반도체및디스플레이장비학회지 제3권 제1호(2004년 3월)
Journal of the Semiconductor & Display Equipment Technology, Vol. 3, No. 1. March 2004.

Carbon Nanofibers with Controlled Size and Morphology Synthesized with Ni-MgO Catalyst Treated by Mechanochemical Process

Fangli Yuan*,, Ho Jin Ryu†*, Yong Ku Kang*, Soo Jin Park*, and Jae Rock Lee***

†*Advance Materials Division, Korea Research Institute of Chemical Technology,
Yusung-Gu P.O.Box 107, Daejeon 305-600, South Korea
**Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, China

ABSTRACT

Carbon nanofibers (CNFs) with uniform diameter and controlled size were prepared from catalytic decomposition of C_2H_2 with Ni-MgO catalyst treated by mechanochemical (MC) process. The properties of Ni catalyst, such as size, distribution and morphology, can be governed by tuning grinding time in MC process. As a result, size and structure of CNFs can be tailored. The effect of grinding time to the as-grown CNFs was studied. CNFs with diameter from 10-70 nm were synthesized. CNFs with bundle formation sharing one tip and twisted CNFs were also synthesized with catalyst treated by MC process.

Key Words : Carbon nanofibers, Chemical vapor deposition, Mechanochemical process, Morphology

1. Introduction

Carbon nanofibers(CNFs) have excellent electric conductivity, absorbability and mechanochemical property applicable to polymer reinforcement[1], electrode materials[2], catalyst support materials[3-5], and energy storage[6-8].

The growth of CNFs by a catalytic pyrolysis of hydrocarbon gases requires the transition metal catalyst such as Ni, Co, Fe, etc. It suggests that catalyst characteristics such as the shapes, size and surface area are one of the most keys for preparation of CNFs using chemical vapor deposition(CVD) process[9-11]. Three types of CNFs which possess "platelet", "ribbon" and "herring-bone" structures can be produced by tuning the catalyst condition and process parameters[12]. Surface science studies have revealed that certain faces favor precipitation of carbon in the form of graphite, whereas less order carbon will be deposited from other faces [13-15]. So by judicious choice of the catalyst and careful control of the reaction conditions, it is possible to tailor the growth of CNFs to generate structure of a desired conformation.

The catalyst for the growth of CNFs is conventionally prepared by impregnation or ion exchange process. We found that mechanochemical (MC) process is a good method to control the size, distribution and morphology of particles. In this study, we use MC process to prepare Ni-MgO catalyst, so as to tailor the size and structure of as-synthesized CNFs.

2. Experimental

$Ni(OH)_2$ and $Mg(OH)_2$ were used as the staring materials to prepare catalyst for growth of CNFs. 500 mg of $Ni(OH)_2$ and $Mg(OH)_2$ powders(mol ratio of Ni and Mg was 1:1) and aluminia balls of 5-mm diameter were put in an agate pot with inner volume of 20 ml. They were well mixed using mechanochemical process, in which the mixture was ground under dry condition using a mixer mill(MM200, Retsch). The grinding was done at approximately 1800 rpm for 120-720 min. In order to compare, $Ni(OH)_2$ and $Mg(OH)_2$ mixtures were also ground in ethanol with an agate mortar and pestle. The prepared catalysts were labeled as MC and

†E-mail : hjryu@pado.krict.re.kr

MP, respectively.

Carbon nanofibers were grown using the above catalyst by thermal CVD in a quartz-tube electric furnace with C_2H_2 as a carbon source. 50 mg of catalyst was taken in an alumina boat and was loaded into a quartz tube with an inner diameter of 45 mm and a length of 1000 mm and placed at the center of the furnace, in which a uniform heating zone was maintained. An argon stream was first introduced into the furnace and temperature was raised from room temperature with a heating rate of 5°C/min. Once the temperature was achieved, H_2 gas at 100 sccm was flowed to reduce the surface of mixture to obtain Ni particle used as a catalytic active site for 30 min. Next, mixture of C_2H_2 gas at 10 sccm and H_2 gas at 100 sccm were simultaneously flowed for 30 min to synthesize CNFs. Finally, the sample was cooled down to room temperature under an argon stream.

Size and morphology of as-synthesized CNFs were observed by the scanning electron microscope(SEM, JSM-840A and Phillips XL 30S FEG).

3. Results and Discussion

Fig. 1 shows the SEM images of as-synthesized CNFs. As shown in Fig. 1(A), CNFs synthesized using MP catalyst were big size in diameter and very short in length, which due to only simple mixing process for catalyst. However, CNFs with small size and long length were synthesized using MC catalyst. It becomes homogeneous and linear for CNFs prepared with MC catalyst ground for 120 min, and the diameter is about 150-200 nm, as shown in Fig. 1(B). In addition to homogeneity, the diameter becomes finer with the grinding time increasing to 360min, and the diameter of CNFs is about 50-100 nm, as shown in Fig. 1(C). It is found that catalyst characteristics such as the shapes, size and surface area have tremendous impact on the growth of CNFs using CVD process[9,10,16]. In the MC process, Ni particles are ground to finer and narrower in size, so as to synthesize CNFs with smaller size and homogeneous distribution. Therefore it is very easy to tailor size and uniformity of synthesized CNFs with catalyst treated by MC process.

Fig. 2. shows bundle formation of CNFs prepared with MC catalyst. As the arrow indicated in Fig. 2(A),

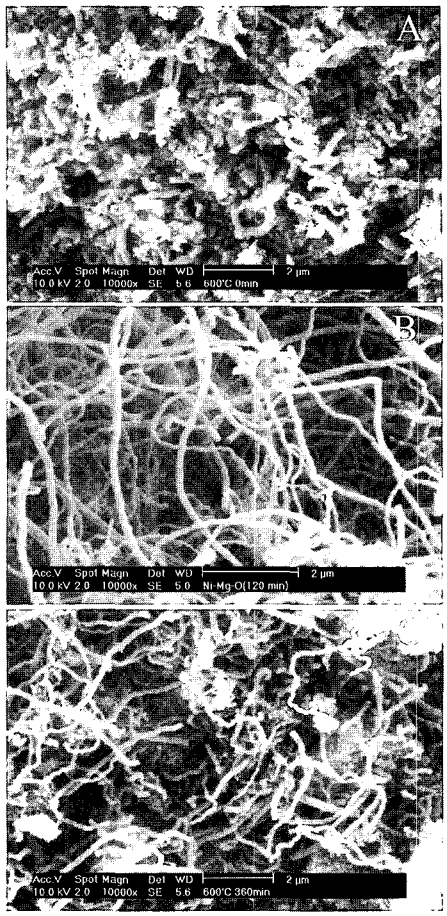

Fig. 1. SEM images of as-grown CNFs. A–MP catalyst, B–MC catalyst treated for 120 min, C–MC catalyst treated for 360 min.

there are many CNF bundles, and CNFs in these bundles are combined close. However there are no CNF bundles found in the MP catalyst. In addition to two CNFs combined as a bundle, bundles combined with four CNFs were also found, as shown in Fig. 2(B). It was also seen that the four CNFs share the one tip as arrow A indicated. Fig. 2(C) shows bundles with two CNFs sharing one tip, as the arrow in indicated.

Mechanochemical process using a high-energy ball-mill has been widely used for preparing nonequilibrium materials like nanocrystalline and amorphous materials. It is an effective way to rapidly refine the particle microstructure, i.e., grain size or crystallite size, during milling[17-18]. It is clear that Ni particles can be refined in the MC process, so that the size of as-grown

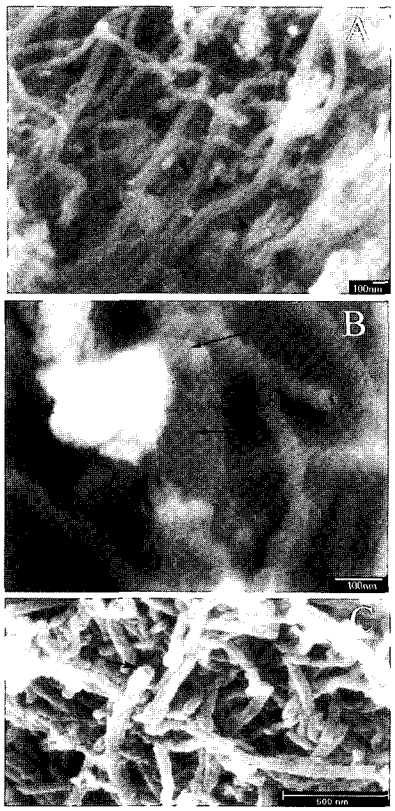

Fig. 2. Bundle formation of CNFs prepared with MC catalyst. A–bundles with two CNFs, B–bundles with four CNFs, C–bundles shared one tip.

CNFs decreases with the increase in the grinding time. More over, Ni particles can be distributed homogeneously on the support MgO, which results in the preparation of uniform CNFs. The most important aspect is that Ni particles can be grind to supply some faces favoring precipitation of carbon and embeded on the support materials using mechanochemical process. It is maybe the embedding that prevents the catalyst Ni particles from agglomerating at high temperature. At the same time, different face in one Ni particles would help to grow bundles with one tip.

In addition to controlling MC grinding time, other parameters such as H_2 flow rate, pyrolytic temperature, ratio of H_2/C_2H_2 can also affect the morphology and size of as-grown CNFs. Fig. 3 shows CNFs with different diameter prepared at various condition using MC catalyst. It shows that CNFs with various diameter would be tailored by tuning the parameters of MC

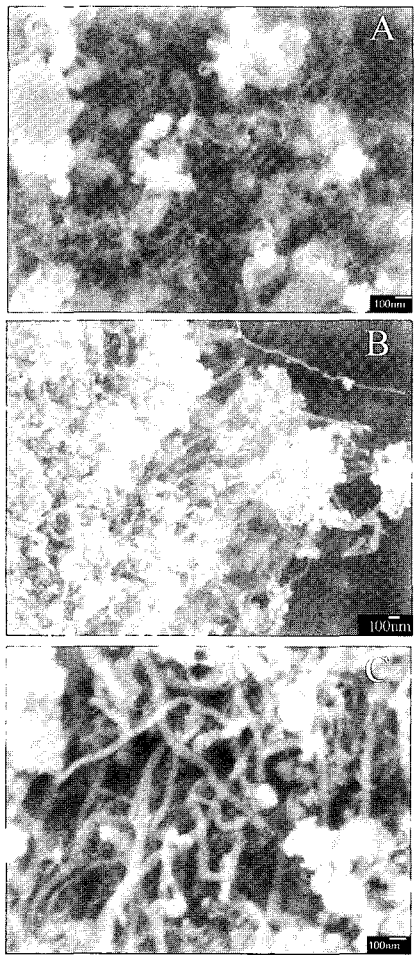

Fig. 3. CNFs with different diameter prepared with MC catalyst. A–10-30 nm, MC 360 min, 700°C, H_2 100 sccm at 700°C; B–30-50 nm, MC 720 min, 700°C, H_2 100 sccm from 200°C, C–50-70 nm, MC 720 min, 600°C, H_2 100 sccm at 600°C.

process and pyrolytic temperature. It can be seen that CNFs of 10-30 nm in diameter are synthesized at 700°C using catalyst treated with MC process for 360 min, as shown in Fig. 3(A), however, CNFs of 30-50 nm in diameter are synthesized at 700°C using catalyst treated with MC process for 720 min, and H_2 gas at 100 sccm flowed into from 200°C, as shown in Fig. 3(B). CNFs of 50-70 nm in diameter are synthesized at 600°C using catalyst treated with MC process for 720 min.

It is worth to mention that the morphology of CNFs can be tailored by treating catalyst with MC process. One of the most apparent features for CNFs prepared

using catalyst treated by MC process is that they have twisted conformation rather than straight conformation. Fig. 4. shows SEM image of as-synthesized CNFs. They were prepared at 550°C with catalyst treated by MC process for 360 min, and the mixture gas of H_2/N_2 ($5\%H_2$) of 100 sccm was introduced to reduce catalyst from 200°C. It is clear that they are twisted conformation with diameter about 65 nm. Compared with the straight CNFs, twisted CNFs have a lot of winds, and they can bend and pucker easily with a small radius of curvature in their growth. Fig. 5. is TEM images of as-grown CNFs. Apparently, CNFs synthesized using catalyst treated by MC process are twisted conformation, and their skin is rough. The catalyst particles can also be seen at the tips as the arrows indicate, and they are near spherical. It can be further seen that twisted CNFs can bend and pucker easily in their growth. As the arrow A in Fig. 5 indicates, the radius of curvature for twisted CNFs is very small, on the other hand, it is always very large for straight CNFs when they loop in some cases.

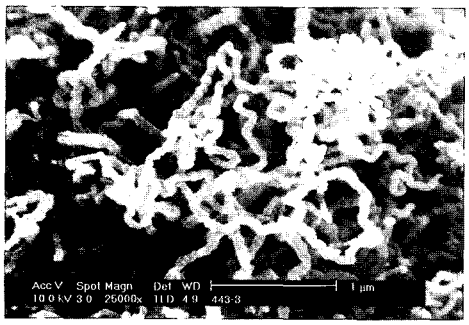

Fig. 4. SEM images of as-grown twisted CNFs.

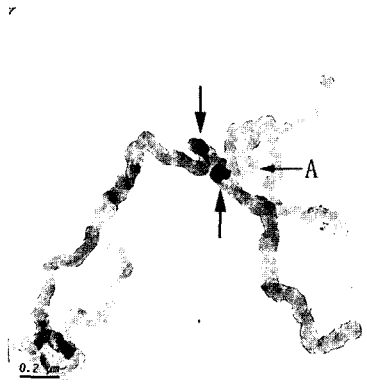

Fig. 5. TEM images of as-grown twisted CNFs.

4. Conclusions

Carbon nanofibers with controlled size and morphology can be synthesized using catalyst treated with mechanochemical process. The size and uniformity of CNFs can be governed by tuning the grinding time in MC process. The diameter of CNFs can be controlled from 10-70 nm by modulating the grinding time in MC process and parameters in pyrolytic process. CNFs with bundle formation sharing one tip are synthesized with the catalyst treated using MC process. It would be contributed to the MC process that makes Ni particles embeded on the support materials and several faces favoring precipitation of carbon on one Ni particle. Twisted CNFs of 65 nm are prepared at 550 with catalyst treated by MC process for 360 min.

Acknowledgments

One of the authors (Yuan Fangli) is thankful for the Brain Pool Program fellowship of KOFST.

References

1. Wang, X., Wang, S., and Chung, D.D.L., *J. Mater. Sci.* Vol. 34, pp. 2703-2713 (1999).
2. Endo, E., Kim, Y.A., Hayashi, T., Nishimura, K, Matusita, T., Miyashiya, K., and Dresselhaus, M.S., *Carbon,* Vol. 39, pp. 1287-2897 (2001).
3. Rodriguez, N.M., Kim, M.S., and Baker, R.T.K., *J. Phys. Chem.,* Vol. 98, p. 13108-13111 (1994).
4. Park, C., and Baker, R.T.K., *J. Phys. Chem. B,* Vol. 102, pp. 5168-5177 (1998).
5. Baker, R.T.K., Laubernds, K., Wootsch, A., and Paal, Z., *J. Catal.,* Vol. 193, pp. 165-167 (2000).
6. Park, C., Anderson, P.E., Chambers, A., Tan, C.D., Hidalgo, R., and Rodriguez, N.M., *J. Phys. Chem. B,* Vol. 103, pp. 10572-10581 (1999).
7. Fan, Y.Y., Liao, B., Liu, M., Wei, Y.L., Lu, M.Q., and Cheng, H.M., *Carbon,* Vol. 37, pp. 1649-1652 (1999).
8. Gupta, B.K. and Srivastava, O.N., *Int. J. Hydrogen Energy,* Vol. 25, pp. 825-830 (2000).
9. Rodriquez, N.M., *J. Mater. Res.,* Vol. 8, pp. 3233-3250 (1993).
10. Rodriquez, N.M., Chambers, A., and Baker, R.T.K., *J. Phys. Chem. B,* Vol. 102, pp. 2251-2258 (1998).
11. Takizawa, M., Bandow, S., Yudasaka, M., Ando, Y., Shimoyama, H., and Iijima, S., *Chem. Phys. Lett.* Vol.

326, pp. 351-357 (2000).
12. Rodriguez, N.M., Chambers, A., and Baker, R.T.K., *Langmuir,* Vol. 11, pp. 3862-3866 (1995).
13. Goodman, O.W., Kelley, R.D., Madey, T.E.; and Yates, J.T., *J. Catal.,* Vol. 63, pp. 226-234 (1980).
14. Nakamura, J., Hirano, H., Xie, M., Matsuo, I., Yamada, T., and Tanaka, K., *Surf. Sci.,* Vol. 222, pp. L809-817 (1989).
15. Yang, R.T. and Chen, J.P., *J. Catal.,* Vol. 115, pp. 52-64 (1989).
16. Jong, K.P.D. and Geus , J.W., *Catal. Rev.,* Vol. 42, pp. 481-510 (2000).
17. Surayanarayana, C., *Prog. Materi. Sci.,* Vol. 46, pp. 1-184 (2001).
18. Koch, C.C., *Nanostructured Mater.,* Vol. 9, pp. 13-22 (1997).