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PRODUCTION OF NANO-CARBON USING ARC DISCHARGE IN LIQUID NITROGEN

Yusran Sulaiman[1], Nor Aziah Buang[1], Suhaila Sanip[1], and Ahmad Fauzi Ismail[2]
[1]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
[2]Membrane Research Unit, Faculty of Chemical Engineering and Natural Resource, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.

ABSTRACT

Arc discharge is a well-known method for the production of carbon nanotubes (CNTs). From the arc discharge method, various kinds of CNTs such as single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) and carbon onion can be produced. Other than these structures, single-walled nanohorns (SWNHs) and their metal-including form can also be synthesized by modifying the system i.e. replacing the vacuum system with liquid nitrogen (LN). They are considered as a novel nanocarbon structure. This method can be an economical route for the mass production of CNTs.

Keyword: arc discharge, carbon nanotubes, liquid nitrogen

1. INTRODUCTION

Since the first discovery by Iijma in 1991, the study of carbon nanotubes (CNTs) has been receiving increasing attention all over the world because of their wide range of applications from nanoelectronics to energy storage [1]. Basically, CNTs can be classified into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) or open-ended and closed CNTs according to their morphologies. CNTs can be produced via many methods but arc discharge is still the most practical one for scientific purposes and yields the most highly graphitized tubes. This technique is very simple and has been established as a method for massive production of both SWNTs and MWNTs. The conventional arc discharge method, however, require a complicated vacuum apparatus. Generally, the temperature in the vacuum chamber is not controlled and the walls of the chamber are cooled by water. After arcing, the soot deposited on the chamber walls consists of useless metal catalyst and carbonaceous particles other than few CNTs. Most CNTs are produced in the center of the core deposited at the head of the cathode and also around the anode rod [2]. In the past few years, many researchers have developed many methods that could produce cheap and high quality CNTs.

Recently, arc in liquid nitrogen [3-5] method has been developed to synthesize many kinds of nano-carbon. This modified arc discharge method was first proposed by Olk [6] and Ishigami *et al.* [7]. Liquid nitrogen (LN) prevents the electrodes from contamination with unwanted gases and effectively lowers the temperature of the electrodes also provides the inert environment. Furthermore, CNTs produced with this technique resulted in clean sample of CNTs. This technique is also considered as a low-cost method compared to conventional methods because it does not require expensive equipments such as vacuum systems, cooling system, reactive gases etc. Since this technique has been developed, many nano-carbons have been synthesized such as MWNTs [7-8], nano-onion [9-10], single-walled carbon nanohorns (SWNHs) [5], and their metal-including forms [5, 11].

2. EXPERIMENTAL

2.1 Preparation of the catalyst

The technique used for this preparation is called solid-solid mixing because both starting materials are in solid form. Synthetic graphite powders (Fluka) and Ni were mixed with the weight ratio of 98.5 :1.5 . They were dispersed in acetone by ultrasonic for 30 minutes in order to get perfect mixing. Acetone acted as a mixing medium. After the mixing process was over, the mixture was left at room temperature until the acetone vaporized.

2.2. Production of nano-carbon

The experimental set-up used in our study is illustrated in Fig 1. Direct current was supplied to the apparatus using a power supply. The anode and cathode is a pure carbon rod of 4 mm diameter. Both electrodes were submerged horizontally in LN contained in stainless steel Dewar flask (2000 cm^3), and arc discharge was generated between these electrodes. The gap between the electrodes was adjusted to 0.10 mm and was kept constant. The discharge current and voltage were set at 80 A and 4 V, respectively. Carbon was evaporated from the anode and deposited to the cathode. When the arc was over, carbon materials deposited on the cathode and at the bottom of the flask were collected for further analysis after removing the LN.

Figure 1. Schematic diagram of arc discharge system.

3. RESULTS AND DISCUSSION

Ni was chosen as the catalyst because it is known to play a critical catalytic role in CNTs formation. Ultrasonic technique can mix two solid compounds perfectly in liquid medium. In other words, homogenous mixing can be obtained by using this method. During the mixing process, the small catalyst particle can penetrate or permeate through the slit shape pore between the graphite layers. Acetone was used as a mixing medium because of its volatility property and easily obtained. After the mixing process is over, the mixture was left at room temperature for all the acetone to vaporize. In this study, LN was used to replace the vacuum system in order to provide the inert condition.

Ishigami *et al.* [7] proposed a simple method for the continuous production of CNTs without using the vacuum system. From their study, high yield MWNTs can be obtained. After their findings have been reported, many other methods have been developed which was considered as an economical technique by replacing the LN with water [11, 12]. Sano *et al.* [3] found that high purity SWNHs were obtained when anode without catalyst was used. When the Ni (0.64% mol) was used as the catalyst, Ni-included SWNHs were found among the normal SWNHs but the SWNTs were not found. The Ni was encapsulated by several graphitic shells. When the anode was doped with Ni (1.8 mol%), most SWNHs turned to include Ni nano-particles as shown in Fig. 2. When the Ni concentration increased over than 6.4 mol%, SWNHs and SWNTs were not observed. Only agglomerated nearly-spherical particles including Ni particle were seen. From TEM (Fig. 3) observation, SWNTs with net-worked between catalyst can be seen. The structure is similar to the as produced 'arc in gas'.

Figure 2. TEM image of Ni-included SWNHs produced by arc in LN with Ni-doped graphite anode. Inset shows high magnification image of protruded horns [3].

Figure 3. TEM image of SWNTs produced by arc in LN with Ni-doped graphite anode (1.8mol %). (a) show some bundled SWCNTs (b) separated SWNTs [3].

Jung *et al.* [4] firstly reported that high-yield MWNTs can be produced from this modified system. This study shows that by using pure graphite (anode) without doping with any metal, MWNTs and carbon onion can be formed (Fig. 4 a & b). From their Raman study, the first and second order peak of the Raman spectra of carbon deposit (Fig. 4c) was observed. The first order (G-band) represents graphite sheet and the second order (D-band) represent the defect structure.

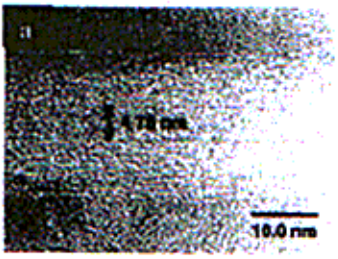

Fig. 4a. TEM image of MWNT [4].

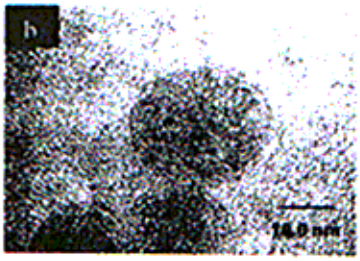

Fig. 4b. TEM image of a carbon onion particle.

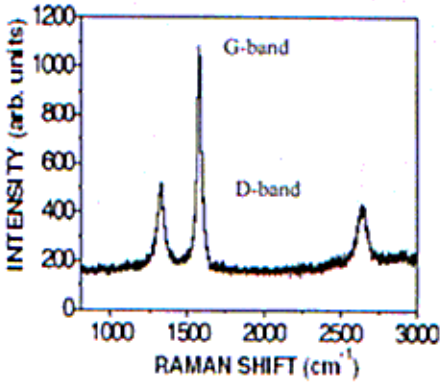

Fig. 4c. Raman spectrum of the carbon deposit synthesized at 27.5V by arc discharge in LN [4].

From the observation of the recent work, it is obtained some transformations of graphite structure. Fig. 5 (a) shows the morphology of cathode before the reaction occurs. The graphite flaky particle present is not even in term of shape, size and distribution. Transformation of structure can clearly be seen after the reaction was carried out which fullerene-like structure was found on the tip surface of cathode (Fig. 5 b). The micrograph indicates that the vertically aligned CNTs bundles with end cap of fullerenes were formed. Fig. 5 (c) shows one of the CNTs is coming out from the bundles. The CNT is surrounded with fullerene-like structure particles.

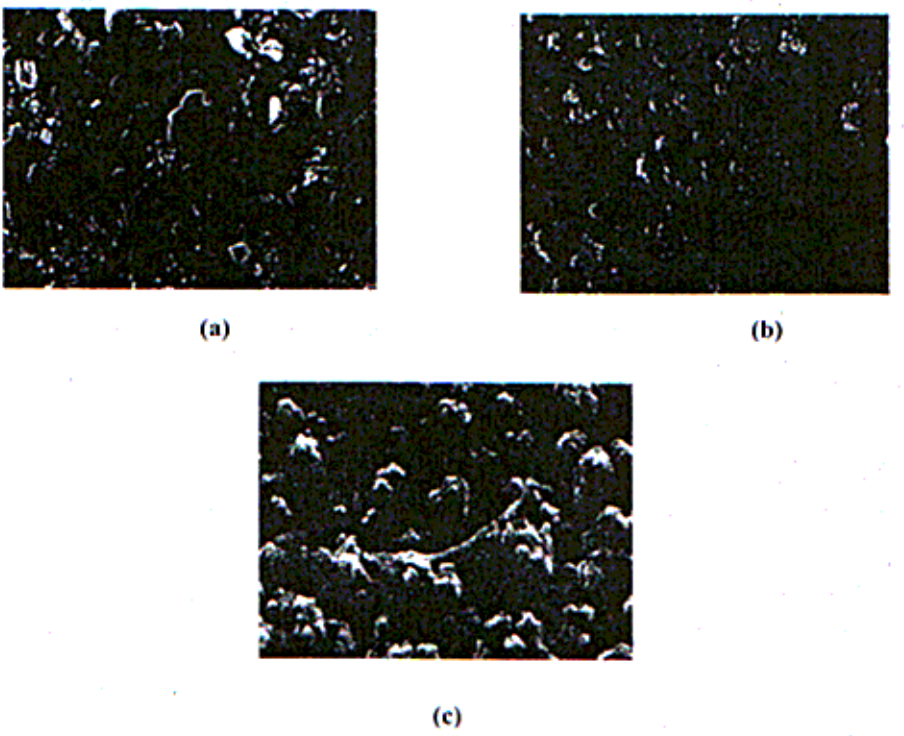

Figure 5. SEM micrographs of (a) unreacted cathode surface (b) cathode surface after reaction (4000 x) (c) magnified cathode surface with single CNT thread coming out from the bundles (10000 x).

Besides using LN, water has also been used as a quenching medium. Lange *et al.* [11] found that the arc in water is erratic, thus it is critical to control precisely the gap between the electrodes. They describe the formation of well-crystallized nano-onion, nanotubes and fully or partly filled with crystallized metal encapsulated.

4. CONCLUSIONS

From our preliminary study using customed built arc-discharge system, we are able to get some structure transformations of the carbon source used in our study supported by the SEM images obtained. Further characterizations are still undergoing in our group. In summary, arc in LN can be an alternative synthesis route for production of CNTs. Since the technique is simple and easily operated, the scaling-up is feasible. This technique is considered to be a low cost-effective method because it does not require expensive

equipment. It is expected that this method will be able to produce highly crystallined and 80-90% purity of MWNTs, SWNTs or SWNHs.

REFERENCES

1. Dresselhaus, M.S. and Dresselhaus G., "Carbon Nanotubes: Synthesis, Structure, Properties and Applications." *Springer*, Berlin, 2001.
2. Park, Y.S., Kim, K.S., Jeong, H.J., Kim, W.S., Moon, J.M., and An K.H., *et al.* "Low Pressure Synthesis of Single-walled Carbon Nanotubes by Arc Discharge. *Synth Met.* vol. 126, 2002, pp. 245-251.
3. Sano, N., Nakano, J., and Kanki T., "Synthesis of Single-walled Carbon Nanotubes with Nanohorns by Arc in Liquid Nitrogen.", *Carbon*, vol. 42, 2004, 667-691.
4. Jung, S.H., Kim, M.R. Jeong, S.H., Kim, S.U., Lee, O.J., Lee, K.H., Suh, J.H., and Park, C.K., "High Yield Synthesis of Multi-walled Carbon Nanotubes by Arc Discharge in Liquid Nitrogen." *Appl. Phys. A*, vol. 76, 2004, pp. 285-286.
5. Sano, N., Kikuchi, T., Wang, H., Chhowalla, M., and Amaratunga, G.A.J., "Carbon Nanohorns Hybridized with A Metal-included Nanocapsule." *Carbon*, vol. 42, 2003, pp. 95-99.
6. Olk, C.H, *US Patent* No. 5753088, 1998.
7. Ishigami, M., Cuming, J., Zettl, A., and Chen, S., "A Simple Method for The Continuous Production of Carbon Nanotubes." *Chem. Phys. Lett*, vol. 319, 2000, pp. 457-459.
8. Sano, N., Wang, H., Alexandrou, I., Chhowalla, M., Teo, KBK., and Amaratunga G.A.J. *et al.*, "Properties of Nano Carbon Particles Produced by An Arc Discharge in Water. " *J. Appl. Phys*, vol. 92, 2002, pp. 2783-2788.
9. Sano, N., Naito, M, Chhowalla, M., Kikuchi ,T., Matsuda, S., Iimura, K. *et al.*, "Pressure Effects on Nanotubes Formation using The Submerged in Water Methods." *Chem. Phys. Lett*, vol. 378, 2003, pp. 29-34.
10. Sano, N., Wang, H., Chhowalla, M., Alexandrou, I., and Amaratunga G.A.J., "Synthesis of Carbon 'Onions' in Water." *Nature*, vol. 414, 2001, pp. 506-507.
11. Lange, H., Sioda, M., Hucko, A., Zhu, Y.Q., Kroto, H.W., and Walton, D.R.M. "Nanocarbon Production by Arc Discharge in Water." *Carbon*, vol. 41, 2003, pp.1617-1623.
12. Sano, N., "Low-cost Synthesis of Single-walled Carbon Nanohorns Using The Arc in Water Method with Gas Injection." *J. Phsy. D*, vol. 37, 2004, pp. L17-L20.