J. of Korean Oil Chemists' Soc.,
Vol. 30, No. 3. September, 2013. 423~430
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2013.30.3.423

산화알루미늄 세라믹 보트 기판을 이용한 탄소마이크로 코일의 대량 합성

김성훈†

신라대학교 에너지응용화학과
617-736 부산광역시 사상구 괘법동 산 1-1
(2013년 8월 10일 접수; 2013년 9월 25일 수정; 2013년 9월 26일 채택)

Large scale synthesis of the geometrically controlled carbon coils using Al_2O_3 ceramic boat for the supporting substrate

Sung-Hoon Kim†

Department of Engineering in Energy & Applied Chemistry, Silla University, Busan 617-736, Republic of Korea
(Received August 10, 2013 ; Revised September 25, 2013 ; Accepted September 26, 2013)

Abstract : Carbon coils could be synthesized using C_2H_2/H_2 as source gases and SF_6 as an incorporated additive gas under thermal chemical vapor deposition (CVD) system. Prior to the carbon coils deposition reaction, two kinds of samples having different combination of Ni catalyst and substrate were employed, namely, a commercially-made Al_2O_3 ceramic boat with Ni powders and a commercially-made Al_2O_3 substrate with Ni layer. By using a commercially-made Al_2O_3 ceramic boat, the synthesis of carbon coils could be enhanced as much as 10 times higher than that of Al_2O_3 substrate. Furthermore, the dominant formation of the microsized carbon coils could be obtained by using Al_2O_3 ceramic boat. The surface roughness of the supporting substrate of Al_2O_3 ceramic boat was understood to be associated with the large scale synthesis of carbon coils as well as the dominant formation of the larger-sized, namely the microsized carbon coils.

Keywords : Carbon coils, Al_2O_3 ceramic boat, Ni catalyst, Geometry control, large scale synthesis, Thermal CVD

1. Introduction

Due to their unique spring-like single helix or DNA-like double helix geometry, carbon coils have been attracted as the high potential materials for nanomechanical engineering.[1-4] Furthermore, carbon coils was supposed to have unique electrical and optical properties that could be used in nanoelectronics.[5-8]

The synthesis of carbon coils is usually too low for their applications in diverse nano/micro electronics or mechanical

†Corresponding author
(E-mail : shkim@silla.ac.kr)

engineering field, therefore the enhancement of their production is preferential problem to overcome.[9,10] Recently catalytic chemical vapor deposition (CCVD) method has been noticed for the enhancement of the synthesis of carbon coils. For the research of CCVD method for carbon coils synthesis, the system parameters for CCVD such as the reaction temperature and the gas flow rate have been understandably considered. Besides the system parameters, the used metal catalyst, the incorporated additives, and the supported substrate would be also the important factors for the synthesis of carbon coils. For the metal catalyst, iron family (Fe, Co, Ni), especially Ni, were known as an effective catalyst for the formation of carbon coils.[11,12] For the incorporated additives, meanwhile, a trace of the sulfur-incorporated species was regarded as the promising additives for the synthesis of carbon coils.[13-15] Despite many efforts to enhance the synthesis of carbon coils, the reports regarding the supporting substrate effect on the synthesis of carbon coils are few up to the present.

In this work the enhancement of carbon coils synthesis is presented by using Al_2O_3 ceramic boat as a substrate and Ni powders as a catalyst. SF_6 was also added in the source gases to take an advantage for sulfur and fluorine species properties which can enhance the formation of carbon coils.[16] To avoid the highly hazardous problem to the health and the environment, the amount of sulfur incorporated chemical species, namely SF_6 in this work, was minimized by reducing the SF_6 injection time down to 5 minutes. By using Ni powders and Al_2O_3 ceramic boat, the geometry control as well as the enhancement of the synthesis for the microsized carbon coils could be achieved. According to the different supporting substrates and catalysts, the characteristics of the as-grown carbon coils, namely the formation density and the geometry, were examined and discussed.

2. Experimental

A commercially-made Al_2O_3 ceramic boat, usually used for crucible, and a commerciall y-made Al_2O_3 substrate (about 1.0 × 1.0 ㎠) were prepared (see Fig. 1). For Ni powders on Al_2O_3 ceramic boat, about 1.0 g Ni powders were directly dropped and

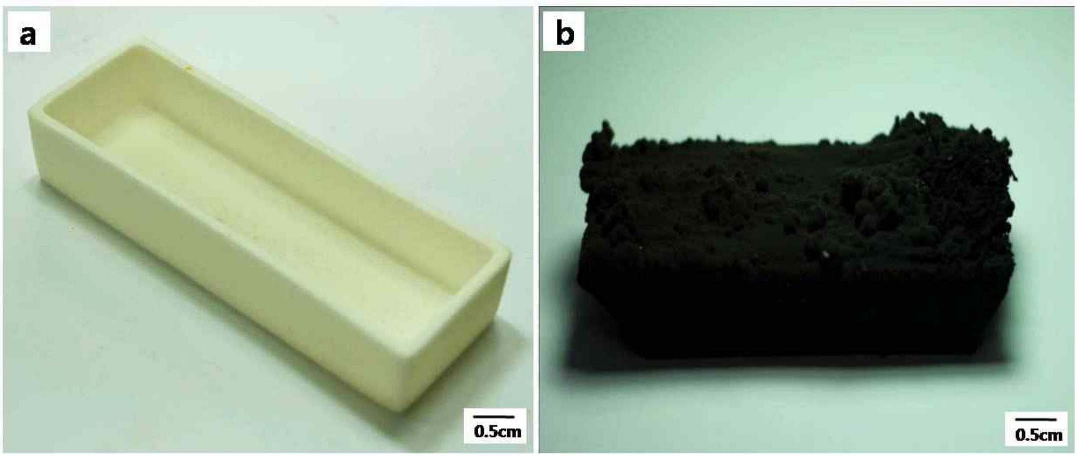

Fig. 1. Photographs of (a) Al_2O_3 ceramic boat and (b) the as-grown carbon materials on Al_2O_3 ceramic boat.

Table 1. Experimental conditions for the deposition of carbon coils

Processes	Conditions / Samples	C_2H_2 Flow Rate (sccm)	H_2 Flow Rate (sccm)	SF_6 Flow Rate (sccm)	Total Pressure (Torr)	Total Deposition Time (min)	The injection time of source gases flow (min)			Substrate temperature (°C)	Types of Catalysts and Substrates
							C_2H_2	H_2	SF_6		
I	Sample A	15	35	35	100	90	90	90	5	750	Ni powders on Al_2O_3 boat
II	Sample B	15	35	35	100	90	90	90	5	750	Ni layer on Al_2O_3 substrate

manually spread on the surface of the boat and then placed into the reaction chamber.

For Ni layer on Al_2O_3 substrate, a 0.5 g Ni powder (99.7 %) was evaporated for 1 minute to form Ni catalyst layer on the substrate using thermal evaporator. The estimated Ni catalyst layer on the substrate was estimated about 400 nm.

For carbon coils deposition, thermal CVD system was employed. C_2H_2 and H_2 were used as source gases. SF_6, as an incorporated additive gas, was injected into the reactor during the reaction. SF_6 was injected for 5 minutes during the initial reaction stage. The flow rate for C_2H_2, H_2, and SF_6 were fixed at 15, 35, and 35 sccm, respectively. The reaction conditions were shown in Table 1. Detailed morphologies of carbon coils-deposited substrates were investigated using field emission scanning electron microscopy (FESEM). The qualities of carbon coils according to the samples were investigated in the range of 800 ~ 2000 cm^{-1} by a micro-Raman spectrometer (Renishaw 2000) with about 50 mm spot size of Ar-ion laser.

3. Results and Discussion

The syntheses of carbon coils were simultaneously carried out on both Ni powders-boat (Ni powders spreading on Al_2O_3 ceramic boat) and Ni layer-substrate (Ni layering on Al_2O_3 substrate). Figure 1 shows the photographs of the boat (Fig. 1a) and the as-grown carbon materials on the boat (Fig. 1b). As a naked eye, a lot of carbon materials seemed to be formed on the boat. The density of the deposited carbon materials were about 0.5g/cm^2 for Ni powders-boat. Microscopic images for the as-grown carbon materials were also investigated using FESEM. Figure 2 shows FESEM image revealing the formation of carbon coils on Ni powders-boat. For Ni powders-boat case, the dominant formation of the microsized carbon coils having a few micrometer-sized coils diameters could be observed.

For Ni layer-substrate, the surface morphologies of the as-grown substrates were measured by FESEM as shown in Fig. 3. Figure 3a shows the formation of carbon materials on Ni layer-substrate. Figures 3b, c and d show the magnified images of Figures 3a, b and c, respectively. As shown in these figures, for Ni layer-substrate, this regular carbon coil has constant coil pitch of ~ 0.2mm without any coil gap and have coil diameter of ~ 1.5mm. The as-grown carbon coils have the slightly reduced diameter compare with that of Ni powders-boat. The carbon nanofilaments that built up the carbon coil have a circular type shape. Furthermore, the nanosized carbon coils with the microsized carbon coils were also observed on the surface of Ni-layer substrate. The estimated density of the deposited carbon materials was about 0.05g/cm^2 for Ni layer-substrate. The combined results of Figures 2 and 3 indicate that the use of Ni powders-boat could dramatically enhance the amount of as-grown carbon coils as much as 10 times compared

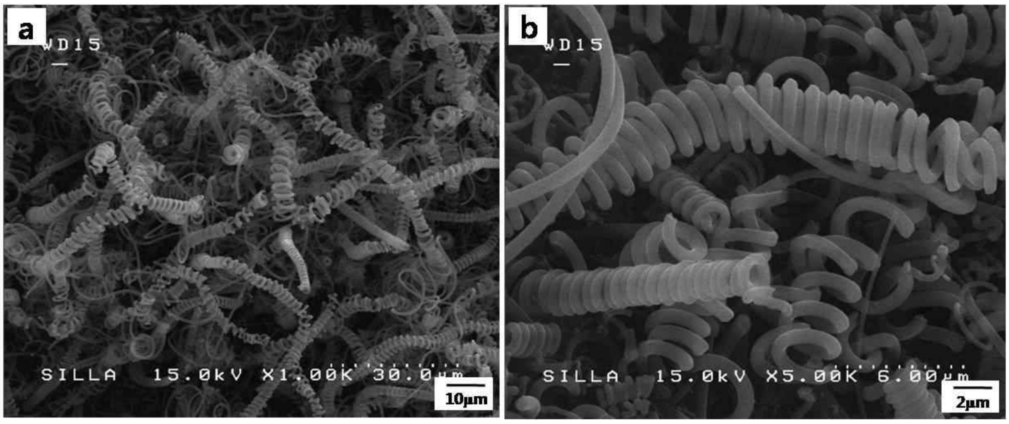

Fig. 2. (a) FESEM images for the formation of carbon coils on Ni powders-boat and (b) the high-magnified image of Fig. 2a.

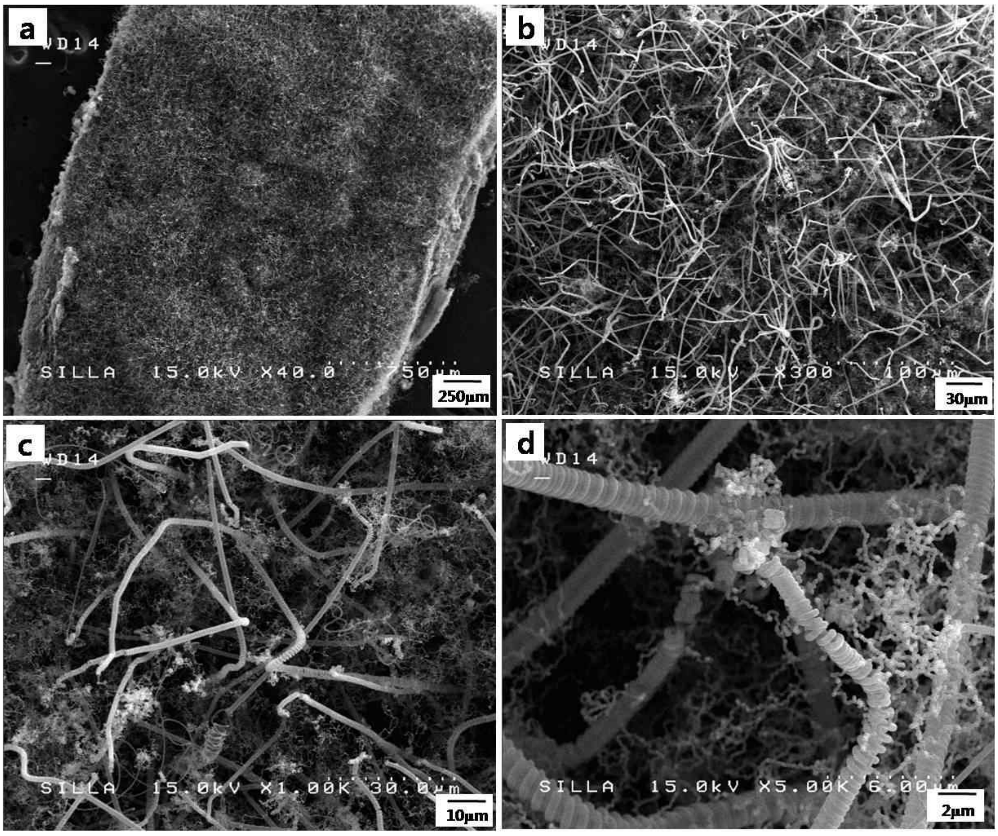

Fig. 3. (a) FESEM images for the formation of carbon coils on Ni layer-substrate, (b) high-magnified image of Fig. 3a, (c) high-magnified image of Fig. 3b, and (d) high-magnified image of Fig. 3c.

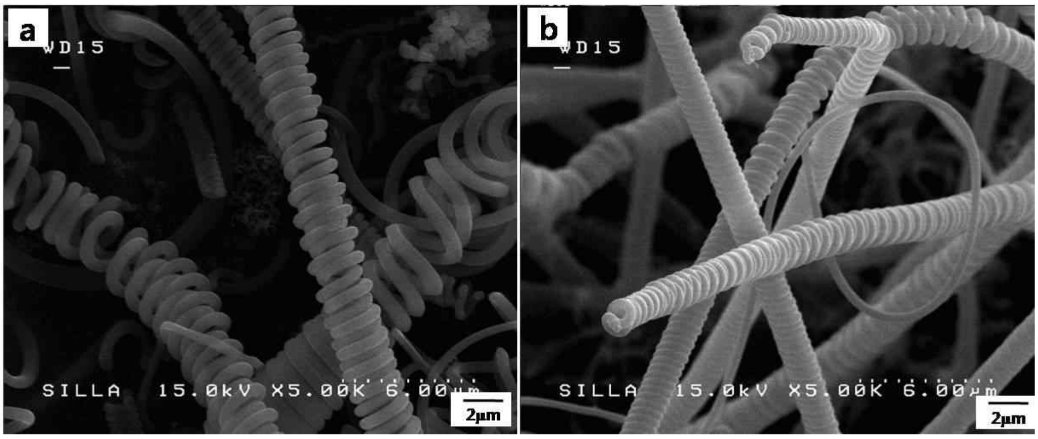

Fig. 4. FESEM images for as-grown carbon coils on (a) the center and (b) the side positions of Ni powders-boat.

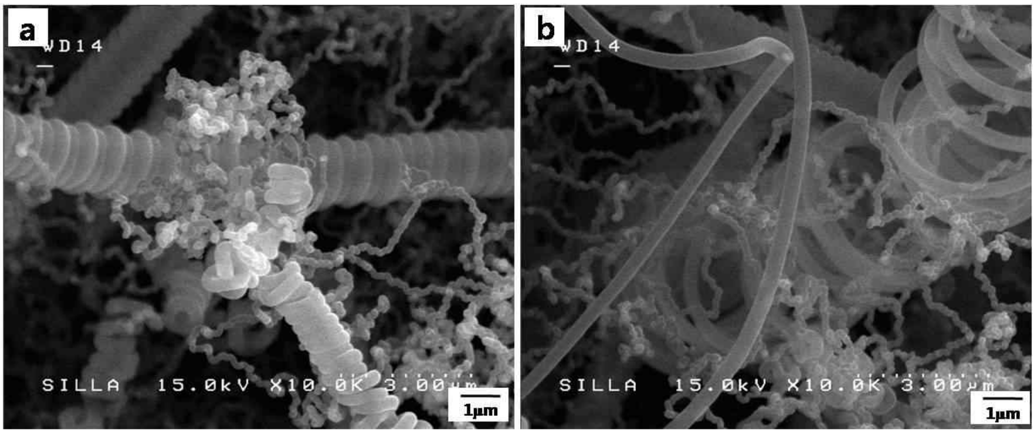

Fig. 5. FESEM images for as-grown carbon coils on (a) the center and (b) the side positions of Ni layer-substrate.

with that of Ni layer-substrate. Furthermore, Ni powders-boat can provoke the dominant formation of the microsized carbon coils.

In general, many types of carbon coils-related geometries could be formed on the substrate, so they could be usually classified into four geometrical categories, namely linear, microsized coil, nanosized, and wave-like nanosized types.[17] Interestingly, Ni powders-boat may give rise to the dominant formation of the microsized carbon coils with few amount of nanosized ones (see Fig. 2). On the other hand, Ni layer-substrate gives rise to the formation of the microsized carbon coils with the nanosized ones (see Figs. 3c and d).

We also investigated the geometry shapes of as-grown carbon coils according to the position on Ni-powders boat and on Ni layer-substrate. Figure 4 shows FESEM images showing the formation of carbon coils on the center (Fig. 4a) and side (Fig. 4b) positions of Ni powders-boat. The geometries of microsized carbon coils were dominant irrespective of the position difference on Ni-powders boat. Figure 5 shows FESEM

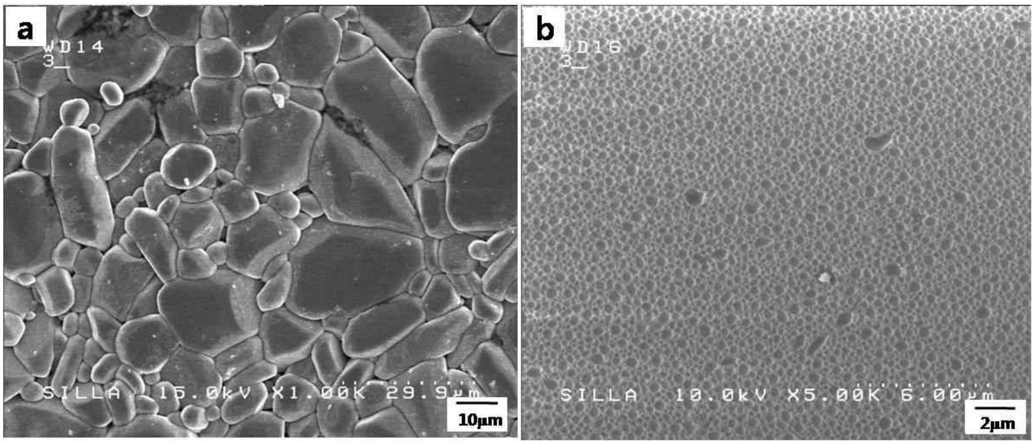

Fig. 6. FESEM images for the surface morphologies of (a) Ni powders-boat and (b) Ni layer-substrate after immediately terminating the reaction process when the substrate temperature reaches up to 750° C under vacuum.

images showing the formation of carbon coils on the center (Fig. 5a) and side (Fig. 5b) positions of Ni layer-substrate. As shown in Fig. 5, Ni layer-substrate gave rise to the formation of many types of carbon coils-related geometries, namely the nanosized carbon coils as well as the microsized carbon coils irrespective of the positions on Ni layer-substrate. The combined results of Figures 4 and 5 confirm that the use of Ni powders-boat surely provide the dominant formation of the microsized carbon coils on the whole surface of the boat.

Based on the results of Figs. 1 ~ 5, it is understood that the geometry control to the microsized carbon coils could be possible merely via Ni powders-boat usage. The cause for this result was understood as follows. Fig. 6 shows FESEM images showing the surface morphologies of Ni powders-boat (Fig. 6a) and Ni layer-substrate (Fig. 6b) after immediately terminating the reaction process when the substrate temperature reaches up to 750° C under vacuum. By comparing FESEM image of Fig. 6a with that of Fig. 6b, it is understood that the surface roughness of Ni powders-boat would be much higher than that of Ni layer-substrate. Because higher surface roughness would provoke the interaction between as-growing carbon elements, they may enhance more active sites for the initiation of the microsized carbon coils. Consequently, the higher surface roughness of the boat seems to produce the dominant formation of the microsized carbon coils. The suggestion based on the surface roughness difference for the main cause of the microsized carbon coils formation could be confirmed even in a same Ni-layer substrate case. Fig. 7 shows the entirely different coils geometries between the cross section area and the edge area on Ni-layer substrate. Indeed, the cross section of Ni-layer substrate could give rise to the dominant formation of the microsized carbon coils. Namely, various microsized carbon coils could be dominantly observed at the cross section area. So, it is understood that the rougher surface like the cross section may give rise to the active properties for the interaction of as-growing carbon elements and consequently producing the microsized geometries of carbon coils. Finally, Ni powders-boat having the rougher surface than that of Ni layer-substrate would give the

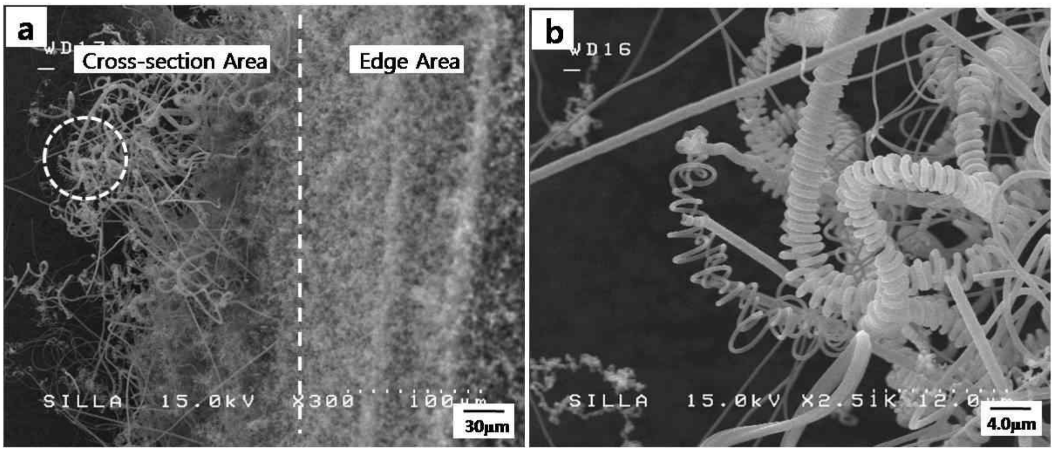

Fig. 7. FESEM images for (a) the cross section and the edge areas of Ni-layer substrate and (b) the magnified images of the circle area of Fig. 7a.

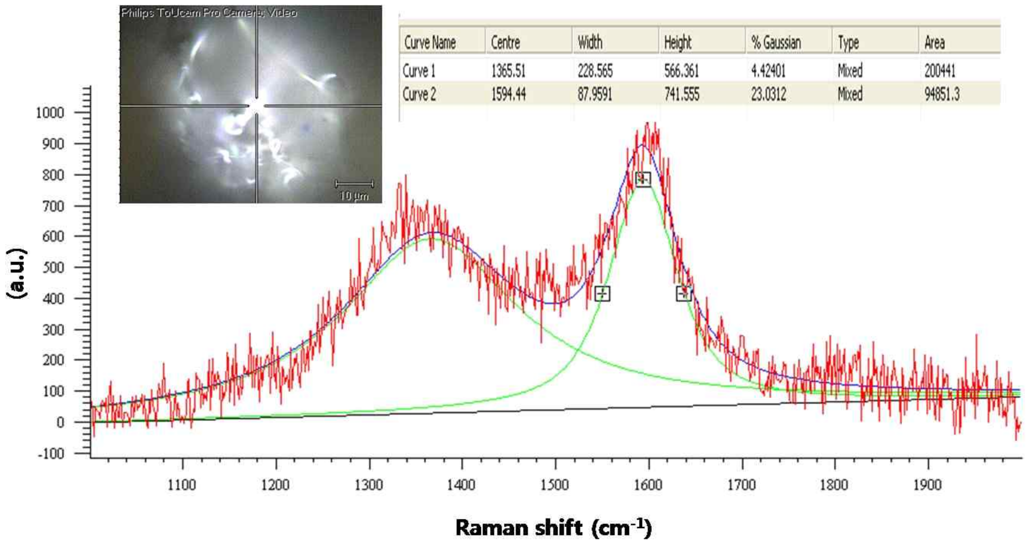

Fig. 8. Micro-Raman spectrum of the individual carbon microcoil. The inset shows the focused image on the individual carbon microcoil. Curve-fit data were also shown.

higher production of carbon coils as well as the dominant formation of the larger-sized, namely the microsized carbon coils.

Previously, a few researchers reported that tuning of carbon morphology could be achieved by appropriately modifying the supporting substrate, the catalyst and the interaction between them.[18,19] Bai obtained a more or less controlled morphology of carbon coils according to the different alumina substrate pore size.[18] Veziri et al. reported that the morphology of carbon nanostructures grown by CVD on porous supports is strongly affected by the porosity of the supporting substrate.[19] In this work, we suggest that the surface roughness of the supporting substrate would be a primary step to control the geometry of carbon coils.

Meanwhile, the qualities of the individual carbon coil was also investigated in the range of 800 ~ 2000 cm^{-1} by a micro-Raman spectrometer as shown in Fig. 8. The D and G peaks in all the samples were observed around $1350cm^{-1}$ and $1600cm^{-1}$, respectively. Curve fitted values of the area intensity ratios of I(D)/I(G) for the individual carbon coil are around 2.1, which indicates the existence of the nanocrystalline aromatic p-bonded clusters in the carbon coils.[20] Based on the value of I(D)/I(G), we could conjecture that the well-developed polycrystalline structure would be somewhat existed in this carbon microcoils.[21-22]

4. Conclusions

Large scale synthesis of carbon coils could be possible simply by Al_2O_3 ceramic boat usage. Using Al_2O_3 ceramic boat, furthermore, the formation of micro-sized carbon coils could be dominantly achieved. So, the geometry control of carbon coils to the microsized one could be possible. The higher surface roughness of the boat seems to be the main cause for the dominant formation of the microsized carbon coils.

REFERENCES

1. S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V.Ivanov, and J.B. Nagy, *Science*, 265, 635 (1994).
2. Z.C. Ouyang, Z.B. Su, and C.L. Wang, *Phys. Rev. Lett.* 78, 4055 (1997).
3. V. Bajpai, L.M. Dai, and T. Ohashi, *J. Am. Chem. Soc.* 126, 5070 (2004).
4. L.J. Pan, T. Hayashida, M. Zhang, and Y. Nakayama, *Jpn. J. Appl. Phys.* 40, L235 (2001).
5. A. Fonseca, K. Hernadi, J.B. Nagy, Ph. Lambin, and A. Lucas, *Carbon*, 33, 1759 (1995).
6. K. Akagi, R. Tamura, and M. Tsukada, *Phys. Rev. Lett.* 74, 2307 (1995).
7. K. Hernadi, L. Thien-Nga, and L. Forro, *J. Phys. Chem.* B, 105, 12464 (2001).
8. J. Wen, Y. Zhang, N. Tang, X. Wan, Z. Xiong, W. Zhong, Z. Wang, X. Wu, and Y. Du, *J. Phys. Chem. C*, 115, 12329 (2011).
9. X. Wang, Z. Hu, Q. Wu, X. Chen, and Y. Chen, *Thin Solid Films*, 390, 130 (2001).
10. A. Huczko, *Appl. Phys. A*, 74, 617 (2002).
11. N. M. Rodriguez, M. S. Kim, F. Fortin, I. Mochida, and R. T. K. Baker, *Appl. Catal. A: General*, 148, 265 (1997).
12. S. Motojima, Y. Itoh, S. Asakura, and H. Iwanaga, *J. Mater. Sci.* 30, 5049 (1995).
13. X. Chen, T. Saito, M. Kusunoki, and S. Motojima, *J. Mater. Res.* 14, 4329 (1999).
14. X. Chen and S. Motojima, *J. Mater. Sci.* 34, 5519 (1999).
15. S. Motojima, S. Asakura, T. Kasemura, S. Takeuchi, and H. Iwanaga, *Carbon*, 34, 289 (1996).
16. M. Asmann, J. Heberlein, and E. Pfender, *Diamond Relat. Mater.* 8, 1 (1999).
17. J.-H. Eum, S.-H. Kim, S.S. Yi, and K. Jang, *J. Nanosci. Nanotechnol.*, 12, 4397 (2012).
18. J.B. Bai, *Mater. Lett.* 57, 2629 (2003).
19. Ch. M. Veziria, G. N. Karanikolosa, G. Pilatosa, E. C. Vermisogloua, K. Giannakopoulosb, Ch. Stogiosb, and N.K. Kanellopoulosa, *Carbon*, 47, 2161 (2009).
20. J. Robertson, *Mater. Sci. Eng. R*, 37, 129 (2002).
21. K. Shibagaki, S. Motojima, Y. Umemoto, and Y. Nishitani, *Carbon*, 39, 1337 (2001).
22. F. Tuinstra, J.L. Koenig, *J. Chem. Phys.*, 53, 1126 (1970).