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Carbon nanotube growth directly on nickel substrate using alcohol

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Abstract

Chemical vapor deposition (CVD), having ethanol vapor as carbon source, is used to synthesize carbon nanotubes on 99.9 wt%Ni polycrystalline materials acting as catalyst bulk metals. At different reacting temperature of 600, 700 and 800°C, synthesized CNTs on 400x400 and single hole Ni grids are visually investigated by a field-emission scanning electron microscope. With 20 minutes feeding time of ethanol under 1000 sccm Ar carrier gas, densely packed CNTs on the substrate are best found at 600 °C. Abundant nanofibers occur at 700 °C while Ni grids are oxidized and broken in small chips at 800°C and it becomes difficult to spot CNTs. Nucleation site of CNTs has been noticed to be at circumferential surface of nanofibers. In addition, CNTs on stainless steel rings that hold the Ni grids in place are found. This indicates the potential application of the CNT growth process on other metals in the near future.

Keywords*:* Carbon nanotube, CVD growth, Nickel substrate, ethanol.

1. Introduction

Nowadays, research works in the field of nanoscience and nanotechnology become highly active among scientists with high expectation that the outcome will change the way of life as semiconductor or polymer did in the last few decades. Since the first discovery of carbon nanotubes (CNTs) in 1991 [1, 2], researches in nanotechnology have been commenced promptly in hi-tech countries with large amount of funding spend in hoping that they are the pioneer countries exploring benefits from such the nanothings. Soon after, unique physical and chemical properties of CNTs have been reported by national laboratories around the world leading to potential applications as an electron field emission source [3], chemical sensor [4], nanoelectronic device [5] electrode for supercapacitors [6], nanocomposite strengthener [7, 8], etc.

CNT synthesis methods can be divided into two major classes depending on phases of carbon source i.e. solid carbon source and gaseous carbon source. After decomposition of the sources into elemental carbon atoms, they must arrange themselves into a

thermodynamically stable form which possesses lowest free energy and CNTs is the stable allotropic form of carbon when 1) no O_2 environment 2) high temperature and 3) suitable catalysts [9]. Among a variety of recent CNTs manufacturing methods, arc discharge or laser ablation processes, using graphite rods containing catalyst particles as solid carbon sources, can produce selective CNTs with less structural defects than other methods. However, high purified CNTs have no use if there is no way to assemble them into a practical structure. The two-fold advantages are gained using Catalyst Chemical Vapor Deposition (CCVD) methods whereby not only CNTs can be synthesized but they can also arrange themselves onto patterned substrates. Such the structure is suitable for fabricating a superior field electron emitter and an electrode in supercapacitors.

CNT synthesis using CCVD is a process in which CNTs nucleate and grow from excess carbon atoms diffusing out of catalyst particles saturated with carbon atoms which are decomposed initially from gaseous carbon source [10]. Gaseous carbon source, the type of metal catalysts, and the processing temperature are three parameters mainly impacting on CNT production and characteristics.

In growing CNTs by CCVD, transition metal catalysts (Fe, Ni, Co, Mo or their alloy) are firstly deposited on a substrate in particle form before introducing carbon containing gas into the reactor. The popular reactive gas is the mixture of inert gas (Ar, He) with either hydrocarbon (CH_4, C_2H_2, C_2H_4, C_6H_6, CH_3OH, or C_2H_5OH) or carbon monoxide (CO). To ensure continuous supply of carbon atoms, the gas must undergo decomposition process through various chemical reactions as catalysis-enhanced thermal cracking ($C_xH_y \rightarrow xC + y/2\ H$) for hydrocarbon gas or catalysis-enhanced disproportionation ($2CO \rightarrow C + CO_2$) for carbon monoxide [9]. The reaction is more complicated for alcohol. It is believe that the vapor can dissociate into many reactive reagents and the intermediate reaction involves methane as gaseous carbon source and OH free radical as etching reagent [11-14].

As mentioned earlier, application in field electron emitters and supercapacitors need CNTs growth on metallic substrates with additional requirement of electrical contact and reasonable mechanical bonding of CNTs to metallic substrates. This couldn't attainable without sophisticate and laborious tasks. In searching for more effective route, some research group runs into studying to grow CNTs directly on metallic substrate without catalyst particle deposition. The effect of Nickel [10, 15, 16] and SS304 [15] as catalyst bulk materials have been reported. However, some kinds of substrate pretreatment are still needed. On contrary, in this work, we report CNT growth directly on as-received nickel grid without pretreatment step except simple cleaning. Ethanol alcohol is used as gaseous carbon source with Ar as the carrier gas. Furthermore, because the technique using alcohol can grow CNT at lower reaction temperature, it promises a scalable production at lower cost. The effect of temperature on the growth of CNTs is investigated by field-emission scanning electron microscope.

2. Experimental

400x400 mesh and single hole nickel grids were used as the catalytic active substrates. Before heated up to 600, 700, 800°C in a tube furnace, as-received grids with purity of 99.9 wt%Ni were ultrasonically degreased in acetone for 1 minute and blown dried in jet air. Six sets of 4 grids, consisting of 2 mesh grids and 2 single hole grids, were prepared. In each set, they were aligned along a 3 cm long screw and held tight between stainless steel rings and nuts as shown schematically in Fig. 1. Ceramic boats were used to carry the samples into a quartz tube (i.d. 27 mm) located in a horizontal tube furnace. A schematic diagram of the CVD reactor equipped with a gas flow system is shown in Fig. 2.

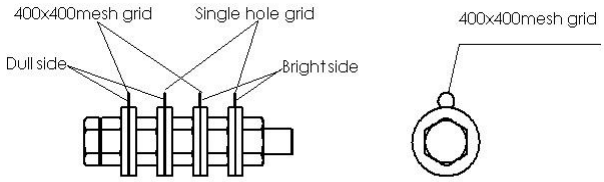


Fig.1 Schematic of a sample set consisting of 4 grids aligned along a screw.

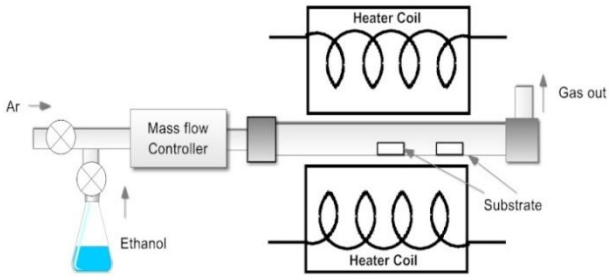


Fig.2 Schematic of tube furnace reactor with gas flow controller for CNTs growth.

Due to the variation of gas mixture temperature and flow velocity along the furnace heating zone [16], one boat then was placed in the middle of the tube furnace while the other was placed at the end of the heating zone. While heating up to the desired temperature Ar gas was kept flowing at 500 sccm. When the sample had reached the temperature, CVD was initiated by introducing 1000 sccm Ar gas flow through Ethanol bubbler. The total mixing gas of Ar and Ethanol vapor then passed through Ni substrates for 20 minutes. After the growth was completed the supply of ethanol vapor was shut off and the system was allowed to cool down to 300°C under 500 sccm Ar flow and to room temperature in still air. The morphology of the synthesized CNTs was characterized via a field-emission scanning electron microscope (FE-SEM; Hitachi model S-4700).

3. Results and Discussions

For reference, Fig.3a-b show SEM images of different sides of a Ni grid regarding to a bright side with respected to a smooth surface (Fig.3a) and a dull side with respected to a rough surface (Fig.3b). Surface discriminated by light reflection is obvious with naked eyes. Such the morphology could be expected due to its manufacturing process by ion sputtering method. Consequently, in our experiment, four grids along a screw was arranged to have two bright surfaces (one of a 400x400 mesh grid and the other of a single hole grid), and the other two dull surfaces facing against the gas flow (see Fig.1). Fig.3c-f indicate growth results by CVD at 600°C. Different positions of Ni substrate yielded different carbon layers if the substrate was located in the middle of the heating zone (Fig. 3c-d) or near the gas outlet of the tube (Fig. 3e-f). By comparing Fig. 3c-d with Fig. 3e-f, the plenty carbon nanofiber could grown when the substrate was placed near

the end of the gas outlet. It is speculated that relatively low flow velocity near the gas outlet and relatively high temperature of the downstream gas would favor alcohol dissociation reaction in term of longer reaction time and more favorable kinetic condition [16]. Nevertheless, the effect of surface morphology (Fig. 3c-e and Fig. 3d-f) is less pronounced than expected due to our too long processing time when CNTs grown directly on Carbon nanofiber instead of Ni substrate (Fig.4b). Surface morphology effect, in addition to CNT growth mechanism, are being investigated at much shorter time in order to verify nanofiber precursor and nucleation sites.

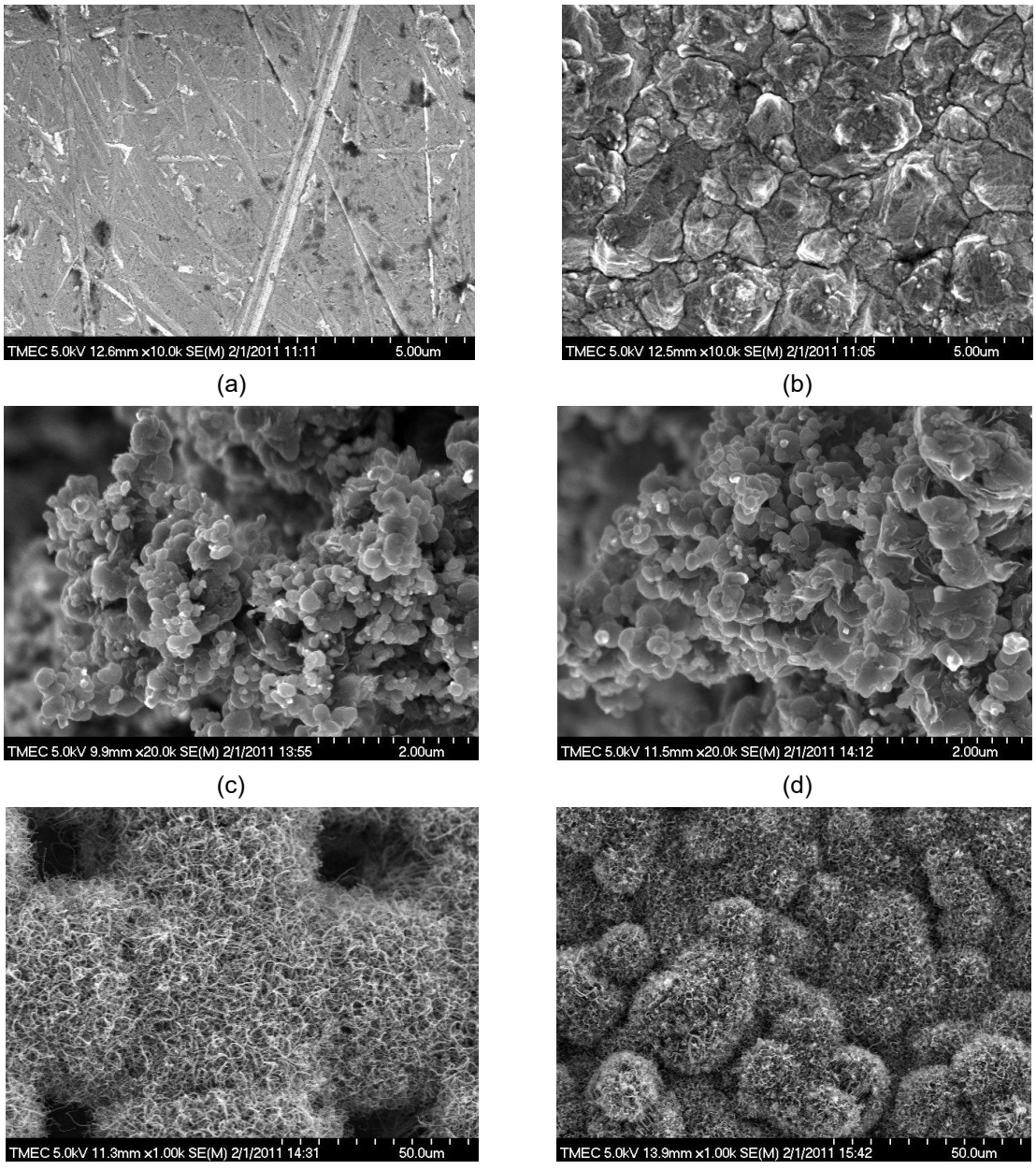
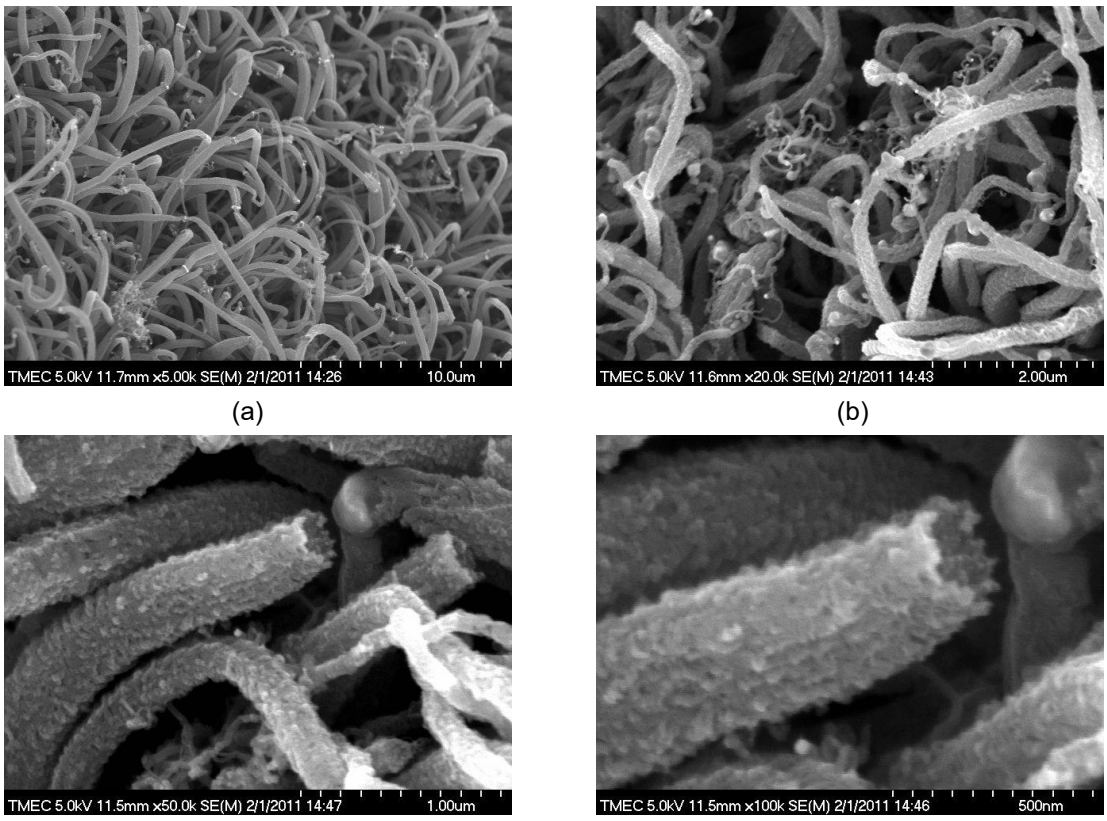


Fig. 3 SEM images of (a) Ni substrate: as-received bright surface; (b) Ni substrate: as-received dull surface; (c) Carbon layer (bright side, middle, 600^{o}C); (d) Carbon layer (dull side, middle, 600^{o}C); (e) Carbon nanofibers (bright side, end, 600^{o}C); (f) Carbon nanofibers (dull side, end, 600^{o}C)

Fig.4 demonstrates higher magnification of Fig. 3e-f. Large amount of nanofibers was synthesized with uniform size of approximately 400 nm in dia. Close up pictures (Fig. 4c-d) at the tip of the nanofiber disclose hollow structure with rosette circumference surface. It becomes interesting to us if the precursor of the fiber really advents from CNTs initially grown on Ni substrate or bidirectional grown from catalyst particle trapped inside. However, using low processing temperature at 600°C, bundles of curl CNTs can favorably nucleate on the rough surface of the fiber (Fig. 4b and 6b).



(a) (b)

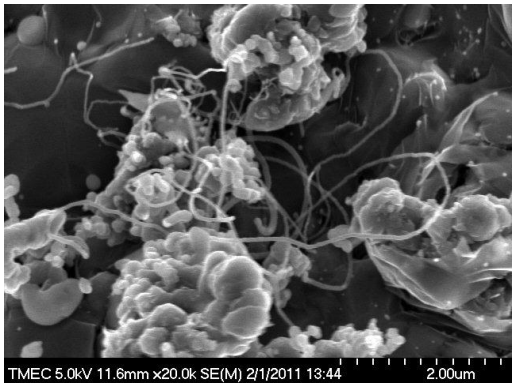
(c) (d)

Fig. 4 SEM images of carbon nanofiber and CNTs grown on Ni substrate near the gas outlet at 600°C

Fig. 5 and 6 show the SEM images of CVD on Ni substrates at 700 and 800°C. As indicated in Fig. 5, Ni substrates were covered by amorphous carbon; thus, stacking up in globular layer in smaller and smaller size until carbon rods can grow (Fig.5c-d). In comparing to the hollow ones, so-called cleaning effect by OH etching agent of amorphous carbon may possess slower rate than carbon dissociation rate. On contrary, OH might become reactivated at higher temperature and suppressed the amorphous morphology as clearly seen by in Fig. 6. Less nanofibers were generated and their surfaces are still the CNT nucleation site even through the surface is more cured and smoother (Fig. 6d). Substrate broke down in pieces at 800°C.

Finally, we accidentally found CNT grown directly on stainless steel ring at 600°C (Fig. 7). Without Carbon nanofiber, Fig. 7 indicates the potential application of the CNT growth process on other cheap metals in the near future

(a)



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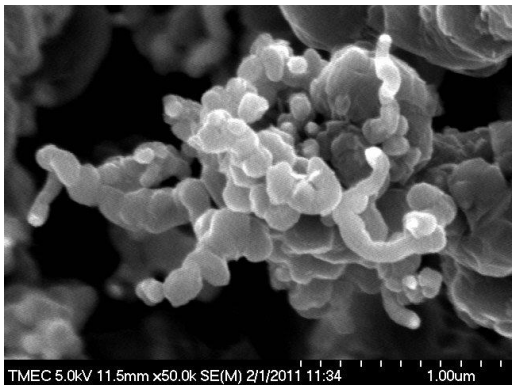

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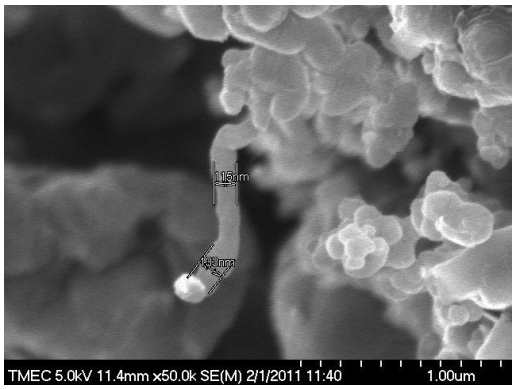
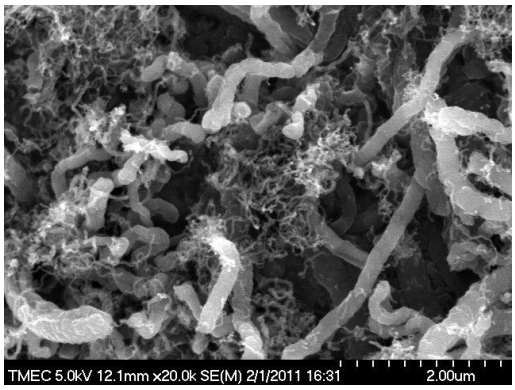
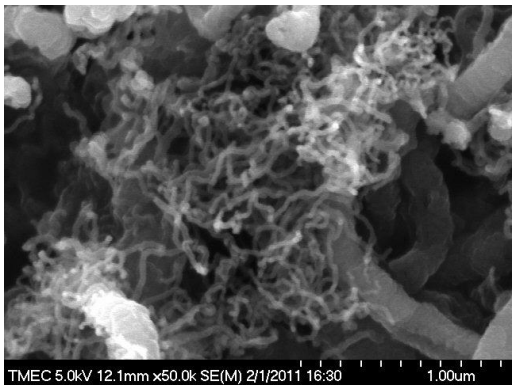


(d)

Fig. 5 SEM images of CVD results on Ni substrate near the gas outlet at 700°C



(a)



(b)

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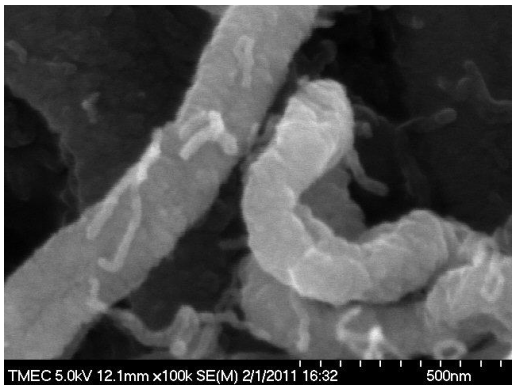
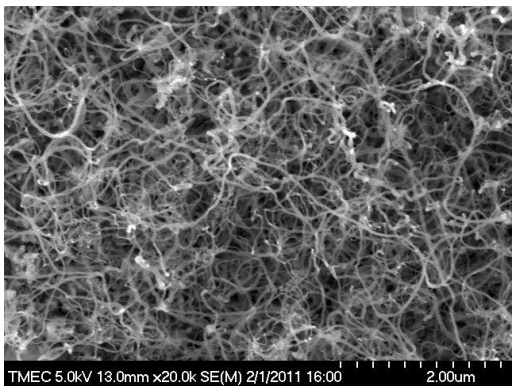
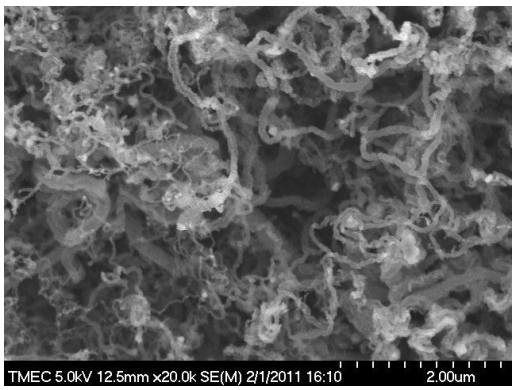


(d)

Fig. 6 SEM images of CVD results on Ni substrate near the gas outlet at 800°C



(a)



(b)

Fig. 7 SEM images of CNTs grown on Stainless Steel rings at 600°C

4. Conclusion

We have directly grown carbon nanotubes on nickel substrates by CVD using Ethanol which does not require chemical pretreatment of the surface. The effect of processing temperature, substrate morphology, and substrate position on morphological characteristics of synthesis CNTs are studied. It was found that densely packed Carbon Nanofibers on the substrate are best found at 600°C with feeding of ethanol under Ar environment. We also observed that nucleation site of CNTs has been at carbonfiber circumferential surface at 600°C and 800°C.

5. Acknowledgement

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