SYNTHESIS AND STATISTICAL STUDY OF MULTI WALL CARBON NANOTUBES ON Cu SUBSTRATE USING ELECTROCHEMICAL CELL

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Abstract

Multi wall carbon nanotubes (MWCNTs) were grown directly on copper substrate and in the acetonitrile / de-ionized water (1% v/v) electrolyte of the electrochemical cell using different growth temperatures.The effects of substrate temperature and growth time over the MWCNTs structure were investigated. MWCNTs were characterized by Scanning Electron Microscopy (SEM), Low Magnification Transmission Electron Microscopy (LMTEM) and Atomic Force Microscopy (AFM). TEM characterization indicate a transition from non growth at 288K to negligible growth at 308K then to excellent growth at 338K, AFM characterization indicate a Gaussian distribution growth on Cu substrate with maximum percentage to 110 nm diameter.

تحضير ودراسة احصائية لأنابيب الكربون النانوية متعددة الجدران على سطح النحاس بأستخدام الخلية الكهروكيميائية

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الخلاصة

تم انماء انابيب الكربون النانوية متعددة الجدران على سطح النحاس وكذلك في الكتروليـت الخليـة الكهروكيميائية بدرجات حرارية مختلفة . تم دراسة تأثير درجة الحرارة وزمن النمـو علـى مواصـفات الانابيب. شخصت انابيب الكربون النانوية بتقنية المجهر الالكتروني الماسـح (SEM) وتقنيـة المجهـر الالكتروني النافذ واطئ التكبير (LMTEM) وتقنية مجهر القوة الذرية (AFM).تشخيص الـ (SEM) أظهر نمو أنابيب الكربون النانوية متعددة الجدران بقطر يتراوح حوالي الـ ٢٩ نانومتر في حين تشخيص (TEM) كشف عن الانتقال من حالة عدم النمو عند ٢٨٨ و٢٩٨ كلفن الى نمو مهمل عند ٣٠٨ كلفن ثـم الى نمو ممتاز عند ٣٣٨ كلفن. أما تشخيص الـ (AFM) فقد كشف عن توزيع كاوس لنمو انابيب الكربون النانوية على سطح النحاس وبأعلى نسبة نمو لقطر ١١٠ نانو متر.

Introduction

Since their discovery in 1991 by Iijima and coworkers [1-3], carbon nanotube have been investigated by many researchers all over the world. Their large length (up to several microns) and small diameter (a few nanometers) result in a large aspect ratio. They can be seen as the nearly one-dimensional form of fullerenes. Therefore, these materials are expected to possess additional interesting electronic, mechanic and molecular properties [4]. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one-dimensional structure on molecular and electronic properties [5].

The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface. Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube [6]. For the same reason, a smaller nanotube diameter results in increased reactivity [7]. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. Though, direct investigation of chemical modifications on nanotube behavior is difficult as the crude nanotube samples are still not pure enough [8].

To integrate CNTs in electronic applications, CNTs would need to be grown on different metal layer. Therefore, it is important to understand the effects of heating supporting metal layer on nanotubes growth. Cu and Al are commonly used in IC technology. Hence, investigating the effects of using these metals as supporting layer for catalyst would be essential [9, 10].

There are many important factors that affect the yield and quality of CNTs, including the surface area of the supporting material, reaction temperature and feeding carbon atoms. The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure [11].

In this study Cu was used as supporting layer in electrochemical cell and its effects are studied with temperature varied from 288 to 348 K.

Experimental

All chemicals were regent grade or the highest available commercial grade and were used as received. Deionized water was obtained from an Auto still water system (YAMATO Co., Ltd. WG25). MWCNTs were synthesized by electrolysis using acetonitrile and de-ionized water (1% v/v) as electrolyte. Electrolysis was carried out at atmospheric pressure and the temperature was varied as (288, 298, 308, 318, 328, 338 and 348) K using hotplate. Carbon nanotubes were deposited onto Copper sheet size (0.2x30x100mm) attached to a copper cathode. Graphite was used as the counter electrode (anode). Before mounting the substrates on the cathode, they were thoroughly cleaned in ultrasonic bath two times; the first with mixture of ethanol, acetone, chloroform, the second was with de-ionized water. The electrodes were separated by a distance of ~10mm. The applied d.c. voltage between the electrodes was kept at ~24 V using a d.c. power supply capable of generating stabilized voltage (24 V, 24A).6264B DC power supply HEWLETT.PACKARD. The deposition was carried out for ~ (4-6) h. The deposit was characterized by Scanning Electron Microscope (SEM), Low Magnification Transmission Electron Microscope (LMTEM), and Atomic force microscope (AFM).

Results and Discussion

In the present work we got two types of carbon nanotubes, the first grew in the electrolyte and the second grew on Cu substrate, growth condition was kept constant (except temperature). Only particles with diameters ranging from 5 nm to 12 nm can be observed in the

electrolyte, while, the diameters of carbon nanotubes on Cu substrate was ranging from 40 nm to 220 nm, this greatness and wide range of diameters was due to roughness of Cu electrode surface and the diversity in the sizes of growing nuclides on Cu electrode surface as shown in Figure 1.

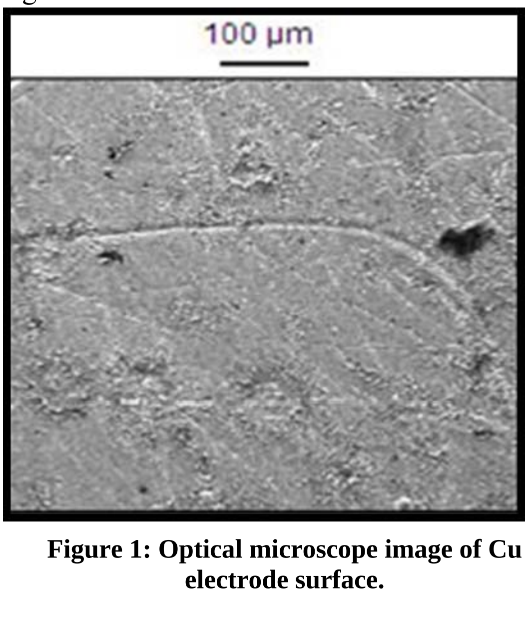


Figure 1: Optical microscope image of Cu electrode surface.

Scanning Electron microscope image Figure 2 shows MWCNTs precipitated in the electrolyte with diameter about 29 nm.

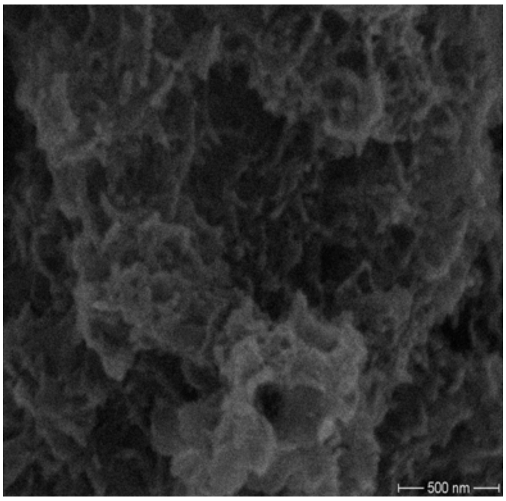
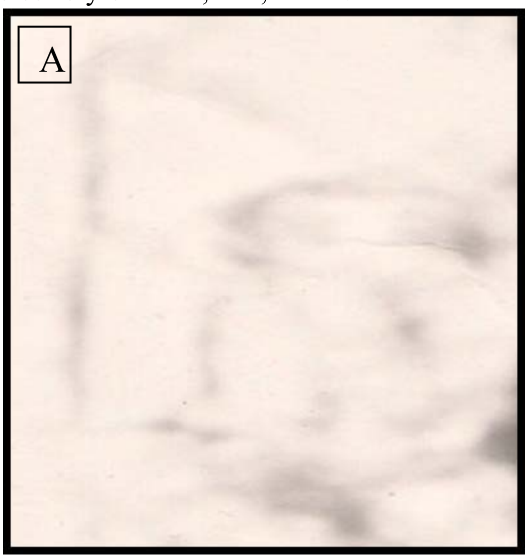


Figure 2: SEM nanograph of 50000X

Figure (3) shows the LMTEM nanographs of carbon nanotubes grown in the electrolyte. It was discovered that electrolyte temperature affected the growing process significantly. There are no CNT growth obtained when electrolyte temperature was 288 and 298K, we found a trace amount of nanotubes obtained at 308K as shown in the TEM image in Figure 3(A), In contrast to that, the LMTEM images in Fig.3 (B, C and D) show well-grown nanotubes with uniform diameter that grown in the electrolyte at 318, 328, 338 K.



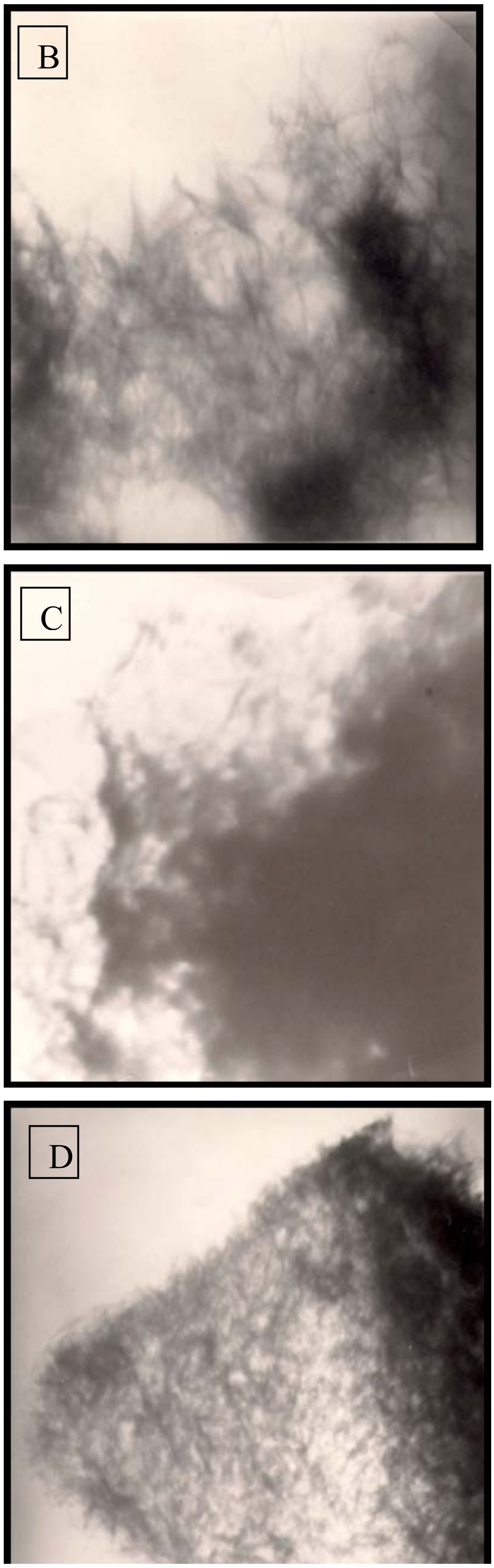


Figure 3: LMTEM nanographs of X64000 / 80KV / 5 – 12 nm carbon nanotubes grown in the electrolyte (A, B, C, D at 308 K, 318 K, 328 K, 338 K respectively).

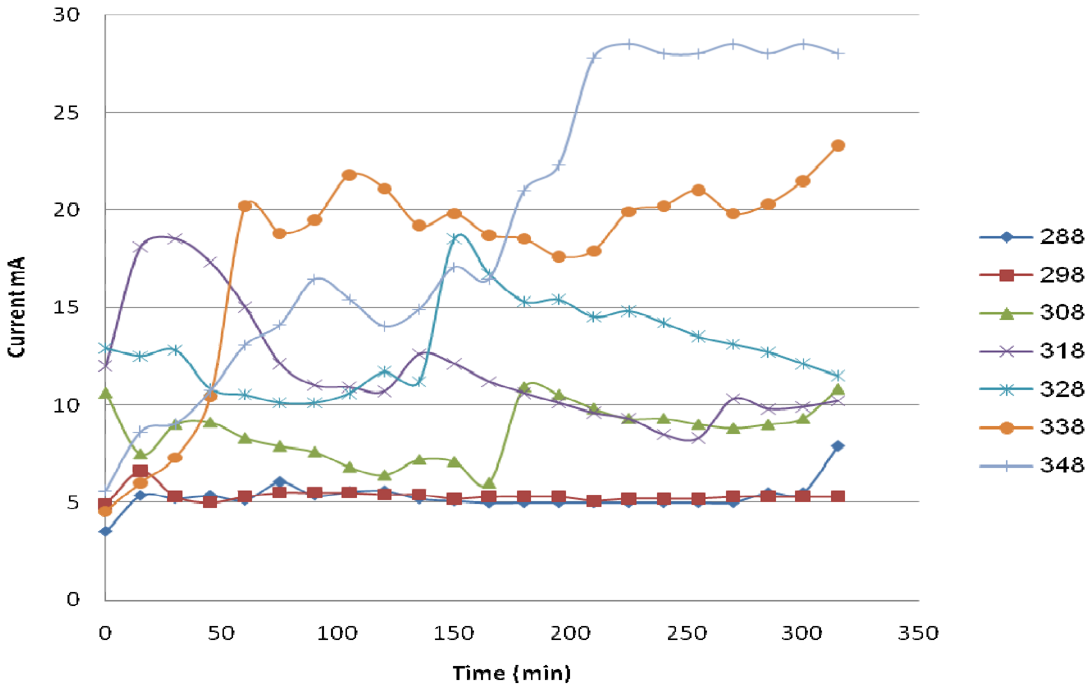


Figure 4: Temperature effect on cell efficiency (Current Vs Time at different temperatures)

The nanotubes grew dense and faster as the electrolyte temperature was increased; the increasing temperature caused increasing the energy of carbon atoms in the outer surface, and help them to escape from the surface of graphite electrode, Figure 4 describes this phenomenon, we can see for (288 and 298 K) there are no increasing in the current during the electrochemical reaction, that means that no ions transferred between electrodes, and for (308 K) there is a poor increasing in current, while for higher temperatures there is a clear increasing in current. We can choose the degree 338 K as the efficient temperature for growing MWCNTs in this electrochemical cell due to the exponential current rise and the fixed current after 60 minutes of reaction.

Atomic Force Microscope images Figures 5 and 6 of MWCNTs grew on Cu surface (cathode) show significant qualitative differences between films grown below and at 338K. We found that there are no CNT`s deposited on Cu substrate at 288, 298, 308 K. These observations coincide with the TEM observations and with curves of the relation between cell efficiency and temperature Figure 4. The films deposited on Cu substrate at 318 and 328K are composed of submicron particles Figure 5. They grew faster as the substrate temperature was increased. The films deposited at 338K for 150 minutes Figure 6. show entangled clusters of nanotubes or nano-fiber structures that were analyzed in more detail by AFM statistical analysis**.**

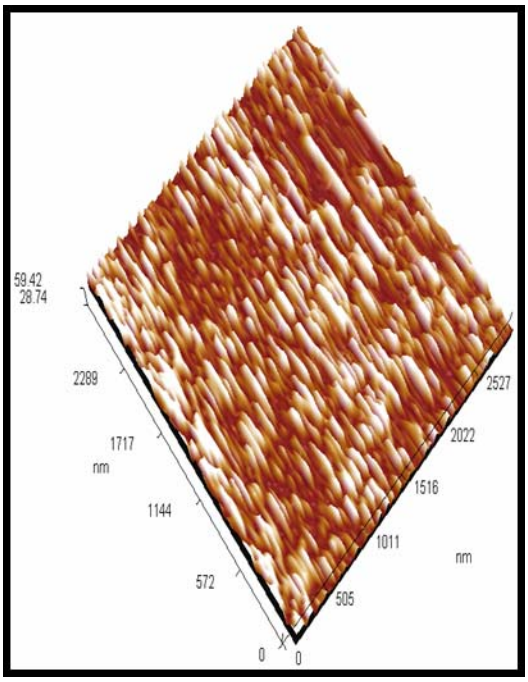


Figure 5: Atomic Force Microscope image of MWCNTs grown on Cu surface below 338K.

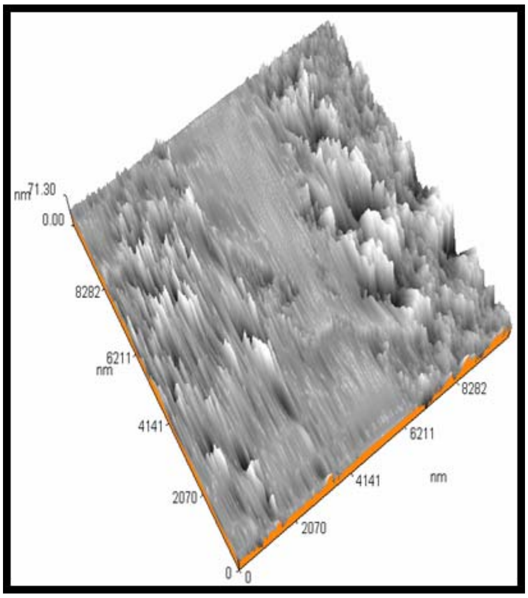


Figure 6: Atomic Force Microscope image of MWCNTs grew on Cu surface at 338K.

The table below shows the statistical analysis of AFM results, it contains:

Normal (%) =Quantity of any size of nanotubes / Quantity of the major size nanotubes

Volume (%) =Normal (%) of any size of nanotubes / the summation of Normal (%)

This table shows that the main deposited CNTs diameter was 110 nm while a diameter above 200 nm was rare. We found that the average diameter was 120.85 nm, and the volume percentages of diameters were about 10% for deposited MWCNTs diameter less than or equal to 50 nm, more than 33% for the diameters less than or equal to 100 nm, 50% for diameters less than or equal to 120nm and 90% for diameters less than or equal to 180nm. The statistical analysis shows Gaussian distribution of MWCNTs diameters deposited on Cu substrate at 338 K as shown in charts 1 and 2 we found that 110 nm has the maximum volume percent and the diameters less than 50nm and greater than 200nm got the tail of Gaussian shape.

Table 1: Granularity volume distribution of MWCNTs deposited on Cu substrate.

Avg. Diameter:120.85 nm **<=10% Diameter:50.00 nm**
<=50% Diameter:120.00 nm **<=90% Diameter:180.00 nm**

Diameter(nm)<	Volume (%)	Normal(%)	Diameter(nm)<	Volume (%)	Normal(%)	Diameter(nm)<	Volume (%)	Normal(%)
40.00	3.16	36.84	110.00	8.58	100.00	180.00	5.19	60.53
50.00	5.19	60.53	120.00	6.32	73.68	190.00	5.87	68.42
60.00	4.06	47.37	130.00	6.77	78.95	200.00	2.26	26.32
70.00	4.51	52.63	140.00	8.13	94.74	210.00	2.03	23.68
80.00	3.39	39.47	150.00	8.35	97.37	220.00	1.81	21.05
90.00	6.55	76.32	160.00	7.22	84.21			
100.00	6.55	76.32	170.00	4.06	47.37			

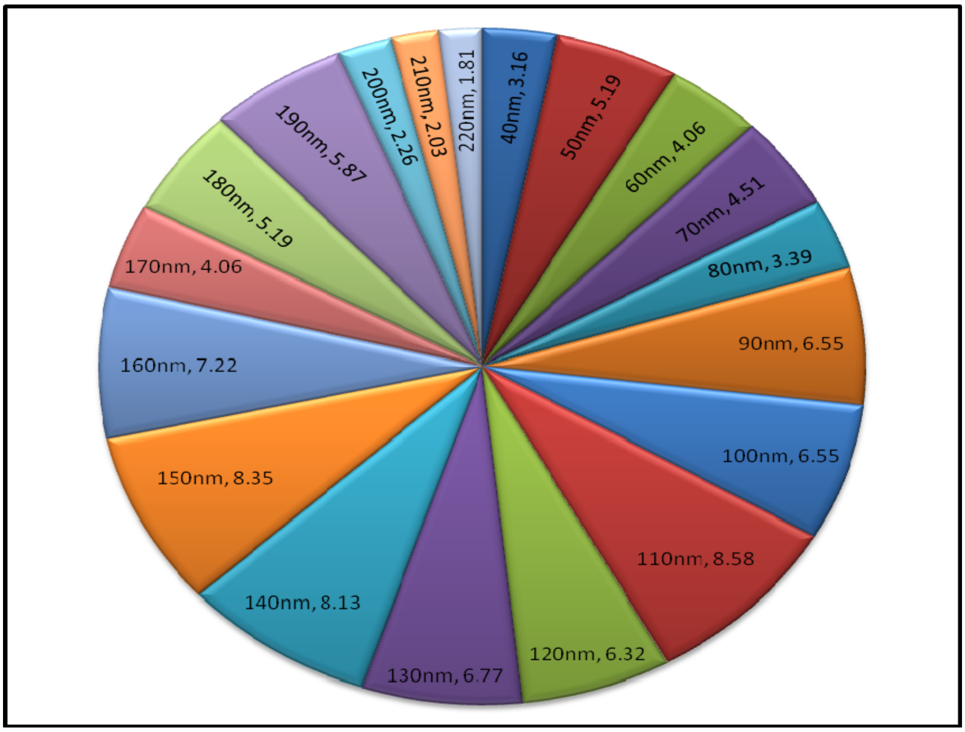


Chart 1: Granularity volume distribution of MWCNTs deposited on Cu substrate.

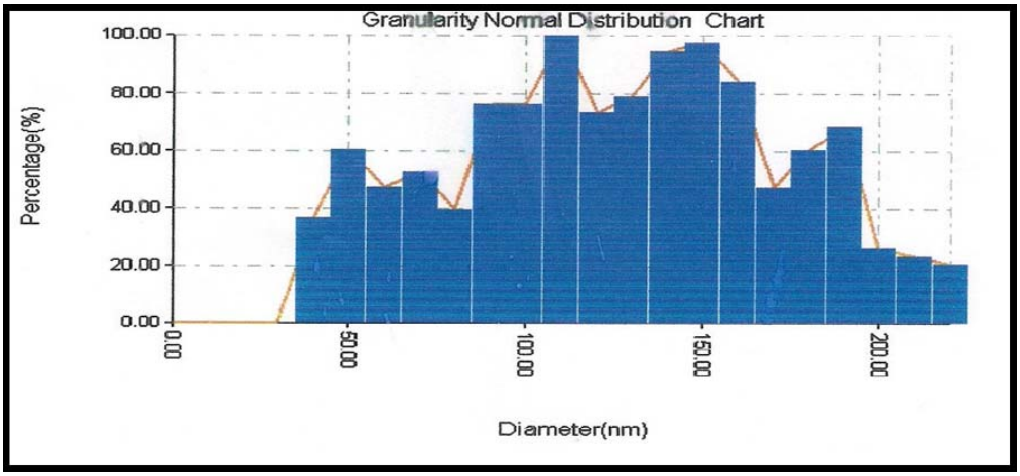


Chart 2: Granularity normal distribution of MWCNTs deposited on Cu substrate.

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