Synthesis of Carbon Nanotubes Growth Using $FeCl_3$ / Ethanol Catalyst by CVD Method

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ABSTRACT

Carbon nanotubes (CNTs) were grown by chemical vapor deposition (CVD) method. $FeCl_3$ was used as the precursor of iron which acts as the catalyst .Solution of $FeCl_3$ in ethanol at concentration of (0.05 mole/litter) has been chosen. Silicon (100) substrates were spin- coated with the prepared catalyst solution ($FeCl_3$) .Carbon nanotubes were grown on Si (100) substrate coated with catalyst in tube furnace using argon and acetylene gases at temperature of 750°C for 30 minutes. The structures of the produced material were characterized with Raman spectroscopy and FESEM. Raman spectra showed MWCNTs with the presence of radial breathing mode (RBM) at low frequency. The morphology of carbon nanotubes called noodles–like CNTs with an average diameter of 45nm was observed with FESEM micrograph.

Keywords: Carbon nanotubes; Chemical vapor deposition; $FeCl_3$ catalyst.

دراسة نمو الكاربون الانبوبي النانوي باستخدام عامل مساعد - كلوريد الحديديك \الايثانول بطريقة الترسيب بالبخار الكيمياوي

الخلاصة

تم اجراء تنمية انابيب الكاربون النانوية بطريقة الترسيب بالبخار الكيمياوي (CVD). استخدمت مادة كلوريد الحديديك ($FeCl_3$) كمصدر لعنصر الحديد والذي يعتبر كعامل مساعد. تم تحضير محلول كلوريد الحديديك باذابته بالايثانول وبتركيز 0.05 مول/لتر. استخدمت شرائح نظيفة من السليكون كقواعد . ان هذه القواعد السليكونية قد تم تغطيتها في المحلول المحضرسابقا بطريقة الطلاء المغزلي.تم تنمية انابيب الكاربون النانوية على السليكون المطلي بالمحفز في فرن انبوبي مستعملا غاز الاركون وغاز الاستيلين وبدرجة حرارة 750 درجة مئوية ولمدة 30 دقيقة . تم تشخيص المركبات الناتجة باستخدام مطيافية رامان و المجهر الالكتروني الماسح ذات الانبعاث المجالي (FESEM) . اظهر طيف رامان وجود انابيب الكاربون النانوية ذات الجدران المتعددة (MWCNTs) مع وجود نمط التوزيع النصف قطري (RBM) عند التردد الواطئ . لقد اظهرت اشكال المجهر الالكتروني الماسح تكون مايسمى بانابيب الكاربون النانوية – المشابهة لاحد اشكال المعكرونة (نودلز). وبمعدل قطر مقداره 45 نانومتر .

الكلمات المرشدة: انابيب الكاربون النانوية، الترسيب بالبخار الكيمياوي ، محفز كلوريد الحديديك .

INTRODUCTION

Since the development of carbon nanotubes (CNTs) in 1991[1] , there has been considerable interest in CNTs with unique properties. Due to the unique mechanical, electrical and chemical properties of nanometer-scale tubular of CNTs [2,3], they have been considered as important components of numerous micro scale and/or nano scale sensor [4,5,6] and also other nano scale applications.Various methods have been used for growing CNTs in the presence of catalyst particles. These methods are: arc discharge method [7, 8, 9, 10], laser ablation method [11] and chemical vapor deposition (CVD) method [12, 13]. Chemical vapor deposition is the most popular method of producing CNTs nowadays .As compared to arc- discharge and laser ablation methods, CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure. The formation of SWCNTs or MWCNTs is governed by the size of the catalyst particle [14]. MWCNTs and SWCNTs are synthesized using CVD method with metals catalyst (Ni,Co or Fe) and (Cu, Ag, and Au) respectively [15]. Metal salt (Fe ($NO_3.6H_2O$) in ethanol was used as a catalyst for CNFs and MWCNTs using CVD technique [16]. Synthesis of carbon nanostructures is quite interesting using $FeCl_3$- ethanol solution to study their structures .these have been done by many workers. [17, 18, 19].. Carbon nanotubes and carbon nanowires were synthesized by using /$FeCl_3$ as catalyst precursor solution to the copper plate. The effect of concentration on growth and structural changes of the as-grown nanomaterials are illustrated and discussed. [20].

The aim of the present work is to synthesized carbon nanotubes on silicon (100) substrate by spin coated of FeCl3/ethanol solution using chemical vapor deposition method in a high temperature tube furnace. Optimized parameters for CNTs deposited by using CVD method at high temperature tube furnace were selected

EXPERIMENTAL METHODS

Sample Preparation

Silicon (100) with dimensions (1x1x0.5 cm^3) was used as substrate. The substrate was degreased in acetone, washed in deionized water for several minutes , cleaned in ultrasonic bath with propanol ,washed again with deionized water and then dried at 100 ^{0}C in oven for 2 hr. Solution of $FeCl_3$ /ethanol was prepared at concentration of (0.05 mole/litter). The cleaned substrate was then dipped into $FeCl_3$ /ethanol solution for 10 minutes. Another Si- substrate was spin coated using spin coater (TC 100 spin coater -MTI Corp.) at speed of (2000 rpm) for 1 minute. The substrate was then dried in an oven at 100 $^\circ$C for 2 hr.

CARBON NANOTUBES GROWTH

The preparation of carbon nanotubes was conducted using alumina tube furnace. A quartz tube with an outside diameter of 30 mm and length of 80 cm was inserted into the alumina tube furnace. The coated Si substrate was put inside an alumina boat. The substrate and the boat were inserted in the middle zone of the quartz tube where the maximum temperature is located. Argon gas was fed through the quartz tube at a rate of (0.2 litter /min), which was preheated to a temperature of 750 °C. Then acetylene gas with rate of (0.5 litter /min) was introduced into the tube furnace in addition to the argon gas for 30 minutes at 750°C. The substrate was removed from the furnace after the furnace was cooled down.

RESULTS AND DISCUSSIONS

CNTs were prepared using 0.05 mole/litter of $FeCl_3$/ ethanol solution as carbon source on silicon substrate using spin coating at (2000 rpm, 1min). CNTs grown by spin coating method have a noodle shape and the tube produced was reasonably small in size. This indicates that spin coating can produces small catalyst particles.

RAMAN SPECTROSCOPY ANALYSIS

Features of Raman Spectroscopy

Raman spectroscopy is a powerful technique to determine the presence of different sorts of carbon nanotubes in the analyzed sample. In Raman spectrum, the so called $G_{graphite}$ – line is a characteristic feature of the graphitic layers and corresponding to the tangential vibration of the carbon atoms. The second characteristic mode is typical sign for defective graphitic structures (D_{defect} – line). The I_D / I_G intensity ratio is a direct measure of the quality of the sample. In addition, there is a third mode, named the radial breathing modes (RBM). These are an important diagnostic feature for the characterization of CNT sample. Firstly, because they are only seen for SWNTs [21] whereas for MWNTs, they are too weak to be observed due to their multiple walls construction [22].

Spectrum Analysis

Raman spectroscopy (in Via Raman microscope - RENISHAW-UK) operated with He – Ne – laser at excitation wavelength of 663 nm was used to characterize CNTs product. Raman spectrum was used to identify the structure of CNTs using $FeCl_3$/ ethanol solution as a catalyst prepared on silicon (100) substrate, which is shown in Figure (1).

At high frequency (1000cm^{-1} - 2000cm^{-1}), the first order Raman spectroscopy has a strong band at 1329 cm^{-1}, which corresponds to the D – line of Multiwall carbon nanotubes. An additional strong band appears at 1593 cm$^{-1,}$ as an observed for CNTs. The degree of graphitization is an indicator of the carbon nanotubes disorder level, and is evaluated by intensity ratio of the D to G peak (I_D / I_G). The intensity ratio derived from Fig. (1) is equal to 1.2. This value is close to one, suggesting high quantity of structural defects, which is due to its multiple graphite layers. Therefore Raman spectrum provides evidence that the CNTs are multiwall with graphitic structure.

At low frequency (150 cm^{-1} - 350cm^{-1}), Raman analysis shows that RBM is present in the spectrum shown of Fig. (1). This could be generated from small diameter MWNTs. The observed Raman modes are reasonably in a good agreement with literature results for MWCNT's [23].

FESEM Analysis

Field emission scanning electron microscope (FESEM – Carl Zeiss, Supra 35VP, Germany) was used to characterize the morphology, sizes and distribution of CNTs produced. FEESM micrograph of CNTs surface prepared using $FeCl_3$/ ethanol solution as a catalyst on silicon (100) substrate are shown in Figure (2)

.Figure (2a) shows carbon nanotubes at magnification 3KX. Figure (2b) shows uneven distribution of carbon nanotubes. The prepared MWCNTs have a noodles structure and they are randomly oriented. Small bright catalyst particles were seen at the tip of the carbon nanotubes in Figure (2 c). These catalyst particles are Fe metal. This suggests that the tip growth mechanism is likely to be responsible for MWCNTs synthesized under the present conditions. These results are confirmed by other workers [23, 24]. Figure (2d) shows the average diameter of MWCNTs around 45nm .The length of CNTs was rather long, therefore it could not be accurately measured due to the randomly structured. However, it was obviously larger than one micron.

CONCLUSIONS

The main conclusion in this work is the growth of MWCNs using spin coated Si substrate with Fe process. The structure of carbon nanotubes MWCNTs is noodles in shape with an average diameter of 45 nm. Raman spectroscopy provides a direct measure of the CNTs quality from I_G/I_D.

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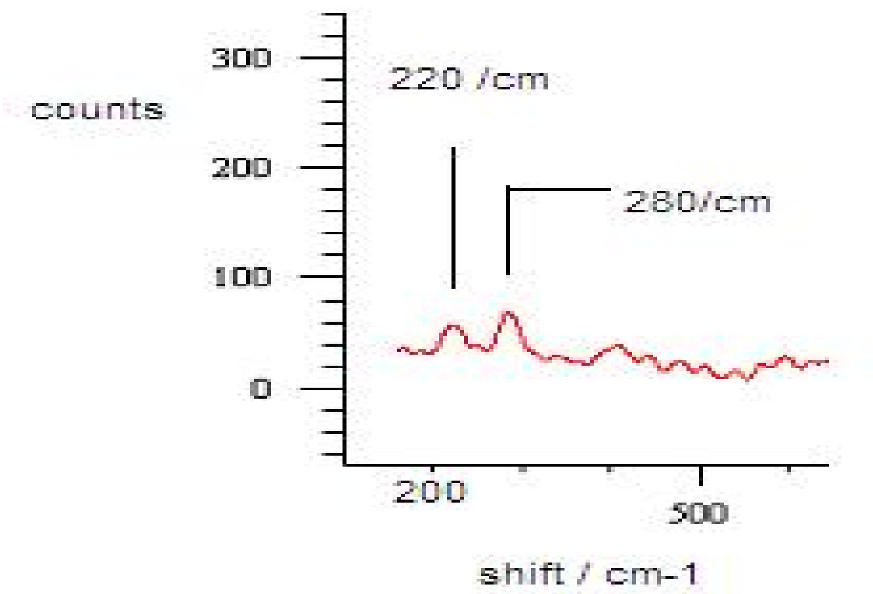

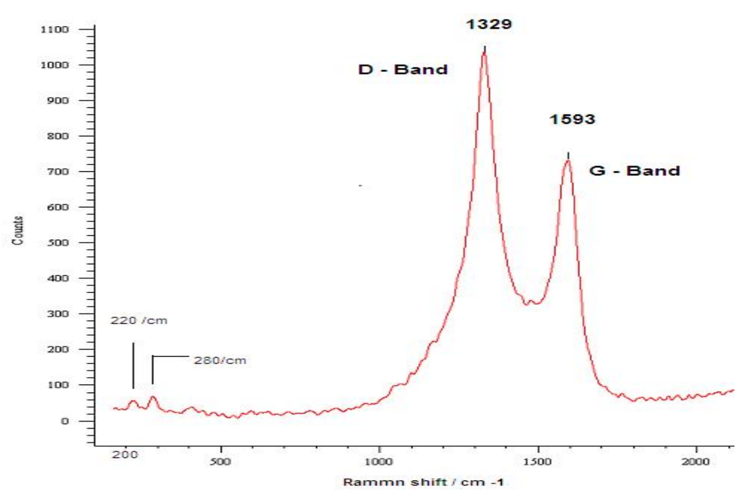

Figure (1) Raman spectra of CNTs as prepared on silicon substrate by CVD method using $FeCl_3$ catalyst; (I_D / I_G = 1.2).

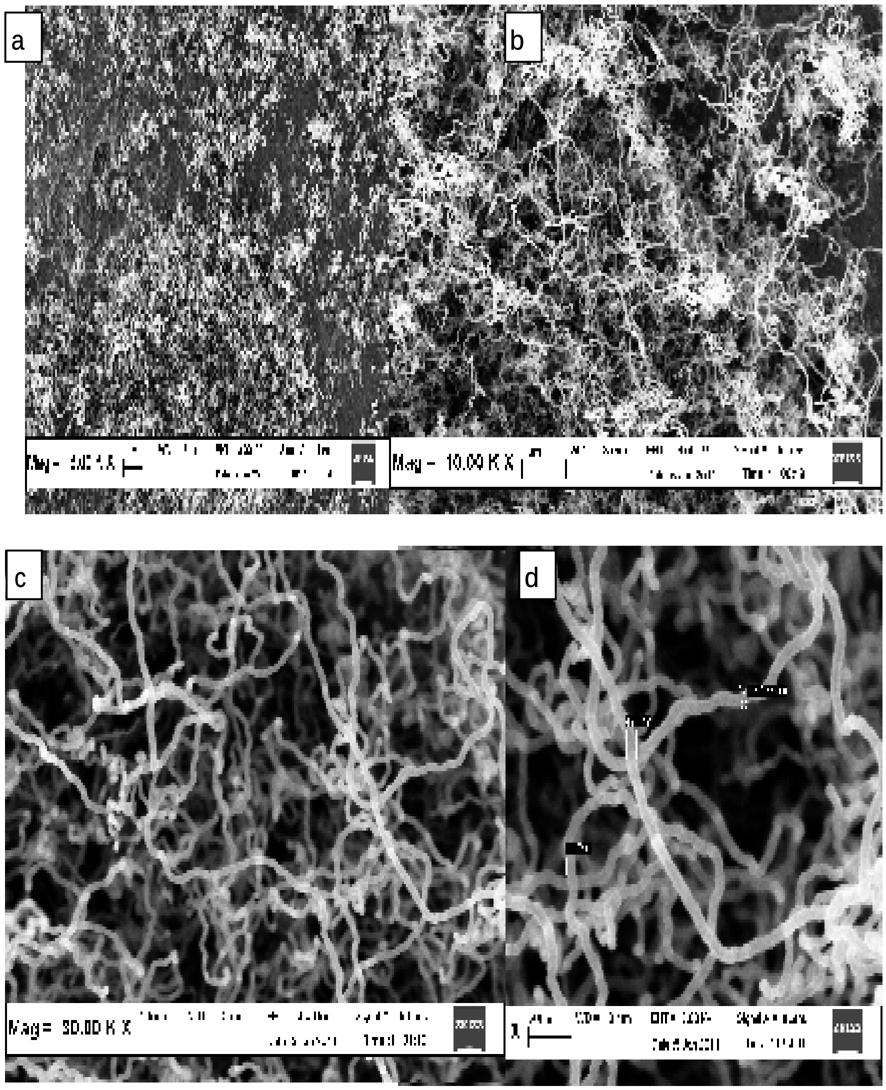

Figure (2) : FESEM micrograph of the grown CNTs deposited on Si(100) spin coated with 0.05mole/l of FeCl3/ethanol solution using CVD method at different magnifications .a) Mag.= 3KX, b) Mag.= 10KX, c) Mag.= 30KX, and d) Mag.= 50 KX .