Applied Mechanics and Materials Vol. 420 (2013) pp 154-159 *Online: 2013-09-27*

doi:10.4028/www.scientific.net/AMM.420.154

Investigation on Fe-Sn-O Catalyst Activity for the Growth of Carbon Nanocoils

Xin Fu[a], Dawei Li[b], Lujun Pan[c]

Institute of Near Field Optics and Nanotechnology, Dalian University of Technology, Dalian, Liaoning 116024, China

[a]fuxin@mail.dlut.edu.cn, [b]765335980@qq.com, [c]lpan@dlut.edu.cn

Keywords: Carbon nanocoils; Catalysts; Growth curve; Catalytic activity; Statistics

Abstract. We have investigated the relationship between the catalyst and the growth of CNCs. It is found that with the increase of deposition time the yield of CNCs gradually increased, while their growth rate decreased exponentially. The short reaction time would lead to the growth of CNCs with smaller coil diameters, however, CNCs with larger coil diameters are increased gradually after a long-time reaction. The Fe-Sn-O catalyst particles are not uniform in sizes. It is considered that CNCs with smaller/larger coil diameters can be synthesized from the smaller/larger catalyst particles. A further fitting of the growth curve indicates that the as-prepared catalyst particles have different activities. It can be inferred that catalyst particles with different sizes have different catalytic activities. The smaller catalyst particles have a higher activity but a shorter lifetime, and the coil diameter of CNCs synthetized from it is smaller.

Introduction

Carbon nanocoils (CNCs), as a new kind of three-dimensional carbon nano-materials, have outstanding electrical and mechanical properties[1,2]. Because of these properties, CNCs have many potential applications, such as nanosprings[3], electron guns for flat panel field emission displays[4], electromagnetic wave absorbers[5] and micro-sensors[6], etc. In recent years, more efforts have been focused on studying the synthesis and growth mechanisms of CNCs. In the field of synthesis, chemical vapor deposition (CVD) is known as an effective method in growing CNCs, due to its controllable and simple operation. In this method, selection of highly efficient catalysts and enhancement of their catalytic activity are crucial for the growth of CNCs. Among the metal catalysts currently used, Fe, Co, Ni and their alloys are proven to be the efficient catalysts. However, the study on the catalytic activity of these catalysts for the CNC growth has seldom been reported. It is known that the catalyst composition and the reaction condition can affect the catalyst activity and the yield of carbon nanotubes (CNTs)[7]. Futaba et al. have investigated the super growth of CNTs through a quantitative time-evolution analysis based on a growth model where decay of catalyst activity was similar to that of radioactive decay[8]. They found that adding small amount of water plays an important role in enhancing the catalyst activity. Similarly, Florian et al. have prepared CNCs by using Pd/C_{60} catalysts, the yield of CNCs has been enhanced by adding a little amount of water during the CVD process[9]. Zheng et al. found that reaction temperatures affect greatly on the catalytic activity of Ni/alumina catalysts, which resulted in different carbon nanostructures at different temperatures[10]. In addition, our previous study revealed that a short-time dependence of the yield of CNCs by using Fe-Sn-O catalysts was found to be similar to that of super grown CNTs[11]. It is noted that the study of long-time catalytic behavior of catalyst particles, including their lifetimes and activities, is very important for accurately controlling the CNC growth. In this work, we have investigated the catalyst activity for the CNC growth through the evolution of the reaction time. A new growth curve of CNCs has been established, which can be fitted well by a modified CNC growth formula. SEM observation and statistical results further indicate that there exist catalysts with different sizes and different catalytic activities for the CNC growth.

Experimental details

$Fe_2(SO_4)_3/SnCl_2 \cdot 2H_2O$ solution with molar ratio of 30:1 were used as the catalyst precursor. 150 ml solution was dip-coated on SiO_2 substrates (8×8 mm^2), dried at 40 ^oC for 10 min, and heated at 700 ^oC in air for 30 min. The oxidized catalysts were placed in a CVD furnace and heated to 700 ^oC under argon gas with a flow rate of 260 sccm. Then CNCs were synthesized by introducing acetylene and argon gases with flow rates of 30 and 230 sccm, respectively for 2 to 600 min. Scanning electron microscopy (SEM; S-4800, Hitachi, Japan) was used to analyze the grown carbon deposits.

Results and discussion

Fig. 1 (a) shows the typical SEM images of the CNCs synthesized at 700 ^oC for 30 min by Fe-Sn-O catalysts. A high yield of CNCs with narrow coil diameter distribution is obtained. The catalyst particles are observed at the tips of the CNCs (Fig. 1 (b)), indicating a tip growth mechanism.

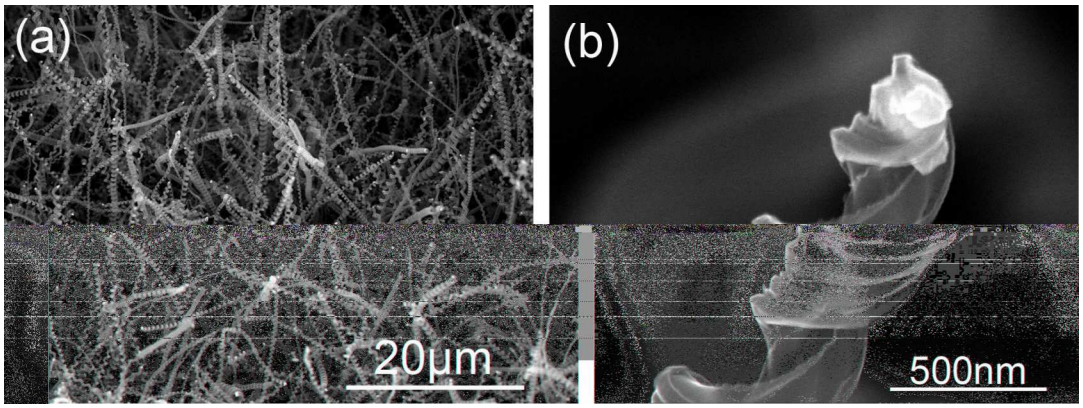


Fig. 1 (a) SEM image of the CNCs synthesized at 700 ^oC by Fe-Sn-O Catalysts, and (b) an enlarged image of the CNC tip.

In order to investigate the relationship between the catalyst activity, the yield and morphology of the CNCs, the CNCs have been synthetized with a series of deposition time. Fig. 2 (a) shows the relationship between the relative production and the reaction time. The relative production is the mass ratio of deposits to catalyst particles and reflects the yield of CNCs. It is found that, in a long period (0 to 600 min), the yield of CNCs is gradually increased with increasing the deposition time, indicating that the used catalysts for CNC growth have a longer lifetime than those for the multi-walled CNTs. The growth formula for super growth of CNTs is as following:

$$H(t) = \beta\tau_0\left(1-\exp\left(-t/\tau_0\right)\right),$$

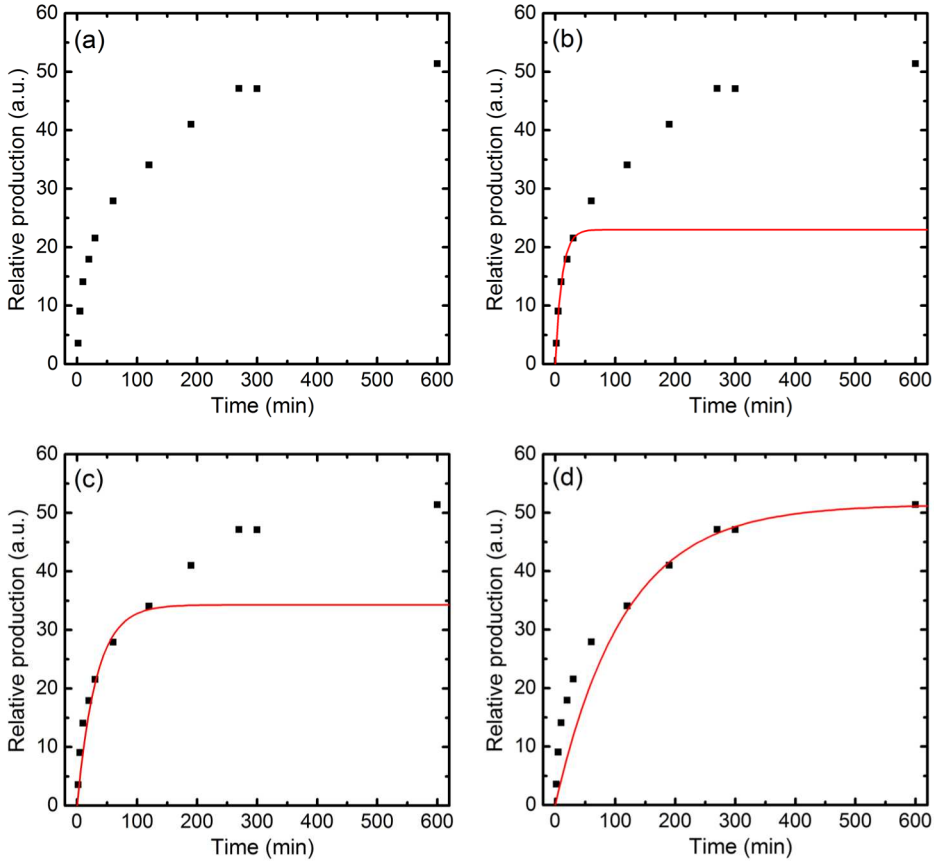


Fig. 2 (a) relationship between relative production and deposition time, fitting curve with the parameter (b) $\tau = 11$, $\beta \times \tau = 23$, (c) $\tau = 32$, $\beta \times \tau = 34.3$, (d) $\tau = 115$, $\beta \times \tau = 51.4$.

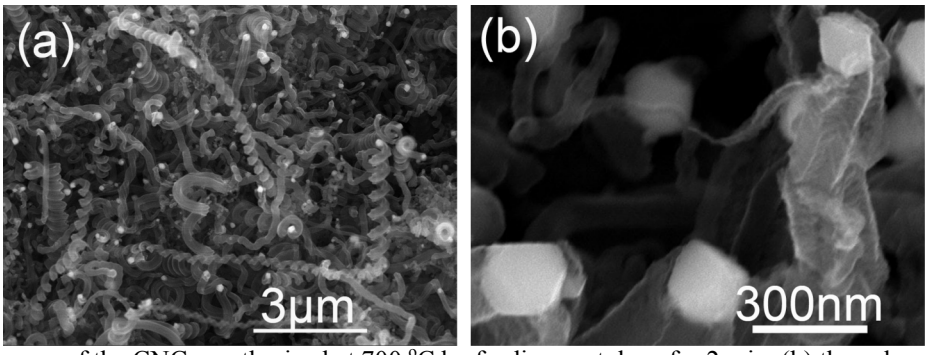


Fig. 3 (a) SEM image of the CNCs synthesized at 700 ^{o}C by feeding acetylene for 2 min, (b) the enlarged image of the CNCs with catalyst particles on their tips.

where β is the initial growth rate (IGR) and τ_0 is the characteristic catalyst lifetime[8]. This formula is used to fit our experimental data. Fig. 2 (b) to (d) shows the solid fitting curves calculated by three groups of parameters (β, τ) that are (2.09, 11), (1.07, 32), and (0.45, 115), respectively. It is found that the growth formula with one group of parameter can only fit one part of the experimental data. For example, the data within the periods of 0 to 30 min can be fitted well using the parameter group of (2.09, 11) (Fig. 2 (b)); in the periods of 30 to 120 min and 120 to 600 min, the data can be fitted by the formula with parameter groups of (1.07, 32) (Fig. 2 (c)) and (0.45, 115) (Fig. 2 (d)), respectively. This result suggests that the activity and lifetime of Fe-Sn-O catalyst particles used for the growth of CNCs are not uniform. Fig. 3 shows SEM images of the CNCs synthesized by the Fe-Sn-O catalysts for 2 min. It is clearly observed in Fig. 3 (b) that the size and morphology of catalyst particles are different with each other. From the overall results, it is reasonable to consider that the experimental data can be fitted well by a growth formula with multi-parameters.

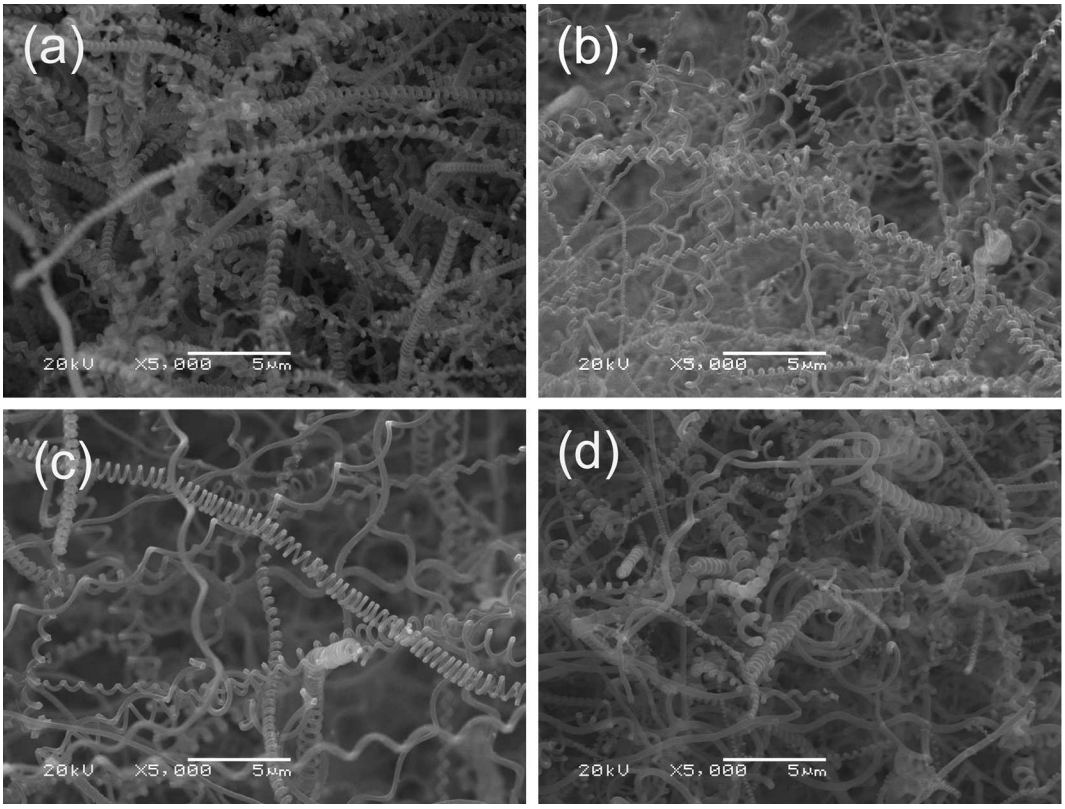
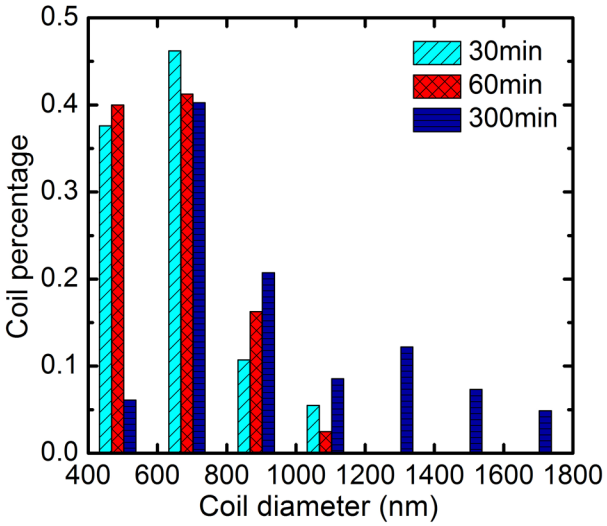


Fig. 4 SEM images of the CNCs synthesized at 700 °C by feeding acetylene for (a) 30 min, (b) 60 min, (c) 300 min, and



(d) 600 min.

Fig. 5 Distributions of coil diameters for the CNCs synthesized under the deposition time of 30, 60, and 300 min.

Figure 4 shows the typical SEM images of the CNCs synthesized at 700 °C by feeding acetylene for (a) 30 min, (b) 60 min, (c) 300 min and (d) 600 min. It is found that the coil diameters of the CNCs synthesized in short time are relatively uniform and small (Fig. 4 (a) and (b)), while with increasing the deposition time their coil diameters are widely distributed and more CNCs with larger coil diameters are observed (Fig. 4 (c) and (d)). The distributions of the CNC coil diameters with different deposition time were analyzed statistically, as shown in Fig. 5. A careful observation of Fig. 5 reveals that the proportions of CNCs with coil diameters in the range of 600 to 800 nm and 800 to 1000 nm are stable. It is also found that the CNCs with large coil diameter increased gradually with increasing the deposition time. According to the above speculation, the experimental data has been refitted using the super growth formula with multi-parameters. It is found that the super growth formula with three groups of parameters can fit the experimental data well as shown in Fig. 6. The formula with three groups of parameters is written as

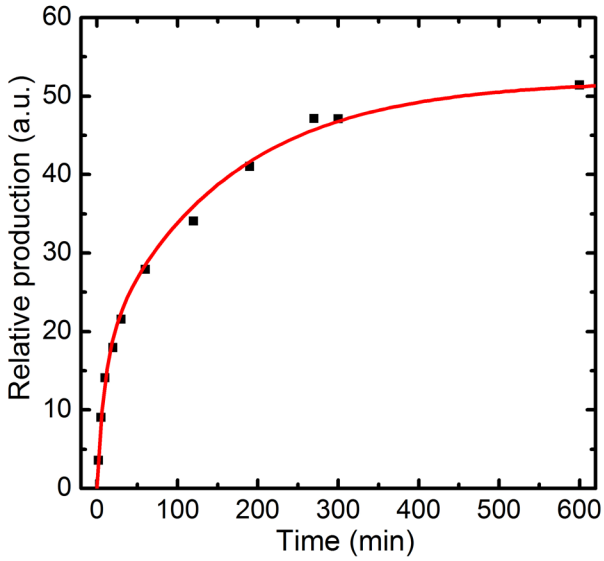


Fig. 6 Fitting curve of CNC growth with three β and three τ, $M_{max} = 52$, $M_{max1} = \beta_1 \times \tau_1 = 15$, $\tau_1 = 13$ min, $M_{max2} = \beta_2 \times \tau_2 = 20.5$, $\tau_2 = 90$ min, $M_{max3} = \beta_3 \times \tau_3 = 16.5$, $\tau_3 = 230$ min.

$$M = M_{max} - M_{max1} \cdot \exp(-t/\tau_1) - M_{max2} \cdot \exp(-t/\tau_2) - M_{max3} \cdot \exp(-t/\tau_3),$$

where $M_{max} = 52$, $M_{max1} = 15$, $\tau_1 = 13$ min, $\beta_1 = 1.15$, $M_{max2} = 20.5$, $\tau_2 = 90$ min, $\beta_2 = 0.23$, $M_{max3} = 16.5$, $\tau_3 = 230$ min, $\beta_3 = 0.07$. The three groups of parameters further indicate that the catalyst particles with a higher activity (β) have a shorter lifetime (τ) during the CVD process and vice versa. Combined with the statistical result as shown in Fig. 4, it is found that the catalyst particles with short lifetime contribute to the growth of CNCs with small coil diameters (short-time growth) and the catalyst particles with long lifetime contribute to the growth of CNCs with large coil diameters (long-time growth). Catalyst particles with smaller diameters are considered to have a higher catalytic activity but a relatively shorter lifetime, while catalyst particles with larger diameters have a lower activity but longer lifetime. CNCs with small coil diameters would be formed from the small catalysts in a short reaction time, with increasing the deposition time CNCs with large coil diameters would be grown from the large catalysts.The reason why different sizes of catalysts have different catalytic activity has not been fully understood, which is a subject for our further study.

Conclusion

The time evolution analysis on the growth of carbon nanocoils by Fe-Sn-O catalyst has been studied. It is found that the yield of CNCs is gradually increased with increasing the deposition time, which can be fitted by a multi-parameter growth formula. The formula with multi-parameters indicates that the catalyst activities for the CNC growth are not uniform. The catalyst particles with a higher activity have a shorter lifetime and vice versa. It is easily found that the coil diameters of the CNCs synthesized in short time are uniform and small, while long deposition time leads to wide distribution of coil diameters and more CNCs with larger coil diameters. It indicates that the sizes of the Fe-Sn-O catalyst particles used for the CNC growth are not uniform. Based on the experimental and calculation results, it can be inferred that the catalyst particles with different sizes have different catalytic activities. The smaller catalyst particles have a higher activity but a shorter lifetime and vice versa.

References

[1] T. Hayashida, L.J. Pan , Y. Nakayama: Physica B, 2002, 323: 352-353.

[2] M.MJ. Treacy, T.W. Ebbesen, J.M. Gibson: Nature, 1996,381: 678-680.

[3] X.Q. Chen, S.L. Zhang, D.A Dikin, W.Q. Ding, R.S. Ruoff, L.J. Pan: Nano, Lett, 2003,3: 1299-1304.

[4] L.J. Pan, T. Hayashida, M. Zhang, Y. Nakayama: Jpn. J. Appl. Phys, 2001, 40: 235-237.

[5] S. Motojima, Y. Noda, S. Hoshiya, Y. Hishikawa: J. Appl. Phys, 2003, 94: 2325-2330.

[6] S.M. Yang, X.Q. Chen, S. Motojima: Carbon, 2006, 44: 3352-3355.

[7] E. Mora, A.R. Harutyunyan: J. Phys. Chem. C, 2008, 112: 4805-4812.

[8] D.N Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura, S. Iijima: Phys. Rev. Lett, 2005, 95: 056104-(1)–(4).

[9] F. Nitze, E. Abou-Hamad, T. Wågberg: Carbon, 2011, 49: 1101-1107.

[10] G.B. Zheng, K. Kouda, H. Sano, Y. Uchiyama, Y.F. Shi, H.J Quan: Carbon, 2004, 42: 635-640.

[11] D.W. Li, L.J. Pan, J.J. Qian, D.P. Liu: Carbon, 2010, 48: 170-175.

Recent Trends in Materials and Mechanical Engineering II
10.4028/www.scientific.net/AMM.420

Investigation on Fe-Sn-O Catalyst Activity for the Growth of Carbon Nanocoils
10.4028/www.scientific.net/AMM.420.154