed combination is both pretreatment and growth taken place under Ar atmosphere. CNTs with larger diameters were obtained. However, amorphous carbon ratio was lower. Observation of low amorphous carbon content may also be attributed to the well-known annealing effect of an an inert atmosphere at high temperatures [29]; Ar increases the purity of the treated material by eliminating amorphous

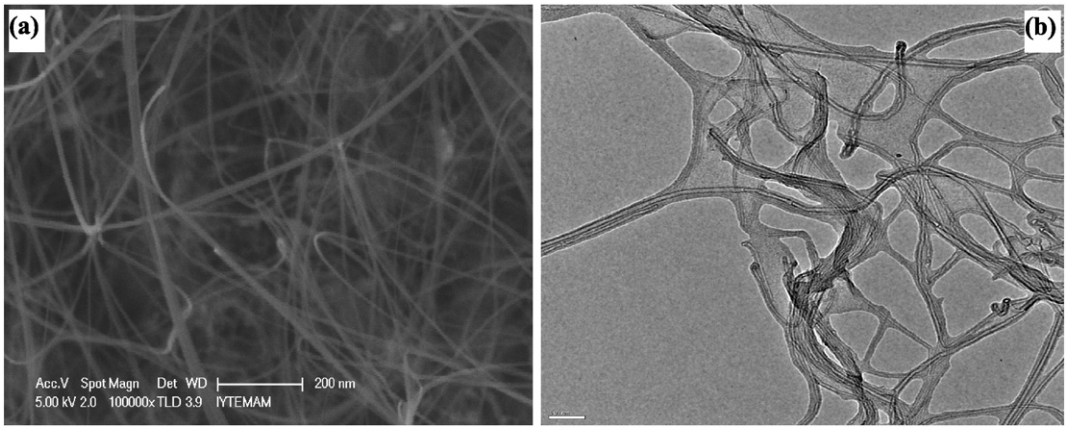

Fig. 4. (a) SEM image and (b) TEM image of the sample pretreated and grown under H_2 atmosphere.

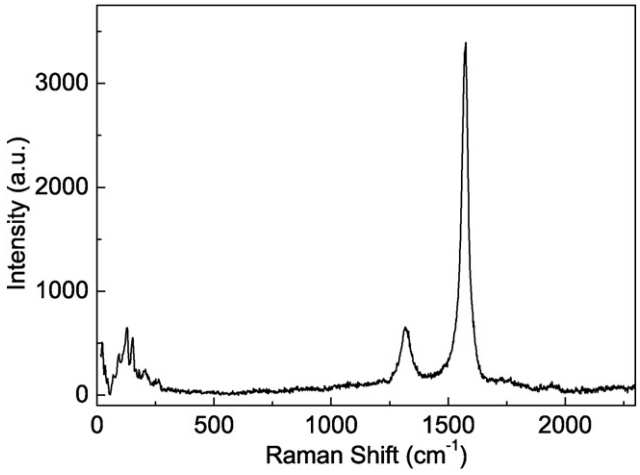

Fig. 5. Raman spectrum of the sample pretreated and grown under H_2 atmosphere at flow of 200 sccm.

carbon and other non-desired materials, which therefore improves the purity of the synthesized CNTs.

Raman spectra I_G/I_D ratios are plotted against pretreatment and growth parameters in Fig. 7. I_G/I_D ratios indicated that the growth carried out under H_2 atmosphere gave very small disorder level for all four pretreatment conditions. On the other hand, growths carried under Ar + H_2 atmosphere showed higher disorder level for both H_2 and Ar pretreatments. However, Ar + H_2 and H_2 for 1 h pretreatments resulted with relatively higher graphitization. For growths under Ar atmosphere, the highest graphitization was obtained for H_2 for 1 h pretreatment. The disorder level increased when Ar only pretreatment was applied. CNTs obtained under Ar growth atmosphere were more disordered, compared to those obtained under H_2 and Ar + H_2 growth atmospheres with the same pretreatment conditions. As a result, the highest I_G/I_D ratio was obtained for the sample grown with H_2 pretreatment followed by H_2 atmosphere growth.

Rashidi et al. synthesized Co–Mo/MgO catalyst using different organic additives and tested these catalysts for CNT growth. Among investigated organic additives, sorbitol gave the best results in terms of CNT quality and yield. Obtained CNT was single walled with yield of 180 wt.% and Raman I_G/I_D value of 9.3 [43]. The results presented in our study represent an extremely high yield SWCNT growth with 292 wt.% yield value by using Co–Mo/MgO catalyst synthesized by the gel-combustion method using sorbitol as organic additive and CH_4 as a carbon precursor at 1000 °C. However, in this study, by decreasing the CNT growth temperature to 850 °C, yield was increased higher

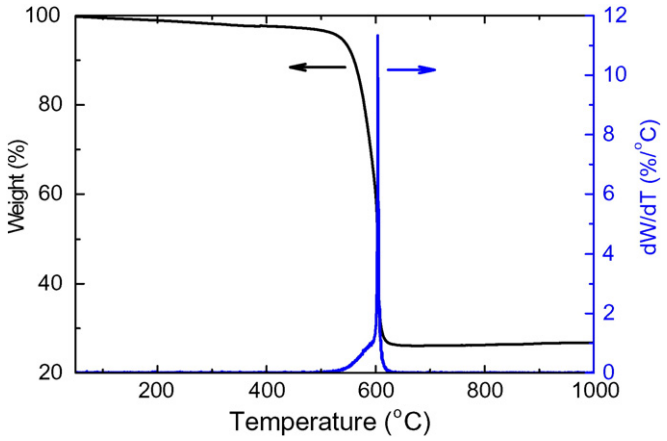

Fig. 6. TGA–DTA curve of the sample pretreated and grown under H_2 atmosphere.

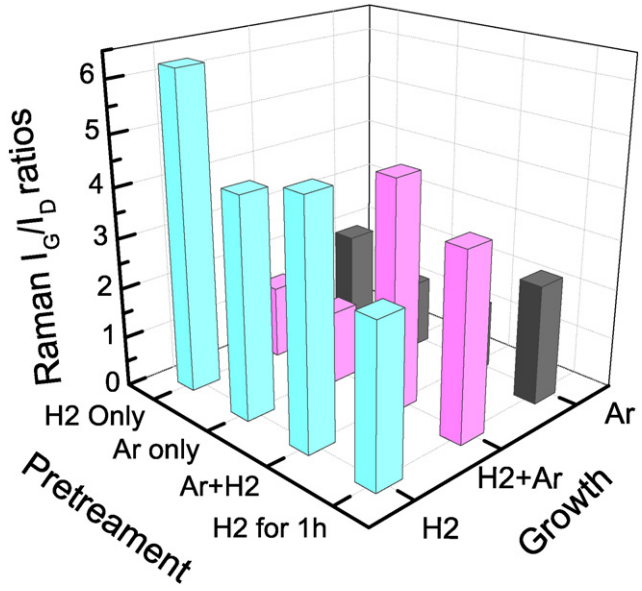

Fig. 7. Raman I_G/I_D ratios of CNTs grown under H_2, Ar + H_2 and Ar atmospheres at 1000 °C for 40 min for four different catalyst pretreatment conditions.

than 1500 wt.%. There is a significant correspondence between high growth temperatures and high crystalline quality for CH_4 catalytic decomposition, therefore, graphitization decreased at lower growth temperatures. In our study, the solution of this problem was found with H_2 positive effect on CNT crystalline quality. As seen from Raman spectra even at low growth temperatures Raman I_G/I_D ratios were high indicating a good graphitization degree at high H_2 flow rates. In the absence of H_2 yield and quality both decreased. Yeoh et al. obtained 304 wt.% MWCNT yield with Co–Mo/MgO catalyst using citric acid as organic additive at 800 °C [46] using N_2 as an ambient gas for catalyst pretreatment and CNT growth processes. In literature large scale MWCNT synthesis was available with different catalysts. MWCNT with 4–7 wall number was achieved by catalytic decomposition of CH_4 on Fe-Mo/MgO catalyst with 450 wt.% yield [47]. Using Ni–Mo/MgO catalyst synthesized by the combustion method using polyethylene glycol 200 (PEG200) as combustion additive and H_2–CH_4 mixture for CNT growth MWCNTs with 9–20 nm diameter were synthesized. Obtained yield with this Ni–Mo/MgO catalyst was about 4500 wt.% [48]. Milone et al. investigated the effect of Co phase on the on CNT growth [49]. Catalytic behavior of physically mixed CoO/MgO + $MgMoO_4$ and $CoMoO_4$ + $MgMoO_4$ was studied and citric acid was used as combustion additive. They found that the crystalline phase of Co was also important for large scale CNT production. Co in the form of $CoMoO_4$ + $MgMoO_4$ gave the best result with 2407 wt.% MWCNT yield. Overall, our study was in agreement with literature about the catalytic activity of Co–Mo/MgO catalyst for CNT growth. However, compared to other studies sorbitol as an organic additive for the combustion method provided SWCNT with high quality. Different catalyst pretreatment and CNT growth conditions were investigated in this study and large scale SWCNT growth was obtained and improved by using H_2 and high temperature positive effects on CNT yield and quality.

4. Conclusion

CNT quality and yield were affected by growth temperature, atmosphere and pretreatment. High growth temperatures (950 and 1000 °C) provided high structural quality CNT growth, however, CNT yield was higher at lower temperatures. At H_2 flow rates, higher quality, straighter, and largely amorphous carbon free CNTs were obtained. For the growth parameters used in this study, the maximum yield of 1526%,

and of high quality, with I_G/I_D ratio of 7.01 CNTs were obtained at 950 °C under 200 sccm H_2 flow rate.

H_2 was found to be necessary for both pretreatment and growth atmosphere for high quality CNT growth. H_2 provided cleaner and higher crystalline CNT formation. It reduced carbonaceous product formation at growth stage. Using Ar CNT yield could be increased, but the growth resulted with larger diameter CNTs with more defects.

Acknowledgments

This study was supported by funding from projects 2008IYTE35 and 105T462. We thank IYTE Material Research Center for SEM images.

References

[1] J.-F. Colomer, C. Stephan, S. Lefrant, G.V. Tendeloo, I. Willems, Z. Konya, A. Fonseca, C. Laurent, J.B. Nagy, Large-scale synthesis of single-wall carbon nanotubes by catalytic chemical vapor deposition (CCVD) method, Chem. Phys. Lett. 317 (1) (2010) 83–89.
[2] V. Shanov, W. Cho, R. Malik, N. Alvarez, M. Haase, B. Ruff, N. Kienzle, T. Ochmann, D. Mast, M. Schulz, CVD growth, characterization and applications of carbon nanostructured materials, Surf. Coat. Technol. 230 (2013) 77–86.
[3] A. Star, Y. Lu, K. Bradley, G. Gruner, Nanotube optoelectronic memory devices, Nano Lett. 4 (9) (2004) 1587–1591.
[4] X. Zang, Q. Zhou, J. Chang, Y. Liu, L. Lin, Graphene and carbon nanotube (CNT) in MEMS/NEMS applications, Microelectron. Eng. 132 (2015) 192–206.
[5] Z. Ozturk, C. Baykasoglu, A.T. Celebi, M. Kirca, A. Mugan, A.C. To, Hydrogen storage in heat welded random CNT network structures, Int. J. Hydrog. Energy 40 (1) (2015) 403–411.
[6] Y. Yun, V. Shanov, Y. Tu, M.J. Schulz, S. Yarmolenko, S. Neralla, J. Sankar, S. Subramaniam, A multi-wall carbon nanotube tower electrochemical actuator, Nano Lett. 6 (4) (2006) 689–693.
[7] D.W. Kim, J.S. Lee, G. Lee, L.J. Overzet, M.E. Kozlov, A. Aliev, Carbon nanotubes based methanol sensor for fuel cells application, J. Nanosci. Nanotechnol. 6 (11) (2006) 3608–3613.
[8] Y.M. Wong, W.P. Kang, J.L. Davidson, A. Wisitsora-at, K.L. Soh, A novel microelectronic gas sensor utilizing carbon nanotubes for hydrogen gas detection, Sensors Actuators B Chem. 93 (1) (2003) 327–332.
[9] P. Mishra, S. Islam, Trace level ammonia sensing by SWCNTs (network/film) based resistive sensor using a simple approach in sensor development and design, Int. Nano Lett. 3 (1) (2013) 1–9.
[10] I.V. Anoshkin, A.G. Nasibulin, P.R. Mudimela, M. He, V. Ermolov, E.I. Kauppinen, Single-walled carbon nanotube networks for ethanol vapor sensing applications, Nano Res. 6 (2) (2013) 77–86.
[11] L.-C. Wang, K.-T. Tang, I.-J. Teng, C.-T. Kuo, C.-L. Ho, H.-W. Kuo, T.-H. Su, S.-R. Yang, G.-N. Shi, C.-P. Chang, A single-walled carbon nanotube network gas sensing device, Sensors 11 (8) (2011) 7763–7772.
[12] A.C. Dupuis, The catalyst in the CCVD of carbon nanotubes—a review, Prog. Mater. Sci. 50 (8) (2005) 929–961.
[13] C.J. Lee, J. Park, Y. Huh, J.Y. Lee, Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition, Chem. Phys. Lett. 343 (1) (2001) 33–38.
[14] M.A. Pasha, R. Poursalehi, M.A. Vesaghi, A. Shafiekhani, The effect of temperature on the TCVD growth of CNTs from LPG over Pd nanoparticles prepared by laser ablation, Phys. B Condens. Matter 405 (16) (2010) 3468–3474.
[15] Q.W. Li, X.F. Zhang, R.F. DePaula, L.X. Zheng, Y.H. Zhao, L. Stan, T.G. Holesinger, P.N. Arendt, D.E. Peterson, Y.T. Zhu, Sustained growth of ultralong carbon nanotube arrays for fiber spinning, Adv. Mater. 18 (23) (2006) 3160–3163.
[16] A. Okita, Y. Suda, A. Oda, J. Nakamura, A. Ozeki, K. Bhattacharyya, Effects of hydrogen on carbon nanotube formation in CH_4H_2 plasmas, Carbon 45 (7) (2007) 1518–1526.
[17] D. Nishide, H. Kataura, S. Suzuki, K. Tsukagoshi, Y. Aoyagi, Y. Achiba, High-yield production of single-wall carbon nanotubes in nitrogen gas, Chem. Phys. Lett. 372 (1) (2003) 45–50.
[18] E. Borowiak-Palen, E. Borowiak-Palen, T. Pichler, X. Liu, M. Knupfer, A. Graff, O. Jost, W. Pompe, R.J. Kalenczuk, J. Fink, Reduced diameter distribution of single-wall carbon nanotubes by selective oxidation, Chem. Phys. Lett. 363 (5) (2002) 567–572.
[19] H. Yu, Q. Zhang, Q. Zhang, Q. Wang, G. Ning, G. Luo, F. Wei, Effect of the reaction atmosphere on the diameter of single-walled carbon nanotubes produced by chemical vapor deposition, Carbon 44 (9) (2006) 1706–1712.
[20] M. Bell, K. Teo, W. Milne, Factors determining properties of multi-walled carbon nanotubes/fibres deposited by PECVD, J. Phys. D. Appl. Phys. 40 (8) (2007) 2285.
[21] J.B.O. Caughman, L.R. Baylor, M.A. Guillorn, V.I. Merkulov, D.H. Lowndes, L.F. Allard, Growth of vertically aligned carbon nanofibers by low-pressure inductively coupled plasma-enhanced chemical vapor deposition, Appl. Phys. Lett. 83 (6) (2003) 1207–1209.
[22] T.Y. Lee, J.-H. Han, S.H. Choi, J.-B. Yoo, C.-Y. Park, T. Jung, Effects of source gases on the growth of carbon nanotubes, Diam. Relat. Mater. 12 (3) (2003) 851–855.
[23] P.E. Nolan, D.C. Lynch, A.H. Cutler, Carbon deposition and hydrocarbon formation on group VIII metal catalysts, J. Phys. Chem. B 102 (21) (1998) 4165–4175.
[24] D.J. Yang, Q. Zhang, S.F. Yoon, J. Ahn, S.G. Wang, Q. Zhou, Q. Wang, J.Q. Li, Effects of oxygen and nitrogen on carbon nanotube growth using a microwave plasma chemical vapor deposition technique, Surf. Coat. Technol. 167 (2) (2003) 288–291.
[25] K.B.K. Teo, Catalytic synthesis of carbon nanotubes and nanofibers, Encycl. Nanosci. Nanotechnol. 10 (1) (2003).
[26] T.D. Makris, L. Giorgi, R. Giorgi, N. Lisi, E. Salernitano, CNT growth on alumina supported nickel catalyst by thermal CVD, Diam. Relat. Mater. 14 (3) (2005) 815–819.
[27] H. Ago, N. Uehara, N. Yoshihara, M. Tsuji, M. Yumura, N. Tomonaga, T. Setoguchi, Gas analysis of the CVD process for high yield growth of carbon nanotubes over metal-supported catalysts, Carbon 44 (14) (2006) 2912–2918.
[28] Q. Liu, Y. Ouyang, L. Zhang, Y. Xu, Y. Fang, Effects of argon flow rate and reaction temperature on synthesizing single-walled carbon nanotubes from ethanol, Physica E 41 (7) (2009) 1204–1209.
[29] C. Vallés, M. Pérez-Mendoza, W.K. Maser, M.T. Martínez, L. Alvarez, J.L. Sauvajol, A.M. Benito, Effects of partial and total methane flows on the yield and structural characteristics of MWCNTs produced by CVD, Carbon 47 (4) (2009) 998–1004.
[30] H.-C. Wen, K. Yang, K.-L. Ou, W.-F. Wu, R.-C. Luo, C.-P. Chou, Carbon nanotubes grown using cobalt silicide as catalyst and hydrogen pretreatment, Microelectron. Eng. 82 (3) (2005) 221–227.
[31] G.Y. Xiong, Y. Suda, D.Z. Wang, J.Y. Huang, Z.F. Ren, Effect of temperature, pressure, and gas ratio of methane to hydrogen on the synthesis of double-walled carbon nanotubes by chemical vapour deposition, Nanotechnology 16 (4) (2005) 532.
[32] M.J. Behr, E.A. Gaulding, K.A. Mkhoyan, E.S. Aydil, Effect of hydrogen on catalyst nanoparticles in carbon nanotube growth, J. Appl. Phys. 108 (5) (2010) (053303–053303-053308).
[33] M. Aksak, Y. Selamet, Carbon nanotube diameter tuning using hydrogen amount and temperature on SiO_2/Si substrates, Appl. Phys. A 100 (1) (2010) 213–222.
[34] S.-i. Honda, M. Katayama, K.-Y. Lee, T. Ikuno, S. Ohkura, K. Oura, H. Furuta, T. Hirao, Low temperature synthesis of aligned carbon nanotubes by inductively coupled plasma chemical vapor deposition using pure methane, Jpn. J. Appl. Phys. 42 (2003) 441.
[35] Y.Y. Lin, H.W. Wei, K.C. Leou, H. Lin, C.H. Tung, M.T. Wei, C. Lin, C.H. Tsai, Experimental characterization of an inductively coupled acetylene/hydrogen plasma for carbon nanofiber synthesis, J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct. 24 (1) (2006) 97–103.
[36] T.X. Li, K. Kuwana, K. Saito, H. Zhang, Z. Chen, Temperature and carbon source effects on methane–air flame synthesis of CNTs, Proc. Combust. Inst. 32 (2) (2009) 1855–1861.
[37] R. Xiang, G. Luo, Z. Yang, Q. Zhang, W. Qian, F. Wei, Temperature effect on the substrate selectivity of carbon nanotube growth in floating chemical vapor deposition, Nanotechnology 18 (41) (2007) (415703).
[38] S. Bandow, S. Asaka, Y. Saito, A.M. Rao, L. Grigorian, E. Richter, P.C. Eklund, Effect of the growth temperature on the diameter distribution and chirality of single-wall carbon nanotubes, Phys. Rev. Lett. 80 (17) (1998) 3779–3782.
[39] C. Fantini, A. Jorio, M. Souza, M.S. Strano, M.S. Dresselhaus, M.A. Pimenta, Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: environment and temperature effects, Phys. Rev. Lett. 93 (14) (2004) 147406.
[40] W. Li, J. Wen, Z. Ren, Effect of temperature on growth and structure of carbon nanotubes by chemical vapor deposition, Appl. Phys. A 74 (3) (2002) 397–402.
[41] D.-H. Kuo, M.-Y. Su, The effects of hydrogen and temperature on the growth and microstructure of carbon nanotubes obtained by the Fe $(CO)_5$ gas-phase-catalytic chemical vapor deposition, Surf. Coat. Technol. 201 (22) (2007) 9172–9178.
[42] Y. Lin, A. Dichiara, D. He, P. Haghi-Ashtiani, J. Bai, Uniform diameter multi-walled carbon nanotubes with a controlled wall number obtained by a simple chemical vapor deposition method, Chem. Phys. Lett. 554 (2012) 137–142.
[43] A.M. Rashidi, M.M. Akbarnejad, A.A. Khodadadi, Y. Mortazavi, A. Ahmadpourd, Single-wall carbon nanotubes synthesized using organic additives to Co–Mo catalysts supported on nanoporous MgO, Nanotechnology 18 (31) (2007) 315605.
[44] T.K. Yamabe, K. Fukui, K. Tanaka, The Science and Technology of Carbon Nanotubes, 1st ed. Elsevier, Japan, 1999.
[45] Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, Purification of single-wall carbon nanotubes, Solid State Commun. 112 (1) (1999) 35–37.
[46] W.-M. Yeoh, K.-Y. Lee, S.-P. Chai, K.-T. Lee, A.R. Mohamed, Synthesis of high purity multi-walled carbon nanotubes over Co–Mo/MgO catalyst by the catalytic chemical vapor deposition of methane, New Carbon Mater. 24 (2) (2009) 119–123.
[47] P. Dubey, S.K. Choi, J.H. Choi, D.H. Shin, C.J. Lee, Synthesis of thin-multiwalled carbon nanotubes by Fe–Mo/MgO catalyst using sol–gel method, Carbon Lett. 13 (2) (2012) 99–108.
[48] Y. Li, X.B. Zhang, X.Y. Tao, J.M. Xu, W.Z. Huang, J.H. Luo, Z.Q. Luo, T. Li, F. Liu, Y. Bao, H.J. Geise, Mass production of high-quality multi-walled carbon nanotube bundles on a Ni/Mo/MgO catalyst, Carbon 43 (2) (2005) 295–301.
[49] C. Milone, E. Piperopoulos, M. Lanza, S. Santangelo, A. Malara, E. Mastronardo, S. Galvagno, Influence of the cobalt phase on the highly efficient growth of MWNTs, Nanomater. Nanotechnol. 4 (1) (2014) 1–8.