

Nanohorns Particle Including Metal-Nanocapsule Formed by Arc Discharge in Liquid Nitrogen

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A hybrid structure, carbon nanohorns (CNHs) particle which includes Ni-contained carbon nanocapsule (CNCs) in its center was synthesized by arc discharge between Ni-contained graphite anode and pure graphite cathode in liquid nitrogen. Transmission electron microscopy revealed that the CNHs particle in nearly spherical shape of diameter around 50-100 nm has one Ni nano particle of diameter 5-20nm encapsulated by graphitic shells as carbon nanocapsules (CNCs). Ni core of these particles are characterized as fcc Ni by EDX, XRD and electron diffraction.

Key words: Carbon nanohorn, Nanocapsule, Arc discharge, Liquid nitrogen

1. INTRODUCTION

Several types of nano carbon structures have been found in a past decade as new functional materials. For example, fullerenes [1], multi-walled carbon nanotubes (MW-CNTs) [2], single-walled carbon nanotubes (SW-CNTs) [3], single-walled carbon nanohorns (SW-CNHS) [4], nano onions [5], and metal-included carbon nanocapsules (CNCs) [6] are widely known. To produce such nano materials, there are several known methods, such as arc discharge in reduced-pressure gases [7,8], plasma-enhanced chemical vapor deposition [9,10], and thermal pyrolysis of hydrocarbon gases [11,12]. In these methods, Ni, Fe and Co are common to use as catalysts to fabricate SW-CNTs and CNCs [3,9-12].

In addition to the above conventional methods, arc-in-liquid method has been recently developed as a relatively new cost-effective method [13-23]. MW-CNTs [13,15,16,18,19,21-23], SW-CNHS [20,22,23], nano onions with C₆₀ core [17], MoS₂ fullerenes [21] were reportedly fabricated by this method. As water can dissolve many electrolyte substances, metal-included nanocarbons were tried to be produced by arc in water with dissolved aqueous metallic ions. It was reported that metal-included CNTs were synthesized by using water with ionic Ni and Co [14]. In addition, non-elongated metal-included nano particles were fabricated by use of metal-doped graphite electrodes or metal-dissolved water [15, 16].

In the arc-in-liquid method, relatively cold liquid is used to quench the hot arc with evaporated materials from electrodes. Liquid component can be selected for target nano materials [22]. This article describes a structure of a unique hybrid structure, CNHs including Ni-contained CNCs, and its formation process using arc plasma generated by a Ni-doped graphite anode in liquid nitrogen [23].

2. EXPERIMENTAL

Experimental set-up used in this study is shown in Fig. 1, which is similar to previous works on arc-in-water

method [17,18]. Here, we used liquid nitrogen in Dewar flask, instead of water in beaker. A Ni-contained (0.7mol%) composite graphite rod commercially available (TOYO TANSO, diameter= 7 mm) was used as an anode. A normal graphite rod (99.99% carbon) of a diameter 12 mm was used as a cathode. These electrodes were submerged in liquid nitrogen, and arc discharge was generated between these electrodes (60A, 25V). Fine powdery products were found at the bottom of the flask after the arc discharge, and these as-grown powders were analyzed by a transmission electron microscopy (TEM) (JEOL2010). Furthermore, a cylindrical solid deposit of approximately same diameter as the anode rod was formed at the tip of the cathode during the arc discharge. This deposit was also analyzed by TEM after it was ground using a mortar and pestle.

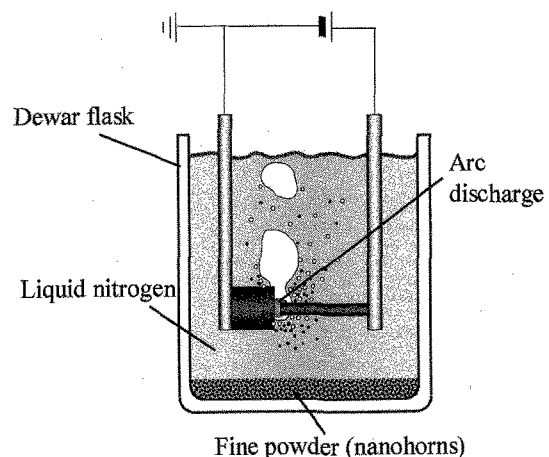


Fig. 1 Apparatus of arc-in-liquid method to synthesis carbon nano particles.

3. RESULTS AND DISCUSSION

3.1 Products from fine powders

Agglomerated CNHs particles were found in the fine powders collected from the flask bottom by TEM observation. Figure 2 shows a TEM image of these CNHs particles. It was observed that the diameter of CNHs particles ranges within 40-120nm.

When the observation was further scanned, a hybrid structure, CNHs particles including Ni-contained CNCs in their centers, were discovered. Figure 3 shows the aggregated such hybrid particles. Energy dispersive X-ray (EDX) analysis revealed that dark spots observed in the centers of nanohorn particles as marked by arrows should contain Ni. As a feature of this hybrid particle, each CNHs particle includes one Ni particle in its center.

Figure 4 shows the single walled carbon horns from the hybrid particles at a high magnification scale. Each horn in these particles shows the same structural feature as the normal CNHs particles. The TEM view of the aggregated-horns particles is considered to be different from that of the aggregated root-grown SW-CNTs around catalytic particles. Such SW-CNTs show their bundled alignment in radial directions from the catalyst [22]. An inset in Fig. 4 shows a high magnification image of the Ni core existing in the hybrid particles. It is shown that the Ni core is encapsulated by shelled fringes. The spacing of the shell was measured as 0.34nm, from which these shells are graphite layers. This feature was kept under tilting TEM observation. This result reveals that the structure of the Ni nano particles are Ni-contained CNCs (Ni-CNCs).

Figure 5 shows tilting observation of the three particles of the hybrid structure. From this observation, the particles seem to be nearly spherical in the projections in all angles. The shift of the relative position of the central particle in this tilting observation indicates that these particles are agglomerated three-dimensionally. If the central particle is located approximately 50 nm higher than the other two particles, the relative position of the central one can be shifted by 20 nm in the TEM view due to 23 degrees tilting.

Figure 6 shows the result of EDX spectrum and electron diffraction of the Ni cores of the hybrid particles. EDX result confirms that the core in the hybrid particles contains Ni. The electron diffraction pattern shown in this figure corresponds to fcc Ni. Beside fcc Ni, a rhombohedral carbide Ni_3C was detected as minor portion. This result that carbide is contained is consistent with a fact that metallic cores of CNCs produced by arc in reduced-pressure gases can contain carbon during the formation process [6,23]. It was observed that the diameter of the Ni-contained nano-particles ranges within 5-20nm.

Although the CNHs-CNCs hybrid particles were observed in the product formed by the present synthesis method, a scanning work was necessary to find such

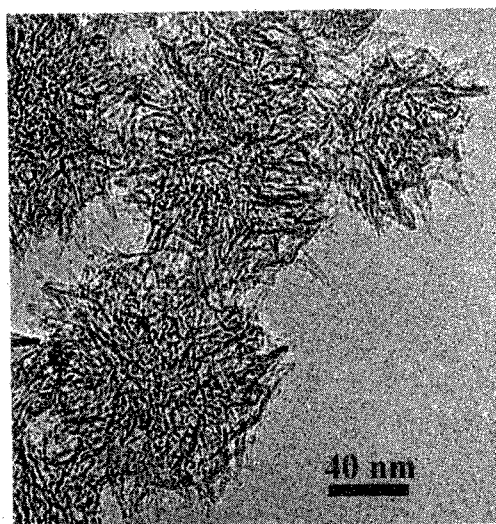


Fig. 2 Carbon nanohorns produced by arc in liquid nitrogen.

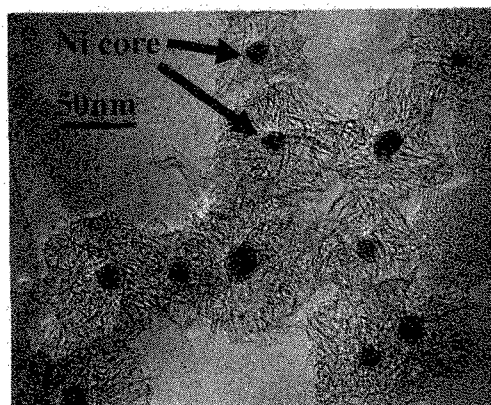


Fig. 3 Aggregates of Ni-included carbon nanhorn particles. Scale bar=50nm.

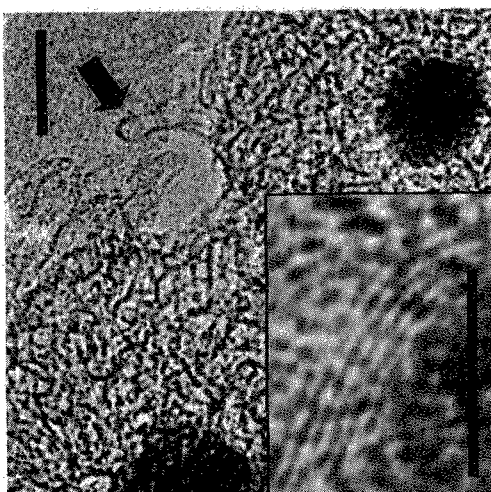


Fig. 4 Protruded horn and graphitic shell of Ni included in nanohorn particles. Horn is marked by arrow (scale bar=20nm). Inset shows shell of Ni core (scale bar=5nm).

structures because the most of nano-structural products here were normal CNHs particles which do not have the Ni-CNC cores. If the concentration of Ni in the composite anode is increased, the higher yield of CNHs-CNCs hybrid particle is expected.

As it is known that SW-CNTs are produced by arc discharge in gas environment with composite graphite anode with metallic catalyst [3,22], one must be interested in the possibility to form SW-CNTs in the present reaction field because the present system also uses metallic catalyst in the anode. However, in spite of this expectation, SW-CNTs were not found in the products collected from the flask bottom. Moreover, MW-CNTs were not observed there. Contrary to these materials of elongated-structures, spherical carbon onions were observed as a minor impurity as agglomerated form.

3.2 Products from cathode deposit

When the deposit formed on the cathode tip was closely analyzed by TEM, high concentration MW-CNTs were found together with caged polyhedrons. This feature was found also in the case when a pure graphite anode was used. The TEM images of the MW-CNTs collected from the cathode deposit formed by the present reactor with liquid nitrogen are shown in Fig. 7. Each MW-CNTs is observed to be straight tubular forms. This feature is consistent with MW-CNTs produced by arc-in-gas method [7,8]. For the structural similarity of the products, the formation mechanism of this deposit may be the same as in the arc-in-gas method. Significant directionality of evaporated carbon in ion current in arc is expected to play a role to form elongated structures. TEM observation revealed that Ni-contained particles were not produced in this cathode deposit.

3.3 Mechanism to form CHNs hybridized with Ni-CNCs

In arc-in-liquid method, it would be reasonable to think that nano-structural particles are formed in the gas phase around the hot arc region by rapid quenching of materials evaporated from anode [18, 21]. Thus, carbonaceous nano particles containing Ni are expected to be produced if Ni doped graphite anode was used. To consider the formation mechanism of the CNHs-CNCs hybrid particle, an experiment replacing liquid nitrogen to water was conducted for reference. When water was used, the CNHs-CNCs hybrid particles were not found although Ni-contained CNCs were observed. Hence, the nitrogen gas environment, which is more chemically inert, may play an important role to form carbon horn structures. If water is used, water vapor, H₂ and CO are expected to be present as main components in the gas bubbles around the arc plasma [14]. Horn structures should be less stable than

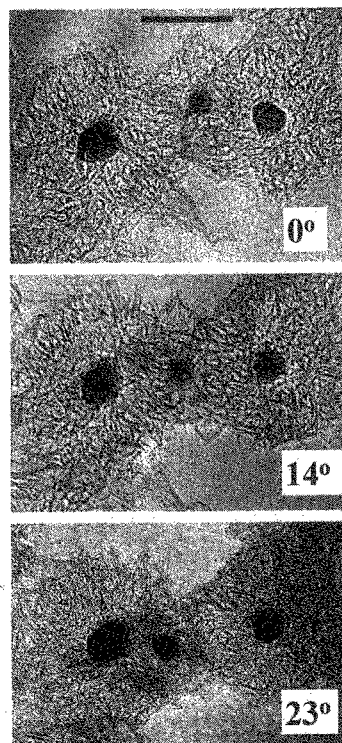


Fig. 5 Tilted TEM images of Ni-included nanohorn particles. Scale bar = 20 nm.

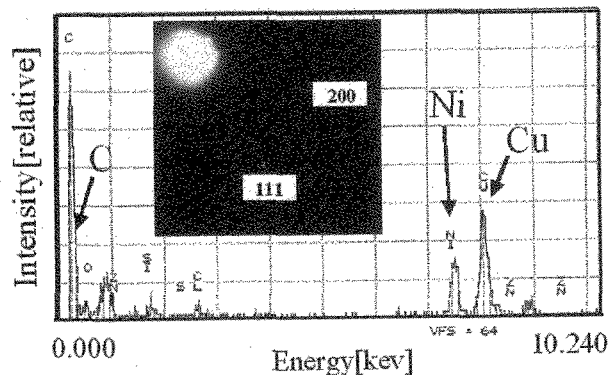


Fig. 6 EDX (Energy Dispersive X-ray) spectrum on core structure of nanohorn particles as shown in Figs. 3-5. Ni is detected. Cu is from TEM grid. Inset shows electron diffraction spots indicating fcc Ni.

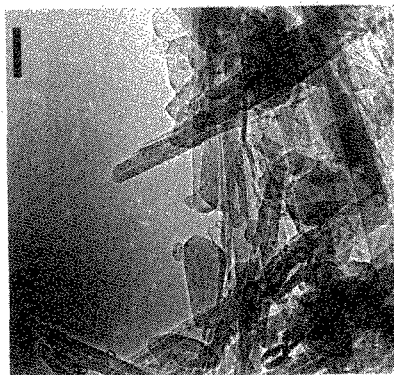


Fig. 7 MWCNTs found in cathode deposit formed in arc in liquid nitrogen method. Scale bar=50nm.

MW-CNTs and onions which can be produced by arc in water because each horn structure is single walled and sharper than MW-CNTs and nano-onions. Therefore, the chemical inertness of N₂ should be important to grow the horn structures without being reacted with gas species.

We have proposed a three-steps model how CNHs-CNCs hybrid particles are formed as a hypothesis [23]. In stage-1, carbon and Ni are evaporated from anode by arc plasma, and carbon is dissolved into the liquidized Ni nano particles in gas bubbles around the arc spot. In stage-2, when the evaporated carbon and Ni nano particles supersaturated with carbon transfer to the cold zone inside the gas bubble, Ni-contained CNCs are formed by salting-out growth of carbons at the Ni particle surfaces. Simultaneously, carbon horns are produced by collision of carbon atoms or carbon clusters [24] in the same gas bubbles. In stage-3, horns are aggregated around the CNCs as a nucleation core to form the CNHs-CNCs hybrid structure.

4. CONCLUSIONS

A hybrid structure, CNHs including Ni-contained CNCs, were synthesized by the submerged arc in liquid nitrogen. To produce the CNHs-CNCs hybrid particle, Ni-contained (0.7mol%) graphite composite anode was used to generate the arc discharge. XRD and electron diffraction analysis indicated that encapsulated core is mainly fcc Ni. Compared with the arc-in-water method, gas bubbles at the arc plasma is quite inert. Horn structures may be produced in such bubbles by self-assembling of evaporated carbon, and they would aggregate around CNCs to form the CNHs-CNCs hybrid particle.

5. ACKNOWLEDGEMENT

Financial support by Grant-in-Aid for Young Scientists (B) of Japan Society for the Promotion of Science (JSPS) (No. 14750618) are acknowledged.

6. REFERENCES

- [1] H. W. Kroto, J. R. Heath, S. C. O. O'Brien, R. F. Curl, R. E. Smalley, *Nature*, **318**, 162-3 (1985).
- [2] S. Iijima, *Nature*, **354**, 56-8 (1991).
- [3] S. Iijima, T. Ichihashi, *Nature*, **363**, 603-5 (1993).
- [4] S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, K. Takahashi, *Chem. Phys. Lett.*, **309**, 165-70 (1999).
- [5] D. Ugarte, *Nature*, **359**, 707-9 (1992).
- [6] R. S. Ruoff, D. C. Lorents, B. Chan, R. Malhotra, S. Subramoney, *Science*, **259**, 346-7 (1993).
- [7] T. W. Ebbesen, P. M. Ajayan, *Nature*, **358**, 220-2 (1992).
- [8] L.-C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, *Nature*, **408**, 50 (2000).
- [9] M. Chhowalla, K. B. K. Teo, C. Ducati, N. L. Rupesinghe, G. A. J. Amaratunga, A. C. Ferrari, D. Roy, J. Robertson, W. I. Milne, *J. Appl. Phys.*, **90**, 5308-17 (2001).
- [10] T. Nozaki, Y. Kimura, K. Okazaki, *J. Phys. D: Appl. Phys.*, **35**, 2779-84 (2002).
- [11] M. Endo, T. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, H. W. Kroto, *J. Phys. Chem. Solids*, **54**, 1841-8 (1993).
- [12] H. M. Cheng, F. Li, G. Su, H. Y. Pan, L. L. He, X. Sun, *Appl. Phys. Lett.*, **72**, 3282-4 (1998).
- [13] M. Ishigami, J. Cumings, A. Zettl, S. A. Chen, *Chem. Phys. Lett.* **319**, 457-9 (2000).
- [14] Y. L. Hsin, K. C. Hwang, R.-R. Chen, J.-J. Kai, *Adv. Mater.*, **13**, 830-3 (2001).
- [15] H. Lange, M. Sioda, A. Huczko, Y. Q. Zhu, H. W. Kroto, D. R. M. Walton, *Carbon*, **41**, 1617-23 (2003).
- [16] N. Sano, M. Chhowalla, H. Wang, K. Iimura, G. A. J. Amaratunga, T. Kanki, Proc. 16th International Symposium on Plasma Chemistry, Taormina (Italy), 680th file in CD-Rom (2003).
- [17] N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, G. A. J. Amaratunga, *Nature*, **414**, 506-7 (2001).
- [18] N. Sano, H. Wang, I. Alexandrou, M. Chhowalla, K. B. K. Teo, G. A. J. Amaratunga, K. Iimura, *J. Appl. Phys.*, **92**, 2783-8 (2002).
- [19] H. W. Zhu, X. S. Li, B. Jiang, C. L. Xu, Y. F. Zhu, D. H. Wu, X. H. Chen, *Chem. Phys. Lett.*, **366**, 664-9 (2002).
- [20] H. Wang, G. A. J. Amaratunga, S. Jia, N. Sano, M. Chhowalla, Proc. 7th Applied Diamond Conference/ 3rd Frontier Carbon Technology Joint Conference 2003 (ADC/FCT), Tsukuba (Japan) 2003.
- [21] N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, G. A. J. Amaratunga, M. Naito, T. Kanki, *Chem. Phys. Lett.* **368**, 331-7 (2003).
- [22] N. Sano, Proc. 17th Diamond Symposium (in Japanese), Ed. New Diamond Forum, Tokyo, in press (2003).
- [23] N. Sano, T. Kikuchi, H. Wang, M. Chhowalla, G. A. J. Amaratunga, *Carbon*, in press.
- [24] S. Subramoney, R. S. Ruoff, D. Lorents, R. Malhotra, *Nature*, **366**, 637 (1993).
- [25] Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya, Y. Nishida, *J. Phys. Chem. Solids*, **54**, 1849-60 (1993).
- [26] H. Lange, K. Saidane, M. Razafinimanana, A. Gleizes, *J. Phys. D: Appl. Phys.*, **32**, 1024-30 (1999).

(Received October 9, 2003; Accepted November 20, 2003)