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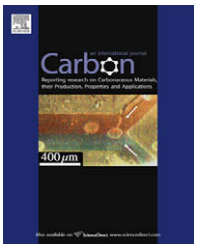

Highly efficient synthesis of carbon nanocoils by catalyst particles prepared by a sol–gel method

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ABSTRACT

Carbon nanocoils (CNCs) have been synthesized by thermal chemical vapor deposition (CVD) using Fe–Sn–O catalyst prepared by a sol–gel process. Three kinds of catalyst precursors, $Fe_2(SO_4)_3/SnCl_2$, $FeCl_3/SnCl_2$ and $Fe(NO_3)_3/SnCl_2$, were selected. It is found that the catalyst prepared by the combination of $Fe_2(SO_4)_3/SnCl_2$ exhibits the highest catalytic activity, which would be resulted from a small amount of sulfur existing in the catalyst. The highest yield of carbon deposits (mass ratio of deposits to catalysts) is 2510 wt.%. The synthesized CNCs are composed of hollow tubules with average coil diameter and line diameter of approximately 500 and 300 nm, respectively. It is also found that the growth of CNCs is greatly affected by reaction conditions, such as reaction time and temperature. Raman spectral analysis indicates that the higher flow rate of acetylene, the more graphite structures in CNCs.

1. Introduction

Carbon nanocoils (CNCs) exhibit outstanding mechanical and electromagnetic properties due to their peculiar helical morphologies in addition to the excellent properties of carbon nanotubes. Nakayama and co-workers reported that CNCs have the conductivity of 100–180 S/cm and Young modulus of 0.1 TPa that is a little smaller than that of straight CNTs [1,2]. Chen et al. also reported that a CNC behaves as an elastic spring with a spring constant *K* of 0.12 N/m in the low-strain regime, with an upturn in *K* in the high-stain regime [3]. These excellent electrical and mechanical properties, as well as their helical shapes, make CNCs suitable for wide applications [4–6]. They are expected for uses in high-performance composites, electromagnetic wave absorbers, field emission devices and micro- or nano-electromechanical systems such as nano-sized springs, generators for electromagnetic waves, etc. Recently, CNCs have attracted much effort for the overall studies. In the field of CNC synthesis, the growth mechanism and the morphology of CNCs have been reported in a lot of papers [7–9]. These CNCs are mainly synthesized by the methods of thermal CVD and plasma enhanced CVD using a kind of transition metallic catalyst usually doped with other elements. The diameters, lengths and densities of these CNCs have been controlled to a certain extent. However, the problem of synthesizing CNCs in large quantity still remains unsettled, which is an obstacle to the overall applications. From all the reported methods for synthesizing CNCs, thermal CVD is considered to be a possible and efficient method for mass production of CNCs, because this method is process controllable, simple in operation and easy to be scaled up for industrial production. In this method, selection of highly efficient catalysts is crucial for the growth of CNCs. Among the metal catalysts currently used in the

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growth of carbon nano-materials so far, iron, cobalt, nickel, titanium and tungsten are found to be relatively effective for the growth of CNCs [10,11]. Zhang et al. have successfully synthesized CNCs in high yield by using iron-coated indium tin oxide as the catalyst [12]. However, this method needs expensive and time-consuming vacuum evaporation to prepare iron film, which is not suitable for mass synthesis. Okazaki et al. have prepared Fe–In–Sn–O fine particles using co-precipitation method for synthesizing CNCs, which provided an effective and low cost method of catalyst preparation for synthesizing CNCs in large quantity [13]. Recently Kanada et al. have successfully synthesized multi-walled CNCs using a deposited thin film consisting of iron and tin as the catalyst [14]. It has been confirmed that Fe–Sn–O is an efficient catalyst even without the addition of indium. Tang et al. have synthesized helical carbon nanotubes in the pyrolysis of acetylene at 450 °C over iron nanoparticles generated by means of a combined sol–gel/reduction method [15]. Similarly over nickel nanoparticles generated by means of a combined sol–gel/reduction method, plait-like CNCs have been synthesized in acetylene pyrolysis at 415 °C [16]. The coil pitch of these nanocoils, however, is too short to exhibit a spring property. It is noted that the sol–gel method used in these studies makes it possible to prepare high-quality powder catalysts in large quantity, in a simple way and low cost.

In this paper, a kind of effective catalyst has been designed for the synthesis of CNCs in high efficiency under taking the advantages of the overall researches. We have fabricated powder catalysts containing oxides of iron and tin by using a sol–gel method. We have also investigated the effects of catalyst composition and CVD conditions on the growth of CNCs.

2. Experimental

Three kinds of compound combinations, $Fe_2(SO_4)_3/SnCl_2$, $FeCl_3/SnCl_2$ and $Fe(NO_3)_3/SnCl_2$, were chosen as the catalyst precursors. The molar ratios of iron to tin in three combinations were maintained at 3:1. A sol–gel process was used to prepare the catalysts, where 0.01 mol $Fe_2(SO_4)_3$ (0.02 mol for $FeCl_3$ and $Fe(NO_3)_3$), 0.0067 mol $SnCl_2$ and 0.03 mol $C_6H_8O_7H_2O$ were mixed with 100 mL ethanol, then the mixture was heated and stirred at 80 °C for 3 h to transform the solution into a sol, and then into a gel. The gel was heated in air at 700 °C for 3 h for the generation of catalyst particles containing the oxides of iron and tin (Fe–Sn–O). The catalysts were labeled as P1, P2 and P3 corresponding to the particles prepared using precursor combinations of $Fe_2(SO_4)_3/SnCl_2$, $FeCl_3/SnCl_2$ and $Fe(NO_3)_3/SnCl_2$, respectively. Catalyst particles of P1, P2 or P3 with a weight of 0.010 g were dispersed on SiO_2 substrates (size: 10×10 mm). CNCs were synthesized on these substrates in a thermal CVD system at 700 °C for 2–30 min by introducing acetylene diluted by argon gas with a total flow rate of 260 sccm. Approximately 0.251 g deposits were collected after CVD. In order to study the effect of CVD conditions on the synthesis of CNCs, the growth temperature was changed from 650 to 800 °C and the flow rate of acetylene was changed from 15 to 60 sccm. The deposits were observed and analyzed by a scanning electron microscope (SEM), a transmission electron microscope (TEM) and a Raman spectrometer.

3. Results and discussion

3.1. Properties of the CNCs prepared by different catalysts

Fig. 1 shows the SEM images of the CNCs grown at 700 °C for 30 min with acetylene flow rate of 60 sccm by Fe–Sn–O catalyst particles of (a) P1, (b) P2 and (c) P3. It is found that the grown CNCs using P1 and P2 are better than those using P3. The properties of the CNCs prepared using the three kinds of catalysts are summarized in Table 1. It is obvious from Table 1 that the yield of CNCs grown by P1 is higher than those grown by P2 and P3. The distributions of coil diameters for the CNCs grown by P1 and P2 are almost the same. The average line diameter of the CNCs grown by P1 and P2 is approximately 300 nm, which is smaller than that grown by P3. The lengths of CNCs grown by the three kinds of catalysts can all reach several tens of micrometers. Fig. 2 shows the SEM images of two kinds of the grown CNCs with (a) spring-like and (b) twisted forms. The catalyst particles are found at the tips of the CNCs indicating a tip growth mechanism, which is consistent with that reported by most of the other researches. The sizes of grain catalysts are approximately 250 and 150 nm in (a) and (b), respectively, which are a little smaller than the line diameters of the CNCs grown from the corresponding catalysts.

TEM observation reveals that the grown CNCs consist of over two carbon tubules [7]. The TEM micrograph of a typical CNC is shown in Fig. 3. It is observed that two carbon tubules forming the CNC have almost same coil diameter and pitch. However, these tubules are almost amorphous, which have the similar structures as carbon fibers.

Fig. 4 shows the energy dispersive X-ray (EDX) spectra of catalyst powder of P1. It is found that the catalyst particles

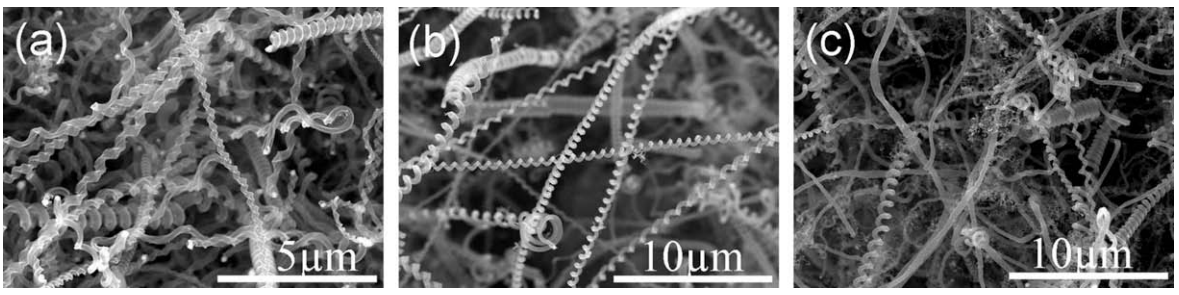

Fig. 1 – SEM images of the CNCs grown at 700 °C for 30 min by the catalyst particles of (a) P1, (b) P2 and (c) P3.

Table 1 – Properties of the CNCs prepared using different catalysts.

Catalyst	P1	P2	P3
Yield of CNCs	90%	70%	50%
Coil diameter (nm)	500–600	600–650	750–900
Average line diameter (nm)	300	300	400
Coil pitch (nm)	300–600	500–600	400–500
Coil length	Tens of micrometers	Tens of micrometers	Tens of micrometers
Morphology of deposits	Coiled and twisted forms	Coiled form	Coiled and twisted forms and some nano-fibers

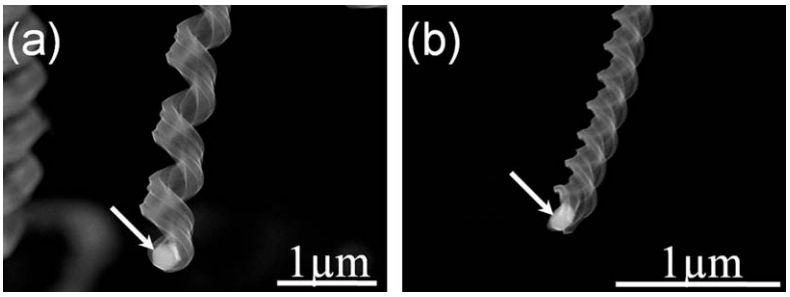

Fig. 2 – SEM images for the tips of (a) a spring-like CNC and (b) a twist-like CNC. The white arrows point to the catalyst particles.

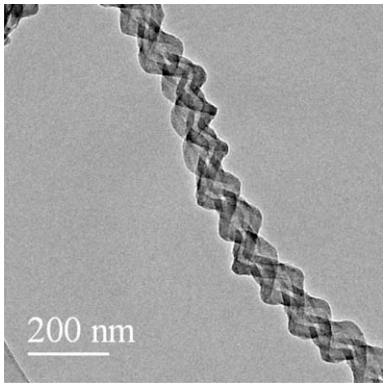

Fig. 3 – TEM image of a carbon coil formed by two tubules with same coil diameter and pitch.

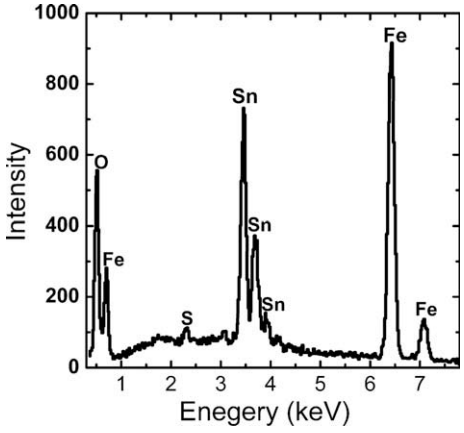

Fig. 4 – EDX spectra for the catalyst powder of P1.

are mainly composed of iron, tin, oxygen and sulfur, in which the molar ratio of iron to tin is approximately 3:1, and the sulfur only accounts for 0.5 at.%. The sulfur is formed by the decomposition of $Fe_2(SO_4)_3$ in the process of heat treatment at 700 °C. On the other hand, no sulfur, but iron, tin, and oxygen are detected in the EDX spectra for the catalyst particles of P2 and P3. It is reported that iron leads to the growth of carbon nanotubes, while indium and tin induce their helical growth [7]. Motojima et al. have synthesized carbon microcoils using a Ni catalyst by introducing a small amount of hydrogen sulfide or thiophene impurities, and the sulfur was considered to be very crucial for the highly efficient synthesis of carbon microcoils [11,17]. Kato et al. found that sulfur could accelerate the diffusion of active species through the metallic catalyst and increase its catalytic activity [18]. Romo-Herrera et al. reported that the sulfur influences the final morphology of deposits by introducing curvature into carbon nanostructures [19]. A similar effect may occur in our system resulting in an efficient synthesis of CNCs by the sulfur contained catalyst.

In order to synthesize CNCs in high yield by using P1 as the catalyst, it is also necessary to optimize the reaction conditions.

3.2. *Dependence of the deposits on growth time*

Fig. 5 shows the SEM micrographs of the CNCs synthesized at 700 °C by introducing acetylene for (a) 2 min, (b) 5 min and (c) 10 min. It is clearly observed that the CNCs have just grown out from the catalyst particles after introducing acetylene for 2 min. The lengths of these CNCs are less than 10 μm (see Fig. 5a). The coil lengths have been increased to more than 10 μm after introducing acetylene for 5 min (see Fig. 5b). After

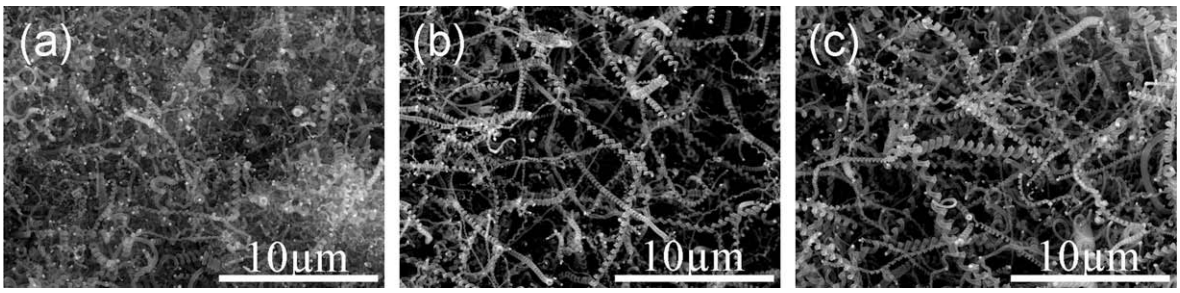

Fig. 5 – SEM images of the CNCs synthesized at 700 °C by introducing acetylene for (a) 2 min, (b) 5 min and (c) 10 min.

10 min deposition, CNCs in a yield of almost 100% are observed to be grown on the SiO_2 substrate as shown in Fig. 5c, which lengths have reached several tens of micrometers. Fig. 1a shows the CNCs grown for 30 min. There is no large difference in coil lengths between the CNCs grown for 10 and 30 min, suggesting that the activity of the catalyst has been reduced after 10 min growth. Fig. 6 shows the time dependence of the relative yield of carbon deposits. The relative yield is defined as mass ratio of deposits to catalyst particles, which indicates the amount of carbon conversion from gas to solid phase by the catalyst of unit mass. The solid circles represent a series of experimental data. It is found that the rate of carbon conversion is highest at the initial stage, gradually decreases over 10 min, and finally ceases. The highest relative yield of carbon materials is 2510 wt.%, which has reached a relatively higher value compared with that reported recently [20]. The further increase of carbon yield is expected by introducing oxidizing gas to increase the lifetime of the catalysts, just like those reported by Hata et al. [21] and Nakayama and co-workers [22]. The dependence of the deposits on growth time is similar to that proposed by Futaba et al. [23] for the super growth of single walled carbon nanotube. In their model, the relative yield of carbon M can be described as $M = \beta \cdot \tau \cdot (1 - e^{-t/\tau})$, where β is the initial growth rate, and τ is the characteristic catalyst lifetime. The experimental data are well fitted by the equation using the fitting parameters of β and τ of 3.22 min^{-1} and 7.98 min, respectively, as shown in Fig. 6. This curve is considered to be corresponding to the growth rate of CNCs. According to the growth equation, the product of β and τ represents the maximum relative yield of carbon deposits, in our case M_{max} = 2569.56% that is very close to the experimental data. The value of τ means that the lifetime of catalyst particles is 7.98 min, which is also reasonable.

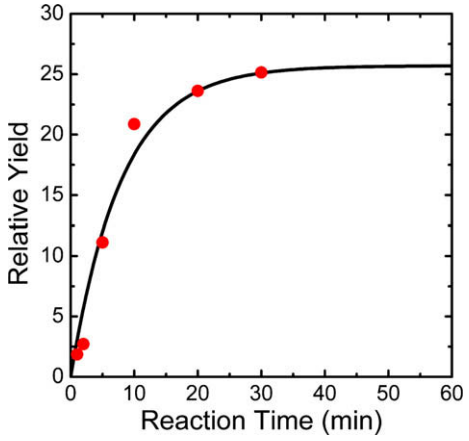

Fig. 6 – Time dependence of relative yield of carbon deposits. The solid circles are the experimental data and the solid line is a fitting curve using the equation of $M = \beta \cdot \tau \cdot (1 - e^{-t/\tau})$.

3.3. *Dependence of the deposits on growth temperature*

Fig. 7 shows morphological differences among the nanostructures synthesized at temperatures of (a) 650, (b) 750 and (c) 800 °C. The SEM image of CNCs synthesized at 700 °C has been shown in Fig. 1a. At the lower temperature of 650 °C, a small amount of CNCs with relatively smaller external diameters and coil lengths is obtained. At 700–750 °C, a high yield of CNCs can be obtained. By careful observation, some carbon fibers appear among the CNCs at 750 °C. It is interesting that when the temperature reaches 800 °C, no CNC but a great number of bean sprout-like carbon nano-fibers are grown from the powder catalysts. The line diameter of the fiber is decreased gradually with the growth time as shown in Fig. 7c. This result is considered to be due to the deposition of amorphous carbon, produced by the gas phase reaction, on the bodies of the carbon fibers, because the decomposition reaction of acetylene at 800 °C is very strong. These results indicate that the catalytic activity of Fe–Sn–O particles is lower at 650 °C and then becomes higher with the increase of temperature. However, higher temperature may induce the loss of tin from the catalyst particles because of its low saturated vapor pressure, which leads to the growth of line shaped tubules. Furthermore, a large amount of amorphous carbon generated from the strong decomposition of acetylene at 800 °C covers the surfaces of these tubules, resulting in the growth of bean sprout-like nano-fibers.

3.4. *Dependence of the deposits on acetylene flow rate*

Fig. 8 shows the SEM image of the CNCs synthesized at 700 °C for 30 min with acetylene flow rate of 15 sccm. The average coil diameter and line diameter of the grown CNCs are all smaller than those synthesized with acetylene flow rate of 60 sccm (see Fig. 1a). This result is consistent with that reported by Pan et al. [7]. It is accepted that the diameter of a tubule is determined by the size of the catalyst particle at its tip, suggesting that the formation of catalyst particles is affected by the reaction gas concentration.

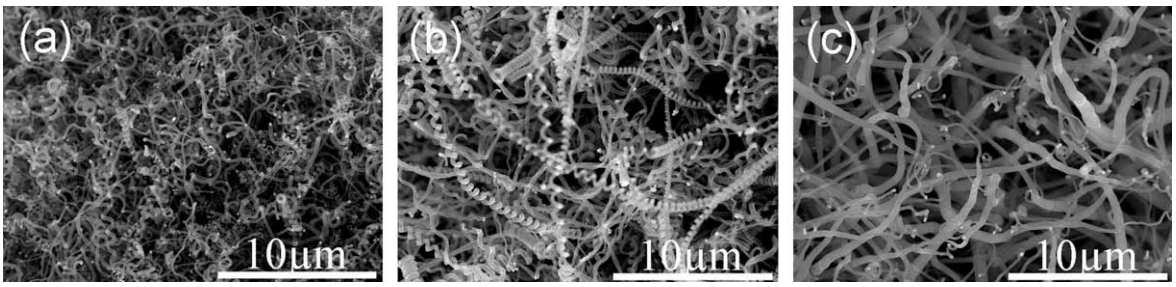

Fig. 7 – SEM images of the CNCs synthesized at reaction temperatures of (a) 650 °C, (b) 750 °C and (c) 800 °C.

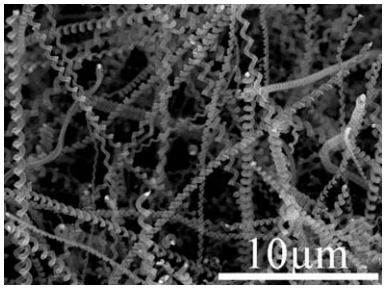

Fig. 8 – SEM image of CNCs synthesized at 700 °C for 30 min with acetylene flow rate of 15 sccm.

3.5. *Dependence of carbon structures on CVD conditions*

The carbon nanostructures in CNCs are inspected by Raman spectral analysis with an excitation laser wavelength of 632.8 nm. Fig. 9 shows the Raman spectra of (a) CNCs synthesized by the catalysts of P1, P2 and P3 with the acetylene flow rate of 60 sccm, and (b) CNCs synthesized with the acetylene flow rate of 15, 30, 45 and 60 sccm by the catalyst P1. There exhibits two main peaks in the Raman spectra, one is around 1322 cm^{-1} known as D-band originated from structural defects in carbon materials, and the other is around 1593 cm^{-1} known as G-band originated from graphite structure. A large peak of D-band and a broad peak of G-band in each spectrum indicate a low graphitization of nanocoils. Comparing the spectra in Fig. 9a, the ratio of I_D/I_G (0.94) corresponding to the CNCs synthesized by P1 is smaller than those synthesized by P2 and P3 (1.03 and 1.00, respectively), indicating that there are more graphite structures in the CNCs synthesized by P1. It is also found that the ratio of I_D/I_G is gradually decreased from 1.18 to 0.91 with increasing of the flow rate of acetylene, suggesting that the higher flow rate of acetylene, the more graphite structures in the grown CNCs.

4. Conclusions

CNCs have been successfully synthesized in high efficiency using Fe–Sn–O catalyst particles prepared by a simple and economic sol–gel method. The catalyst particles prepared by the precursor combination of $Fe_2(SO_4)_3/SnCl_2$ exhibit the highest activity compared with the other two kinds of catalysts. A small amount of sulfur existing in the catalyst particles may enhance their catalytic activity leading to the high yield of CNCs and more graphite structures in the CNCs. The average coil diameter and line diameter of these CNCs are approximately 500 and 300 nm, respectively. The grown CNCs are composed of over two hollow amorphous tubules. The temperature range of 700–750 °C is suitable for the growth of CNCs, while the high temperature of 800 °C induces the growth of bean sprout-like carbon nano-fibers. Increasing of the flow rate of acetylene results in more graphite structures in CNCs.

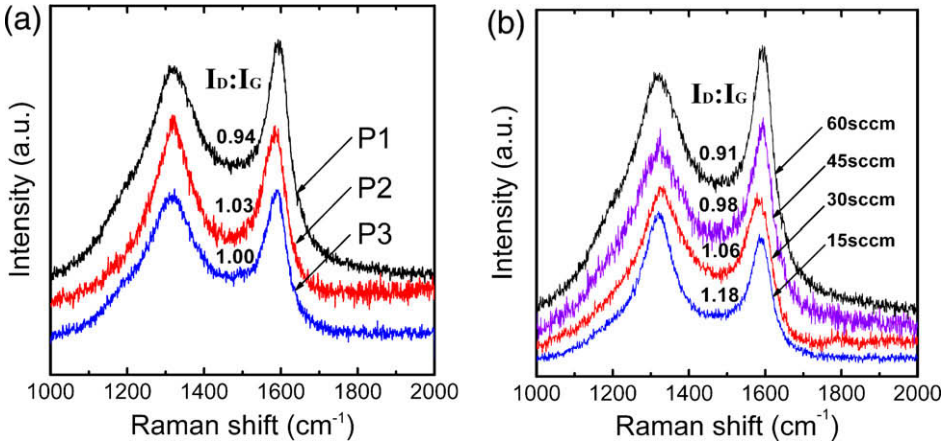

Fig. 9 – Raman spectra of the CNCs synthesized (a) by the catalysts of P1, P2 and P3, with the acetylene flow rate of 60 sccm, and (b) with the acetylene flow rate of 15, 30, 45 and 60 sccm by the catalyst P1.

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REFERENCES

[1] Hayashida T, Pan LJ, Nakayama Y. Mechanical and electrical properties of carbon tubule nanocoils. Physica B 2002;323(1):352–3.
[2] Treacy MMJ, Ebbesen TW, Gibson JM. Exceptionally high Young's modulus observed for individual carbon nanotubes. Nature 1996;381(20):678–80.
[3] Chen XQ, Zhang SL, Dikin DA, Ding WQ, Ruoff RS, Pan LJ, et al. Mechanics of a carbon nanocoil. Nano Lett 2003;3(9):1299–304.
[4] Pan LJ, Hayashida T, Zhang M, Nakayama Y. Field emission property of carbon tubule nanocoils. Jpn J Appl Phys 2001;40(3B):L235–7.
[5] Amelinckx S, Zhang XB, Bernaerts D, Zhang XF, Ivanov V, Nagy JB. A formation mechanism for catalytically grown helix-shaped graphite nanotubes. Science 1994;265(5172):635–9.
[6] Hokushin S, Pan LJ, Konishi Y, Tanaka H, Nakayama Y. Field emission properties and structural changes of a stand-alone carbon nanocoils. Jpn J Appl Phys 2007;46(23):L565–7.
[7] Pan LJ, Zhang M, Nakayama Y. Growth mechanism of carbon nanocoils. J Appl Phys 2002;91(12):10058–61.
[8] Nishimura K, Pan LJ, Nakayama Y. In situ study of Fe/ITO catalysts for carbon nanocoil growth by X-ray diffraction analysis. Jpn J Appl Phys 2004;43(8A):5665–6.
[9] Pan LJ, Hayashida T, Nakayama Y. Growth and density control of carbon tubule nanocoils using catalyst of iron compounds. J Mater Res 2002;17(1):145–8.
[10] Rodriguez NM, Kim MS, Fortin F, Mochida I, Baker RTK. Carbon deposition on iron–nickel alloy particles. Appl Catal A: General 1997;148(2):265–82.
[11] Motojima S, Itoh Y, Asakura S, Iwanaga H. Preparation of micro-coiled carbon fibers by metal powder-activated pyrolysis of acetylene containing a small amount of sulphur compounds. J Mater Sci 1995;30(20):5049–55.
[12] Zhang M, Nakayama Y, Pan LJ. Synthesis of carbon tubule nanocoils in high yield using iron tin oxide as catalyst. Jpn J Appl Phys 2000;39(12A):L1242–4.
[13] Okazaki N, Hosokawa S, Goto T, Nakayama Y. Synthesis of carbon tubule nanocoils using Fe–In–Sn–O fine particles as catalysts. J Phys Chem B 2005;109(37):17366–17371.
[14] Kanada R, Pan LJ, Akita S, Okazaki N, Hirahara K, Nakayama Y. Synthesis of multiwalled carbon nanocoils using codeposited thin film of Fe–Sn as catalyst. Jpn J Appl Phys 2008;47(4):1949–51.
[15] Tang NJ, Zhong W, Gedanken A, Du YW. High magnetization helical carbon nanofibers produced by nanoparticle catalysis. J Phys Chem B 2006;110(24):11772–4.
[16] Tang NJ, Yang Y, Lin K, Zhong W, Chaktong A, Du YW. Synthesis of plait-like carbon nanocoils in ultrahigh yield, and their microwave absorption properties. J Phys Chem C 2008;112(27):10061–7.
[17] Motojima S, Asakura S, Kasemura T, Takeuchi S, Iwanaga H. Catalytic effects of metal carbides, oxides and Ni single crystal on the vapor growth of micro-coiled carbon fibers. Carbon 1996;34(3):289–96.
[18] Kato T, Kusakabe K, Morooka S. Effect of sulphur on formation of vapour-grown carbon fibre. J Mater Sci Lett 1994;13(5):374–7.
[19] Romo-Herrera JM, Cullen DA, Cruz-Silva E, Ramirez D, Sumpter BG, Meunier V, et al. The role of sulfur in the synthesis of novel carbon morphologies: from covalent Y-junctions to sea-urchin-like structures. Adv Funct Mater 2009;19(8):1193–9.
[20] Kumar M, Ando Y. Gigas growth of carbon nanotubes. Defence Sci J 2008;58(4):496–503.
[21] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Lijima S. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. Science 2004;306(5700):1362–4.
[22] Chakrabarti S, Naqasaka T, Yoshikawa Y, Pan LJ, Nakayama Y. Growth of super long aligned brush-like carbon nanotubes. Jpn J Appl Phys 2006;45(28):L720–2.
[23] Futaba DN, Hata K, Yamada T, Mizuno K, Yumura M, Iijima S. Kinetics of water-assisted single-wall carbon nanotube synthesis revealed by a time-evolution analysis. Phys Rev Lett 2005;95(5):056104-(1)–(4).