

Synthesis of Carbon Nanofibers from Carbon Particles by Ultrasonic Spray Pyrolysis of Ethanol

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SUMMARY We report the growth of carbon nanofibers (CNFs) from carbon particles by chemical vapor deposition (CVD) with ultrasonic neblizer using ethanol as carbon source. Dense CNFs having diameters of several tens of nanometers have been successfully synthesized by the CVD without using any metal catalysts. The carbon particles formed from decomposition of fullerene were found to be suitable for the synthesis of CNFs. Details of the optimum conditions for producing CNFs and the expected growth mechanism are also described.

key words: carbon nanofibers, ultrasonic spray pyrolysis, carbon particles

1. Introduction

Carbon nanofibers are filaments or whiskers of carbon which have diameters less than 500 nm. The CNFs have a high aspect ratio, and hence the lengths of nanofibers are usually in the range of few micrometers or more. In general, the carbon nanofibers are constructed by amorphous carbon [1]. It has resulted very attractive materials owing to their unique chemical and physical properties. And many potential applications have been proposed; such as resin material, fuel cell [2], electron field emission source [3], interconnects [4], energy storage [5], capacitors [6], battery electrodes [7] etc.

Several studies have been investigated for synthesis of CNFs by chemical vapor deposition (CVD) [8]. The CVD technique is a simple and low-cost method, and it is thought to be used for mass production. In traditional method, the horizontal furnace is the most popular configuration for the production of carbon nanofibers [9]. Synthesis of CNFs involves supporting of metallic (Ni, Fe, and Co or alloys) particles on oxides form or other materials for carbonization of gaseous precursor by catalytic pyrolysis (thermal CVD synthesis) [10]. For example the CNFs having diameter of about 100 nm have been synthesized by using Co and acetylene as catalyst metal and carbon source, respectively [11].

The CNFs samples synthesized by CVD generally need the purification processes, because of the existence of metal catalysts. In this use of Co-catalyst as case, the TGA of an as-produced sample shows that the sample contains 23wt.% catalysts. Even after purification with hydrochloric acid the sample still has 10wt.% of the remained catalyst metal. Thus, this is obviously that achieving completely purified

CNFs for device application is still a challenging work. To obtain CNFs sample having no metal catalysts, novel synthesis method without using any catalyst metals is required.

In the present study, we have obtained CNFs that have diameter of about 20 nm without using any metal catalyst. This method produces mist of carbon sources by ultrasonic spray pyrolysis for the synthesis of CNFs. This is the promising method to grow carbon nanofibers.

2. Experimental

Figure 1 shows the schematic diagram of the CVD apparatus. The ultrasonic nebulizer is connected to quartz tube and N₂ gas cylinder. Si (100) substrates of size 10 mm × 10 mm were cleaned in acetone and methanol by ultrasonicator followed by deionized water and finally dried using nitrogen blower. The substrates were kept in the quartz boat, which was then placed at the center of the quartz tube. The one end of the quartz tube was attached to ultrasonic spray pyrolysis and other to the gas bubbler. Deposition was performed at different reaction temperatures ranging from 650°C to 950°C. Fullerene was used as the source of carbon particles and ethanol was used as carbon source. Before allowing ethanol/fullerene (100 ml/0.1 g) mixture to enter into the quartz tube, the electric furnace was allowed to attain the desired temperature. When electric furnace has reached the desired temperature, ultrasonic nebulizer was switched on. Ethanol/fullerene mixture was change to thin mist. Flow of N₂ was maintained to pass this mist inside the electric furnace. After deposition the furnace was switched off and allowed to cool down the temperature below 100°C.

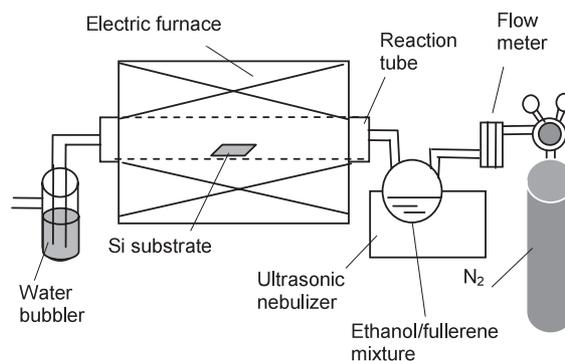


Fig. 1 Schematic image of the apparatus of the CVD.

Manuscript received February 27, 2009.

Manuscript revised July 15, 2009.

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DOI: 10.1587/transle.E92.C.1432

In spray pyrolysis method [12], mist of fullerene/ethanol can not be produced, although vaporization and pyrolysis of carbon source occurs simultaneously. But fullerenes will not dissolve in ethanol. So, a simultaneous passes of ethanol and fullerenes is not possible in spray pyrolysis, whereas in ultrasonic spray pyrolysis, electric vibrators (1.65 MHz, Atom Medical Corp-Modle 303) produces mist of ethanol and fullerene. Finally, CNFs were removed from the Si for characterization by scanning electron microscope (SEM, Hitachi S-3000H), transmission electron microscope (TEM, JEOL JEM-4000 EXII), thermo-gravimetric analysis (TGA, THERMOFLEX TG-DTA TG8110) and Raman spectroscopy (JASCO, NRS-1500 W). The excitation wavelength in the Raman measurements was 532 nm.

3. Results and Discussion

3.1 Synthesis of CNFs from Carbon Particles by Ultrasonic Spray Pyrolysis of Ethanol

Figure 2(a) shows a SEM image of CNFs synthesized at 750°C. Dense CNFs were successfully deposited on the Si substrates. Figure 2(b) shows a TEM image of an individual CNF, having a diameter of about 20 nm. The TEM observation indicates that the present CNFs were amorphous carbon condition as shown in Fig. 2(c). However, in the case of ultrasonic spray pyrolysis method using ethanol and metal catalyst at 850°C CNTs were obtained [13]. We found that the present CNFs have a black spot on the bottom of CNFs by the TEM observations which are shown in Figs. 2(b) and (d).

We expect that such particles have been originated from the fullerene. To identify whether the particles are constituted from the carbon, we used TGA by measuring the amount of residue. Figure 3 shows the TGA curve of CNFs sample synthesized at 750°C. TGA was measured in the static-air. TGA analysis was normalized at 200°C. The reason for this normalization is that CNFs might have absorbed water vapor from air, which could influence TGA curve. At 200–500°C, TGA curve was slightly declined; that is attributed to organic decomposition of thermally unstable carbon group formed on the surface of CNFs [14]. The weight loss of CNFs was clearly observed from 500°C. We have observed no impurity residues after the measurements. This result indicates that the present sample has no metal catalysts and the particles at the bottom of CNFs are consisted of carbon materials originated from the fullerenes.

To investigated the structure of fullerene under the CVD temperature, we measured Raman spectra of fullerene samples annealed at the reaction temperatures (650–950°C) in N₂. Figure 4(a) shows the typical Raman spectra of the pristine fullerenes sample. We observed a peak around 1460 cm⁻¹ corresponding to tangential A_g mode [15]. The two peaks (G and D) are clearly observed from the samples annealed at 650°C to 950°C. G-peak corresponds to tangential stretching mode (E_{2g}) of sp² carbon atoms and D-peak originates from disorder in the sp² hybridized carbon [16].

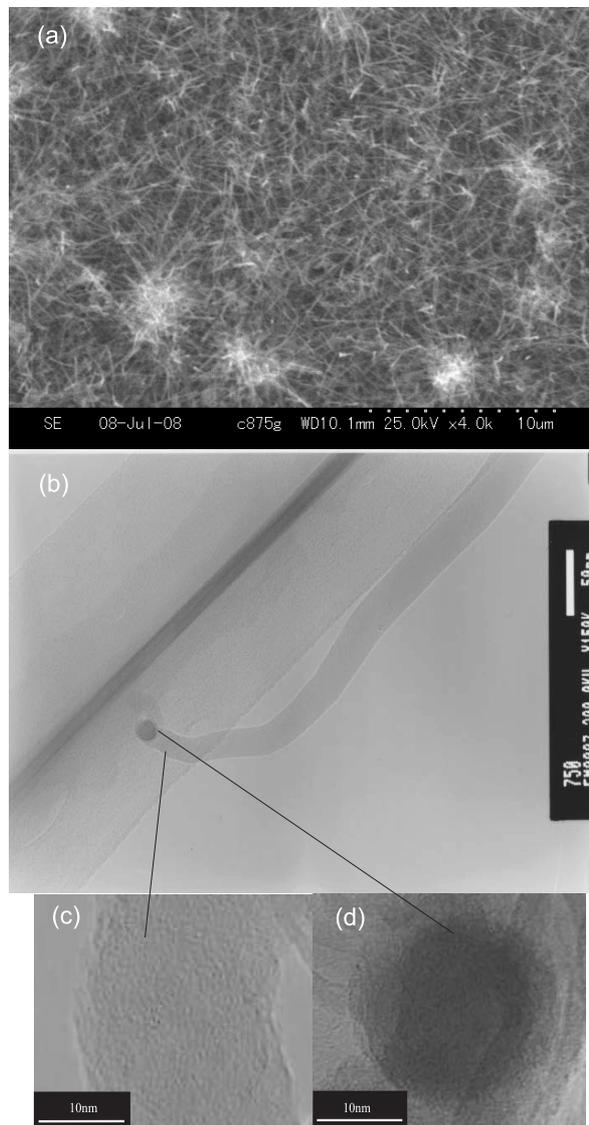


Fig. 2 SEM and TEM images of carbon nanofibers synthesized on Si substrate: (a) SEM image of CNFs synthesized at 750°C, (b) TEM image of an individual CNF, (c) enlarged TEM images of the body, and (d) the bottom of the CNF.

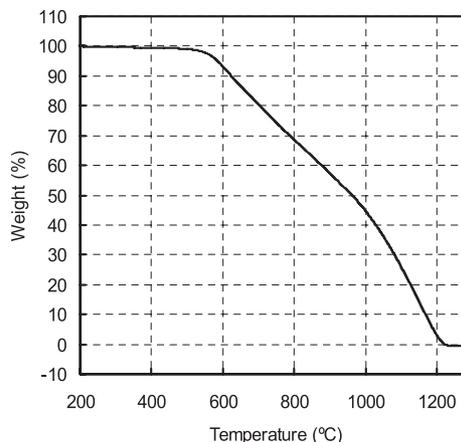


Fig. 3 TGA curve of the CNFs sample synthesized at 750°C substrate.

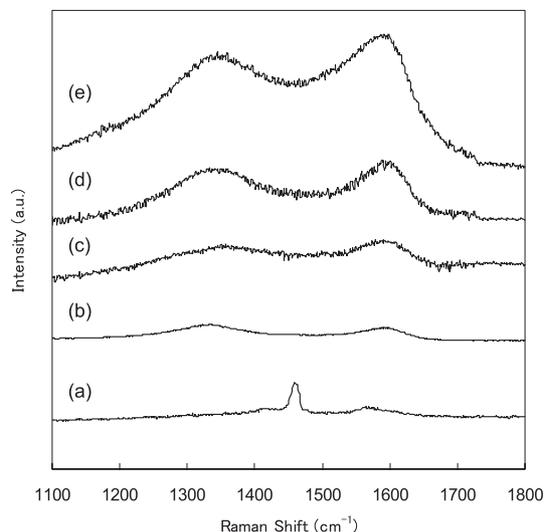


Fig. 4 Raman spectra of (a) pristine fullerene sample and those after heating at (b) 650°C, (c) 750°C, (d) 850°C, and (e) 950°C.

This result indicates that the structured fullerene was destroyed and converted to amorphous carbon in the present conditions. And the structure of carbon particles on the bottom of CNFs were speculated amorphous like one.

3.2 Growth Temperatures Dependence of Synthesis of CNFs

Figure 5 shows the SEM image of CNFs synthesized at different temperatures after passing the mist of fullerene/ethanol into the quartz tube. The carbon nanofibers were synthesized at all the temperatures ranging from 650°C to 950°C. Figure 5(a) shows a SEM image of CNFs synthesized at 650°C. Short carbon nanofibers were observed. The yields of CNFs synthesized at 750°C and 850°C are high compared to other temperatures. At 950°C, aggregation of carbon particles originated from fullerene were observed.

According to these images, we expected that the growth temperature can affect the synthesis of CNFs. The amounts of active carbon increase with increasing growth temperature. However, aggregation of carbon particles are prompted by higher temperature heating, as shown in Fig. 5(d).

Figure 6(a) shows the Raman spectra of CNFs at different temperatures ranging from 650°C to 950°C. At 750°C and 850°C, the intensity of G peak is slightly higher than that of D peak. This indicates that the better graphitization of carbon nanofibers was obtained at these temperatures. Figure 6(b) shows the ratio of intensity of I_D/I_G decreases at 750°C, which suggests better formation of sp^2 hybridized CNFs at this temperature.

3.3 Growth Mechanism of CNFs

To clarify the growth mechanism of CNFs in the present

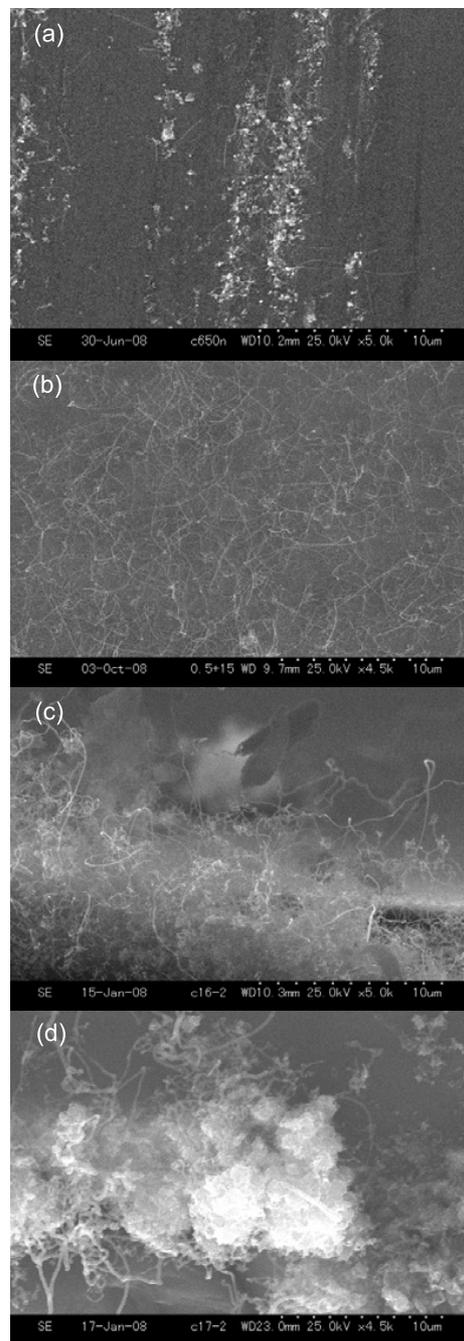


Fig. 5 SEM images of CNF synthesized at (a) 650°C, (b) 750°C, (c) 850°C, and (d) 950°C.

CVD method, we investigated growth time dependence of synthesis of CNFs. Figure 7(a) shows a SEM image of CNFs formed in 3 minutes deposition. CNFs can be observed in this image. Figure 7(b) shows a SEM image of CNFs obtained after 30 minutes growth. In this condition, longer CNFs can be seen as compare to 3 min growth. Figure 7(c) shows a SEM image of CNFs synthesized at 60 minutes. The number of longer CNFs increase with increasing reaction time as shown in Figs. 7(b) and (c). However, the diameters of CNFs of these samples are almost same as

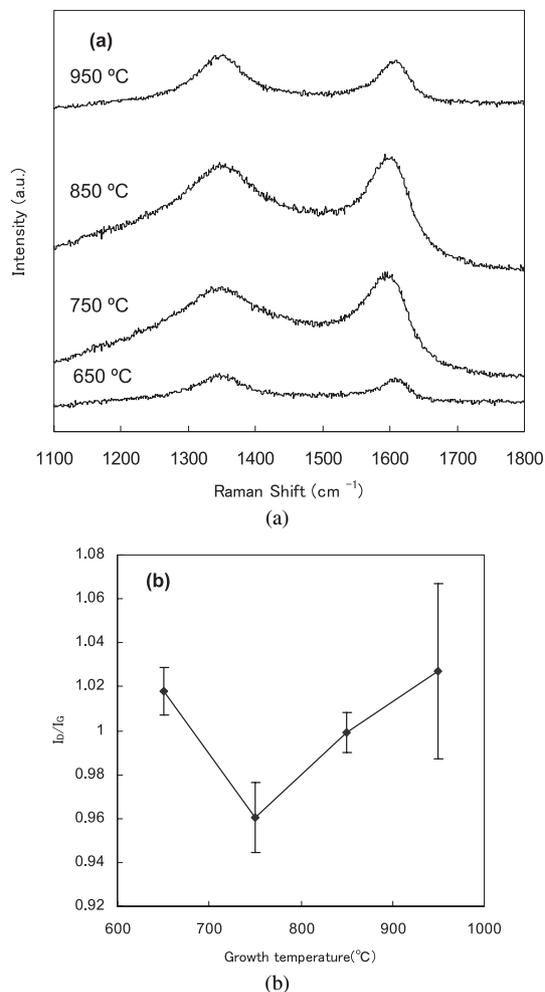


Fig. 6 (a) Raman spectra of CNFs synthesized at: 650 °C, 750 °C, 850 °C, 950 °C. (b) Growth temperatures dependent of I_D/I_G ratio.

shown in the insets of Figs. 7(a)–(c).

In general, the growth of CNFs occurs by catalytic decomposition of the carbon feedstock and bulk diffusion of carbon atoms [17]. According to this reference, length of CNFs depends on the growth time. The expected growth mechanism of the present CNFs is as follows. First, fullerenes become carbon particles by heating under the CVD temperature as shown in Fig. 2(d). Secondly, ethanol is rapidly decomposed and carbon sources are supplied to the carbon particles. The supplied carbon atoms diffuse on the surface of the carbon particles and form the body of CNFs, as shown in Fig. 2(c).

As shown in Figs. 7(b) and (c), short CNFs are also observed with longer ones. The short CNFs observed in Figs. 7(b) and (c) are CNFs, which are deposited on Si substrate in short time. After introducing fullerene/ethanol mixture, the growth of CNFs occurs during flowing of carbon sources along the quartz tube. A part of flowing CNFs successively falls on the Si substrate. The deposited CNFs become longer on the Si substrate by continuous supply of carbon sources. Finally, mixtures of longer and short CNFs are

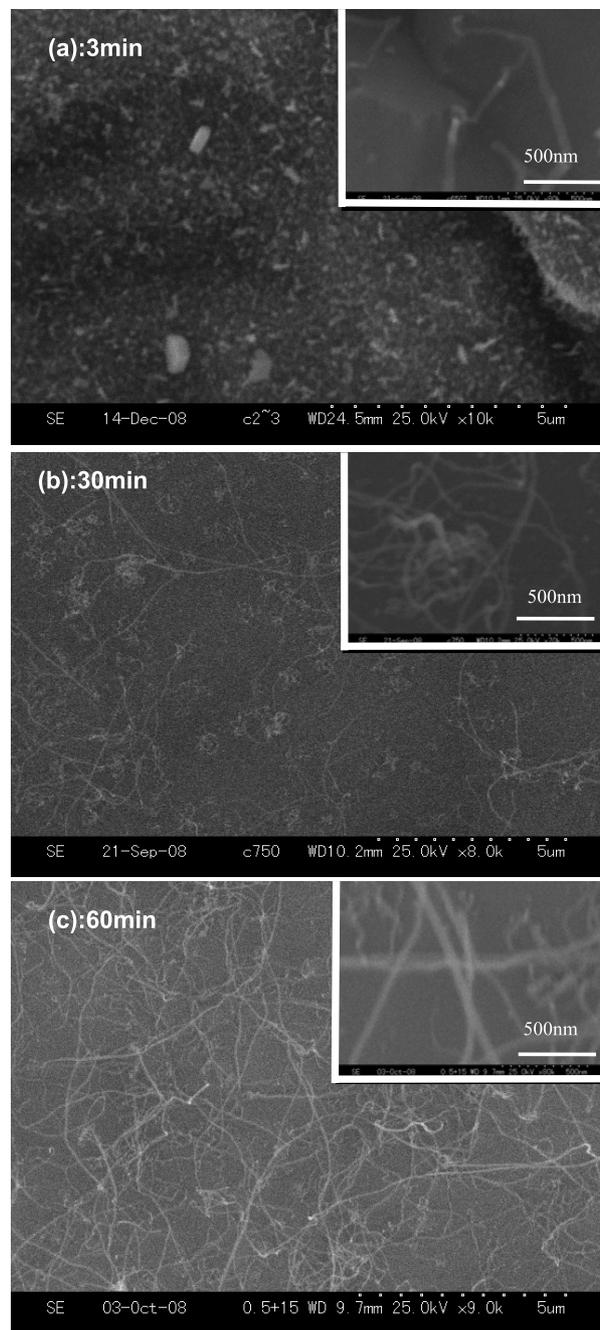


Fig. 7 SEM images of carbon nanofibers synthesized for SEM image of (a) 3 min, (b) 30 min and (c) 60 min. The insets show the high magnification images of each SEM pictures.

formed on the substrate.

4. Conclusion

In this study, we achieved synthesis of CNFs without using any catalyst metals. We expect that carbon particles originated from fullerene, which acts as the nucleating site for the formation of CNFs. This process can be a good alternative to achieve all the properties of carbon nanofibers because it does not require any further acid treatment process, which

may destroy and reduce the nature of CNFs. A part of the short CNFs formed during flowing of mist of carbon falls on the Si substrate. CNFs deposited on the Si become longer with increasing reaction time.

References

- [1] J.P. Tu, L.P. Zhu, K. Hou, and S.Y. Guo, "Synthesis and frictional properties of array film of amorphous carbon nanofibers on anodic aluminum oxide," *Carbon*, vol.41, no.6, pp.1257–1263, 2003.
- [2] D. Sebastián, I. Suelvesa, M.J. Lázaro, and R. Molinera, "Carbon nanofibers as electrocatalyst support for fuel cells: Effect of hydrogen on their properties in CH₄ decomposition," *J. Power Sources*, vol.192, no.1, pp.51–56, 2008.
- [3] H. Li, J. Li, and C. Gu, "Local field emission from individual vertical carbon nanofibers grown on tungsten filament," *Carbon*, vol.43, no.4, pp.849–853, 2005.
- [4] J.C. Coiffic, H. Le Poche, D. Mariolle, N. Chevalier, S. Olivier, M. Fayolle, and S. Maitrejean, "Toward the integration of single carbon nanofiber as via interconnect," *Microelectronic Engineering*, vol.85, no.10, pp.1971–1974, 2008.
- [5] X. Chen, Y. Zhang, X.P. Gao, G.L. Pan, X.Y. Jiang, J.Q. Qua, F. Wua, J. Yana, and D.Y. Songa, "Electrochemical hydrogen storage of carbon nanotubes and carbon nanofibers," *International Journal of Hydrogen Energy*, vol.29, no.7, pp.743–748, 2004.
- [6] S.-U. Kim and K.-H. Lee, "Carbon nanofibers composites for the electrodes of electrochemical capacitors," *Chemical Physics Letters*, vol.400, no.1-3, pp.253–257, 2004.
- [7] L. Ji and X. Zhang, "Manganese oxide nanoparticle-loaded porous carbon nanofibers as anode materials for high-performance lithium-ion batteries," *Electrochemistry Communications*, vol.11, no.4, pp.795–798, 2009.
- [8] D.B. Thakur, R.M. Tiggelaar, J.G.E. Gardeniers, L. Lefferts, and K. Seshan, "Growth of carbon nanofiber coatings on nickel thin films on fused silica by catalytic thermal chemical vapor deposition: On the use of titanium, titanium–tungsten and tantalum as adhesion layers," *Surface and Coatings Technology*, vol.203, no.22, pp.3435–3441, 2009.
- [9] M. José-Yacamán, H. Terrones, L. Rendón, and J.M. Domínguez, "Carbon structures grown from decomposition of a phenylacetylene and thiophene mixture on Ni nanoparticles," *Carbon*, vol.33, no.5, pp.669–678, 1995.
- [10] G. Xie, W. Sun, and W. Li, "Synthesis and catalytic properties of amorphous Ni-Co-B alloy supported on carbon nanofibers," *Catalysis Communications*, vol.10, no.3, pp.333–335, 2008.
- [11] S.A. Manafi and S.H. Badiiee, "Production of carbon nanofibers using a CVD method with lithium fluoride as a supported cobalt catalyst," *Research Letters in Materials Science*, vol.2008, pp.1150–1155, 2008.
- [12] R.A. Afre, T. Soga, T. Jimbo, M. Kumar, Y. Ando, M. Sharon, P.R. Somani, and M. Umno, "Carbon nanotubes by spray pyrolysis of turpentine oil at different temperatures and their studies," *Microporous and Mesoporous Materials*, vol.96, no.1-3, pp.184–190, 2006.
- [13] I. Khatri, T. Soga, T. Jimbo, S. Adhikari, H.R. Aryal, and M. Umeno, "Synthesis of single walled carbon nanotubes by ultrasonic spray pyrolysis method," *Diamond and Related Materials*, vol.18, no.319, pp.50–61, 2009.
- [14] M. Chipara, K. Lozano, A. Hernandez, and M. Chipra, "TGA analysis of polypropylene-carbon nanofibers composites," *Polymer Degradation and Stability*, vol.93, no.4, pp.871–876, 2008.
- [15] B. Liu, Y. Hou, L. Wang, D. Liu, S. Yu, B. Zou, T. Cui, G. Zou, A.I. Wabning, and B. Sundqvist, "High pressure and high temperature induced polymeric C₆₀ nanocrystal," *Diamond and Related Materials*, vol.17, no.4-5, pp.620–623, 2008.
- [16] V.B. Golovko, M. Cantoro, S. Hofmann, B. Kleinsorge, J. Geng, D. Jefferson, A.C. Ferrari, J. Robertson, and B.F.G. Johnson, "Selective growth of vertically aligned carbon nanofibers in sub-micron patterns and Raman mapping of produced arrays," *Diamond and Related Materials*, vol.15, no.4-8, pp.1023–1028, 2006.
- [17] R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates, and R.J. Waite, "Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene," *J. Catalysis*, vol.26, no.1, pp.51–62, 1972.



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