

***In Situ* Synthesis of Carbon Nanotubes by Polymer Materials**

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ABSTRACT

Catalytically grown carbon nanotubes were prepared by *in situ* thermal decomposition of the polymer materials. Polymer material (PEG, polyethylene glycol) was employed as carbon source and nickel-based materials were used as catalytic precursors. These materials were well mixed and thermal treated at the desired temperature. The synthesis process includes the removal of solvent, dehydrogenation, thermal decomposition, carbonization, graphitization, and formation of carbon nanotubes by catalytic effects. The results showed that carbon nanotubes can be formed without any additional hydrocarbon gases during the fabrication process at 750 °C in the nitrogen atmosphere. By the field emission-scanning electron microscopy (FE-SEM) and high resolution-transmission electron microscopy (HR-TEM) observation, it revealed that the carbon nanotubes possesses highly graphitic structures and the diameters were about 20-30 nm.

Keywords: carbon nanotubes, polymer, *in situ*

1 INTROCTION

Carbon nanotubes (CNTs) have attracted increasing attention since their discovery by S. Iijima in 1991 [1], it have been intensive studied and used in advanced devices such as single electron transistors(SET) [2], quantum wire [3], flat panel display (FED) [4-6], hydrogen storage materials [7], and scanning probe microscopy (SPM) [8-10]. To date, primarily synthesis methods of carbon nanotubes were arc-discharge [11], laser ablation [12], catalyzed chemical vapor deposition (CVD) [13-15]. In the above studies carbon nanotubes were formed through vapor-solid reaction or through gaseous hydrocarbon gas cracked into solid carbon with presence of catalysts. Some preparation methods are claimed to be appropriate for the large scale production of carbon nanotubes [16-17]. However a cost-effective, large scale and continuous production process is still under development. Synthesis of carbon nanotubes by polymer interacted with catalyst under a desired thermal process is an other route [18-23]. Up to the present, rarely attention has been focused on this method. Cho et al [18] were the first group to use the bulk polymer obtained by polymerization between citric acid and ethylene glycol to form carbon nanotubes by thermal process at 400 °C for 8 hours in air on an Al₂O₃ boat. Later some research groups used PE [19], PVA [20], diamond-like carbon (DLC) [22]

and fine core-shell polymer microspheres [23] as carbon source to form CNTs. The method is based on the interaction between polymer (carbon source) and transition catalysts (Fe, Co, Ni) at elevated temperatures. During the pyrolyzing process, the polymer undergoes dehydration, dehydrogenation, decomposition to light hydrocarbons and then transition to amorphous carbon forms on a substrate [20]. By increasing temperature to a certain level, catalysts are active with carbon species such as amorphous carbon (liquid-solid growth) or light hydrocarbon (vapor-liquid-solid growth), so that carbon nanotubes can be therefore formed. In this type of process, carbon nanotubes can be fabricate without additional gaseous hydrocarbon, which is explosive and flammable, as it is common used for the general CVD synthesis method.

In this study, polyethylene glycol (PEG) and nickel-contained catalysts were used to investigate the feasibility of *in situ* synthesis of carbon nanotubes. Thermal process were carried out under a nitrogen atmosphere in the temperature range from 650~750 °C. Nickel chloride was utilized individually as the source of catalyst. The polymeric precursors and carbon nanotubes were characterized by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC), high-resolution transmission electron microscopy (HR-TEM), field-emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD).

2 EXPERIMENTAL

Polyethylene glycol (PEG, M.W., 8000) with a structural formula $\text{-(CH}_2\text{-CHO)}_n\text{-}$ was used as the source of carbon material while NiCl₂ · 6H₂O (purity 97.0%) were employed as catalyst precursor for the formation of carbon nanotubes. The mixture of PEG and catalytic solution was stirred by magnetic stirrer in a water bath until it became gel. The resulting gel was then spin-coated onto silicon wafer following by drying at room temperature until the mixture reached a constant weight to ensure all the water/solvent had been vaporized. The catalyst-contained polymeric precursors was placed in a quartz boat and loaded into a tubular furnace. Thermal process were carried out by heating the material in a nitrogen flow at 400 and 500 °C kept for 1 hour for the removal of volatile from PEG decomposition and dehydration of catalyst precursor. The process then elevated to 750 °C and kept for 1 hour for the synthesis of carbon nanotubes in a nitrogen flow.

The carbon nanotubes were observed by scanning

electron microscopy (FE-SEM; HITACHI S-4800) for the analysis of CNTs morphology while transmission electron microscopy (TEM; JEOL JEM 2010) was employed to understand the inner structure and crystal forms of carbon nanotubes. The crystallographic data were collected with X-ray diffractometer (XRD; Shimadzu XRD-6000) using Cu K α radiation from the rotating anode X-ray source. In addition, thermogravimetry (TGA; TA Instrument 5100) /differential scanning calorimetry (DSC; Netzsch Instrument HT-DSC 404) of mixture were carried out as an index of pyrolysis of the polymers before thermal decomposition experiments.

3 RESULTS AND DISCUSSION

3.1 Thermal analysis

The temperature of thermal decomposition of PEG and the mixture of PEG and catalysts were firstly studied by TGA-DSC for a better understanding of pyrolysis temperature of these materials. Approximately 10mg of the material was heated in an open platinum pan at the ramping rate of 15 °C /min to 950 °C under the nitrogen atmosphere. Results of TGA, DSC and DTG thermograms were shown in Fig. 1 for the mixture of PEG and catalysts (NiCl₂). It is clear that the fastest thermal decomposition of the mixture materials occur at a temperature about 400 °C which is assumed due to the decomposition of the polymeric precursors. Therefore, the first constant temperature was set up at 400 °C and kept for 1 hour for removal of volatile and liquid products of PEG decomposition.

Fig. 1 also shows the differential scanning calorimetry (DSC) thermograms on the polymeric precursor that were heated to 950 °C. These thermograms are useful for determining endothermic and exothermic transitions occurring during thermal treatments to elevated temperatures. The polymeric precursors appear of exothermic transition peaking at approximately 700 °C which was thought that nickel catalyst were interacted with carbon matrix to form carbon nanotubes.. As a result, the second constant temperature was set up at 650-750 °C and kept for 1 hours for synthesis of carbon-based materials

3.2 CNTs analysis

A novel polymer material (PEG) has developed for the formation of carbon nanotubes by in situ thermal pyrolysis method. PEG materials were used as carbon source because of well-dispersion of catalyst in the matrix domain during the heat treatment and the bonds between the carbon and other elements can be removed by simple thermal treatment. The ultimate size and separation of the nickel nanoparticles is dependent on the time to a gelation at a given temperature. Thermal treatment of the mixture above 650 °C result in the interaction of nickel and carbon atom for the formation the carbon nanotubes. The Ni atoms and/or Ni nanoparticles directly aid in the formation and the size of

CNTs. Besides, CNTs can be formed without additional gaseous hydrocarbon by this method. The growth of CNTs depended on the temperature, ramping rate and the time of exposure. This method offers an easy and safe operation for synthesis of CNTs possessing highly graphitic structure with low cost materials. At the heating of the PEG samples without catalyst up to 750 °C in the above regime, carbon nanotubes could not be formed.

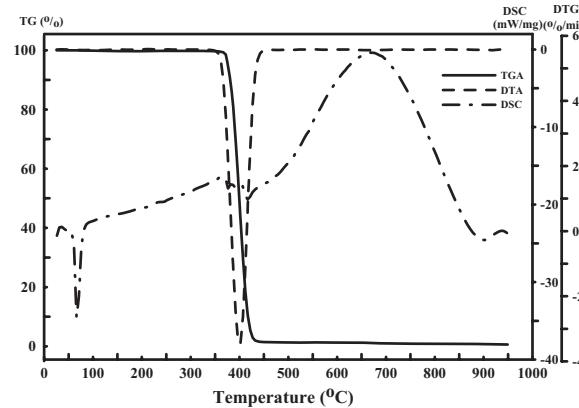


Figure 1: TGA, DSC and DTG thermograms of the mixture of PEG and catalyst (NiCl₂).

3.3 X-ray Diffraction analysis

X-ray diffraction scans of the sample were measured at a scan rate of 3°/min by using Cu K α radiation from the rotating anode X-ray source. Fig. 2 shows the X-ray diffraction patterns for CNTs formed from the mixture after in situ thermal decomposition process at 750 °C. Two main crystalline peaks, C(002) and C(101), are clearly centered at 26° and 45° on these XRD pattern, indicating the presence of a graphite crystalline structure on these CNTs.

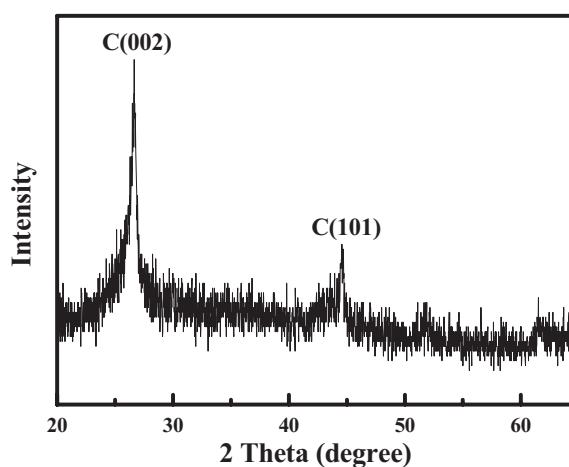


Figure 2: X-ray diffraction pattern of CNTs.

3.4 FE-SEM and HR-TEM analysis

Fig. 3a shows the FE-SEM image of straight and uniform diameter of carbon nanotubes on the surface of silicon wafer after in situ thermal decomposition process at 750 °C. The diameter of carbon nanotubes were about 20-30 nm in diameter and few micrometer in length. As shown in fig. 3b and 3c, it could be observed that carbon nanotubes were long individual and grown from amorphous carbon matrix with catalysts particle on their ends. It can be thought that CNTs were fabricated by top-down method. Fig. 4 shows the low-magnification TEM image of CNTs derived from the mixture after thermal treatment at 750 °C and insert image is the end of CNTs containing catalyst particle. Figure 5 shows the high-resolution image of the walls of carbon nanotubes. It can be easily observed that CNTs possesses exceptionally highly ordered graphitic wall structures with axially parallel planes (002) and wide hollow channels (50-80% of the tube cross-section).

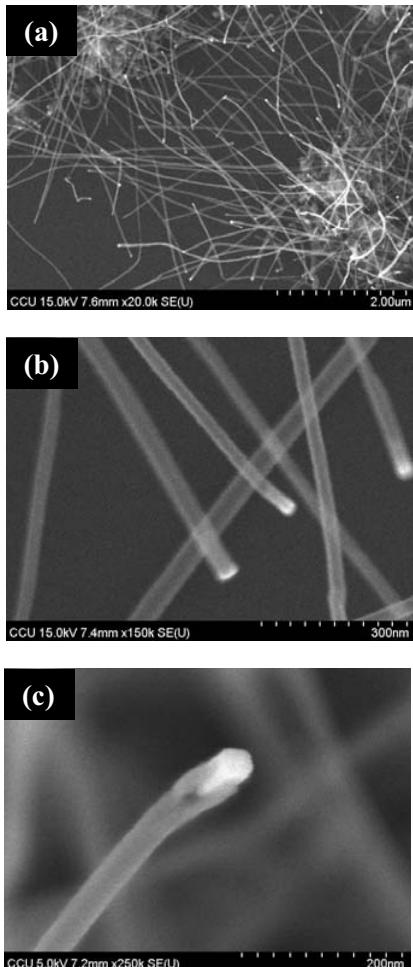


Figure 3: (a) SEM images of the synthesized carbon nanotubes at 750 °C; (b) and (c) were HR-SEM image of the end of carbon nanotubes containing catalyst particle.

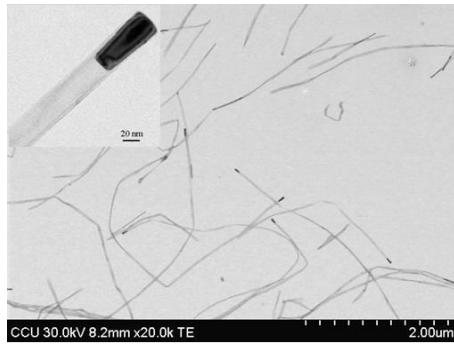


Figure 4: low-magnification TEM images of CNTs derived from the mixture after thermal treatment at 750 °C: insert image is the end of CNTs containing catalyst particle.

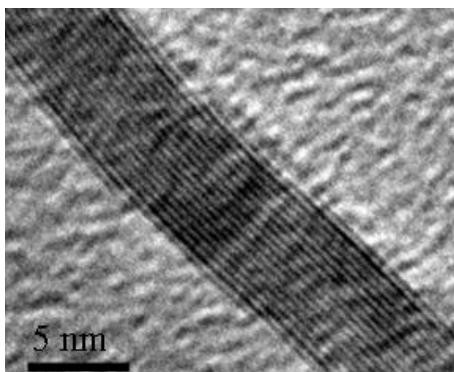


Figure 5: high-resolution image of the walls of carbon nanotubes possesses highly graphitic structures with axially parallel planes (002).

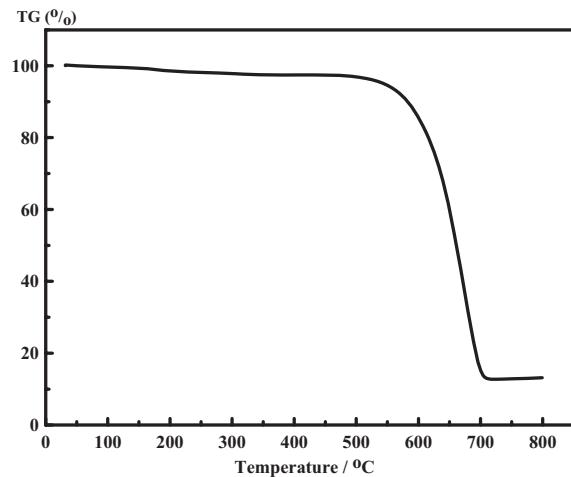


Figure 6: TGA thermograms of CNTs.

3.5 Oxidation analysis

The oxidation of obtained highly graphitic nanotubes has been studied by thermogravimetric experiments. Approximately 10 mg of the material was heated heated in

an open platinum pan at the ramping rate of 10 °C /min to 800 °C under the air atmosphere. Fig. 6 shows the TGA thermograms for carbon nanotubes. It is clear from the observation that the thermal decomposition of the CNTs occurs at a temperature about 550 °C which is higher than normal CNTs. It shows a high resistance to complete the CNTs oxidation up to 700 °C in the air.

4 CONCLUSIONS

The growth of carbon nanotubes from the mixture of PEG and nickel chloride by in situ thermal pyrolyzed method has been demonstrated in this process. These carbon nanotubes possess highly graphitic structures with axially parallel planes (002) and wide hollow channels (50–80%). The diameter of these CNTs was about 20-30nm and few micrometers in length. By this method CNTs can be formed without additional gaseous hydrocarbon as a result it offers an easy and safe operation for synthesis of CNTs.

REFERENCES

- [1] S. Iijima, Nature. 354, 56, 1991.
- [2] S. J. Tans, A. R. M. Verschueren and C. Dekker, Nature. 393, 49, 1998.
- [3] L. J. Geerligs and C. Dekker, Nature. 386, 474, 1997.
- [4] D. W. A. Heer, A. Chatelain and D. Ugarte, Science. 17, 1179, 1995.
- [5] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell and H. Dai, Science. 283, 512, 1999.
- [6] N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H. Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee and J. M. Kim, Diam Relat Mater. 10, 265, 2001.
- [7] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M.J. Heben, Nature. 386, 377, 1997.
- [8] H. Dai, J .H. Hafner, A. G. Rinzler, D. T. Colbert and R. E. Smalley, Nature. 384, 147, 1996.
- [9] C. L. Cheung, J. H. Hafner, T. W. Odom, K. Kim and C. M. Lieber, Appl Phys Lett. 76, 3136, 2000.
- [10] C. L. Cheung, J. H. Hafner and C. M. Lieber, P Natl Acad Sci USA. 97, 3809, 2000.
- [11] C. Jourmet, W. K. Maser, P. Bernier, A. Loiseau, M. L. D. L. Chapelle, S. Lefrant, P. Deniard, K. R. Lee and J. E. Fischer, Nature. 388, 756, 1997.
- [12] F. Kokai, K. Takahashi, M. Yudasaka and S. Iijima, Journal of Physical Chemistry B. 104, 6777, 2000.
- [13] M. Su, B. Zheng and J. Liu, Chem Phys Lett. 322, 321, 2000.
- [14] Q. Li, Y. Hao, X. Li, J. Zhang and Z. F. Liu, Chemistry of Materials. 14, 4262, 2002.
- [15] B. C. Satishkumar, A. Govindaraj, R. Sen and C. N. R. Rao, Chem Phys Lett. 293, 47, 1998.
- [16] Y. Ando, X. Zhao, K. Hirahara, K. Suenaga, S. Bandow and S. Iijima, Chem Phys Lett. 323, 580, 2000.
- [17] P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith and R. E. Smalley, Chem Phys Lett. 313, 91, 1999.
- [18] W. S. Cho, E. Hamada, Y. Kondo and K. Takayanagi, Appl Phys Lett. 69, 278, 1996.
- [19] E. F. Kukovitskii, L. A. Chernozatonskii, S. G. L'vov and N. N. Mel'nik, Chem Phys Lett. 266, 323, 1997.
- [20] O. P. Krivoruchko, N. I. Maksimova, V. I. Zaikovskii and A. N. Salanov, Carbon. 38, 1075, 2000.
- [21] J. Liberaa and Y. Gogotsi, Carbon. 39, 1307, 2001.
- [22] D. Sarangi, C. Godon, A. Granier, R. Moalic, A. Goullit, G. Turban and O. Chauvet, Appl Phys A-Mater. 73, 765, 2001.
- [23] D. Hulicova, K. Hosoi, S. Kuroda, H. Abe and A. Oya, Adv Mater. 14, 452, 2002.