

Effect of Multi-catalysts on Carbon Nanofiber Synthesis in CVD

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The catalytic chemical vapor deposition (CVD) method has been widely utilized for synthesis of carbon nanomaterials. One of important key parameters in catalytic CVD to synthesize the carbon nanofibers or nanotubes is an appropriate selection of catalytic agents. In the present study, first, various kinds of micron-size powder catalysts and their mixtures were combinatorially tested, concerning to the macroscopic disposition of carbon in CVD with C₂H₂ source gas. It was found that the catalytic efforts of some composite catalysts brought remarkable enhancement as compared with single metal catalysts. The maximum fibrilliform carbonaceous deposition was obtained when using Fe+Ni+Sn mixture catalyst. Through the first experiment, unique formation shapes of carbon nanomaterials were obtained using NiO+In₂O₃ combination catalyst, called nanotube-bur-particle (NBP) and jointed-fiber-web (JFW). Secondly, the influence of CVD process parameters such as gas flow rate, deposition time, temperature, and position, on these unique materials synthesis was experimentally investigated.

Keywords: carbon nanofiber, multi-element catalysts, CVD, nanotube bur particle, jointed fiber web

1. INTRODUCTION

Carbon nanomaterials such as nanotubes, nanofibers, and nanocoils, have been attracting numerous scientific and engineering attentions because of their unique structure and properties [1]. A variety of synthesis methods of such materials have been developed, including arc-discharge [2, 3], laser ablation [4], and chemical vapor deposition (CVD) [5, 6]. The CVD technique is a simple and low-cost method, and is thought to be realized the mass production. In CVD method, catalyst is required for the growth of carbon nanomaterials. Typical catalysts are the transition metals of Fe, Co, Ni, their oxides and alloys [7]. Recently, it was reported that when the other element was mixed, unique nanofibers has been obtained. The carbon nanocoils and nanotwist have been synthesized by using Fe/ITO (indium tin oxide) [8], and Ni/Cu or Zn/Cu film/substrate [9] as catalyst. This indicates that the selection of appropriate combination of elemental catalysts is one of the key factors to fabricate carbon nanomaterials in controlled shape or mass-production.

In the present study of carbon nanomaterials synthesis in CVD, first, various combinations of catalysts were tested and the production rate of carbonaceous materials was investigated. During that experiment, the combination of NiO and In₂O₃ provided unique structural carbonaceous materials. Then the influences of the process parameters on the production of the materials were experimentally investigated.

2. EXPERIMENTAL

The CVD apparatus with a cylindrical quartz tube reactor (300 mm long, 40 mm inner diameter) has been shown in previous paper [9]. However, a hot-filament was not used this time. In the present study, commercial powders of Fe, Ni, Sn, In, and their oxides with 1-3 μm

diameter were used as catalyst, scattering on the quartz substrate (7.5 mm × 2.5 mm, 1 mm thickness) as thinner as possible. The basic experimental conditions were as follows: source gas, C₂H₂ (180 sccm); purge and dilute gas, He (420 sccm); process temperature, 700°C; deposition time, 3 min; substrate setting location, center of reactor tube; pressure, 1 atm; total weight of powdery catalyst, 10 mg. When the multi element catalyst was tested, each powder was equally mixed in weight.

The deposited carbonaceous materials were weighted with an electronic balance, and observed and analyzed with a scanning electron microscope SEM (JEOL, JSM-6300), energy dispersive X-ray EDX (PHILIPS, DX-4), and transmission electron microscopy TEM (JEOL, JEM-2010).

3. RESULTS AND DISCUSSION

3.1 Carbon deposition rate

After the deposition process, the weight of the product including the catalyst was measured. Then the carbon deposition rate (CDR) was evaluated, dividing the amount of carbonaceous material by the amount of catalyst and unit time (1 min). Therefore, CDR indicates that how many times the amount of carbonaceous material fabricated in the unit time is higher than the amount of the fed catalyst in weight.

The results of CDRs are listed in Tables I and II, for using Fe and/or Ni and Fe₂O₃ and/or NiO powdery catalyst, respectively. First, it was found that Sn, In, SnO₂, In₂O₃ and their mixture did not work as catalyst for carbon deposition at all. However, these elements obviously worked as additive secondary catalyst to enhance the carbonaceous deposition by using together with primary catalysts of Fe, Ni, Fe₂O₃, and/or NiO.

Concerning to the metallic primary catalyst, Fe or Ni

Table I. Carbon deposition rate per unit catalyst weight of various mixture catalysts prepared with Fe and/or Ni as primary catalyst.

Primary catalyst		Secondary catalyst		Carbon deposition rate (min^{-1}) CDR
Fe				0.15
	Ni			0.07
		Sn		0
			In	0
Fe	Ni			0.19
Fe		Sn		0.85
Fe			In	0.04
	Ni	Sn		0.68
	Ni		In	0.18
		Sn	In	0
Fe	Ni	Sn		4.44
Fe	Ni		In	0.05
Fe		Sn	In	0.27
	Ni	Sn	In	0.14
Fe	Ni	Sn	In	0.19
Fe			In_2O_3	0.31
	Ni		In_2O_3	0.22
		Sn	In_2O_3	0
Fe	Ni		In_2O_3	1.93
Fe		Sn	In_2O_3	0.51
	Ni	Sn	In_2O_3	0.16
Fe	Ni	Sn	In_2O_3	1.07

alone had a catalytic function for carbonaceous deposition. Mixture of Fe and Ni provided higher CDR than Fe or Ni alone. When the secondary catalysts of Sn, In, and/or In_2O_3 were added to the primary catalysts of Fe and/or Ni, CDR became higher. These secondary catalysts obviously have an ability to enhance the carbonaceous deposition. In precise, Sn, In_2O_3 and their mixture marvelously brought quite higher CDR, although the addition of In often decreased the CDR. The maximum CDR was remarkably obtained when Fe+Ni+Sn mixture catalyst was used. This mixture catalyst was found to be superb catalytic function and brought 20-60 times higher than the primary and their mixture catalyst.

Concerning to the metal oxide primary catalyst, the following tendency was found. Mixture of primary metal oxide catalysts (Fe_2O_3 +NiO) brought considerable enhancement as compared with metal oxide alone. For Fe_2O_3 , the addition of SnO_2 brought the higher CDR, although the addition of In_2O_3 acted as impediment for carbonaceous reaction. Contrariwise, for NiO, the addition of In_2O_3 brought the higher CDR, although the addition of SnO_2 acted as impediment. The maximum CDR was obtained by using Fe_2O_3 + SnO_2 .

Figures 1 and 2 show the micrographs of deposited carbon materials with higher CDR catalysts for metal and metal oxide primary catalyst, respectively. The materials were consisted of carbon nanofibers, microfibrs, nanocoils, nanotwists, and clod of beads-like badly grown fiber.

Table II. Carbon deposition rate per unit catalyst weight of various mixture catalysts prepared with Fe_2O_3 and/or NiO as primary catalyst.

Primary catalyst		Secondary catalyst		Carbon deposition rate (min^{-1}) CDR
Fe_2O_3				0.04
	NiO			0.07
		SnO_2		0
			In_2O_3	0
Fe_2O_3	NiO			0.34
Fe_2O_3		SnO_2		1.33
Fe_2O_3			In_2O_3	0.06
	NiO	SnO_2		0.08
	NiO		In_2O_3	0.43
		SnO_2	In_2O_3	0
Fe_2O_3	NiO	SnO_2		0.55
Fe_2O_3	NiO		In_2O_3	0.13
Fe_2O_3		SnO_2	In_2O_3	0.28
	NiO	SnO_2	In_2O_3	0.05
Fe_2O_3	NiO	SnO_2	In_2O_3	0.62

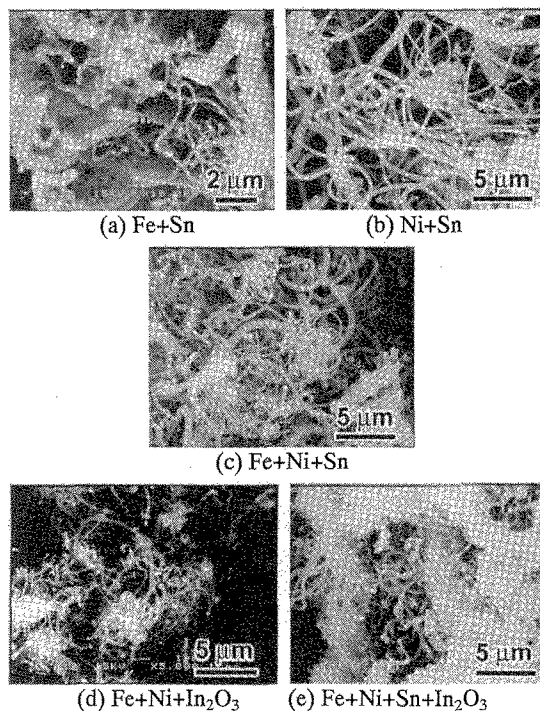


Fig. 1. SEM micrographs of carbon depositions when the higher carbon deposition rate was obtained for metal primary catalyst.

3.2 NiO+ In_2O_3 mixture catalyst

As shown in Fig.2(b), when the NiO+ In_2O_3 composite catalyst was used, quite unique deposit was obtained. Then, the influence of process parameters on the deposit using NiO+ In_2O_3 catalyst was intensively investigated.

There were two different types of macroscopic structure, as shown in Fig. 3. The illustrative models of

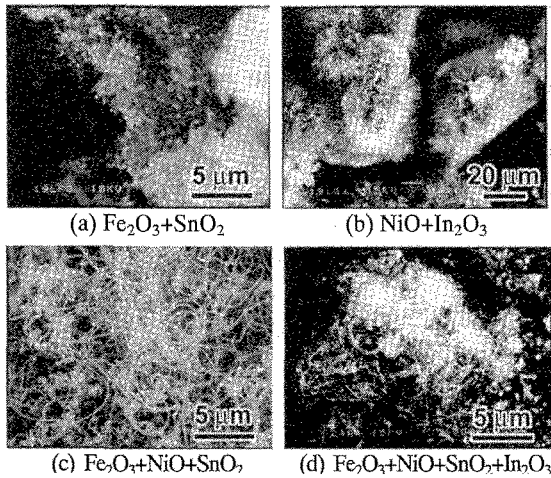


Fig. 2. SEM micrographs of carbon depositions when the higher carbon deposition rate was obtained for metal oxide primary catalyst.

these structures are presented in Fig. 4. After EDX analysis, we presumed that there were core catalyst particles of Ni or NiO which were covered with Ni+In and/or the oxide. A small amount of Ni+In or its oxide separated from the core catalyst surface during the carbonaceous growth formed the seed catalysts in the triangular or rectangular projection shape. When the seed catalyst took the triangular projection shape, the amorphous carbon nanotube with somewhat herring

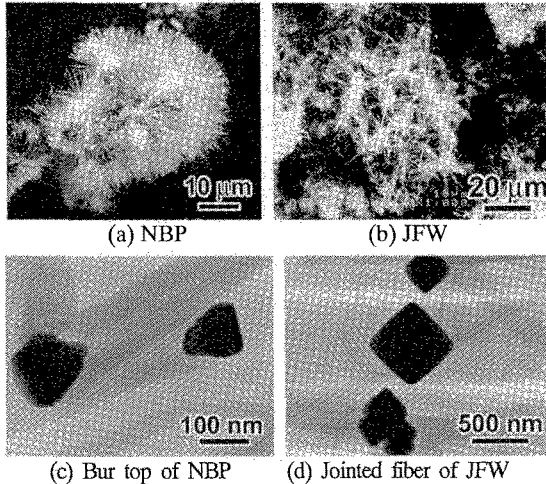


Fig. 3. SEM (a), (b) and TEM (c), (d) micrographs of nanotube-bur-particle (NBP) and jointed-fiber web (JFW).

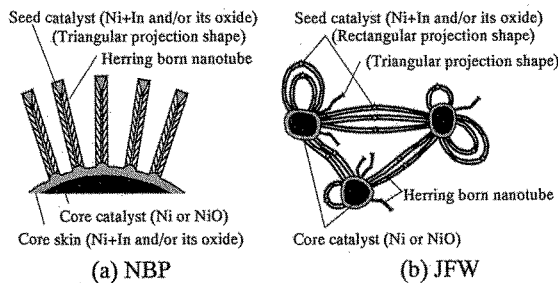


Fig. 4. Illustrative structure models of NBP and JFW.

bone-like density distribution was grown, resulting that the macroscopic shape looked like bur-chestnut or sea urchin, called nanotube-bur-particle (NBP).

On the other hand, when the seed catalyst took rectangular projection shape, the several times thicker nanofiber with a hollow was grown to two directions from the seed catalyst. Namely, in this case, the two nanofibers looked like being jointed by the catalyst. This jointed nanofiber sometimes interconnected the two core catalysts, and sometimes looped from the single core catalyst. When the jointed nanofiber was grown, overall view looked like 3-dimensional spider web, so that the products were called jointed (nano)fiber web (JFW). The JFW also had the similar nanotubes with a rectangular projection shaped catalyst at the top, observed in NBP. The JFW was also obtained for $\text{Fe}_2\text{O}_3+\text{NiO}+\text{In}_2\text{O}_3$ compound catalyst. The NBP and JFW were also obtained for Ni+In composite catalyst.

Whether the product took which shape of NBP or JFW was found to be dependent on process parameters of catalyst composition ratio, source/dilute gas flow, deposition time, and substrate location in the reactor. The followings were the result summary. When one parameter was changed, other parameters were same as basic parameters as described previously in the experimental section, except the catalyst composition ratio. The optimum composition ratio NiO:In₂O₃ was 40:60 and this composition was used in the following experiments.

Figure 5 shows the dependence of gas flow rate and source gas mixing ratio. It was found that the NBP tended to grow at relatively lower total gas flow rate and lower source gas ratio, although the JFW tended to grow

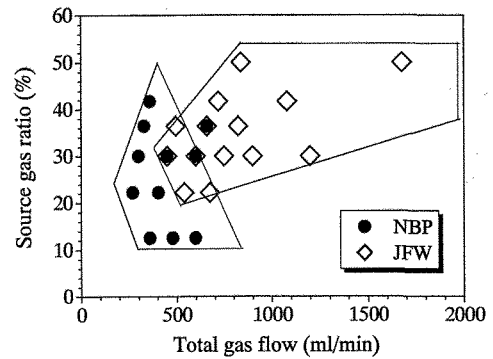


Fig. 5. Dependence of total gas flow rate and source gas ratio on NBP or JFW growth.

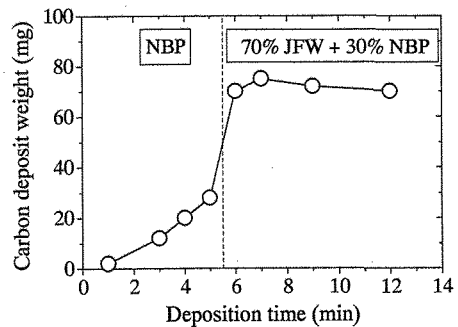


Fig. 6. Yield of NBP or JFW as a function of deposition time for 3 min with 10 mg catalyst.

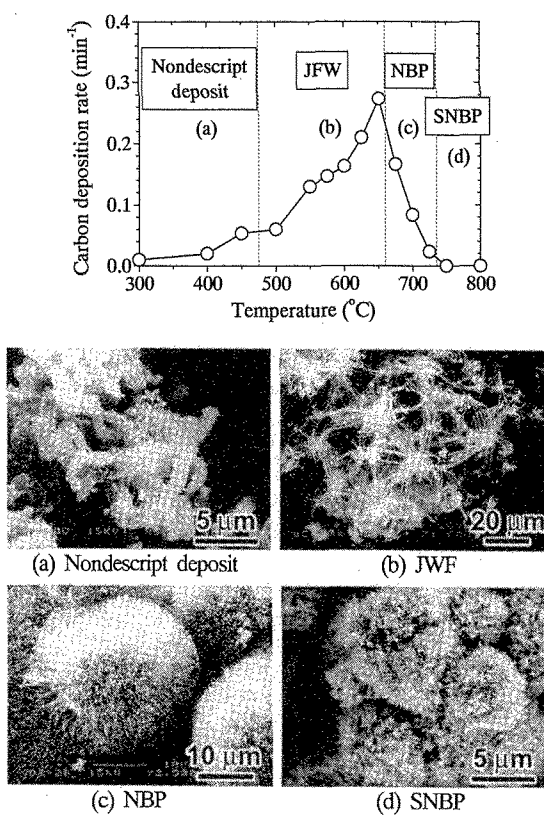


Fig. 7. Dependence of process temperature on the macroscopic shape of carbonaceous product.

at higher total gas flow rate and higher source gas ratio.

Figure 6 shows the dependence of deposition time. When the deposition time was shorter than 5 min, the NBP was mainly obtained and its deposition yield increased with the deposition time. However, for longer deposition time than 6 min, 70% of the product was JFW and the deposit weight was saturated. This means that the NBP gradually grows, although the JFW comparatively suddenly grows at some conditions.

Process temperature dependence on the product shape is shown in Fig. 7 with typical SEM images. At lower temperature below 500°C, nondescript carbonaceous deposit was obtained including thick and short carbon fibers. At the temperature between 500–650°C, JFW was obtained and the amount of JFW increased with the temperature. At the temperature above 600°C, NBP was obtained and the amount of NBP decreased with the temperature. Especially, at the temperature above 750°C, deposition amount was very low, although the NBP with sharper, finer, shorter nanotube was obtained, referred as SNBP.

It was found that the deposition amount and the product were dependent on substrate position, as shown in Fig. 8. The CDR decreased, as the substrate was placed at downstream. At upstream, center, and downer stream, the JFW, NBP and SNBP were obtained, respectively.

4. CONCLUSIONS

The present study concerning with catalytic CVD for carbon nanotube synthesis revealed the following principal results. Mixing the additives of Sn, In and their

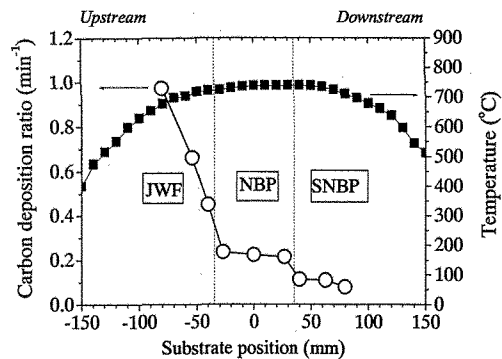


Fig. 8. Dependence of substrate position on the macroscopic shape of carbonaceous product.

oxides as secondary catalytic agents with the primary catalysts of Fe, Ni, and their oxides, remarkably enhance the carbonaceous deposition rate. The optimization mixture was Fe+Ni+Sn. Further optimization of the catalyst with additives is considered to improve and realize the mass production of carbon nanotubes.

The mixture catalyst of NiO and In₂O₃ provided the products with unique macroscopic structures: NBP, SNBP, and JFW. The NBP and SNBP is considered to be useful for electron emitter for screen-print preparation, since some nanotubes among their burs can be faced to the anode in the field emission device when they are printed on the cathode.

5. ACKNOWLEDGEMENTS

This work was partly supported by the excellent research project of the Research Center for Future Technology, Toyohashi University of Technology, by the research project of the Venture Business Laboratory, Toyohashi University of Technology, and by the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and by a Grant-in-Aid from The Japan Society for Promotion of Science.

6. REFERENCES

- [1] S. Iijima: *Physica B*, **323**, 1 (2002)
- [2] S. Iijima: *Nature*, **354**, 56 (1991)
- [3] T.W. Ebbesen, P.M. Ajayan: *Nature*, **358**, 220 (1992)
- [4] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, & R. E. Smalley: *Chem. Phys. Lett.*, **243**, 49 (1995)
- [5] M. José-Yacamán, M. Miki-Yoshida, L. Rendón, & J. G. Santiesteban: *Appl. Phys. Lett.*, **62**, 657 (1993)
- [6] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, & H. W. Kroto: *J. Phys. Chem. Solids*, **54**, 1841 (1993)
- [7] R.-M. Liu, J.-M. Ting: *Mater. Chem. Phys.* (in press)
- [8] M. Zhang, Y. Nakayama, L. Pan: *Jpn. J. Appl. Phys.*, **39**, L1242 (2000)
- [9] H. Takikawa, M. Yatsuki, R. Miyano, M. Nagayama, T. Sakakibara, S. Itoh, Y. Ando: *Jpn. J. Appl. Phys.*, **39**, 5177 (2000)

(Received October 15, 2003; Accepted November 20, 2003)