

Reductive Heat Treatment of Austenitic Stainless Steel Substrate for Growth of Hybrid Carbon Nanostructures

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Abstract— Single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and carbon nanofibers (CNFs) in hybrid structures were synthesized on austenitic stainless steel substrates (Type:304). The formation of nanoparticles on substrates occurred under hydrogen gas (H_2) with temperature of 720 °C. The effects of reductive heat treatment on the growth of carbon nanostructures at 15, 45, 60, 75 and 80 minutes were examined with scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffractometer (XRD) and thermogravimetric analysis (TGA). The samples were synthesized using thermal chemical vapor deposition (Thermal CVD) under atmospheric pressure of acetylene gas (C_2H_2). The combination of carbon nanotubes and carbon nanofibers in hybrid structure was synthesized on a substrate using a long time to adjust the surface by heating treatment. The hybrid structure of carbon could not be observed when used in surface treatment time was 80 minutes. Shorter (<45 min) or longer (>75 min) substrate heat treatments did not produce hybrid carbon nanostructures at this temperature.

Keywords— hybrid nanostructure, chemical vapor deposition, carbon nanotubes

I. INTRODUCTION

Carbon nanotubes and carbon nanofibers are discussed as excellent materials due to their spectacular physical, chemical and mechanical properties. The techniques used for the growth of any carbon nanostructures are arc discharge [1], chemical vapor deposition (CVD) [2-7], and laser ablation [8]. Thermal chemical vapor deposition has been accepted as a advantageous method for the large-scale synthesis of CNTs and CNFs. This is because thermal CVD can be performed continuously due to the active supply of both carbon source and catalysts. Furthermore, it can be managed at relatively low temperatures (600–1000 °C). Stainless steel (SS) plate has been proposed as cost-effective dual purpose substrates and catalysts [9-12]. Stainless steel contains transition metals (iron, nickel, etc.) which are well-documented to be effective catalysts for CNT growth [13–14]. For instance, type 304 SS

is readily available and reason-ably purchased, its application as catalyst is of technological interest to CNT manufacturing [15,16]. However, the systematic study of the pretreated duration effect on the growth of hybrid carbon nanostructures is still not much documentary reported.

This study illustrated the heat pretreatments of 304 stainless steel substrates under reducing environments (such as hydrogen gas). The growth of hybrid carbon nanostructures was directly synthesized on stainless steel surfaces without additional catalysts. The results demonstrated an appropriate method to activate the 304 stainless steel substrate in controllable carbon nanostructures.

II. MATERIALS AND METHOD

A. Preparation of samples

Austenitic stainless steel substrate (Type:304) with an area of 6 cm² was used as a catalytic substrate for the growth of carbon nanostructures. The substrate was cleaned using 99.99% of methanol. Then, it was placed into a stainless steel chamber of thermal CVD system with pressure less than 10⁻² mbar using a rotary pump (Acatel, 2012). To achieve conversion of hydrocarbon gas to carbon nanostructures, a tubular furnace (Nabertherm, R13) was used as a heating source. Argon gas (Ar) was fed into the chamber with flow rate of 50 standard cubic centimeters per minute (sccm) while waiting for the chamber to heat up to prevent the oxidation on the surface of samples. Acetylene gas (C_2H_2) with a flow rate of 160 sccm was thermally pyrolyzed inside an electric tubular furnace at 720 °C. Pyrolysis occurred in hydrogen gas (H_2) with a flow rate of 200 sccm, as reductive gas and formation-supported of catalytic nanoparticles. Growth of carbon nanostructures occurred on a catalytic substrate at reductive heat treatment time of 15, 45, 60, 75 and 80 minutes, respectively. Effects of reductive heat treatment time on the growth of carbon nanostructures were examined with SEM, TEM, XRD and TGA.

B. Characterization

Scanning electron microscope (SEM, Quanta 450 FEI) installed with energy dispersive spectroscopy (EDS) was used to investigate the morphology and elemental composition of samples. The voltage and the current during operation was 30 kV and 10 μ A, respectively. The working distance of 6.7 mm and 12 mm were used for SEM imaging and EDS analysis, respectively. Transmission electron microscope (TEM, Hitachi HT 7700) was conducted using an accelerating voltage of 120 kV and a current of 60 μ A to explore the structure of synthesized CNTs. The samples were sonicated with ethanol and dropped on a copper grid. And then the samples were taken into a holder of microscope. X-ray diffractometer (XRD, Bruker D8 Advance) was used to determine the crystal structure of materials. The samples were scanned over the diffraction angle 2θ of 10 to 80 degrees. The scanning speed was set at 3 degree/min and in step of 0.02°. The incident X-ray wavelength was 1.54 angstrom (Cu anode) with the voltage and the current of 40 kV and 40 mA, respectively. Thermogravimetric analysis (TGA, NETZSCH TG 209F3) was used to investigate the thermal properties of samples with a mass of 10 mg. The heating rate was 20 °Cmin⁻¹ under nitrogen flow. The temperature was increase from 25 to 900 °C.

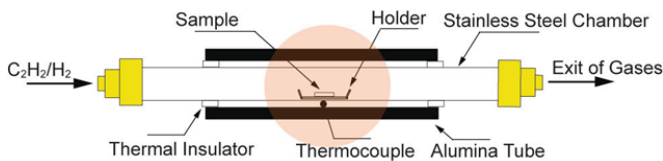


Figure 1. Schematic diagram of thermal CVD chamber.

III. RESULTS AND DISCUSSION

A. Effect of reductive heat treatment on the morphology of substrate surface

The substrate surface is directly involved in CNTs growth. Hydrogen gas was used as reductive pretreatment gas for self-supporting in growing carbon nanotubes. Figure 2(a) shows a smooth surface without any surface pretreatment for comparison with other conditions. The top layer of the surface was exposed at high temperature shown in figure (b-f). The formation of catalytic particles occurred on the surface with heat treatment time of 15 min as shown in figure 2(b). The surface was more exposed and smaller catalyst particles formed in the heat treatment time for 45 minutes and 60 minutes, respectively. The small particles were merged together into a larger catalytic size at the heat treatment time of 75 and 80 minutes.

The investigation of the evolution of surface morphology with reductive heat treatment duration, the surface chemical composition was also examined by EDS analysis (Fig.3). The mass concentration of Cr, Mn, Fe and Ni did not obvious changes upon reductive heat treatment. The mass concentration of oxygen showed a remarkable decrease, such an decrease is attributed to the oxidation of surface at high temperature.

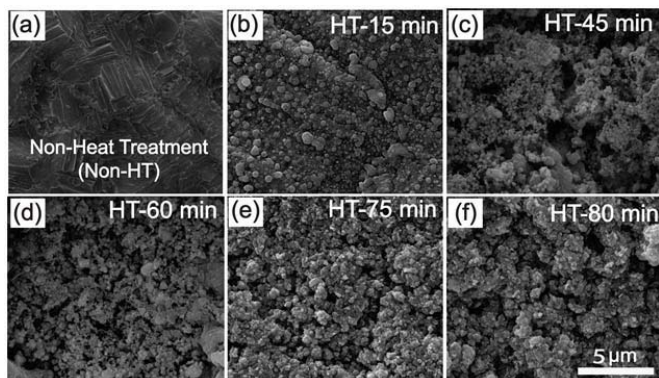


Figure. 2 SEM images of stainless steel substrates after reductive heat treatment of (a) 0 min, (b) 15 min, (c) 45 min, (d) 60 min, (e) 75 min and (f) 80 min.

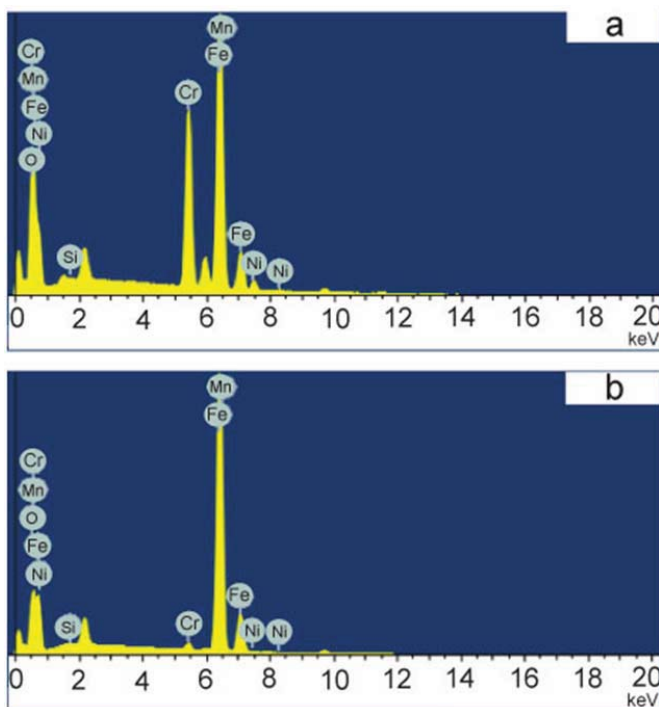


Figure. 3 EDS spectra of stainless steel substrates after reductive heat treatment of (a) 15 min, (b) 75 min.

B. Effect of reductive heat treatment on the growth of carbon nanostructures.

Carbon nanostructures did not form on a SS without any pretreatment. The single structure of MWCNTs was observed only in the condition of heat treatment for 15 min. The appearance of carbon hybrid structures such as CNTs and CNFs was observed on SS with heat treatment of 45 min, 60 min and 75 min. The pure CNFs were grown on substrate for reductive heat treatment conditions of 80 min. Figure 4 showed the structural change from nanotubes structure into nanofibers structure.

The low magnification of TEM images (see Fig. 5a and 5b) clearly showed the single-walled and multi-walled structures of carbon nanotubes grown on CNFs as hybrid structures. Additionally, the quality of the hybrid structures was examined using XRD (Fig.5C). XRD reveals a significant degree of graphitization and metal catalytic crystals.

The yields and the structures of the synthesized carbon products were readily controlled by simply varying the reductive heat treatment durations. The catalytic particles across each other on their moving path, they might fuse together to form a larger catalytic particle, which would then catalyze the growth of a resulting carbon.

The collected carbonaceous material was further examined by TGA. As shown in Fig. 7, a rather slow weight loss was evident until 550 °C, after that a rapid decline was appeared until oxidation was completed at 780 °C.

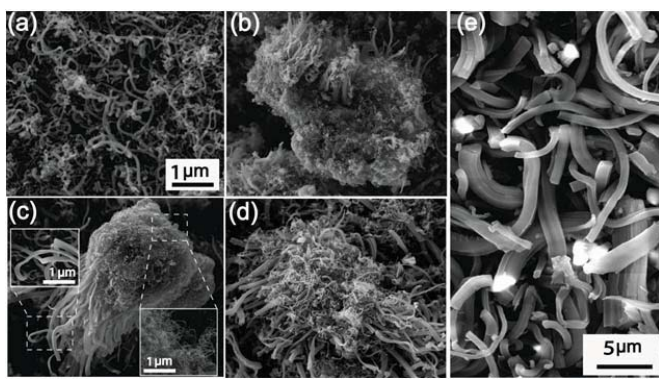


Figure. 4 SEM images of carbon nanostructures for reductive heat treatment of (a) 15 min, (b) 45 min, (c) 60 min, (d) 75 min and (e) 80 min.

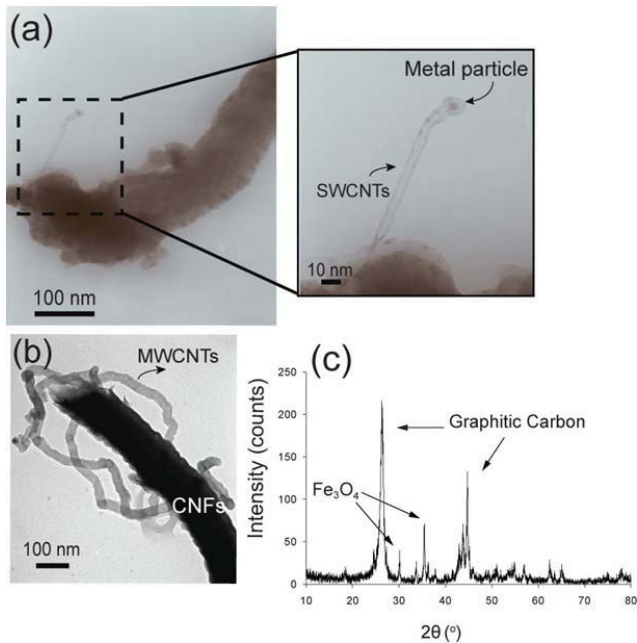


Figure. 5 (a-b) TEM images of hybrid carbon nanostructure after reductive heat treatment of 75 min and (c) XRD spectrum.

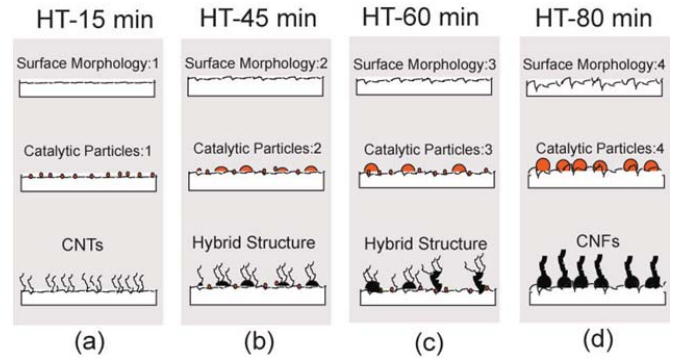


Figure. 6 Schematic representations of the growth processes of various carbon structures for reductive heat treatment of (a) 15 min, (b) 45 min, (c) 60 min and (d) 80 min.

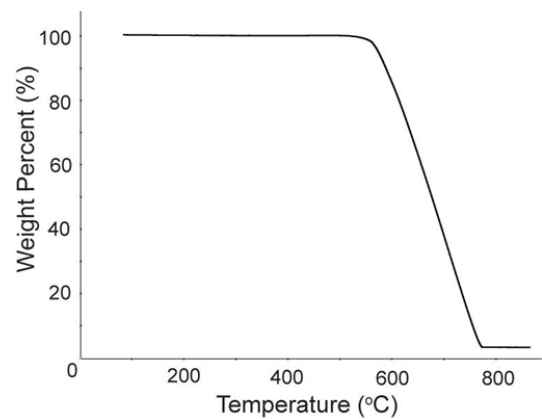


Figure. 7 TGA plot of synthesized carbon nanostructures. Reaction occurred in air at a heating rate of 20°C min⁻¹.

IV. CONCLUSION

In summary, it has been proven possible to activate the surface of the 304 stainless steel using reductive heat treatments, in hydrogen gas at 720°C. The stainless steel was used as both a substrate and a catalyst to produce various carbon nanostructures. The pretreatments such as etching and reduction with hydrogen gas of the substrates were necessary. Acetylene gas was used as a carbon containing gas for growth of carbon products. The structures of the resulting carbon, such as nanotubes, nanofibers and hybrid structures were clearly manipulated by simply chanceful reductive heat treatment durations. This finding may open a new alternative way of synthesizing a variety of carbon nanostructures with future technological importance.

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REFERENCES

- [1] Y.S. Park, K.S. Kim, H.J. Jeong, W.S. Kim, J.M. Moon, K.S. An, D.J. Bae, Y.S. Lee, G.S. Park, and Y.H. Lee, "Low pressure synthesis of single-walled carbon nanotubes by arc discharge," *Synthetic metals*, vol. 126, pp. 245-251, 2002.
- [2] M. Jung, K.Y. Eun, J.K. Lee, Y.J. Baik, K.R. Lee and J.W. Park, "Growth of carbon nanotubes by chemical vapor deposition," *Diamond and Related Materials*, vol. 10, pp. 1235-1240, 2001.
- [3] H. Liu, G. Cheng, Y. Zhao, R. Zheng, C. Liang, F. Zhao, and T. Zhang, "Controlled growth of Fe catalyst film for synthesis of vertically aligned carbon nanotubes by glancing angle deposition," *Surface & Coatings*, vol. 1, pp. 1-5, 2006.
- [4] C. Huiqun, Z. Meifang, and L. Yaogang, "Decoration of carbon nanotubes with iron oxide," *Journal of Solid State Chemistry*, vol. 179, pp. 1208-1213, 2006.
- [5] L. Kim, E. Lee, S.J. Cho, and J.S. Suh, "Diameter control of carbon nanotubes by changing the concentration of catalytic metal ion solutions," *Carbon*, vol. 43, pp. 1453-1459, 2005.
- [6] J. Jiang, T. Feng, X. Cheng, L. Dai, G. Cao, B. Jiang, X. Wang, X. Liu, and S. Zou, "Synthesis and growth mechanism of Fe-catalyzed carbon nanotubes by plasma-enhanced chemical vapor deposition," *Nuclear Instruments and Methods in Physics Research B*, vol. 244, pp. 327-332, 2006.
- [7] S. Zhu, C.H. Su, S.L. Lehoczy, I. Muntele, and D. Ila, "Carbon nanotube growth on carbon fibers," *Diamond and Related Materials*, vol. 12, pp. 1825-1828, 2003.
- [8] F. Kokai, I. Nozaki, T. Okada, A. Koshio, and T. Kuzumaki, "Efficient growth of multi-walled carbon nanotubes by continuous-wave laser vaporization of graphite containing B₄C," *Carbon*, vol. 49, pp. 1173-1181, 2011.
- [9] R.L.V. Wal, and L.J. Hall, "Carbon nanotube synthesis upon stainless steel meshes," *Carbon*, vol. 41, pp. 659-672, 2003.
- [10] G.T. Liu, D.Y. Zhong, S.H. Xia, S.F. Cheng, Y.G. Ding, Y.J. Lu, Y.J. Shao, H.Y. Li, L.J. Hangfu, and E.G. Wang, "CNTs grown on the surface of various materials by large volume MP-CVD for VME applications," *Applied Surface Science*, vol. 215, pp. 209-213, 2003.
- [11] Y.S. Li, T.J. Pan, Y. Tang, Q. Yang, and A. Hirose, "Selective synthesis of diamond and CNT nanostructures directly on stainless steel substrates," *Diamond & Related Materials*, vol. 20, pp. 187-190, 2011.
- [12] M. Karwa, Z. Iqbal, and S. Mitra, "Scaled-up self-assembly of carbon nanotubes inside long stainless steel tubing," *Carbon*, vol. 44, pp. 1235-1242, 2006.
- [13] C. Zhuo, B. Hall, H. Richter, and Y. Levendis, "Synthesis of carbon nanotubes by sequential pyrolysis and combustion of polyethylene," *Carbon*, vol. 48, pp. 4024-4034, 2010.
- [14] C. Zhao, X. Wang, W. Yiannis, and A. Levendis, "Oxidative heat treatment of 316L stainless steel for effective catalytic growth of carbon nanotubes," *Applied Surface Science*, vol. 313, pp. 227-236, 2014.
- [15] C.L. Lin, C.F. Chen, and S.C. Shi, "Field emission properties of aligned carbon nanotubes grown on stainless steel using CH₄/CO₂ reactant gas," *Diamond and Related Materials*, vol. 13, pp. 1026-1031, 2004.
- [16] B. Kim, H. Chung, K.S. Chu, H.G. Yoon, C.J. Lee, and W. Kim, "Synthesis of vertically-aligned carbon nanotubes on stainless steel by water-assisted chemical vapor deposition and characterization of their electrochemical properties," *Synthetic Metals*, vol. 160, pp. 584-587, 2010.
- [17] N.V. Chuc, C. T. Thanh, N. V. Tu, V. T. Q. Phuong, P. V. Thang, and N. T. T. Tam, "A simple approach to the fabrication of graphene-carbon nanotube hybrid films on copper substrate by chemical vapor deposition," *Materials Science & Technology*, vol. 31, pp. 479-483, 2015.
- [18] H. Vijwani, M. N. Nadagouda, V. Nambodiri, and S. M. Mukhopadhyay, "Hierarchical hybrid carbon nano-structures as robust and reusable adsorbents: Kinetic studies with model dye compound," *Chemical Engineering Journal*, vol. 268, pp. 197-207, 2015.
- [19] S. Kugler, K. Kowalczyk, and T. Spychaj, "Hybrid carbon nanotubes/graphene modified acrylic coats," *Progress in Organic Coatings*, vol. 85, pp. 1-7, 2015.
- [20] J. Berkman, A. Jagannatham, M. R. Reddy, and D. P. Haridoss, "Synthesis of thin bundled single walled carbon nanotubes and nanohorn hybrids by arc discharge technique in open air atmosphere," *Diamond & Related Materials*, vol. 55, pp. 12-15, 2015.
- [21] G. B. Hwang, K. M. Sim, G. N. Bae, and J. H. Jung, "Synthesis of hybrid carbon nanotube structures coated with *Sophora flavescens* nanoparticles and their application to antimicrobial air filtration," *Journal of Aerosol Science*, vol. 86, pp. 44-54, 2015.
- [22] L. Shahriary, H. Ghourchian, and A. A. Athawale, "Graphene-multiwalled carbon nanotube hybrids synthesized by gamma radiations: Application as a glucose sensor," *Journal of Nanotechnology*, vol. 2014, pp. 1-10, 2014.