

Investigation of the Solution Electrical Conductivity Effect upon the Synthesis of Carbon Nanotubes by Arc Discharge Method

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(Received: September 25, 2012; Accepted in Revised Form: February 4, 2013)

Abstract: Some techniques have been developed to produce carbon nanotubes (CNTs) in sizeable quantities, including arc discharge, laser ablation and chemical vapor deposition (CVD). Arc discharge in liquid environment is a new, simple and cheap method of synthesizing CNTs. CNTs in this study were fabricated by arc discharge in liquid. The present work was undertaken to study the effect of electrical conductivity of liquid on CNTs production and was fabricated using arc discharge between two graphite electrodes submerged in different aqueous solutions of NaCl, KCl and LiCl. For comparative study, CNTs were synthesized under different electrical conductivity conditions and the results were analyzed, compared and discussed. The scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy were employed to study the morphology of these carbon nanostructures. Based on LiCl 0.25 N, high-crystalline and a longed multi MWCNTs, SWCNTs were synthesized by using this technique.

Key words: Electrical Conductivity • Carbon nanotubes • Arc discharge in liquid • Purification • Synthesize carbon nanotube

INTRODUCTION

Carbon nanotubes (CNTs) were first described by Iijima [1]. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. CNTs have been constructed with length-to-diameter ratio of high. The remarkable properties of CNTs have attracted extensive interest since they were first reported in 1991 and making them superior choices in a large variety of applications in classical chemical and process engineering. CNTs are categorized as single wall nanotubes (SWNTs) and multi wall nanotubes (MWNTs).

The usual methods of synthesizing CNTs include arc discharge [1, 2], laser vaporization [4, 5] and chemical vapor deposition [6-8]. Arc discharge in liquid environments is a new method of synthesizing CNTs developed recently [9-10].

This method does not require vacuum equipment, reacted gases, a high temperature furnace or a heat exchange system. Consequently, this method is extremely

simple and cheap. Ishigami et al. reported the first production of CNTs by arc discharging in liquid nitrogen [10]. Moreover, Hsin et al. produced CNTs by using an arc in deionized water [11]. Furthermore, Zhu *et al.* fabricated CNTs in deionized water or aqueous solution of NiSO₄, CoSO₄ and FeSO₄ [12]. Lange et al. constructed CNTs and carbon onions in deionized water [13] and Antisari et al. compared arc discharge in liquid nitrogen and deionized water [14].

In this study, some new results by investigating the morphologies and microstructures of CNTs that prepare by arc discharge in solution under different condition are presented. Subsequently a modified acid treatment method will apply for purification stage. The arc discharge in this work takes place between two electrodes; they are submerged in the liquid solutions in a beaker. This research is going to study the effect of electrical conductivity of solution on synthesise, morphology as well as characterization of fabricated CNTs.

MATERIALS AND METHODS

Materials: All chemicals were of analytical grade and aqueous solution was prepared by dissolving LiCl (Fulka, Sweden), NaCl (Fulka, Sweden) and KCl (Fulka, Sweden) in de-ionized water. Ni (Merck) and Mo (Sigma, Uk) were purchased as catalyst.

A graphite rod of diameter 6 and 12 mm (Germany) was used for anode and cathode respectively. The products were treated with HCl (Merck, Germany) for observation by using electron microscopy to analyze the samples.

Set up: A schematic of arc discharge apparatus is shown in Fig. 1. The graphite anode and cathode were submerged in liquid media and sustained vertically. Both electrodes were connected with a digital controllable DC power supply and submerged in 3000 cm³ of aqueous solution in a steel beaker (15×20×20 cm³) [15]. Evaporation of the solution during the arc discharge is ignored.

Fabrication: The cathode-anode gap was controlled at approximately 1 mm to maintain a stable discharge current of 10 A and a voltage of 20-25 V, while the synthesis time was 60s [11]. The anode was drilled a 2 mm diameter hole and filled with Ni/Mo powders as a catalyst and the ½ as a catalyst ratio according to literature [16].

Arc discharge in deionized water and liquid nitrogen are erratic due to their electrical insulation [9]. According to the physical model set out in [12], the plasma produced from arc discharge in liquid, can supply enough energy for carbon atoms to evaporate from anode. These atoms leave the anode surface with certain velocity due to pressure gradient and some of them become ionized as a result of collisions with electrons emitted from cathode. In the mean time, some other carbon species including atoms and ions move from anode to cathode.

In this method, a direct current dc arc discharge was generated between two electrodes. The raw products were collected, filtered out and purified. The scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy were employed to study the morphology of these carbon nanostructures. This study was investigated the effect of electrical conductivity of solution on the structure of CNT. To find this effect, CNTs have been produced in three different electrical conditions namely, LiCl, KCl and NaCl and the results have been compared and analyzed.

Purification: A separation and purification process was applied upon the deposit. The following purification steps for all tests were put: A Millipore filter was used to separate solid material, sonicating deposits in 12 N HCl for 30 minutes, refluxing in 6 N HCl for 6 hours. Therefore the resulting solution was diluted with distilled water and centrifuged. After that material separates with a Milipore again and the residue was dried in an oven at 80-100°C for 5 hours. Then the CNTs were kept in desiccators [15, 16]. To study the morphology of the products a scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and Raman spectroscopy were applied.

RESULTS AND DISCUSSION

In the first sample, CNTs were synthesized by arc discharge method in the LiCl (0.25N) as liquid media with a voltage 25 v while Ni and Mo was used as catalyst [23]. The all conditions for two other samples were constant except aqueous solution. Here, NaCl, KCl, LiCl were used as aqueous solution with different electrical conductivity and the same concentration. Table 1 shows the electrical conductivity of the salty solution used in this study.

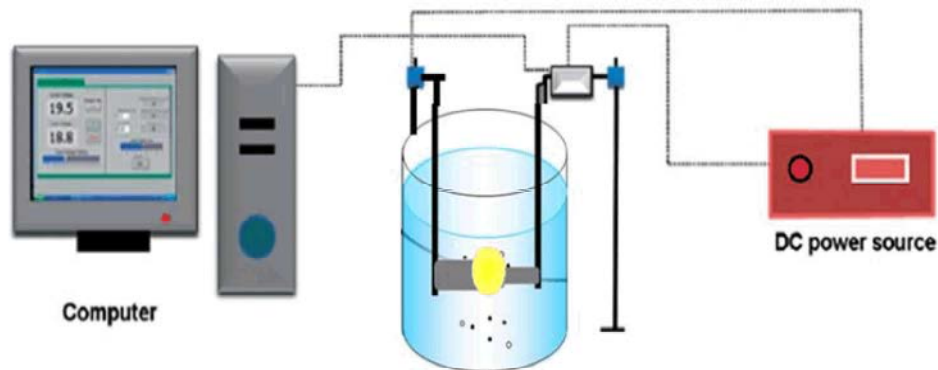


Fig. 1: A schematic of arc discharge

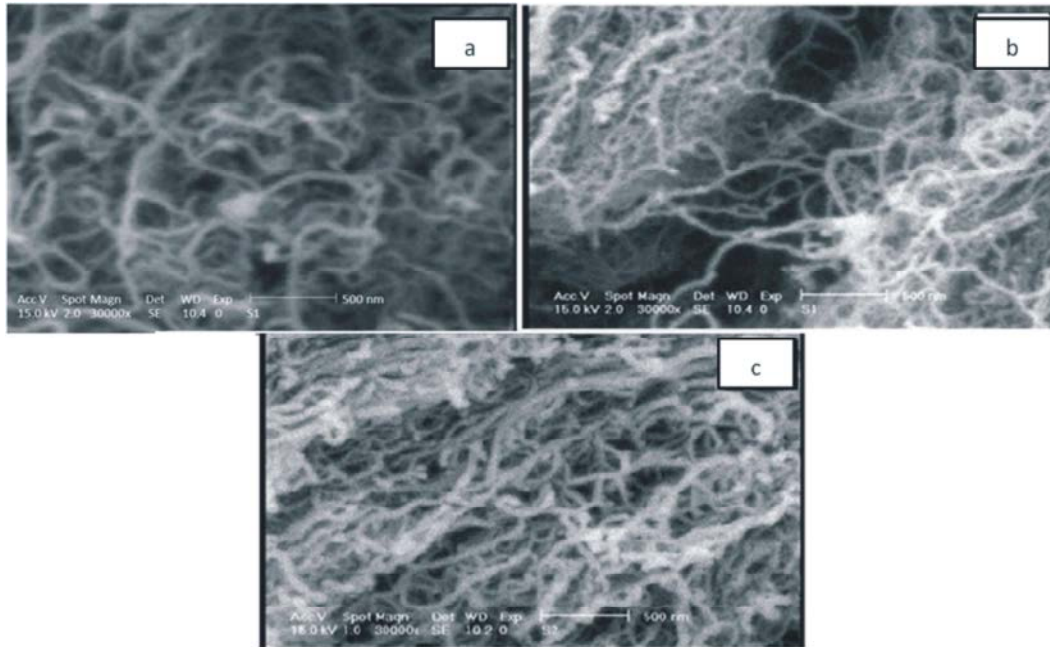


Fig. 2: a) SEM image of CNTs produced by arc discharge in LiCl 0.25 N, b) NaCl 0.25N, c) KCl 0.15N

Table 1: Electrical conductivity of LiCl, NaCl, KCl (0.25N)

0.25 N of aqueous solution	LiCl	KCl	NaCl
Electrical Conductivity (mS/cm)	22.7	24.4	33.1

Table 2: Electrical conductivity of KCl in different concentration

Concentration(mole/l)	0.1	0.2	0.3	0.4
Electrical Conductivity(mS/cm)	13.1	26	35.8	43.9

Figure 2a shows SEM image of the first sample. CNTs were synthesized in the NaCl 0.25N [22] in second sample while the other conditions were the same as the conditions of the previous experiment.

In third sample, KCl 0.25N has been applied as a solution, but in this condition no CNTs were produced because of high electrical conductivity of the solution. However, the arc has been found to be unstable. The electrical conductivity of KCl in different concentration was determined subsequently. Table 2 shows the electrical conductivity of the KCl. whereas; CNTs were produced in LiCl 0.25N and NaCl 0.25N with 22.7 and 24.4 as a electrical conductivity respectively.

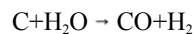
Therefore KCl 0.15 N with 19.8 mS electrical conductivity was selected for the effect of electrical conductivity study. To study the morphology of the products a transmission electron microscopy was applied. Figure 2b shows SEM image of the second sample. Also Figure 2c illustrates SEM image of third sample after purification step. Figure 2 shows that the diameter of produced CNTs based on arc discharge in LiCl 0.25 N was smaller and more suitable dispense than others.

Electrical Conductivity Effect on Crystallinity:

The Raman spectra of the CNTs in LiCl 0.25 N are shown in Figure 3A and in NaCl 0.25 N are shown in Figure 3B. In the Raman spectra D-band is an indication of the presence of defective material and G-band refers to the well-ordered graphite.

The decrease in D-peak intensity indicates a reduction in the relative amount of disordered carbon of the samples [10]. In Figure 3B, it can be observed that distance between the D-band peak and G-band is low while in Figure 3A the D-band peak is decreased and this distance is much more. TEM images show that the products are mainly CNTs with 5-10 nm in diameter (Figure 4). The images also indicate that produced CNTs have quite uniform and good quality structures.

During the arc discharge process in aqueous solutions, the gas bubbles of CO and H₂ were formed around the hot arc region as follows as explained before [6]:



The gas mixture further forms a chamber of reducing environment, which can lead to cooling of the reactants. The liquid hosting the arc plasma causes rapid quenching of the carbon vapor emitted from the consumed anode.

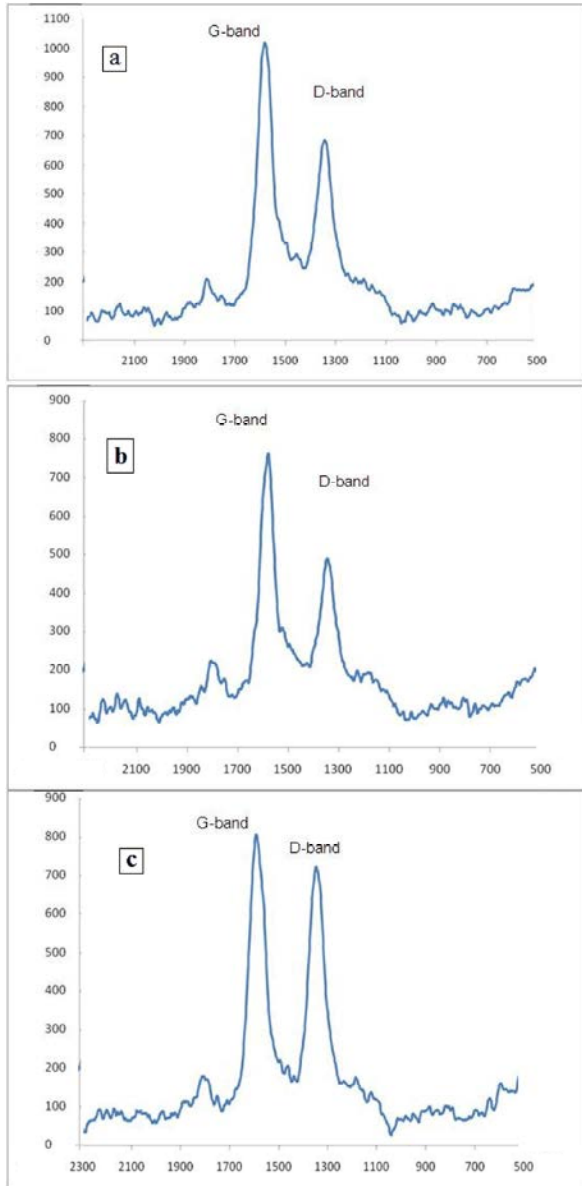


Fig. 3: Raman spectrums of CNTs were fabricated a) in LiCl 0.25N b) in NaCl 0.25 c) in KCl 0.15N

Despite the extremely high electrical conductivity of KCl 0.25 N was caused the turbulence media and unstable arc because of the high moving ions and the operation of the arc discharge did not allow a good thermal exchange between the synthesized material and its surroundings but the arc discharge in LiCl 0.25N solution was found to be extremely stable.

Therefore, it could be said that KCl 0.25 N solution provided less efficient cooling than LiCl 0.25N solution and the fabricated CNTs exhibit a distorted morphology and a degraded structure. The arc discharge in LiCl 0.25N

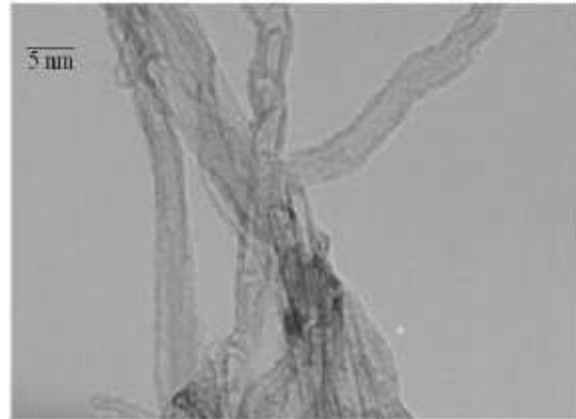


Fig. 4: TEM image photograph of the product fabricated by arc discharge in LiCl 0.25N aqueous solution

Table 3: Amount of fabricated CNTs in 3 varies aqueous solutions

Amount of CNTs (mg)		Aqueous solution
Run 1	Run 2	
5.8	6.6	LiCl (0.25 N)
5.3	5.1	NaCl (0.25 N)
3.42	4.15	KCl (0.25 N)

solution was found to be extremely stable and this was thought to be owing to the excellent electrical conductivity induced by Cl^- and Li^+ ions. Too many Li^+ ions are believed to hinder carbon ions flying from anode towards the center of cathode [9].

Table 3 was indicated the amount of produced CNTs in three different solutions. This was suggested that LiCl yields the maximum amount of product at different runs.

CONCLUSIONS

In this study, CNTs were successfully synthesized using arc discharge in aqueous solutions. The CNTs fabricated while the anode and cathode were submerged in salty solutions of NaCl, KCl and LiCl with different electrical conductivity. The extremely high electrical conductivity of KCl 0.25 N was caused the turbulence media and unstable arc because of the high exchange ion and the operation of the arc discharge did not allow a good thermal exchange between the synthesized material and its surroundings but the arc discharge in LiCl 0.25N solution was found to be extremely stable. SEMs, TEM and Raman showed that the produced CNTs in LiCl 0.25N with 22.7mS as an electrical conductivity were with long length, narrow distribution diameters and crystalline structure without any defect and followed with a good yield. To the best of our knowledge the current study is

one of the first one have demonstrated application of a arc discharge in liquid media with electrical conductivity effects upon CNT preparation and deserves further study.

ACKNOWLEDGMENTS

Authors would like to thank Nanobiotechnology research group, Babol University of Technology. Also special thanks to Kashan University for their cooperation in various aspects of this collaborative work.

REFERENCES

1. Iijima, S. and T. Ichihashi, 1993. Single shell carbon nanotubes of one nanometer diameter. *Nature*, 363: 603-605.
2. Baughman, R.H., A.A. Zakhidov and W.A. Heer, 2002. Carbon Nanotubes - The Route Towards Applications. *Science*, 297: 787-792.
3. Mansour, A., M. Razafinimanana, M. Monthioux, M. Pacheco and A. Gleizes, 2007. A significant improvement of both yield and purity during SWCNT synthesis via the electric arc process. *Carbon*, 45: 1651-1661.
4. Ando, Y., X.L. Zhao, K. Hirahara, K. Suenaga, S.J. Bandow and S. Iijima, 2000. Mass production of single-wall carbon nanotubes by the arc plasma jet method. *Chemical Physics Letters*, 323: 580-585.
5. Sano, N., H. Wang, M. Chhowalla, I. Alexandrou and G.A.J. Amaratunga, 2001. Synthesis of carbon 'onions' in water. *Nature*, 414: 506-507.
6. Nikolaev, P., M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert and K.A. Smith, 1999. Gas-phase Catalytic Growth of Single-Walled Carbon Nanotubes from Carbon Monoxide. *Chemical Physics Letters*, 313: 91-97.
7. Cheng, H.M., F. Li, G. Su, H.Y. Pan, L.L. He and X. Sun, 1998. Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons. *Applied Physics Letters*, 72: 3282-3284.
6. Andrews, R., D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, 1999. Continuous production of aligned carbon nanotubes. a step closer to commercial realization. *Chemical Physics Letters*, 303: 467-474.
9. Sano, N., H. Wang, I. Alexandrou, M. Chhowalla, K.B.K. Teo, G.A.J. Amaratunga and K. Iimura, 2002. Properties of carbon onions produced by an arc discharge in water. *Applied Physics*, 92: 2783-2788.
10. Ishigami, M., J. Cumings, A. Zettl and S. Chen, 2000. A Simple Method for the Continuous Production of Carbon Nanotubes. *Chemical Physics Letters*, 319: 457-459.
11. Hsin, Y.L., K.C. Hwang, F.R. Chen and J.J. Kai, 2001. Production and in situ metal filling of carbon nanotubes in water. *Advanced Materials*, 13: 830-835.
12. Zhu, H.W., X.S. Li, B. Jiang, C.L. Xu, Y.F. Zhu and D.H. Wu, 2002. Formation of carbon nanotubes in water by the electric-arc technique. *Chemical Physics Letters*, 366: 664-669.
16. Lange, H., 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.
14. Antisari, M.V., R. Marazzi and R. Krsmanovic, 2003. Synthesis of multiwall carbon nanotubes by electric arc discharge in liquid environments. *Carbon*, 41: 2393-2401.
15. Jahanshahi, M., J. Raoof and R.J. Seresht, 2009. Voltage effects on the production of nanocarbons by a unique arc-discharge set-up in solution. *Experimental Nanoscience Journal*, 4: 331-339.
16. Jahanshahi, M., R. Jabari Seresht and S. Hajizadeh, 2009. Catalysts effects on the production of carbon nanotubes by an automatic arc discharge set up in solution, *Physica Status Solidi*, 6: 2174-2178.
17. Lange, H., M. Sioda, A. Huczko, Y.Q. Zhu, H.W. Kroto and D.R.M. Walton, 2003. Nanaocarbon production by arc discharge in water. *Carbon*, 41: 1617-1623.
18. Jahanshahi, M., J. Raoof, S. Hajizadeh and R. Jabari Seresht, 2007. Application of Taguchi method in the optimization of ARC-Carbon nanotube fabrication, *Nanotechnology and its application*. American Institute of Physics, 929: 77-81.
19. Wang, S.D., M.H. Chang, M.D. Lan, C.C. Wu, J.J. Cheng and H.K. Chang, 2005. Lipophilic functionalization of multi-walled carbon nanotubes with stearic acid. *Carbon*, 43: 1778-1814.

20. Zhao, H.P., Y.D. He, X.H. Kong and W. Gao, 2007. Carbon nanotubes and diamond-like carbon films. *Materials Letters*, 61: 4916-4919.
21. Jahanshahi, M., J. Raoof, S. Hajizadeh and R. Jabari Seresht, 2007. Application of Taguchi method in the optimization of ARC-Carbon nanotube fabrication. *First Sharjah International Conference on nanotechnology and its applications*. UA.
22. Jahanshahi, M., J. Raoof, S. Hajizadeh, R. Jabari Seresht, 2009. Synthesis and subsequent purification of carbon nanotubes by arc discharge in NaCl solution. *Physical Status Solidi (A)*, 206: 101-105.
23. Jabari Seresht, R., M. Jahanshahi and F. Toubi, 2010. Applying the Multiple Linear Regressions and Taguchi Design Method for Controlled Fabrication of Carbon Nanotubes in Solution, Fullerenes, Nanotubes and Carbon Nanostructures, 18: 148-159.