Morphology Investigation of Carbon Nanostructures Synthesized with Gold Catalytic Chemical Vapor Deposition CCVD.

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Abstract:

Carbon nanostructures with chemical vapor deposition (CVD) were successfully grown on silicon (100) pre-coated with gold nanoparticles as a catalyst using electrochemical method. Different thicknesses of gold films (10nm, 20nm, 80nm,140nm, 170nm, and 280nm) were used. These films were thermally annealed at temperature of 600ºC for 1h with argon environment. The CNTs were grown at 700ºC, argon and acetylene as a precursor source of carbon (Ar -500sccm, C_2H_2 -200sccm). The gold deposition after annealing was characterized by atomic force microscopy (AFM). The produced carbon nanostructures were also characterized with scanning electron microscope (SEM), and transmission electron microscope (TEM). The observed carbon structures of the SEM and TEM results are straight, curved, helical, and Y-junction with diameter rang of 100nm-200nm, which is attributed to carbon nano fibers with different size and shape of gold catalyst nanoparticles.

Keywords: CNT's Nanostructures; CNT's Synthesis, Gold Catalyst.

التحقق من مورفولوجية التراكيب النانوية للكاربون المحضرة بطريقة الترسيب بالبخار الكيمياوي المحفزة بالذهب

الخلاصة :

لقد تم وبنجاح تنمية التراكيب النانوية للكاربون بطريقة الترسيب بالبخار الكيمياوي على السليكون المغطى مسبقا بالجسيمات النانوية للذهب كعامل مساعد باستعمال طريقة الترسيب الكهروكيميائي . تم ترسيب اسماك مختلفة من اغشية الذهب (10نانومتر-20نانومتر-80 نانومتر-140نانومتر-170- نانومتر- 280نانومتر) .تم تلدين هذه الاغشية حراريا عند درجة حرارة 600 درجة مئوية لمدة ساعة واحدة في جو من غاز الاركون. تم تنمية الكاربون الانبوبي النانوي عند درجة حرارة 700 درجة مئوية بوجود غاز الاركون وضخ غازالاستيلين كمصدرلانتاج الكاربون (معدل جريان الاركون 500سم^3- قياسي بالدقيقة ومعدل جريان الاستيلين 200سم^3- قياسي بالدقيقة) شخص الذهب المترسب بعد عملية التلدين بواسطة مجهر القوى الذرية (AFM) وسخصت ايضا التراكيب النانوية للكاربون بواسطة المجهر الالكتروني الماسح (SEM) والمجهر الالكتروني النافذ (TEM) . بينت النتائج المرصودة بالمجهر الماسح والنافذ للتراكيب النانوية للكاربون بشكل مستقيم ومنحني وحلزوني ومرتبط بشكل حرف Y ويمتلك قطر بمدى يتراوح من 100نانومتر الى 200نانومتر، والذي يعزى الى وجود الفايبر النانوي من الكاربون و بابعاد واشكال مختلفة لجسيمات الذهب المحفزة.

الكلمات الافتتاحية : التراكيب النانوية للكاربون الانبوبي: تحضير الكاربون الانبوبي النانوي: محفز الذهب.

1.Introduction:

Since the first discovery of carbon nanotubes (CNTs) in 1991 [1] ,CNTs have attracted much attention because of many potential applications in the field emission display [2], as a tips for scanning probe microscopy [3] , hydrogen storage [4], chemical sensors [5] , and high strength composites [6] . For the production of CNTs, various synthesis methods such as arc discharge [7], laser vaporization [8], and catalytic chemical vapor deposition (CCVD) [9] have been developed. Among the various growth methods, CCVD process is widely used technique that generates a relatively high yield of pure carbon nanomaterials. Carbon nanotubes have been widely synthesized by chemical vapor deposition in the presence of transition- metal catalyst such as Fe and Co [10], because they have strong catalytic activities for both the decomposition of hydrocarbon feedstock and the formation of graphitic carbon. A noble metals catalyst such as gold was used to synthesize CNTs and CNFs with different structures [11]. The catalytic activity of Au catalyst through decomposition of acetylene for the synthesis of CNTs over Au nanoparticles supported catalysts. The results of screening tests indicated that Au catalysts show CNT formation activity at the relatively low temperature of 550ºC [12]. The synthesis of single wall carbon nanotubes (SWCNT's) was presented using gold nanoparticles catalyst with thermal chemical vapor deposition (CVD). Nanotubes were successfully grown using monodispersed gold nanoparticles prepared through a block copolymer tempting technique [13]. Using optical emission spectra plasma to synthesis of single wall carbon nanotubes (SWCNT's) using an Au catalyst were in situ examined for the purpose of understanding the formation of SWCNT's over the Au catalyst. This growth found to be useful for finding the optimum condition for the SWNT's growth by plasma chemical vapor deposition method [14]. Gold was reported to catalyze the growth of multi-wall and single –wall carbon nanotubes (MWNTs and SWNTs, respectively). Because of the low solubility of carbon in Au and the unique catalytic activity observed for Au nanoparticles, the growth mechanism and yield of nanotubes over Au catalysts are intriguing [10]. Multiwall carbon nanotubes (MWNTs) , and other carbon nanostructures, such as carbon nanofibers and carbon nanoparticles (NP's) was fabricated through structure transformation of metastable carbon layers on Au surface at temperatures 800ºC-850ºC with the thermal decomposition of ethylene [15]. Different shapes of carbon nanostructures (CNTs and CNFs) have been synthesized by CVD, such as coiled [16], helical and zigzag [17, 18], Y-junction [19], etc. These are depending on the deposition parameters catalyst shape and size. Y-Junctions were synthesized by gold catalyzed chemical vapor deposition (CVD) to explain the growth mechanism. [20].

In the present work, gold catalytic chemical vapor deposition CCVD method was developed to grow and investigate the morphology of carbon nanostructures on silicon substrate (100) electrochemically coated with different thicknesses of gold films. SEM and TEM were used to characterize the shape and size of carbon nanostructures produced.

2. Experimental Details:

2.1. Catalyst preparation:

Silicon wafers (100) p – type, were used as a substrates, where ultrasonically cleaned with acetone and propanol then washed with distilled water and dried under nitrogen atmosphere. Different thicknesses of gold nanoparticles as catalyst were deposited on silicon wafers by electrochemical method. The gold nanoparticles were annealed at 600°C for 1h under argon atmosphere using tube furnace quipped with quartz tube. Now the substrate with catalyst becomes ready to use for the CNT's growth process via chemical vapor deposition (CVD).

2.2. Tube Furnace calibration temperature:

Before carrying out our experiments, the temperature controller used for single zone tube furnace was calibrated against external thermocouple. The calibration process done by using external K-type thermocouple as reference temperature measurements. The thermocouple sensor was inserted into the center of the reaction chamber under argon gas flow rate of 500 sccm. The furnace temperature was raised and fixed to a certain values. Then the temperature was recorded using the furnace controller against the external sensor at different points along reaction chamber axis. The selected temperatures were 500°C, 600ºC, 700ºC, and 800ºC to determine the effective temperature zone of the reaction chamber. The experimental results of this calibration are shown in Fig 1. It is clear that the furnace holds a constant temperature over a relatively large zone, about 20cm at the center of the furnace which is the hottest region. This was considered as the working region of the furnace where the substrate was placed.

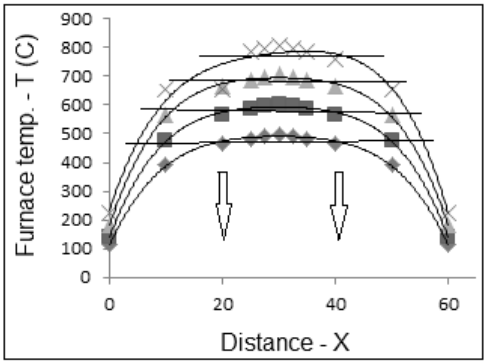

Fig.1 Calibration curves of temperature versus distance of tube furnace along x-axis.

2. 3. Catalytic chemical vapor deposition (CCVD):

Our catalytic chemical vapor deposition (CCVD) system used in this work is shown in Fig. 2 consists of a horizontal ceramic tube furnace with a quartz tube (2.8 cm internal diameter, 3.2 cm external diameter, and 60cm long) as the reaction chamber. The substrates held in alumina boat are loaded at a distance of 15cm from the end of reaction chamber. The furnace temperature was raised to reach the desired value under argon gas with flow rate of 500sccm. Carbon growth was carried out with acetylene gas as the carbon source used with flow rate of 100sccm, and argon as a carrier gas with flow rate of 200sccm. Experiments with different catalyst thicknesses were conducted at 800 ºC for 30 minutes. At the end of experiment, acetylene gas was switched off to cool down leaving argon gas under flow.

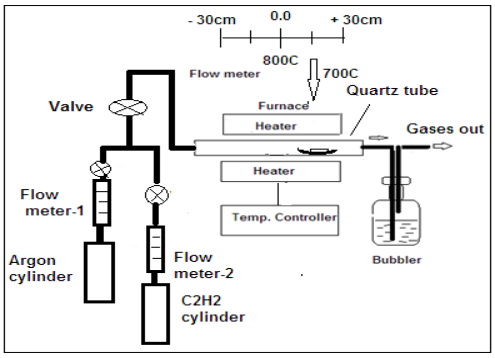

Fig.2 Schematic diagram of CCVD system

2.4. Characterization:

The deposited materials were characterized by atomic force microscopy (SPM - AA3000, -SPM-USA), scanning electron microscope (SEM- Vega II Tescan, Jeek) , transmission electron microscope (TEM -Philips – CM12, Holland) . During SEM and TEM characterization, some types of Y-junction and helical shaped CNF's were found and characterized.

3. Results and Discussion:

The growth of carbon nanostructures by thermal chemical vapor deposition often involves three main steps [21]: i) decomposition of hydrocarbon gas at the surface of catalyst nanoparticles; ii) diffusion of the resultant carbon atom in the nanoparticles to form the nucleation seed; iii) precipitation of carbon atoms at the nanoparticles interface to form nanotubes or nanofibers. The synthesized material was characterized by SEM and TEM.

3.1. AFM Analysis:

Atomic Force Microscopy AFM operated in tapping mode was used to study the surface morphology of gold nanopatricales deposited on silicon substrate (100). Fig.(3) show AFM morphology of 140nm gold nanopatricales , which was deposited in electrochemical method and thermal annealing at 600ºC for 1h as mesioned previously .

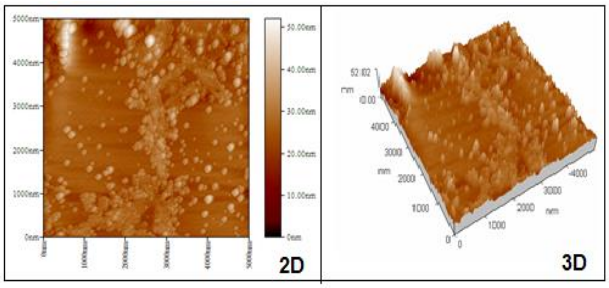

Fig. 3. AFM images in 2D and 3D for 140nm thick gold nanoparticles as deposited.

3.2. SEM Analysis:

Fig. 4.shows scanning electron microscope (SEM) morphology of carbon nanostructures grown on silicon (100) at 800ºC by CVD with gold nanoparticles catalyst at different thicknesses (10nm, 20nm and 80nm) treated by thermal annealing in argon atmosphere. The growth direction of carbon structures is approximately perpendicular to the surface. Most of the carbon growth are slightly curved or bent. Low growth density at 10nm and 20nm of gold catalyst as shown in Fig. 4a, b respectively. These are attributed to low thickness of catalyst. Higher growth density at 80nm gold catalyst was observed as shown in Fig. 4c, d. It was concluded that carbon growth was influenced by catalyst thicknesses.

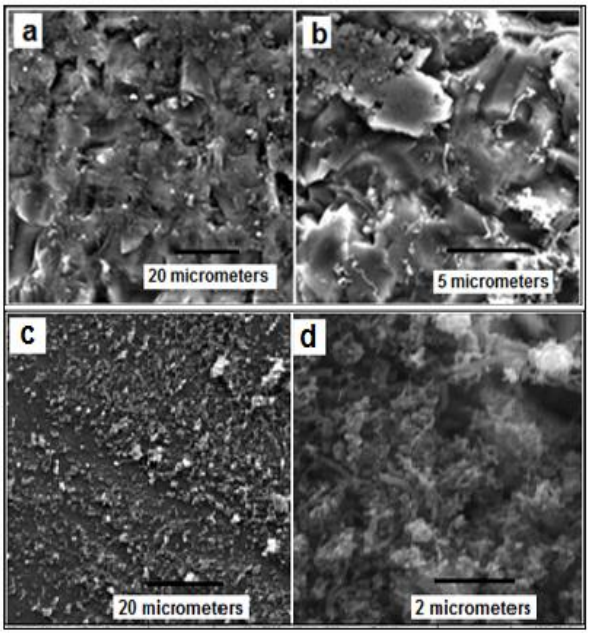

Fig.4. SEM images (top view) of as-synthesized carbon nanostructures as deposited on Si(100) coated with gold catalyst (10nm) (a) ; 20nm (b) ; and 80nm (c and d). at different magnifications .

Fig.5. shows carbon growth on silicon (100) coated with gold nanoparticles about 140nm. Long and high density CNFs within large area of the sample with tube diameter ≤ 200nm. This could be due to larger particle size of gold. These are mostly grown in spaghetti like fashion where they are not particularly aligned with each other. They contain many structural defects, and bend many times through their length. Larger magnification to see fiber details could not achieve due to instrumental problem.

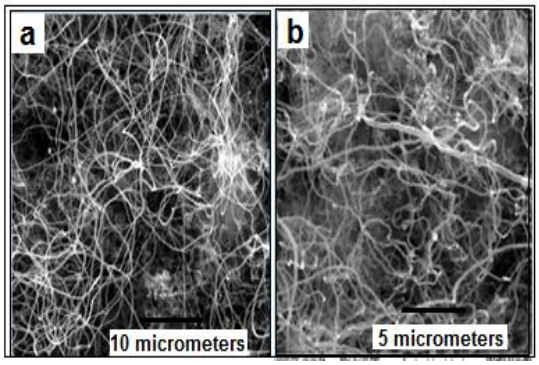

Fig.5 a,b. SEM images of CNFs with different area and magnification(140nm gold film).

The catalyst particles shape has also been proposed to control the carbon growth. It has been shown that different crystal faces of a metal particle could show variable coil growth. From these results it was proposed that coiling could be related to unequal extrusion rates of carbon catalyst faces [22]. Fig. (6) shows SEM images with different area and magnifications of Y- shaped CNFs deposited on silicon (100) coated with 170 nm of gold nanoparticles. From this figure several types of CNFs can be identified: they are i) Y-shaped CNFs with three non-helical CNF branches. ii) Helical Y-shaped CNFs with three helical branches. iii) Helical Y-shaped CNFs with two or more junctions (multiple junctions). These results are confirmed by other workers results [20,23]. The measured diameters and angles between the three branches are approximately in the range of 100- 170nm and 50º – 100º respectively (inset circles). These Y-shaped CNFs also have relatively longer branch with length greater than 5μm. This length is longer than the length of branches of CNFs previously synthesized [20]. We believed that the catalyst size and shape are responsible to the presence of different structures of CNFs.

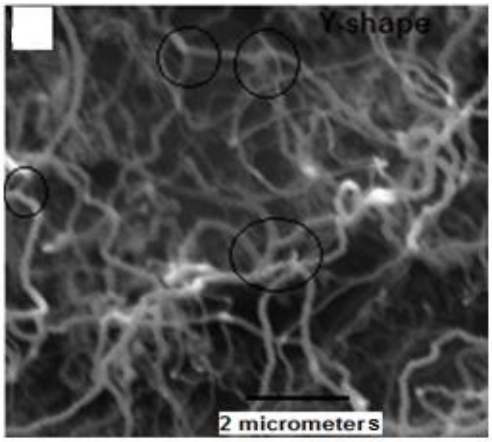

Fig.6. SEM for CNTs –CVD deposition on Si (100) coated with 170 nm Au film.

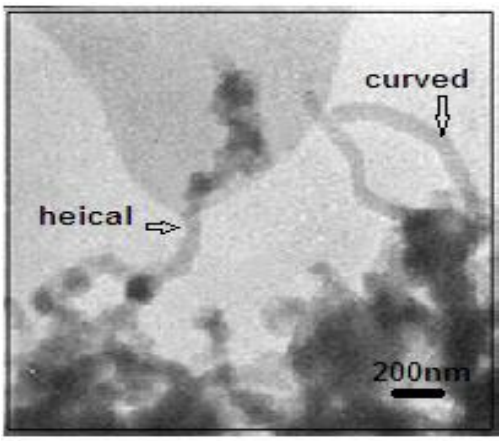

Fig.7 TEM image of CNFs grown at 800°C by CVD with 280nm gold catalyst on Si(100)

3.3. TEM Analysis:

The synthesized material was scratched off the silicon substrate and solicited with ethanol for 10 minutes, a few drops of this suspension were deposited on standard 3.05 mm copper grids for transmission microscopy (TEM) observation. Figure (7) show TEM image of CNFs deposited on silicon (100) substrate coated with thick layer (280nm) of electrodeposited gold nanoparticles which was annealed for 1h at 600ºC The average diameter of CNFs was measured to about 150nm-170nm, with curved and helical shapes are seen. As previously mentioned helical Y-shaped with three CNFs branches can be seen with TEM image. These results are confirmed with the SEM characterization. The dark spots on the fibers in this image are due to gold catalyst nanoparticles.

Finally our experimental results characterization and measurements for CNFs growth are summarized in Table (1). SEM and TEM studies show that most of the carbon products are long and small diameter CNFs .The CNFs entangle with each other and the diameter of CNFs are 150-180nm .Further observations show that the products are of very high quality CNFs with almost no other forms of amorphous carbon deposited. The CNFs are very long form tenth to hundredth of microns. In addition to the usual CNFs some helical CNFs are also observed in these images. The typical helix structure of the CNFs is shown in Figure (7). From the image we can clearly find that the tips of some CNFs contain some gold nanoparticles.

Table1. Summarized results of SEM and TEM characterization of carbon nanostructures.

Deposition type	Characterization	Au-thickness (nm)	CNFs sizes (nm)
CNTs /Au/Si	SEM (Fig.4a,b,c,d)	10nm,20nm 80nm	Not measurable , Mostly ≤ 200
CNTs /Au/Si	SEM (Fig.5a,b)	140nm	Mostly ≤ 200
CNTs /Au/Si	SEM (Fig.6)	170nm	Range ≈ 100-170
CNT's /Au/Si	TEM (Fig.7)	280nm	Range ≈ 150-170

4. Conclusion :

In the present work, it was successfully deposited CNFs with gold catalyst. The CVD process with annealed of different thicknesses electrodeposited of gold on silicon (100) as a catalyst nanoparticles is a good procedure for mass production of carbon nanofibers . SEM and TEM morphology show various types of carbon nanomaterial's: CNFs, curved, helical, CN Coils, and Y-Junction with different diameters. We believed that the catalyst is responsible to the presence of different structures of CNFs. The measured diameters of carbon nanofibers produced at different gold catalyst thicknesses are within the range of 100-200nm.

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