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Etching of 316L Stainless Steel by Different Chemical Etchant Solutions for the Growth of Carbon Nanotubes by Thermal Chemical Vapour Deposition

R. CHERAGHALI[1,*], SH. MORADI[1], M. GHORANNEVISS[2], P. ABEROMAND AZAR[3] and S.A. KHORRAMI[1]

[1]Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran
[2]Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran
[3]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

*Corresponding author: E-mail: ramincheraghali@yahoo.com

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We report and interpret the effectiveness of different etching with different and well-known etching chemical reagents such as Kallings number 1, Kallings number 2, Kellers, kroll, nital, marble, picral reagents on stainless steel as a substrate to synthesize carbon nanotubes. Suitable pretreatment of stainless steel substrates was required for the satisfactory growth of carbon nanotubes on them. Carbon nanotubes were grown on stainless steel by thermal chemical vapour deposition, using acetylene as hydrocarbonic gas and hydrogen as diluted one in atmospheric pressure at 800 ºC. It was found that the density of carbon nanotubes decreases as the roughness on the surface is reduced.

Key Words: Multiwalled CNTs, Steel 316L, Etchant solutions, Surface roughness.

INTRODUCTION

Because of the unique physical and chemical properties and their potential applications of carbon nanotubes (CNTs) in many areas such as microelectronic devices[1], adsorbents, lubricants, hydrogen storage[2], catalyst support, chemical sensor[3,4] *etc*.[5]. Nowadays, many methods have been used for synthesis of carbon nanotube. The most common methods for synthesis of carbon include: arc discharge[6], laser ablation[7] and chemical vapour deposition[8]. Among the synthesis methods, chemical vapour deposition method because of cheapness, simplicity of process and frequency of product has a special significance. Researchers are trying with various factors, the best performance in terms of production quality and quantity to gain. The first step in the synthesis of carbon nanotubes is based on the providing appropriate substrate. For this purpose, researches have done multifarious pretreatments on substrate such as deposition of metal catalyst on substrate or etching the substrate by different methods.

Fang *et al.*[9] grow multiwalled carbon nanotubes (MWCNTs) on a nickel coated silicon substrate, using electron cyclotron resonance chemical vapour deposition. Gao *et al.*[10] synthesized La_2NiO_4 catalyst film on the 304 stainless steel (ss) mesh on which carbon microfibers and nanotubes were grown by cracking of CH_4.

In this paper, we report a simple processing technique involving cost-effective stainless steel that can be used as a conducting substrate for the direct growth of high-density aligned multiwalled nanotubes (MWNTs) by thermal chemical vapour deposition. The chemical composition of the 316 L stainless steel used was (wt. %): 0.03 % C, 18.5 % Cr, 13 % Ni, 2.5 % Mo, 1.0 % Si, 2.0 % Mn and Fe balance (as stated by the manufacturer). Acetylene as a hydrocarbonic source and hydrogen as a diluted gas in atmospheric pressure in 800 ºC were used. An inert gas such as Ar or He can also be used as diluent. The surface properties of the substrates were particularly investigated and the effect of different treatment such as Kallings number 1, Kallings number 2, Kellers, kroll, nital, marble, picral reagent on the CNT growth is critically analyzed. Such thorough understanding is a foundation for the site-selective growth of CNTs on conducting substrates for many prospective applications such as in nanoelectronics, field emission devices and so forth. The results were investigated by atomic force microscope (AFM), scanning electron microscope (SEM) and Raman spectroscopy.

EXPERIMENTAL

Multiwalled carbon nanotubes were deposited by thermal chemical vapour deposition (TCVD). The stainless steel plates had a thickness of 1 mm and cut into required dimension 1 cm

× 1 cm. The substrates did not mechanically polished. Before deposition, all samples were cleaned by 3-stepes ultrasonic vibration cleaning in acetone, ethanol and deionized water for 10 min, sequentially and dried in the air to remove all contaminants and degreased. Afterwards the stainless steel plates were dipped into different chemical etchant solutions with different lengths of time (mentioned in Table-1) at room temperature to etch the surface. They were loaded in the thermal CVD furnace for the CNT growth. The atmospheric pressure thermal CVD system consists of 800 mm (diameter 75 mm) horizontal quartz tube, an electric heating system, reaction gas supply and related mass flow controllers. Sample held in alumina boats were then loaded into the quartz tube were heated to temperatures in 800 ºC in argon flow as an oxygen-free ambient. The reactive gas mixture was C_2H_2, H_2 and Ar with flow rates of 10:25:500 SCCM, respectively. A flow of 500 SCCM Ar was used as diluent and after processing to prevent oxidation during cool-down.

TABLE-1
COMPOSITION OF THE SPENT WET CHEMICAL ETCHANT SOLUTIONS

Etchant	Composition	Conc.	Conditions
Kalling's No. 1	Distilled water $CuCl_2$ Hydrochloric acid Ethanol	33 mL 1.5 g 33 mL 33 mL	Immersion etching at 20 ºC
Kalling's No. 2	$CuCl_2$ Hydrochloric acid Ethanol	5 g 100 mL 100 mL	Immersion etching at 20 ºC
Kellers Etch	Distilled water Nitric acid Hydrochloric acid Hydrofluoric acid	190 mL 5 mL 3 mL 2 mL	10-30 s immersion. Use only fresh etchant
Kroll's reagent	Distilled water Nitric acid Hydrofluoric acid	92 mL 6 mL 2 mL	15 s
Nital	Ethanol Nitric acid	100 mL 1-10 mL	Seconds to minutes
Marble's reagent	$CuSO_4$ Hydrochloric acid Water	10 g 50 mL 50 mL	Immerse or swab for 5-60 s
Picral	Ethanol Picric acid	100 mL 2-4 g	Seconds to minutes

A scanning electron microscope (SEM, Philips model XL30) was used to observe the morphology of the growing samples. The surface morphology of the thin films and roughness parameters were observed using atomic force microscope Autoprobi cp (AFM, Park Scientific Instrument) and Raman spectroscopy (Nicolet) to characterize the quality of the CNTs.

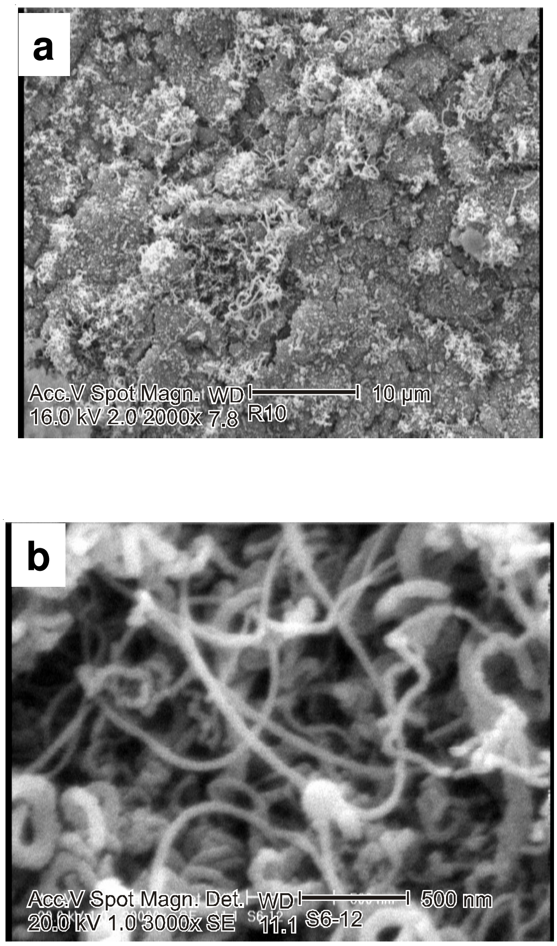
RESULTS AND DISCUSSION

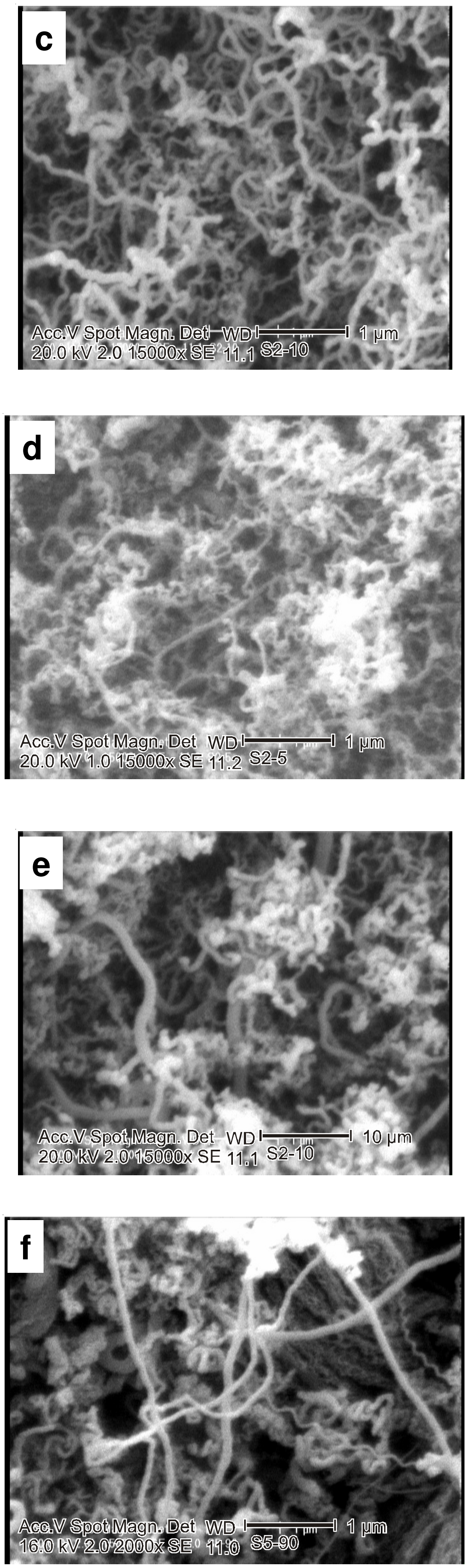
The stainless steel samples (Type 316L) with chemical etchant solutions with different lengths of time were considered to elucidate the effect of surface properties on the CNT growth. The atomic force microscope (AFM) analysis of stainless steel treated with different reagent was listed in Table-2. Considering to surfaces morphology of samples shows that different etching on the stainless steel surface created different size of roughness and there is a relation between surface morphology and the kind of used reagents.

TABLE-2
AVERAGE ROUGHNESS FOR EACH SAMPLE

Sample	Etchant	Time (s)	Ave rough (Å)
1	Kalling's No. 1	5-10	23.3
2	Kalling's No. 2	5-10	18.1
3	Kellers	30	15.4
4	Kroll	15	13.5
5	Nital	50	14.6
6	Marble	30	52.4
7	Picral	75	12.2

Fig. 1 shows the SEM images of MWNTs synthesized on the stainless steel plates treated with different chemical etchant solutions. The as-received stainless steel plate, which was degreased but not mechanically polished, (without any treatment) was performed in order to confirm the growth of CNTs under such conditions. The SEM image of the substrate surface reveals small amount of scattered CNTs and most of the soot is amorphous carbon (Fig. 1a). The nanotubes observed in Fig. 1b are sinuous and entangled multiwalled were grown on treated stainless steel with marble reagent, whose lengths are up to several micrometers with a variety of diameters and mainly grew with random orientation. It is not difficult to observe some amorphous carbon and there are few graphitic particles in the product. Eatching with Kaling No. 1 resulted more irregular morphology of catalyzed CNTs as shown in Fig. 1c. The substrate was etched by Kaling No. 2 etchant was also less active towards CNT synthesis (Fig. 1d).





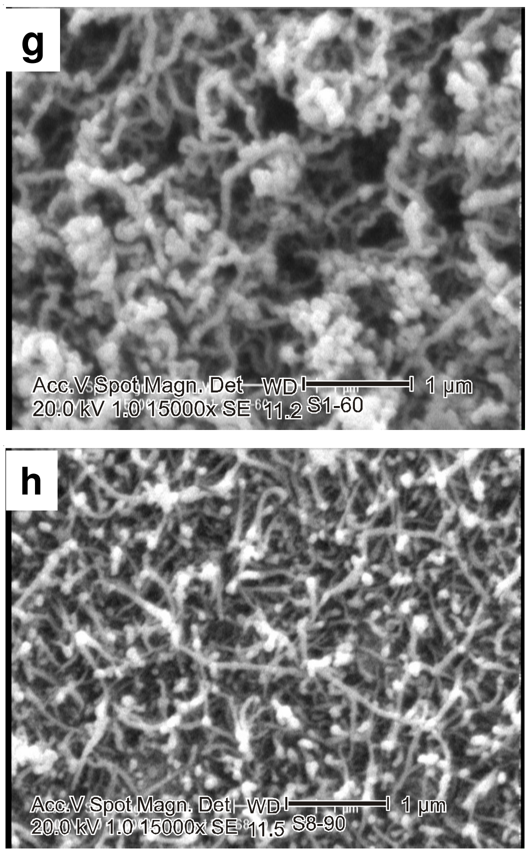


Fig. 1. SEM images of synthesized MWCNTs on stainless steel (a) without etching, (b) etched by Kalling's No. 1, (c) Kalling's No. 2, (d) Kellers, (e) Kroll, (f) Nital, (g) Marble and (h) Picral

Similarly etching with Kellers etchant resulted in a significantly lower yield and shorter, larger diameter nanofibers (Fig. 1e). As seen in Fig. 1f, the CNTs where synthesized by Nital reagent don't exactly follow this procedure and have a little more purity in comparison with previous CNTs. Figs. 1(g) and 1(h) are related to substrate etching by Kroll and Picral reagents, respectively. The growth became sparse with irregular structures. In the latter one, almost no CNTs growth had occurred and the formation of nanostructures was observed.

The SEM images of products rather show that the surface density of MCNTs decreases as the roughness on the surface decreases. As it seen, the substrates were etched by Marble and Picrall solutions with roughness of 5.24 and 1.22 nm, respectively have the best and worst morphology. This observation implies that such asperities promote the growth of CNTs and that a systematic study of the effect of surface roughness on the growth and distribution of CNTs on the stainless steel surface would be of interest[11]. Raman spectroscopy showed peaks at 1281 and 1589 cm^{-1} that indicate carbon nanotubes are multiwalled with carbonaceous particles embedded in them (for example Raman spectroscopy of MWCNTs synthesized on substrate etched by Kalling No. 1 has given in Fig. 2).

Fig. 3 shows vertically oriented pigtail like MWCNTs in a quite dense have grown on substrate's both sides. The substrate has previously been immersed in an etchant solution. It was then placed on porcelain boat. Since the inlet gas can pass over the substrate's either side, carbon nanotubes grow on its both sides that it is one of the most advantages of this method.

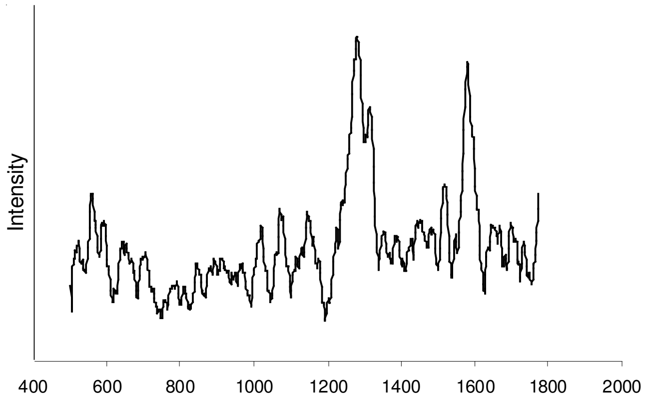


Fig. 2. Raman spectra of synthesized MWCNTs on stainless steel was etched by Kalling No. 1

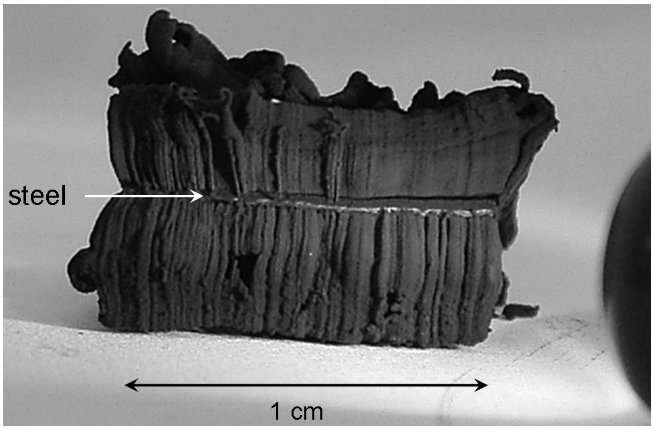


Fig. 3. Oriented pigtail like MWCNTs were grown on substrate's both sides

As seen in Fig. 1, multiwalled carbon nanotubes synthesized in this study were not straight, but curled in shape. One of the reasons for the curly growth of multiwalled carbon nanotubes might be the roughening of the substrate surface by etching with the chemical etchant solutions, which can induce an incoherent growth direction. Another possibility is that carbon nanotubes were not crowded enough to have vander Waals effects that make the aligned growth of nanotubes possible in the absence of strong electrical field[12].

However, no report has hitherto been available on the mechanism behind the growth of CNTs on stainless steel substrates, which is very important for better control of the CNT density and alignment[13].

Conclusion

An efficient and cost-effective method of synthesizing multiwalled carbon nanotubes directly on stainless steel (type 316L) substrates is reported. We discuss the relationship between the surface roughness of substrates and growth of CNTs. Synthesized CNTs were curly in shape and Raman spectroscopy indicated that they were multiwalled. It was found that pretreatment of the substrate surface was very important for successful synthesis. Etching with different chemical etchant solutions (Table-1) rendered the different substrate surface roughness. Atomic force microscope measurements revealed the surface roughness of etched stainless steel, ranged from 12.2-52.4 Å that related to Picral and Marble reagent, respectively. It is qualitatively observed that nanotube density decreases drastically when the roughness on the surface is reduced.

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