SYNTHESIS OF CARBON NANOPARTICLES BY ARC DISCHARGE IN LIQUID NITROGEN USING METAL-GRAPHITE ELECTRODES

T. Charinpanitkul and E. Phattarapongsant, Center of Excellence in Particle Technology (CEPT), Faculty of Engineering, Chulalongkorn University, Bangkok,THAILAND 10330*
W. Tanthapanichakoon, National Nanotechnology Center, National Science and Technology Development Agency, Thailand Science Park, Patumtani 12120
and N. Sano, Department of Mechanical and System Engineering, Faculty of Engineering, University of Hyogo, JAPAN 671-2201

Abstract

An idea of using pure iron and graphite electrodes for arc discharge in liquid nitrogen could be employed to synthesize carbon nanostructures, which are multiwalled carbon nanotubes (MWNT), carbon nanohorns (CNH), and carbon nanocapsules (CNC) containing metal cores. Effect of metallic cathode and discharge current on structure and yield of nanoparticles has been comprehensively investigated. Typical evidence of transmission electron microscopic images reveals that under some certain conditions of discharge in liquid nitrogen the synthesized products mainly consist of CNCs with mean diameter of 50-400 nm. Interestingly, CNHs with some MWNTs could also be obtained when conventional graphitic electrodes are employed. Meanwhile, MWNTs with diameter of 8-25 nm and length 150-250 nm became less selectively synthesized as cathode deposit under the condition of discharge in liquid nitrogen with higher arc current. Finally, it was found that the production yield of carbon nanoparticles synthesized by either carbon-carbon or carbon-iron electrodes became also lower with an increase in the arc current.

Keywords : Arc discharge, iron electrode, carbon nanoparticles

Introduction

Nowadays, carbon nanoparticles, which are considered as promising materials various applications such as electrodes of fuel cell, battery storage, filler of polymer, nanocomposite of solar cell, have gained increasing interest [1-9]. While there are some methods, such as alcohol-catalytic chemical vapor deposition (alcohol-CCVD) [3], pyrolysis of ferrocene [4] and laser ablation [5], 'arc in liquid' has been recognized as one of effective techniques to synthesize carbon nanoparticles (CNPs) with various advantages over others. With this method arc plasma is generated between anode and cathode which are generally made of graphitic carbon. So far there are many teams investigating the effects of various operating parameters on the characteristics as well as yield of the synthesized carbon nanoparticles. For instance, arc discharge under a nitrogen atmosphere essentially needs investment higher than others arc's method [6], while arc discharge in liquid benzene could provide high yields but the product selectivity is pretty low [7]. Meanwhile, Sano et al. conduct arc discharge in liquid nitrogen using Fe-contained graphite anode which could provide single-walled carbon nanotubes but the production yield was relatively low [8]. Thus other alternative synthesis methods with higher effectiveness would be required to decrease operating cost and to increase the production yield. More recently, synthesis of various carbon nanostructures by electrical arc discharge in liquid media (deionization and liquid nitrogen) [9] is further reported that modification of the system components, such as the liquid media, the material of electrodes could provide some novel products with relatively low cost.

With these previous investigations it is widely recognized that arc-in-liquid method will be one of the most promising means for the actual industrial production of carbon nanoparticles. However, further improvement in the increasing production yield and the decreasing operating cost has still been a challenging issue to explore. With previous experiences it has been realized that cathode is seldom consumed during the arc discharge operation. In addition, incorporation of catalytic substance with arc discharge could also be expected to help increase product yield and selectivity of synthesized carbon nanostructures. Therefore, it is noteworthy that novel point of this work is that instead of using graphite rod as general electrodes, a pure iron rod is employed in arc discharge with an aim of catalytic function on its surface.

Experimental

A direct current (DC) welding power supply (ARC, DP300) was used to generate arc plasma. While graphitic carbon rods were employed as the anode either carbon or iron rods were set as the cathode in the arc discharge experiments. These electrodes were aligned in vertical in 2000 ml of liquid nitrogen which was placed in a stainless vessel insulated with PS foam. Schematic diagram of electrode arrangement for arc discharge employed in this work is shown in **Figure 1**. The arc plasma was normally initiated by contacting two electrodes, and then the gaps between the electrodes were carefully controlled at about 1 mm to maintain stable discharge with are current which was varied in a range of 50 – 250 A. After the arc discharge was terminated, two typical products were generally found, (1) deposit at the cathode tip and (2) fine particles settling down at the vessel bottom. After being dried in the oven for 1 day, all products were taken to analyze by Field Emission Scanning Electron Microscope (HITASHI S-900), Transmission Electron Microscope (JEOL, JEOL2010), Dynamic Light Scattering Analyzer (MALVERN, ZETASIZER 300HSA) and Raman Spectroscopy (Renishaw Ramascope System 2000).

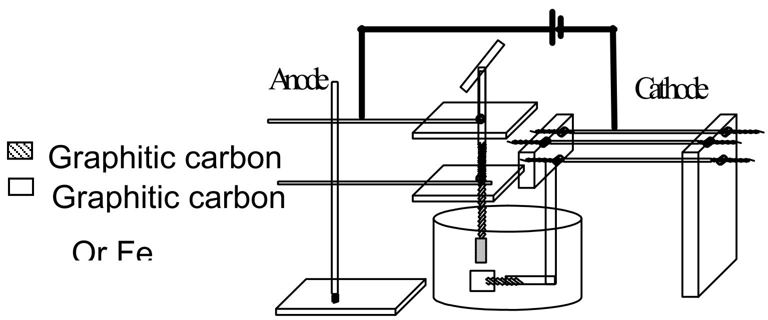

Figure 1. Schematic diagram of electrodes arrangement for arc discharge in liquid nitrogen

Results and Discussion

After the arc discharge, two types of products, cathode deposit and sedimentary particles could be observed. Generally, the graphitic carbon anode was consumed during the arc discharge, resulting in formation of carbon cluster which undergo the self-assembling process to provide carbon nanostructures. When carbon-carbon electrodes were employed there were two types of bulk products obtained; one is the cathode deposit and the other is sedimentary solids. However, with the system of carbon-iron there were only sedimentary particles obtained from arc discharge.

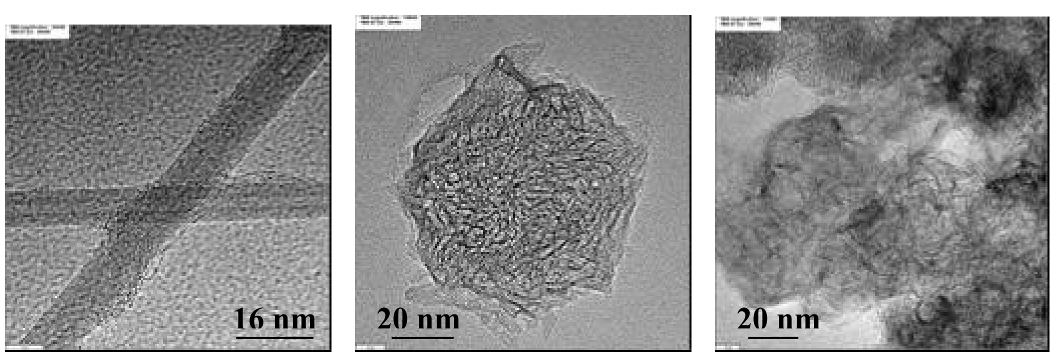

Figure 2. TEM images of carbon nanoparticle existing in sedimentary products which was obtained from arc discharge using carbon-carbon electrodes with arc current of 100 A in liquid nitrogen

Microscopic analyses shown in **Figure 2** reveal that sedimentary particles obtained from arc discharge with arc current of 100A in liquid nitrogen are composed of MW-CNTs with nominal diameter of 8-25 nm and length of 150-250 nm, CNHs with nominal diameter of 50-150 nm and multi-shelled carbon nanoclusters with diameters of 40-100 nm. On the other hand, **Figure 3** shows that cathode deposit obtained from the same condition consists of MW-CNTs with nominal diameter of 8-25 nm and length of 150-250 nm, and multi-shelled carbon nanoparticles with diameters of 40-160 nm. It was found that with an increase in arc current MW-CNTs became less produced while CNHs and multi-shelled carbon nanoclusters became preferably generated. From experimental observation, light emitted from the boiling liquid nitrogen became more intensive in accompany with higher turbulent mixing due to rigorous emergence of gas bubbles. This leads to a logical implication that with the increasing arc current, the evaporation rate of carbon atoms from the anode could become more enhanced. Lange et al. [2] reported that carbon nanotubes are less preferably generated under higher temperature because of its highly exothermic behavior compared with those of carbon nanostructures. As a result, the increasing arc current would lead to a larger average size of carbon nanostructures because of higher formation of carbon nanooinons and polyhedral. Though there is a difference between the particles size analyzed by the microscopic observations and the DLS analyses which are shown in **Figure 4**, trends of effect of the arc current on the average size of synthesized product are in good agreement. With the increasing arc current, the DLS peak size of the synthesized carbon nanoparticles becomes more elevated and achieves a stable value of ca. 295 nm when the arc current is higher than 100 A.

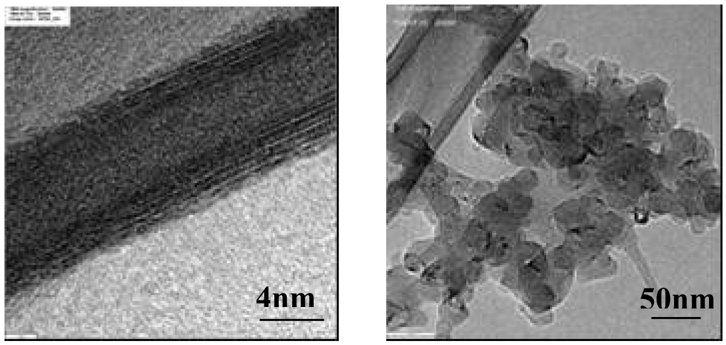

Figure 3. TEM images of carbon nanoparticles existing in cathode deposit which was obtained from arc discharge using carbon-carbon electrodes with arc current of 100 A in liquid nitrogen

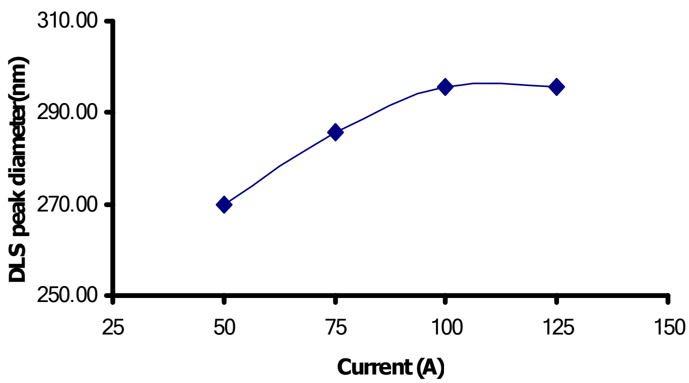

Figure 4. Effect of arc current on peak size of synthesized carbon nanoparticles analyzed by DLS method

It should be noted that when an iron rod was employed as the cathode there was only sedimentary products obtained from the arc discharge. No cathode deposit could be observed. In **Figure 5**, typical TEM micrographs of carbon nanoparticles synthesized by C-Fe electrodes reveal that the synthesized products exhibit remarkable characteristics of Fe nanopartciels encapsulated in graphitic carbon layers. Energy dispersive X-ray analyses reveal that dark zones inside the nanostructures contain iron or iron carbide. Average size of the iron core is in a range of 40 – 150 nm while the nominal size of the carbon nanocapsules is in a range of 50 -400 nm. Much larger size of carbon nanocapsules obtained from the arc discharge using C-Fe electrodes provide an implication that formation of Fe core particles could provide catalytic function to enhance growing of carbon nanolayers on the surface of the Fe particle themselves. Similar to the case of arc discharge using carbon-carbon electrodes, an increase in the arc current could result in an elevating DLS size of carbon nanostructures synthesized by arc discharge with carbon-iron electrodes.

Production yield of CNPs was determined from ratio of weight of as-received product to that of consumed anode. Figure 6 reveals that the production yield of the CNPs synthesized by arc discharge using either carbon-carbon or carbon-iron electrodes are significantly dependent on the arc current. The increasing are current leads to a decrease in production yield of CNPs because a higher emerging rate of gas bubbles generated in the arc zone would lead to higher loss of carbon atoms and clusters. This is in good agreement with the experimental results of Cui et. al. reporting that a decrease in partial pressure of nitrogen around the arc discharge zone could result in a continuous decrease in yield of cathode deposit product [6].

Meanwhile, it should be further remarked that with the same arc current the production yield of carbon-iron electrodes system is significantly higher than that of carbon-carbon system. Xu et al have experimentally revealed that existing of metallic catalytic clusters plays an important role in formation of hybridized carbon nanoparticles which are elementary metal-containing CNCs [11]. The metal particles are encapsulated by dozens of carbon shells, which help protect the encapsulated metal particles from reactive environments (acidic, corrosive and oxidative). With arc temperature of higher than 2000 K iron atoms on the surface of iron electrode surface could be vaporized to form iron nanoclusters which could enhance formation rate of carbon nanostructures due to their catalytic capability. Therefore, the higher production yield as well as the elevated average size of carbon nanocapsules could be obtained from our proposed electrode system. Another attributable reason would be contribution of existing Fe clusters of which density is much higher than carbon.

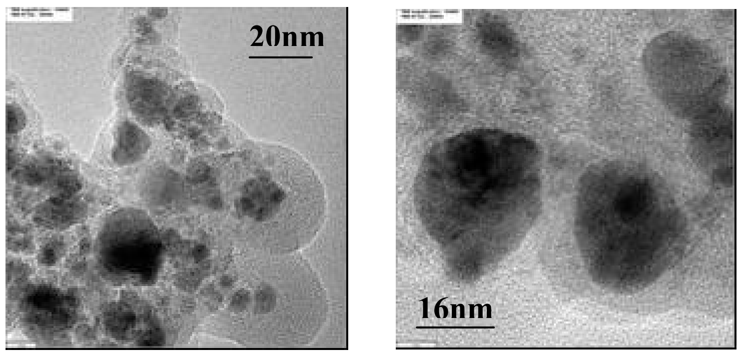

Figure 5. TEM images of carbon nanoparticles existing in cathode deposit which was obtained from arc discharge using carbon-iron electrodes with arc current of 100 A in liquid nitrogen

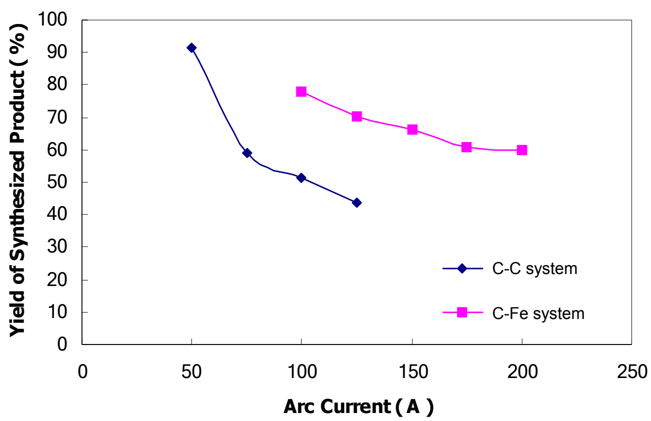

Figure 6. Effect of arc current on production yield of CNPs synthesized by arc discharge using carbon-carbon and carbon-iron electrodes

Conclusion

It is worth to mention that CNHs with some MWNTs could be synthesized when carbon-carbon electrodes were employed. Meanwhile, MWNTs with diameter of 8-25 nm and length 150-250 nm could be selectively synthesized as cathode deposit under the condition of discharge in liquid nitrogen with low arcing current. Use of iron rod as cathode could provide carbon nanocapsules with iron nanoclusters as the core. Typical TEM analyses reveal that under some certain conditions of are discharge in liquid nitrogen carbon nanocapsules (CNCs) with mean diameter of 50-400 nm could be synthesized. However, the production yield of carbon nanoparticles synthesized by either carbon-carbon or carbon-iron electrodes became lower with the increasing arc current due to loss of carbon atoms leaving with more violently emerging gas bubbles.

Acknowledgement

This work was supported by Silver Jubilee Endowment Fund of Chulalongkorn University for CEPT and Research Team Award of Thailand Research Fund for WT. TC and NS gratefully acknowledge Thailand-Japan Technology Transfer Project (TJTTP-JBIC) of CU. Financial support of Faculty of Eng., CU. for TC to participate CARBON2007 is also gratefully acknowledged.

References

[1] H.W. Zhu, X.S. Li, B. Jiang, C.L. Xu, Y.F. Zhu, D.H. Wu and X.H. Chen (2002), Formation of carbon nanotubes in water by the electric-arc technique, *Chem. Phys. Lett.* 366, 664–669

[2] H. Lange, M. Sioda, A. Huczko, Y.Q. Zhu, H.W. Kroto and D.R.M. Walton (2003), Nanocarbon production by arc discharge in water, *Carbon* 41, 1617–1623

[3] D. Nishide, H. Kataura, and S. Okubo(2004), Growth of single-wall carbon nanotubes from ethanol vapor on cobalt particles produced by pulsed laser vaporization, *Chem. Phys. Lett.* 392, 309–313

[4] N. Sano, H. Akazawa, T. Kikuchi and T. Kanki (2003), Sepparated synthesisof iron-inclued carbon nanocapsules and nanotubes by pyrolysis of ferrocene in pure hydrogen, *Carbon* 41, 2159-2179

[5] E. Bekyarova, Y. Hanzawa, K. Kaneko, J. Silvestre-Albero, A. Sepulveda-Escribano, F. Rodriguez-Reinoso, D. Kasuya,M. Yudasaka and S. Iijima (2002), Cluster-mediated .lling of water vapor in intratube and interstitial nanospaces of single-wall carbon nanohorns, *Chem. Phys. Lett.* 366, 463–468

[6] S. Cui, P. Scharff, C. Siegmund, L. Spiess, H. Romanus, and J. Schawohl (2002), Preparation of multiwalled carbon nanotubes by DC arc discharge under a nitrogen atmosphere, *Carbon* 41, 1645– 1687

[7] N. Sano (2004), Formation of multi-shelled carbon nanoparticles by arc discharge in liquid benzene, *Mats. Chem. Phys.* 88, 235–238

[8] N. Sano, J. Nakano and T. Kanki (2004), Synthesis of single-walled carbon nanotubes with nanohorns by arc in liquid nitrogen, *Carbon* 42, 667–691

[9] M.V. Antisari, R. Marazzi and R. Krsmanovic (2003), Synthesis of multiwall carbon nanotubes by electric arc discharge in liquid environments, *Carbon* 41, 2393–2401

[10] N. Sano, T. Kikuchi, H. Wang, M. Chhowalla and G.A.J. Amaratunga (2004), Carbon nanohorns hybridized with a metal-included nanocapsule, *Carbon* 42, 95–99

[11] B.S. Xu, J.J. Guo, X.M. Wang, X.G. Liu and H. Ichinose (2006), Synthesis of carbon nanocapsules containing Fe, Ni or Co by arc discharge in aqueous solution, *Carbon* 44, 2631-2634