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GROWTH OF CARBON NANOTUBES ON CATALYSTS OBTAINED FROM CARBON RICH FLY ASH

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We report a novel carbon nanotube (CNT) synthesis method by chemical vapor deposition (CVD) using catalysts obtained from carbon rich fly ash. In this approach two fly ash samples (S1 and S2) were treated by heating at 750 ^{0}C, and then analyzed using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). EDS results show that the treated fly ash contains the main components needed in the catalysis of CNTs growth such as Fe, Ni, Al and Si in their oxide forms. Iron levels are found to be higher in S1 than those in S2, while S2 contains an elevated amount of Ni. The as-grown CNTs on S1 and S2 were analyzed by SEM, transmission electron microscope (TEM) and Raman spectroscopy. The nanotubes grown on S1 have diameters in the range of 30-50 nm and lengths in the order of a few micrometers, while those grown on S2 have smaller diameters. These CNTs have around 12 walls as revealed by TEM, while Raman spectrum shows a good degree of wall graphitization (I_G/I_D = 1.35). These results suggest that this approach is quite suitable to obtain low cost catalysts for producing CNTs on a large-scale.

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Keywords: Carbon nanotubes, chemical vapour deposition, electron microscopy (TEM and SEM).

1. Introduction

Carbon nanotubes (CNTs) are nanometer-size cylinders made out of carbon atoms. They can be thought of as layers of graphite rolled-up into cylinders to form single or multiwall nanotubes and have diameters ranging from a few nm to hundreds of nm. They are of increasing scientific interest due to their extraordinary mechanical and unique thermal and electronic properties [1,2] and therefore have great value to many practical applications [3-7]. Iijima in 1991[8] was the first scientist, who discovered CNTs, thereafter these CNTs have attracted huge interest and used in a wide variety of applications including electronic devices [9], field emitters [10], probe tips for microscopy [5], hydrogen storages [11], and composite materials [12]. These CNTs have a potential to be used also in other products once they can be produced in large quantities at a low price.

Several methods were developed to produce CNTs. The most common are arc discharge [13] laser ablation [14,15] and chemical vapor deposition (CVD)[16]. These techniques have aspects that make them potentially viable as a large-scale process, but each method has drawbacks. In the arc discharge method [13] the arc process requires very high-temperatures (~3000 ^{0}C) and produces other carbonaceous material. The production rate is low. Similarly, in the laser ablation method [14,15] the yield is low, particularly, at low temperatures.

In the CVD method, a hydrocarbon gas is allowed to flow over a heated layer of catalyst particles [16]. This process does not require high-temperatures (<1200 ^{0}C) and different version processes of this technique have been able to produce substantial amounts of nanotubes. Thus, this

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method has advantages and potential to be the most suited for producing CNTs in sizeable quantities. However, a significant drawback to this method is the cost of the metal catalyst particles, which add to the overall expense of CNTs synthesis. Even the question of yield still remains with limitations, particularly if we suggest on extending CNT industrial applications into a variety of products. In order for CNTs to reach their full potential, a new approach for the production of large-scale quantities must be developed. We suggest that this approach be rapid, efficient, and of low-cost.

Carbon fly ash is composed of fine particles of ash, produced during solid fuel combustion carried by waste gases out through a furnace flue. It is transported from the combustion chamber via exhaust gases and then collected by electrostatic precipitators or fabric filters. Water desalination and power plants generate large quantity of fly ash every day [17]. There are several studies and suggestions to identify ways to utilize fly ash in order to reduce the amount that is land filled, causing a serious environmental problem [18]. Few studies suggested the use of coal fly ash (contains small percentage of carbon and oxides of aluminum and silicon) as a catalyst for CNTs, as it was adopted by Yasui *et al* [19]. Another group has suggested impregnating coal fly ash with iron nitrite and using it as a substrate to produce CNTs [20]. However, no previous efforts were adopted whereby they would utilize the catalysts that already exist in carbon rich fly ash needed for CNTs synthesis. Carbon rich fly ash is produced in Saudi Arabia in huge quantities and has not been utilized for any application. Therefore, testing these ashes as catalysts for CNTs growth might provide an ideal solution and solve the high cost of CNTs production and allow for fabrication of large scale CNTs for commercial propose. Expectantly, this might lead to extended applications of CNTs into a variety of products.

In this work we report on testing two samples of fly ash powders as catalysts for CNTs growth. They were treated by pre-heating at 750 ^{0}C to release the unburned carbons and then used to grow CNTs by the CVD method. After the heat treatments samples were analyzed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The morphology and quality of the as-grown CNTs were studied by scanning electron microscopy, transmission electron microscope and Raman spectroscopy.

2. Experimental

Carbon nanotubes were synthesized using a low-pressure CVD (by Syskey Technology, Taiwan). Catalysts obtained from fly ash powder were used to grow CNTs. Two samples of fly ash powders (S1 and S2) were collected from two different water desalination plants in Saudi Arabia. They were treated by pre-heating in air at 750 ^{0}C to release the unburned carbon and then analyzed using a scanning electron microscope (Quanta, FEI) and energy dispersive spectroscopy (EDS) (EDAX, Ametec). To grow carbon nanotubes using the treated S1 and S2 as catalysts, acetylene gas was used as a carbon precursor, while N_2 is used as a carrier gas. The obtained treated fly ash powder (carbon free fly ash) is kept in a quartz boat, which then placed in the quartz tube of the CVD system. The reactor tube was evacuated up to 10^{-3} Torr, and heated at about 20 ^{0}C/min. Once the temperature reached to 750 ^{0}C a mixture of N_2:C_2H_2 gases was flowed with a flow rate of 200:50 sccm, respectively. The growth time was kept fixed at 20 minutes, while the chamber pressure was maintained at 15 Torr.

The morphology of the as-grown CNTs was analyzed by scanning electron microscopy using Quanta, FEI and transmission electron microscope using Titan 80, 300 kv(st), FEI. TEM and SEM measurements were performed on the as-synthesized CNTs without treatments or purification. Raman spectra were measured using DXR Raman Microscope, Thermo Scientific using the 532 nm laser as excitation source at 8 mW power. Spectra were measured in the 100-3600 cm^{-1} zone.

3. Results and discussion

Figs. 1 and 2 show SEM images of different magnifications for the collected fly ash samples (S1 and S2, respectively) before heat treatment. Almost spherical particles with sizes

around 70 μm can be seen for S1 (Fig. 1 a and b) and about 20 μm for S2 (Fig. 2 a and b). It is previously reported that these fly ash powders contain more than 80% pure carbon, while the remaining are various oxides [17]. When these fly ash samples i.e. S1 and S2 were heated up to 750 ^{0}C, the big solidified ash particles disappeared. The results are fragments of small particles with sizes in the range of 0.5-3.0 μm that have random shapes as shown in Figs. 3 (a and b) and 4 (a and b) for S1 and S2, respectively.

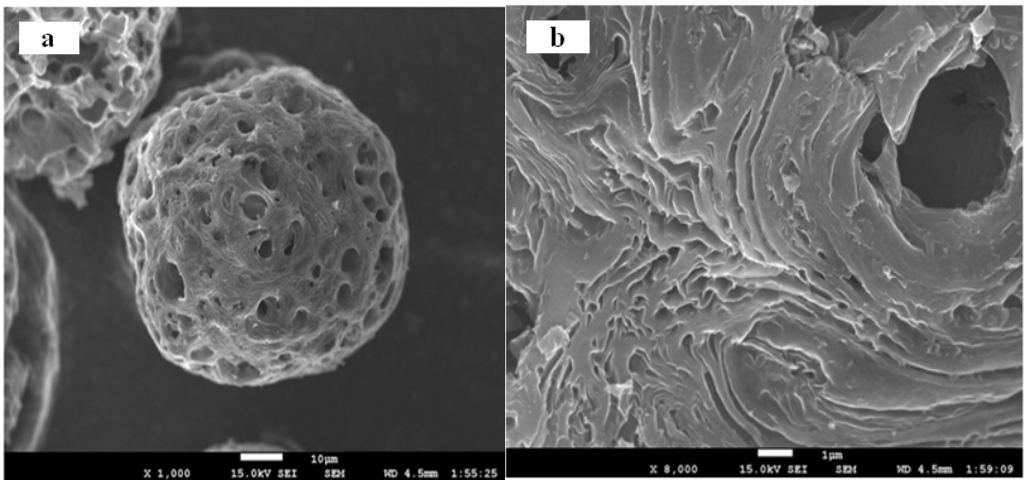

Fig.1: SEM images of different magnifications for the first sample of fly ash (S1) before heat treatment.

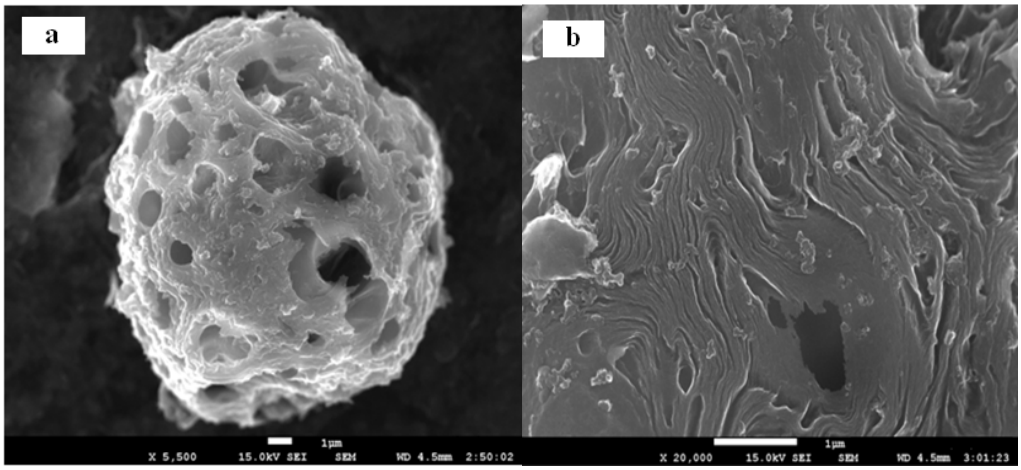

Fig. 2: SEM images of different magnifications for the second sample of fly ash (S2) before heat treatment.

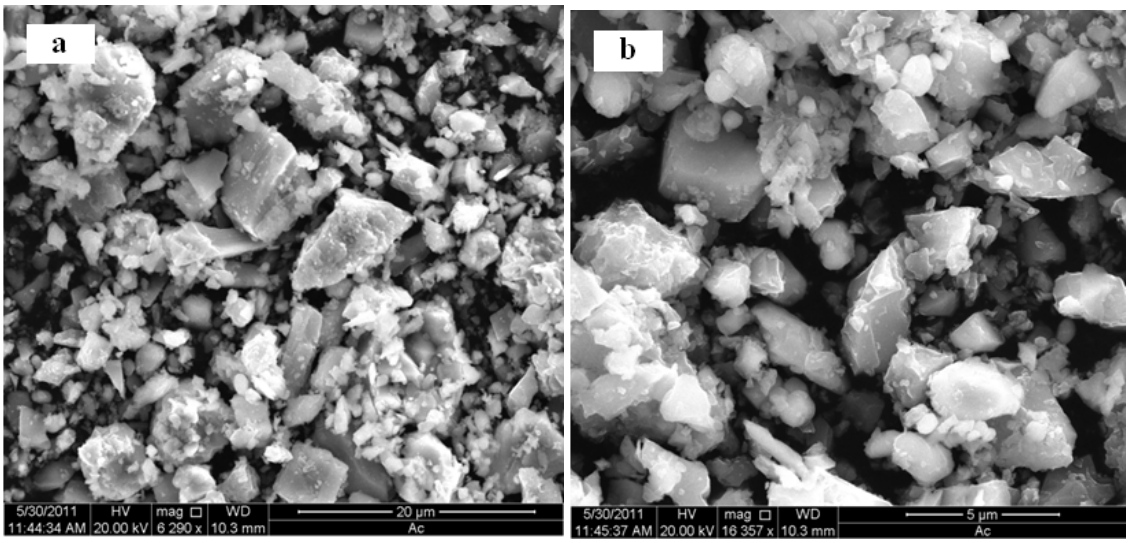

Fig. 3: SEM images of different magnifications for the first sample of fly ash (S1) after heating at 750 ^{0}C.

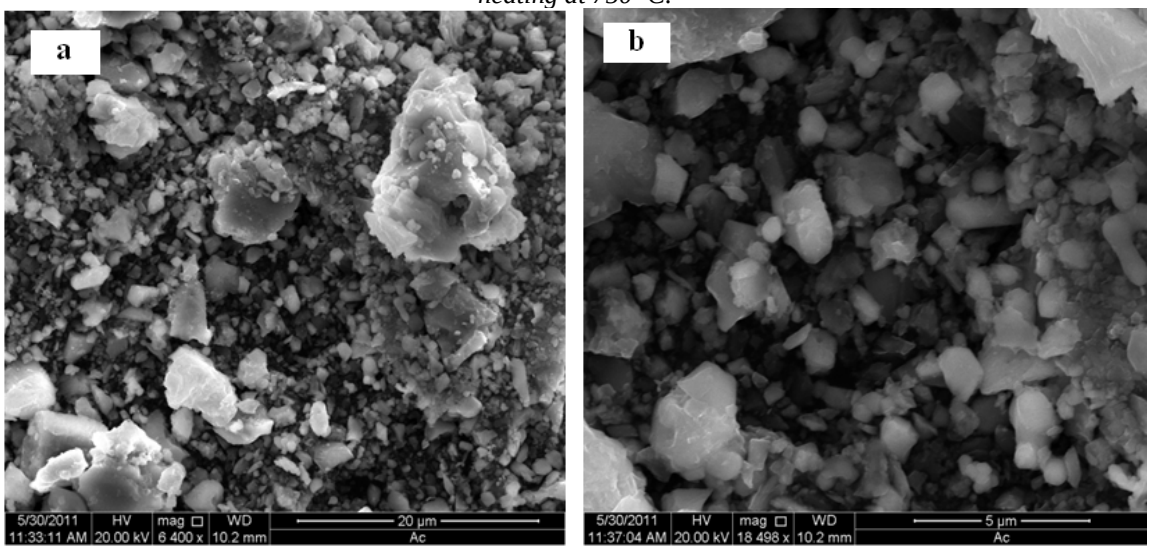

Fig. 4: SEM images of different magnifications for the second sample of fly ash (S2) after heating at 750 ^{0}C.

The fly ash samples treated by heating at 750 ^{0}C were analyzed using energy dispersive spectroscopy (EDS). The EDS results are shown in Figs. 5 and 6 for S1 and S2, respectively. Metals composed the majority in oxide forms as observed in both samples, S1 and S2. The major elements in S1 after heat treatment were iron (Fe), vanadium (V), aluminum (Al) and nickel (Ni). Amongst them, iron is found to be the most abundant element in S1 with around 46 percent (Fig. 5). The second sample S2 had mostly V, Fe, Ni, Si (silicon) and Na (sodium) (Fig. 6). An interesting observation is that the amount of Fe in S2 is found to be lower than that in S1, while it is vice versa for that of Ni; it is greater in S2 than in S1. The latter two elements, i.e. Fe and Ni and their combinations have been widely used as catalysts for CNTs growth [21-23]. Cobalt (Co), which is also reported to be used as a catalyst [24,25] for CNTs growth might exist in a very small quantity in both samples (Figs. 5 and 6). However, it is clear from EDS analysis for both S1 and S2 that the unburned carbons were completely released from the fly ash powders by pre-heating at 750 ^{0}C.

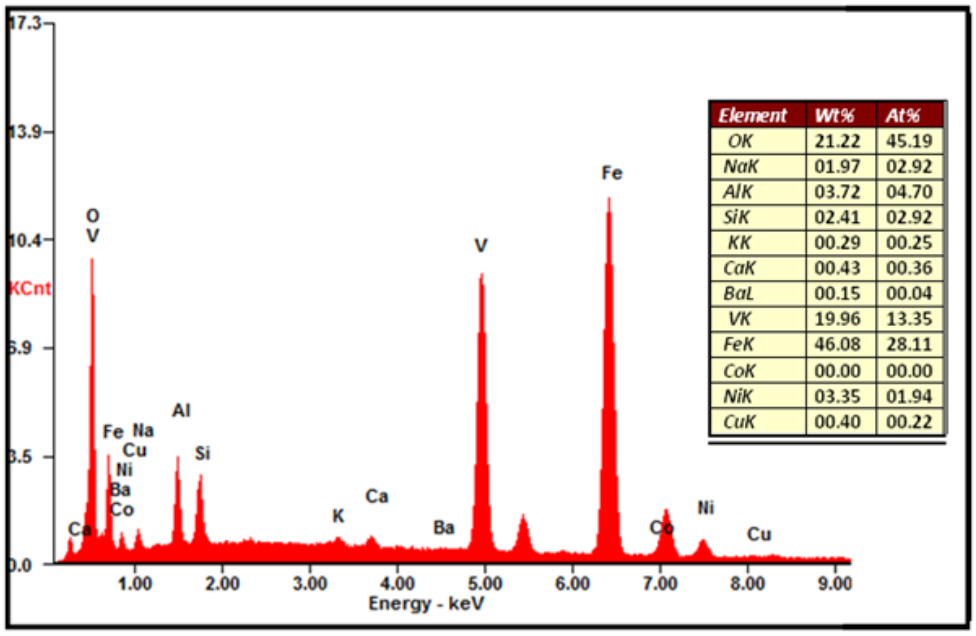

Fig. 5: EDS quantitative and qualitative results for S1, after heat treatment.

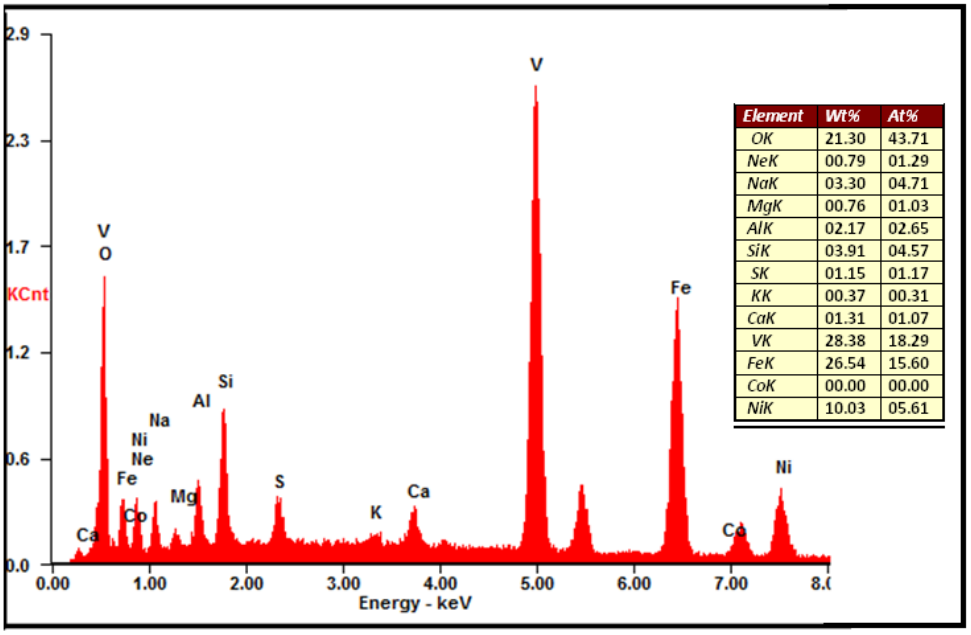

Fig. 6: EDS quantitative and qualitative results for S2, after heat treatment.

Figs. 7 and 8 show SEM images of different magnifications for the as-grown CNTs correlating to S1 and S2, respectively. The nanotubes grown on S1 have diameters in the range of 30-50 nm and lengths in the order of few micrometers (Fig. 7 a and b), while those grown on S2 (Fig. 8 a and b) have smaller diameters. Furthermore, some of the CNTs grown on S2 have very small diameters close to 5 nm. What is a remarkable result is that the type of catalysts and their amount have direct impact on the diameter of the grown CNTs. Nanotubes grown on a catalyst with a majority of Fe tends to have bigger diameters than those grown on Ni. Effect of catalyst type on diameter of the grown CNTs was studied by several authors [21-23]. Lee *et al* [21] have

found that the average diameter of CNTs follows the sequence of Fe, Co, and Ni catalysts, by means that Fe gives bigger diameters, while Ni provide smaller diameters for the CNTs. Similar results are observed in the CNTs grown by Sengupta and Jacob [22]. Their CNTs grown on Fe have diameters bigger that those grown on Ni. Lee *et al* [21] have attributed this effect to the growth rate, which itself depends on the diffusion rate of carbons over the surfaces of the metal catalysts. They reported that carbons can defuse faster over the surface of Ni than that over Fe, which leads to the formation of smaller diameters of CNTs. They also considered the particle size effect of the catalyst on the diameters of the grown CNTs; smaller catalyst particles enabled the synthesis of highly dense, long and narrow-diameter CNTs. Hsieh *et al* [23] have reported that the catalytic activity of $Fe–Al_2O_3$ catalyst was found to be greater than that of $Ni–Al_2O_3$ catalyst. The results from our present study are completely in agreement with the above mentioned studies [21-23]. In this study the main difference is in the composition of the catalysts used, where S1 and S2 differed in the amount of Fe and Ni, which might have direct impact on diameters of the grown CNTs.

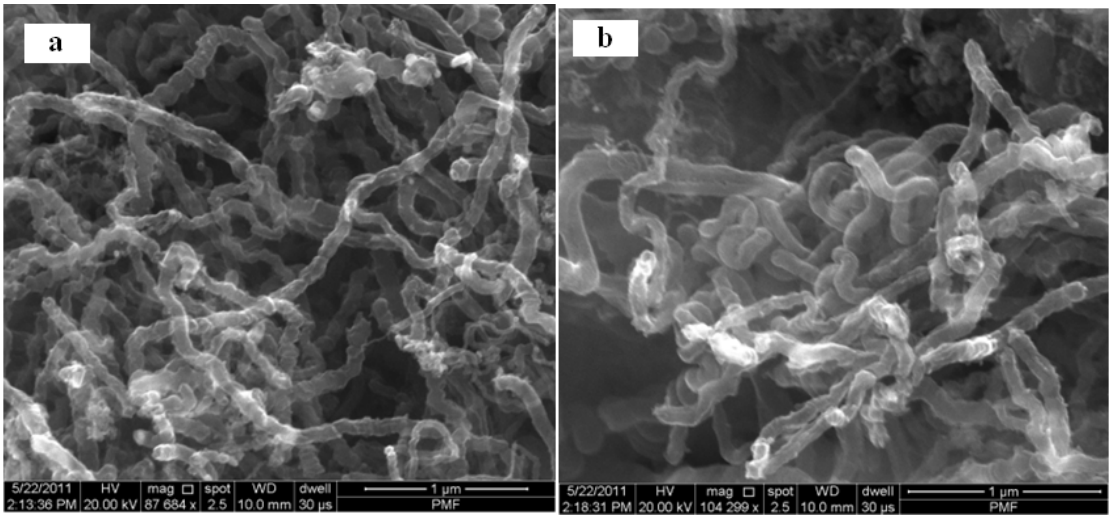

Fig. 7: SEM images for the as-grown CNTs on S1, obtained at different magnifications.

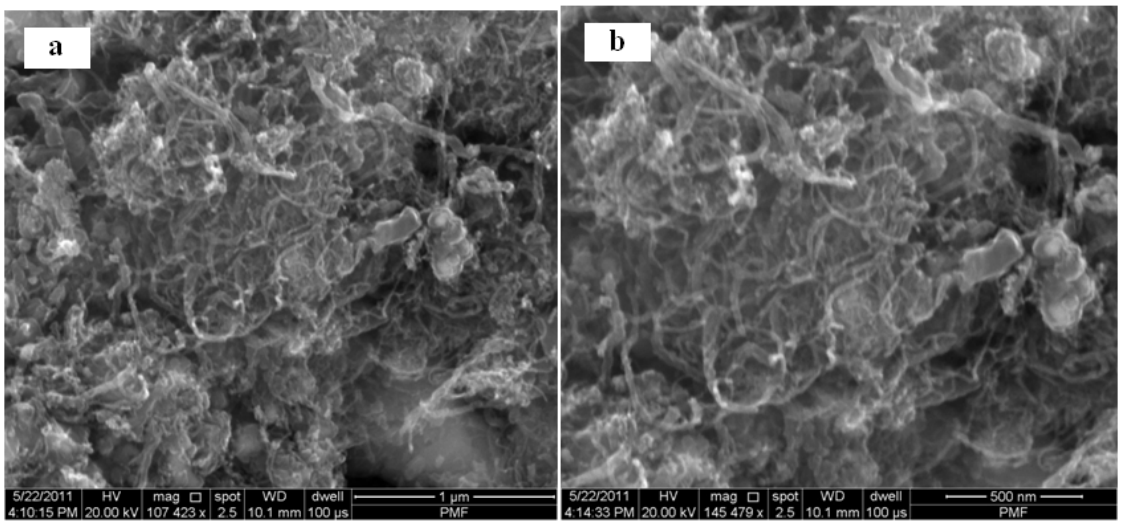

Fig. 8: SEM images for the as-grown CNTs on S2, obtained at different magnifications.

There are also considerable amounts of silicon and aluminum oxides in the treated fly ash samples as can be seen in Figs. 5 and 6. They have also been reported as good catalyst-supporting materials [23, 26-29]. Thus, these catalysts from the used treated fly ash are ideal components for CNTs growth with different diameters. However, more studies are needed to optimize several factors influencing the growth of CNTs and their morphology, quality and yields. These factors might include growth time, temperature, pressure, gas flow rate, size of catalysts particles, etc. They will be studied in our future work.

TEM images given in Figs. 9 and 10 show the as-grown CNTs on S1 and S2, respectively. They show similar pattern to those observed by SEM images (Figs. 7 and 8). The grown nanotubes on S1 have bigger diameters than those grown on S2. These images also show some catalyst particles. The high-resolution TEM images given in Figs. 9b and 10b show multiwall nanotubes in CNTs samples grown on S1 and S2. Around 12 walls can be observed in both cases. Thickness of these walls is around 3 nm, while the inner and outer walls thickness is 0.3 nm. The CNTs grown on S1 seem to have straight walls, better than those grown on S2 (Figs. 9 and 10). Qian *et al* [30] have reported that introducing small amount of nickel into the catalyst can significantly increase the yield of CNTs, but the nanotubes change from straight tubes with concentric parallel carbon sheets to helical tubes of the fish-bone type. They have attributed this effect to the change in the chemical nature of the catalyst. This is in agreement with our results, where the influence of catalyst type on the morphology and microstructure of the CNTs is apparent.

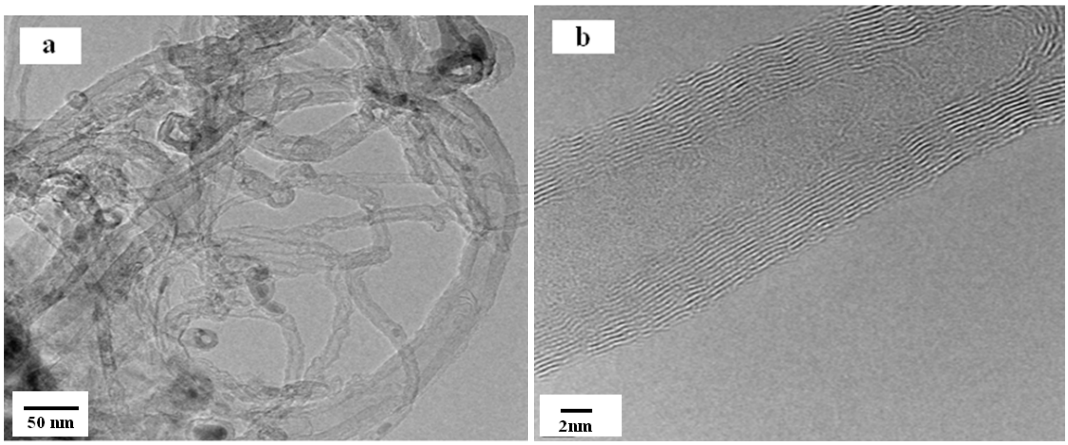

Fig. 9: TEM images for the as-grown CNTs on S1, obtained at different magnifications.

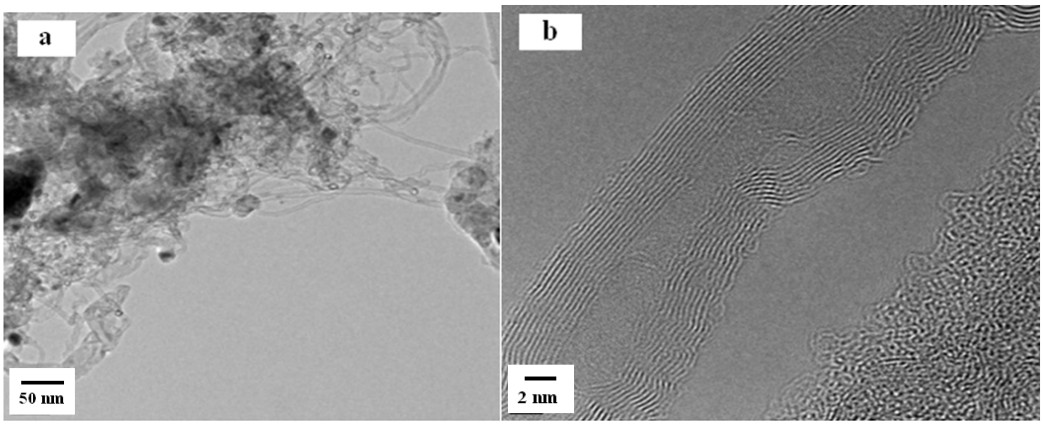

Fig. 10: TEM images for the as-grown CNTs on S2, obtained at different magnifications.

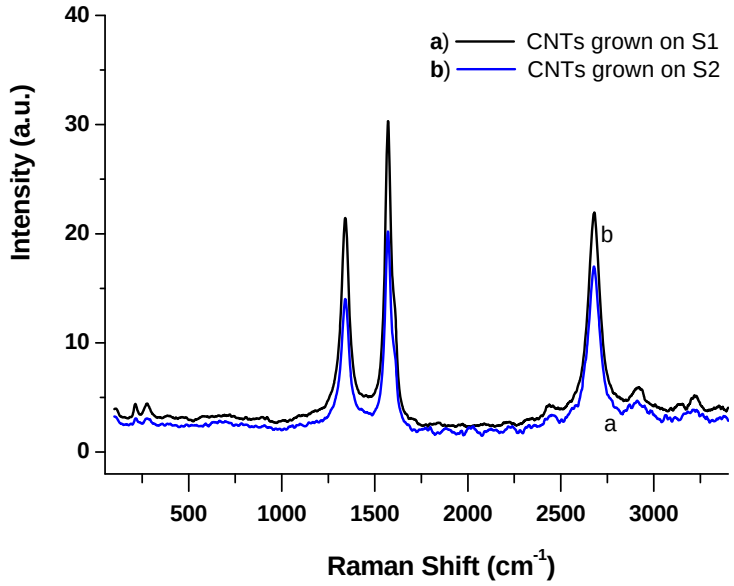

Fig. 11: Raman spectra for the as-grown CNTs on S1 (curve a) and S2 (curve b).

Raman spectra for the as-grown CNTs in both S1 and S2 treated fly ash are recorded and presented in Fig.11 (curves a and b, respectively). Both curves show several bands in the range of 100-3500 cm^{-1}. Three prominent bands can be observed at 1345, 1580 and 2690 cm^{-1} along with two smaller bands at 2925 and 3230 cm^{-1}. The intensity ratios of these bands are similar in both samples. The first band at 1345 cm^{-1} is attributed to the carbon materials disorder-induced band (D-band) and the second band at 1590 cm^{-1} resulted from in-plane vibrations of graphite (G band) [16,17]. The remaining three bands at 2690, 2925 and 3230 cm^{-1} are the overtones/second order resonance 2D, D+G and 2D bands, respectively [18,19]. Experimentally, the intensity ratio of the G and D bands (I_G/I_D) is often used as an indication of the level of defect density on a graphitic carbon sample [16,18]. The intensity of G-band is more than that of D for the as-grown CNTs for both S1 and S2. The value of I_G/I_D is around 1.35. This result is much better than that of Yasui et al. [19], who have used coal fly ash as a catalyst for CNTs growth. This might be due to the poor quality of their fly ash as a catalyst, which contains only silicon and aluminum oxides.

Raman spectrum for the as-grown CNTs in both sample S1 and S2 (Fig. 11, curves a and b, respectively) also show two small bands at 205 and 290 cm^{-1}. These bands are called radial breathing mode features (RBM) [20]. It has been reported that RBM features correspond to coherent vibration of the C atoms in the radial direction, as if the tubes were breathing [20,312]. They can easily be observed in single-walled carbon nanotubes (SWCNTs) and show strong inverse diameter dependence. RBM features are not usual in multi-walled carbon nanotubes (MWCNTs), since the signal from the larger diameter is usually too weak to be observable and the set average of inner tube diameters broadens the signal [20, 31]. In the present case it is very remarkable for some single-walled CNTs to be formed. The presence of these RBM bands in the spectrum of the as-grown CNTs is an indication for the formation of a small percentage of SWCNTs. This might be due to the presence of ultrafine catalysts particles in the fly ash samples used.

From the application point of view, the presented results from these experiments are very promising towards the use of fly ash catalysts for CNTs growth. The low cost of this fly ash is an important factor when producing CNTs in large quantities, which might extend CNTs application into a variety of products.

4. Conclusions

In this work we have treated fly ash powder by pre-heating at 750 ^{0}C and used it as a catalyst for CNTs growth. Two types of fly ash samples (S1 and S2) were analyzed using EDS and found to contain main components needed for catalyzing CNTs growth. Metals were present predominantly in oxide forms in both samples including Fe, Ni, V, Al and Si. Iron is found to be the most abundant element in S1. The second sample S2 had lower abundance of Fe than that in S1, but contained higher amounts of Ni. The as-grown CNTs on S1 and S2 were analyzed by SEM, TEM and Raman spectroscopy. The nanotubes grown on S1 had diameters in the range of 30-50 nm and lengths in the order of few micrometers, while those grown on S2 had smaller diameters with similar length. These CNTs were formed with around 12 walls as revealed by TEM, while Raman spectrum showed a good degree of wall graphitization. These results suggest that this approach is quite suitable for a large-scale production of CNTs with different diameters at low price.

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References

[1] M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, Nature **381**, 678 (1996).
[2] Alina V. Korobeinyk, Raymond L.D. Whitby, Jun Jie Niu, Yury Gogotsi, Sergey V. Mikhalovsky, Mater. Chem. Phys. **128**, 514 (2011).
[3] N. Buang, F. Fadil, Z. Abdul Majid, S. Shahir, Digest Journal of Nanomaterials and Biostructures, **7**, 33 (2012).
[4] G. Y. Chen, B. Jensen, V. Stolojan, S. R. P Silva, Carbon **49**, 280 (2011).
[5] T. Mocan, S. Clichici, AR. Biris, S. Simon, C. Catoi, F. Tabaran, A. Filip, D. Daicoviciu, N. Decea, R. Molcovan, L. Mocan, A. Muresan, Digest Journal of Nanomaterials and Biostructures, **6**, 1207 (2011).
[6] S. Ratkovic, Dj. Vujicic, E. Kiss, G. Boskovic, O. Geszti, Mater. Chem. Phys. **129**, 398 (2011).
[7] J. Donald, C. Xu, H. Hashimoto, E. Byambajav, Y. Ohtsuka, Appl. Catal. A-Gen. **397**, 73 (2011).
[8] S. Iijima, Nature **354**, 56 (1991).
[9] Z. Yao, H. W. Ch. Postma, L. Balents, C. Dekker, Nature **402**, 273 (1999).
[10] Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seelig, R. P. H. Chang, Appl. Phys. Lett. **72**, 2912 (1998).
[11] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, Nature **386**, 377 (1997).
[12] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, Science **287,** 637 (2000).
[13] T. W. Ebbesen, P. M. Ajayan, Nature **358**, 220 (1992).
[14] P. J. F. Harris, Carbon **45**, 229 (2007).
[15] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, R. E. Smalley, Science **273**, 483 (1996).

[16] J. Kong, A. M. Cassell, H. J. Dai, Chem. Phys. Lett. **292**, 567 (1998).
[17] S. S. Habib, J. Nano. Biomaterials **2**, 437 (2009).
[18] M. Ahmaruzzaman, Prog. Energy Combust. Sci. **36**, 327 (2010).
[19] A.Yasui, Y. Kamiya, S. Sugiyama, S. Ono, H. Noda, Y. Ichikawa, IEEJ Trans. Elec. Electron Eng. **4**, 787 (2009).
[20] O. M. Dunens, K. J. Mackenzie, A. T. Harris, Environ. Sci. Technol. **43**, 7889 (2009).
[21] Cheol Jin Lee, Jeunghee Park, Jeong A. Yu, Chem. Phys. Lett. **360**, 250 (2002).
[22] Joydip Sengupta, Chacko Jacob, J. Nanoparticle Res. **12**, 457 (2010).
[23] Chien-Te Hsieh, Yi-Tien Lin, Wei-Yu Chen, Jin-Long Wei, Powder Technol. **192**, 457 (2009).
[24] Xin Dong, Xue-Lian Liang, Hai-Yan Li, Guo-Dong Lin, Peng Zhang, Hong-Bin Zhang, Catal. Today **147**, 158 (2009).
[25] Xiao-Feng Guo, Joong-Ho Kim, Geon-Joong Kim, catal. Catalysis Today **164**, 336 (2011).
[26] T. Murakami, Y. Hasebe, K. Kisoda, K. Nishio, T. Isshiki, H. Harima, Diamond Relat. Mater. **17**, 1467 (2008).
[27] S.-P. Chai, S. H. S., M. Abdul Rahman, Appl. Catal. A-Gen. **326**, 173 (2007).
[28] H. Sugime, S. Noda, Carbon **48**, 2203 (2010).
[29] Pezhman Zarabadi-Poor, Alireza Badiei, Ali Akbar Yousefi, Bradley D. Fahlman, Alireza Abbasi, Catal. Today **150**, 100 (2010).
[30] Weizhong Qian, Tang Liu, Zhanwen Wang, Hao Yu, Zhifei Li, Fei Wei, Guohua Luo, Carbon **41**, 2487 (2003).
[31] L. Alvarez, A. Righi, S. Rols, E. Anglaret, J. L. Sauvajol, E. Muñoz, W. K. Maser, A. M. Benito, M. T. Martínez, G. F. de la Fuente, Phys. Rev. B **63**, 153401 (2001).