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Effect of Acid Treatment on Stainless Steel Substrate on the Growth of Carbon Nanomaterials Using Alcohol Catalytic Chemical Vapor Deposition

Thanattha Chobsilp[1], Visittapong Yordsri[2], Chaisak Issro[3] and Worawut Muangrat[4*]

[1] *Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand.*
[2] *National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani, 12120, Thailand.*
[3] *Department of Physics, Faculty of Science, Burapha University, Chonburi, 20131, Thailand.*
[4] *Materials Engineering Program, Office of Education, Faculty of Engineering, Burapha University, Chonburi, 20131, Thailand.*
*Corresponding author's e-mail address: worawut.mu@buu.ac.th

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ABSTRACT

In this work, the effect of acid treatment on stainless steel (SS) substrate on the morphology and structure of carbon nanomaterials (CNMs) was investigated. CNMs were grown on SS and hydrochloric acid-treated SS (A-SS) substrates by alcohol catalytic chemical vapor deposition (ACCVD) at a growth temperature of 900 °C under atmospheric pressure. Morphology and structure of CNMs on SS and A-SS substrates were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that selective growth of carbon nanotubes (CNTs) with mean diameter of 37.07±8.27 nm, was achieved by using A-SS substrate, while selective growth of carbon nano-onions (CNOs) with mean diameter of 48.70±6.52 nm and some multilayer graphene (MLG), was achieved by using SS substrate. These results demonstrate that acid treatment on the SS substrate is a key parameter to the morphology and structure of CNMs.

INTRODUCTION

Since their discovery three decades ago, carbon nanotubes (CNTs) [1,2] have been extensively studied in many fields of nanotechnology for use in sensor, field emitter and energy storage [3-6] because of their excellent structure and properties. Mainly used methods for production of CNTs compose arc discharge, laser ablation and chemical vapor deposition (CVD). Compared with other methods, CVD is the most effective method for CNTs production due to their simple technique, low cost and mass production with controlled diameter, structure, crystallinity, yield, and orientation. Various parameters such as carbon source, metal catalyst, growth temperature and growth time were studied to obtain the optimum condition for specific application [7-10]. For CNT-based electronic devices, substrate is one of the key factors for CNTs growth. Most previous studies report that CNTs have been grown on silicon substrate, which requires the additional of an external metal catalyst. Metal transition such as nickel, cobalt and iron have been commonly used as catalyst [7-10]. However, it is time-consuming and involves the use of complex techniques for catalyst deposition or dispersion on the silicon substrate.

Recently, growth of CNTs on the stainless steel (SS) substrate become other choice. CNT-based conductive SS substrate is beneficial to the specific application such as field emission and supercapacitors [11-12]. SS contains the metal catalyst in their structure. Thus, SS substrate can be used both as substrate and catalyst for the growth of CNTs without additional external catalysts [13-15]. Although most previous works successfully produced CNTs on the SS substrate, the study on effect of surface treatment by acid on the morphology and structure of CNMs has not been fully explored. In this work, we study on the effect of acid treatment of SS substrate onto CNMs growth by alcohol catalytic CVD (ACCVD). The morphology and structure of as-grown CNMs on SS and hydrochloric acid-treated SS (A-SS) substrates were characterized.

METHODOLOGY

CNMs were synthesized by ACCVD on SS (type 304) mesh substrate. SS substrates were soaked in 37% HCl acid for 30 min and then cleaned by ethanol and deionized water for 10 min, respectively, using ultrasonication. The cleaned A-SS substrates were then heated at 100 °C for 30 min to remove the humidity. A-SS substrates were placed in alumina boat at the reaction zone of CVD system. The temperature of reaction zone was heated at 10 °C/min from room temperature to 900 °C under Ar gas at a flow rate of 500 sccm. The ethanol vapor was introduced into reaction zone by bubbling Ar gas through ethanol at a flow rate of 750 sccm. The growth time was carried

out for 30 min at atmospheric pressure. The as-grown CNMs were cooled down under Ar gas at a flow rate of 500 sccm. For comparison, CNMs was also grown on the SS substrates without HCl acid treatment. The morphology and nanostructure of CNMs were characterized by scanning electron microscopy (SEM; JSM7800F) and transmission electron microscopy (TEM; JEOL, JEM-2100) operated at 3 kV and 200 kV, respectively. The composition was analyzed by TEM equipped with energy dispersed X-ray spectrometer (TEM-EDX; OXFORD X-Max^N(80T)).

RESULTS AND DISCUSSION

From wide-area SEM observation, the main structure of the SS and A-SS substrates were clearly seen as shown in Figure 1. At high-magnification in the specific area of each sample, the morphology of CNMs on the SS and A-SS substrates were clearly revealed in different structure. Figure 1(a-b) and (c-d) show low and high magnification of SEM images of as-grown CNMs on the SS and A-SS substrates, respectively. It was found that the tangled fibrils cover on the substrate when the A-SS was used as substrate (inset of Figure 1(c)). We envision that the surface coverage of tangled fibrils could be increased with increasing the growth time. At high magnification SEM images reveal that the CNMs grown on SS substrate had a particle-like and platelet-like structure (Figure 1(b)), while CNMs grown on A-SS substrate had a high density of tube-shaped structure covered on the surface of substrate (Figure 1(c)).

Next, TEM was utilized to characterize the nanostructure of CNMs. Figure 2 shows TEM bright field images of CNMs grown on the SS substrate. The main structure of as-grown CNMs on SS substrate was onion-like structure that consist of concentric carbon layers, so called carbon nano-onions (CNOs), as shown in Figure 2(a). The average diameter of CNOs was 48.70±6.52 nm, with a size distribution of 43-63 nm. Figure 2(f) shows the histogram of the diameter distribution obtained from TEM statistics of CNOs. Figure 2(b) shows HRTEM of CNOs. The average interlayer distance of graphitic layers was in the range of 0.33-0.35 nm, which is close to sp^2 graphitic shell [16-17]. The growth mechanism of CNOs could be explained by vapor-liquid mechanism. The growth model of CNOs is as follows: carbon atoms decompose from ethanol vapor and then precipitate on the metal catalyst. The graphitic layers were formed around on the surface of metal catalyst until the metal catalyst became poisoned. Normally, the melting temperature of bulk metal in SS is approximately ~1300-1400 °C, which higher than the growth temperature for producing of CNOs. The growth temperature of CNOs in this work was 900 °C. However, the melting temperature of small particles can be significantly decreased with decreasing the particle size [18]. Thus, metal catalyst particle with very small size could be evaporated through the void or interior in the graphitic layers of CNOs during growth process. Finally, the CNOs with an empty core was achieved (Figure 2b) [19-20]. In addition, the elemental composition of CNOs was analyzed by TEM-EDX. The atomic percent of carbon, copper, iron and cobalt are 96.52, 3.38, 0.05 and 0.05 %, respectively (spectrum not shown).

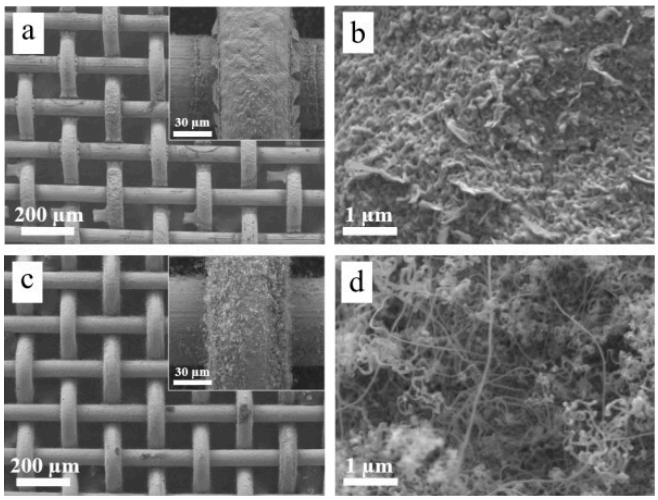

Figure 1. SEM images of CNMs grown on (a-b) SS and (c-d) A-SS substrates.

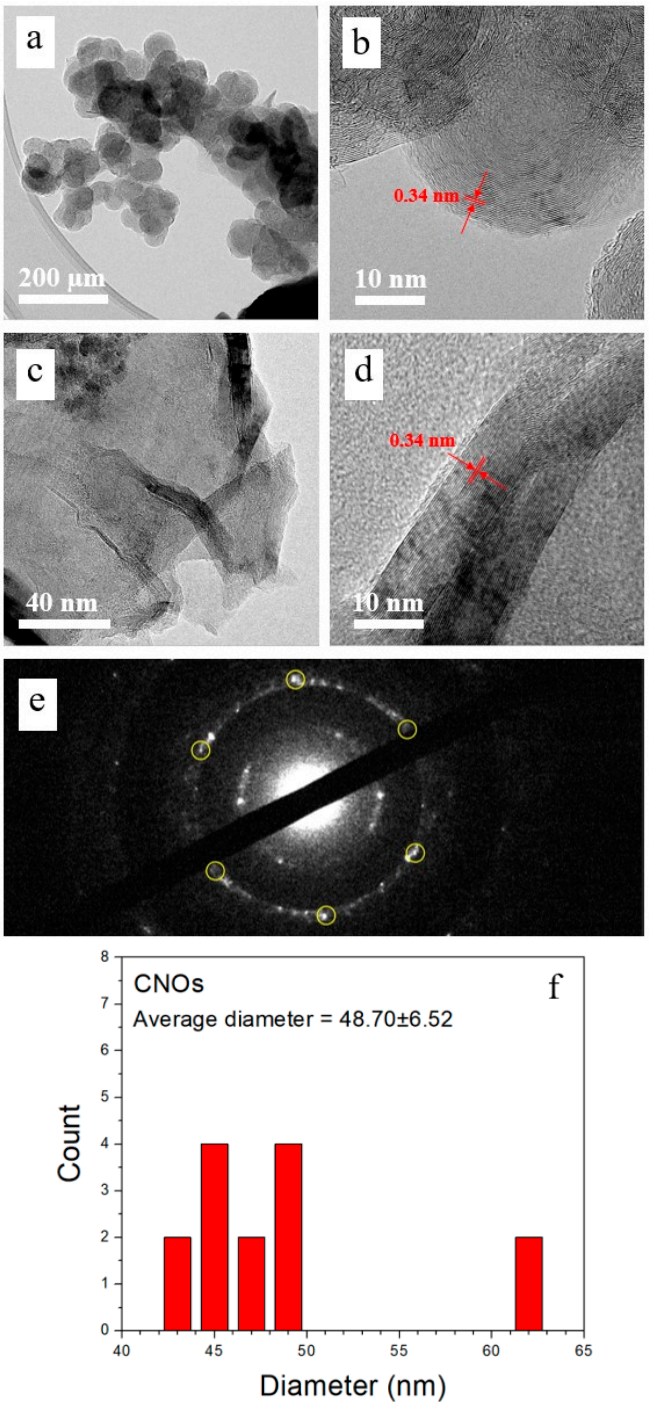

Figure 2. (a,c) Low- and (b,d) high-magnification TEM images of CNOs and MLG, respectively. (e) SAED pattern of MLG. (f) Histogram of the diameter distribution of CNOs.

Furthermore, a few of two-dimension platelet-like structure consisting of several graphitic layers was also found as shown in Figure 2(c). At high resolution TEM image in Figure 2(d) reveal the multilayer of graphene (MLG). The interlayer spacing of MLG is approximately 0.34 nm, which corresponds to the 002 lattices planes of the crystal of graphite [21-22]. Figure 2(e) shows the spot pattern of the selected-area diffraction (SEAD) pattern of MLG, which correspond to the six-fold symmetry of graphene lattice [23]. By TEM-EDX analysis, the atomic percent of carbon, copper, iron and chromium are 96.12, 3.66, 0.18 and 0.04 %, respectively (spectrum not shown). The main element composition both of CNOs and MLG is carbon with a few of residual metal catalyst.

Figure 3 (a-d) shows the TEM bright field images of as-grown CNMs on A-SS substrate. The as-grown CNMs on A-SS substrate are multi-walled carbon nanotube (MWCNTs) with average diameter of 37.07±8.27 nm, with a size distribution of 26-50 nm. Figure 3(e) shows the histogram of the diameter distribution obtained from TEM statistics of MWCNTs. At high resolution TEM in Figure 3(c) clearly show the highly ordered multilayered carbon structure. The graphitic layer of MWCNTs was well aligned along the tube with approximate spacing as 0.34 nm. A metal catalyst at the closed-tip CNTs can be observed as shown in the red circle in the Figure 3(a). Furthermore, metal catalyst clusters along their tubes were also found (data not shown). The growth mechanism can be explained by vapor-liquid-solid mechanism. According to the tip growth model of CNTs, the carbon atoms decomposed from carbonaceous precursor and then precipitated onto the metal catalyst nanoparticle. Due to the weak interaction between metal catalyst and substrate, the carbon atoms dissolved and diffused through the bulk and pushed upward the metal catalyst nanoparticle from the substrate surface and then form graphitic tubular structure around metal catalyst nanoparticles [24-26]. Figure 4 shows the tip-growth model of MWCNTs. We envision that that acid pretreatment to substrate plays an important role for the satisfying growth of CNTs. Due to one of the most important parameters to control the CNT growth mechanism is the catalyst part. Etching treatment on substrate, lead to the formation as nanoparticle catalyst on the substrate's surface that appropriate to be the initial catalyst for the CNT growth [27].

In addition, the bamboo-like structure of MWCNTs were also observed. A high-resolution TEM image shown in Figrue 3(d) reveal the bamboo-like MWCNTs with the curved graphitic layer inside their hollow structure. The formation of bamboo-like MWCNTs could be explained as follows: carbon atoms diffuse via surface and bulk of metal catalyst to form graphitic layers. The carbon atoms accumulated at the inside surface of metal catalyst via bulk diffusion that can form the compartment graphitic layers. Then, the tube grows upward, the next compartment layer is produced on the metal catalyst particle [28].

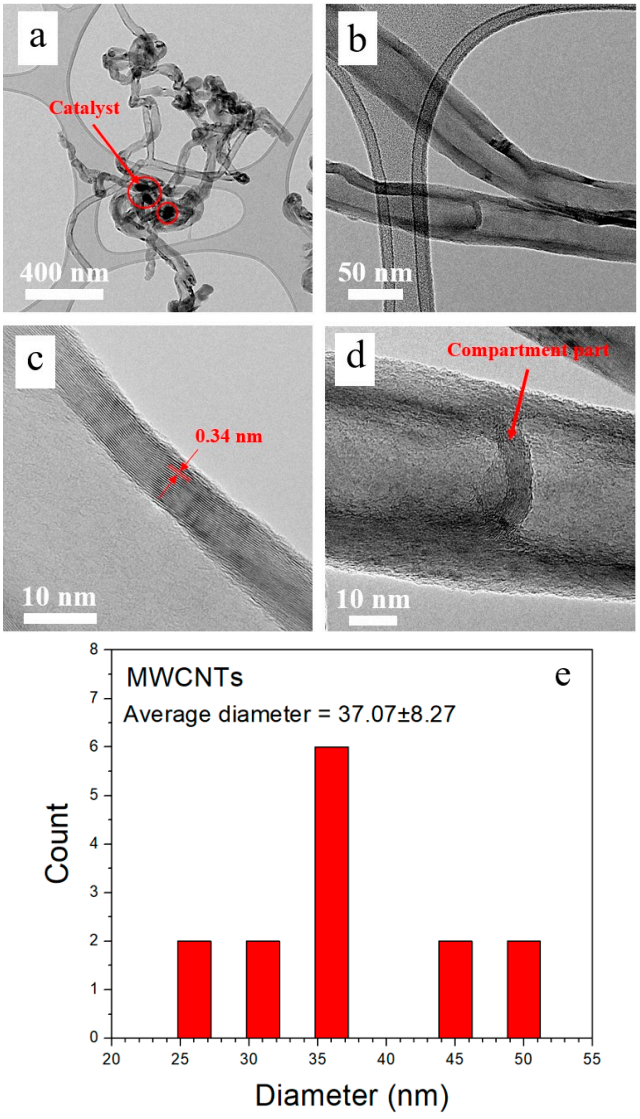

Figure 3. (a) Low- and (b) high-magnification TEM images of CNTs. (c) high-magnification TEM images of interlayer distance of MWCNTs and (d) compartment part of graphite in bamboo-like MWCNTs. (e) Histogram of the diameter distribution of MWCNTs.

CONCLUSION

CNMs were successfully grown on the SS and A-SS substrates by ACCVD at 900 °C under atmospheric pressure. The results show that the HCl acid-treatment on SS substrate directly affect the morphology and structure of CNMs. MWCNTs were obviously produced on the A-SS substrate. Meanwhile, use of SS substrate mainly obtained CNOs with some MLG. The results imply that HCl acid treatment plays a significant role the selective formation of CNMs.

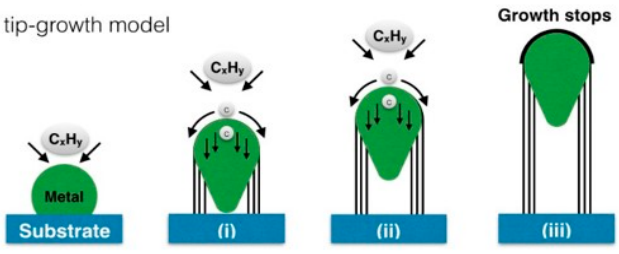

Figure 4. Tip-growth model for CNTs [29].

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