Catalytic Growth of Carbon Nanotubes on Ni Nanoparticals Prepared Using Nd-YAG Pulse Laser Technique

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Abstract:

Carbon Nanotubes were prepared and studied using $NiSO_4.6H_2O$ catalyst irradiated by Nd-YAG laser pulses. Solution of nickel sulfate in distilled water was prepared in different concentrations (2 and 5) mg/ml. Clean Si(100) p-type substrate was coated with $NiSO_4.6H_2O$ solution using dip and spin coating techniques respectively. Samples were then irradiated by different parameters of Nd-YAG pulsed laser in ambient atmosphere to produce catalyst nanoparticles. Carbon nanotubes were grown using a tube furnace. The irradiated Si sample was introduced into the middle of the quartz tube located inside in the furnace. CNT's were grown at 750°C using acetylene and argon gases for about 20 minute. The results were characterized by optical microscope, FESEM and TEM analysis. The study showed that CNT's growth with small MWCNT's diameters (20-70 nm) was successfully achieved with $NiSO_4$ nanocatalyst using pulsed laser as a hammering device. New morphology of carbon nanotubes called noodles –like CNT's was observed with FESEM micrograph.

Keyword: CNT's, $NiSO_4$ catalyst, laser ablation.

1. Introduction:

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [l],CNTs have attracted much attention due to their singular, mechanical, and chemical properties .Potential applications include electrochemical devices[2], field emission devices [3], sensors and probes [4] and electronic devices [5].CNTs can be produced by several methods including arc discharge [6], laser ablation [7], pyrolysis [8], chemical vapor deposition (CVD) [9,10], plasma enhanced chemical vapor deposition PECVD [11] and catalytic chemical vapor deposition (CCVD) [12,13]. In most process, optimization of catalyst preparation is one of the key steps to grow CNTs with desired diameters and size distributions[14].

The catalyst is prepared by many different techniques like: sputtering [15], electron beam evaporation [16], Laser ablation [17].Recently, there is an increasing interest in pulsed-laser processing of nanoparticles [18]. Nanocatalysts were fabricated by Nd-YAG pulsed laser ablation of thin transitional metal films for CNT's growth [19]. Another method of Laser ablation in liquids leads to rapid quench of hot species and formation of gold nanoparticles [20]. Nanocrystals are emerging as key materials to their novel shape and size dependent chemical and physical properties that differ drastically from that counter parts. Ni nanostructured on SiO_2/Si substrate for catalytic growth of carbon nanotube was produced using pulse laser ablation (PLA) and subsequent laser annealing at room temperature.

The generation of Ni and bi-metallic nanoparticles using Nd-YAG PLAL (pulsed laser ablation in liquid) in organic solution [21]. A simply and high efficient process coated with $NiSO_4$ or $FeSO_4$ layer on the pretreatment substrate as catalyst precursors .This novel quality process provides possibility for high quality and mass production of CNTs and CNFs from flames [22]. Nickel sulfate ($NiSO_4$) microclusters on Si substrates were fragmented by pulsed excimer laser irradiation to serve as catalysts for carbon nanotube/nanofiber (CNT/CNF) growth .The size of clusters/nanoparticals were found to be dependent on laser flounce and laser pulse number [21]. Individual single wall carbon nanotubes was synthesized by CVD method using nickel sulfate as a catalyst precursor [22]. Pulsed laser deposition were also used to deposited Fe thin films as a nanocatalyst other than Ni .Carbon nanotubes synthesized on these catalysts were shown to have almost the same size and density as those of the same catalyst [23].

In the present work, carbon nanotubes were prepared and studied using $NiSO_4.6H_2O$ catalyst irradiated by Nd-YAG laser pulses. Solution of nickel sulfate in distilled water was prepared in different concentrations (2 and 5) mg/ml. Clean Si(100) p-type substrate was coated with $NiSO_4.6H_2O$ solution using dip and spin coating techniques respectively .

2. Experimental procedure:

Silicon p-type (100) substrate with dimensions of (1×1) cm^2 were degreased by acetone, washed in distilled water and cleaned in ultrasonic bath for several minutes using acetone and propanol respectively. The samples were then washed with distilled water and dried at 90˚C in oven for 1 hour. Two concentrations (2 and 5) mg /ml of $NiSO_4.6H_2O$ solution and two different were used for silicon coating processes with catalytic solution. Different techniques, dip and spin coating (TC 100 spin coater-MTI Corp.) were used. Firstly; silicon substrate was dipped into $NiSO_4.6H_2O$ solution to mount catalyst for 10 minutes then dried in oven at 90°C. Secondly; another cleaned substrate was spin coated with desired concentration at speed 2000 rpm for 30 sec. and then dried in oven at 90°C for 1 hour. Film of $NiSO_4$ particles was formed on the Si substrate. The previous coating processes with $NiSO_4.6H_2O$ solution dispersed uniformly on the substrate surface. Nd-YAG Q-switched laser (wavelength=532nm, 1064nm and pulse duration 7 ns were used to break the $NiSO_4$ film into nanoparticles at room temperature. In this study, the Si substrate coated with $NiSO_4.6H_2O$ was exposed to laser at certain parameters to produce nanoparticles as a catalyst. Laser energy density of (3-13) J/cm^2 and 30 pulses were used. CNT's were grown on the prepared $NiSO_4$ nanoparticales. The Si-substrate (covered with catalyst and irradiated with laser) was then inserted at the middle of quartz tube, which is located into a 3cm diameter quartz tube located tube furnace. The furnace was heated to a temperature of (750)° C and flashed with argon at a rate of (5ℓ / min). Acetylene gas at a rate of (0.5) ℓ/min was introduced with argon at rate (2 ℓ /min) for 20 minute. Finally, the furnace was cooled down at room temperature and the CNT's grown on silicon sample was collected.

3. Results and discussion:

The Si-substrate covered with ($NiSO_4.6H_2O$) catalyst at a concentration of 2 mg/ml by dipping method .Laser irradiated the same substrate using Nd-YAG laser pulses at 2nd harmonic wavelength=532nm, energy density =6 J/ cm^2, pulse duration=7 ns and 30 pulses.

3.1. Optical microscope analysis:

The qualitative imaging of the CNT growth was firstly characterized by an optical microscope

[Olympus BX51M -Japan - fitted with high resolution CCD camera (Kruss DCM 35). For carbon structure growth using CVD process, different concentrations (2 and 5) mg/ml of ($NiSO_4.6H_2O$) catalyst coated the Si using dip and spin methods .These were irradiated with laser at a certain conditions. The growth results of carbon structures are shown in Figure (1). It can be seen that most of the carbon structures are long, relatively straight and some of them are not uniformly distributed as shown in Fig. 1a. This structure is called spaghetti – like carbon nanotubes. Some carbon structure was grown out of the substrate surface and not vertically aligned. One can easily observe small amount of fine structure in the catalyst agglomeration area. Figure (1b) shows different size and shape of carbon structure growth on silicon substrate coated with the same catalyst using spin coating method. Very fine, short, and accumulated structure can be seen compared to the structure in Figure (1a). These are preliminary investigation results by high resolution optical microscope with CCD camera. Detailed structure investigation using TEM is shown in Figure (3).

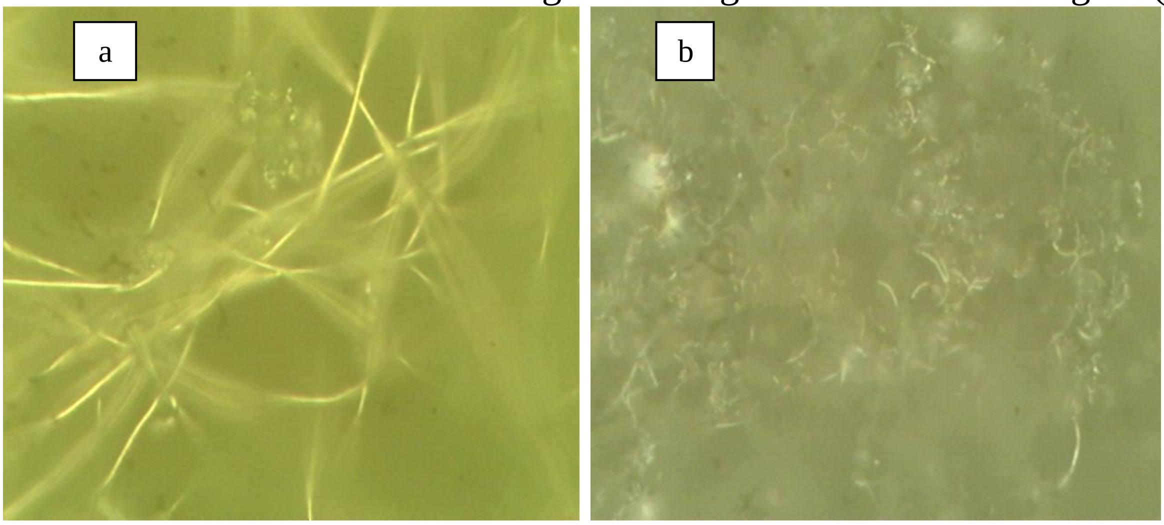
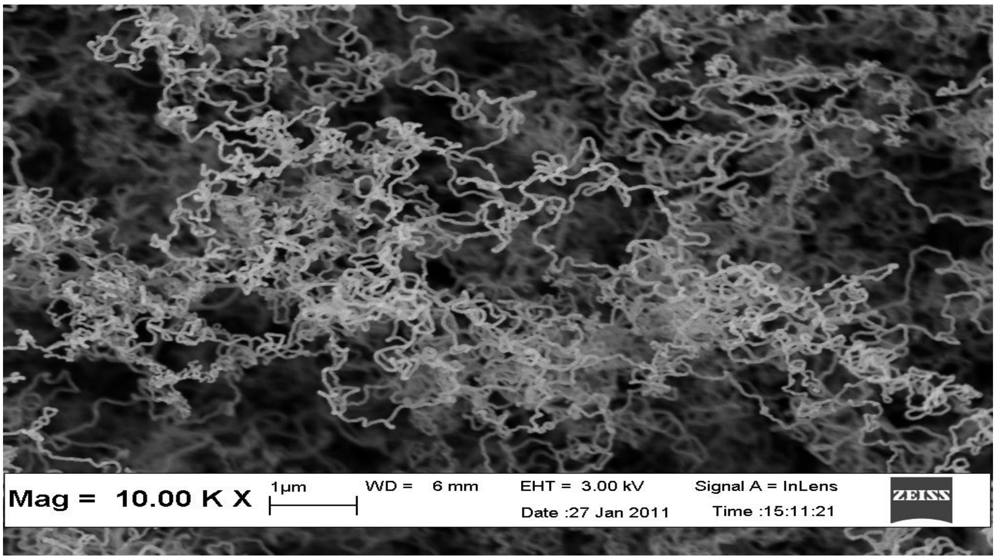
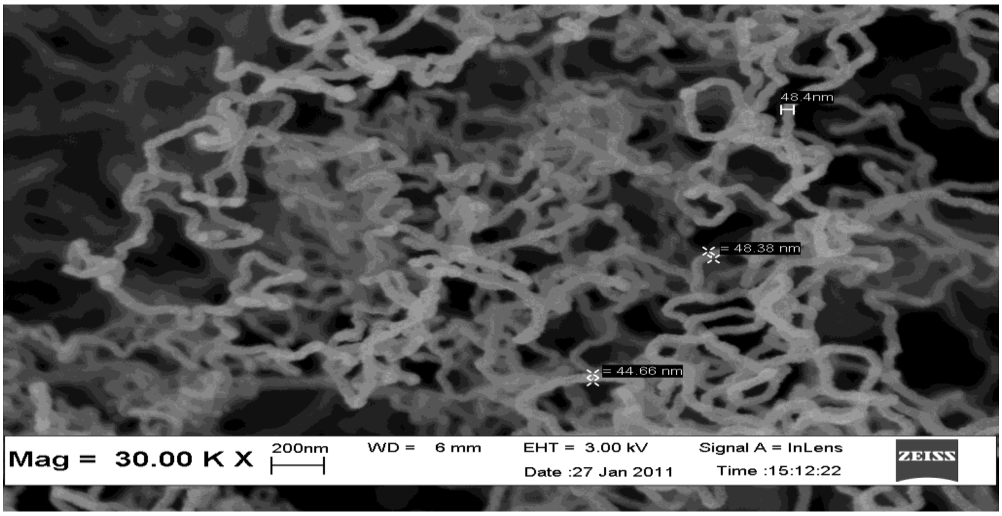


Figure (1): Optical micrograph at magnification of 1500 X for carbon structure grown on Si (100) irradiated with laser. a) Dip coating and b) spin coating at concentration (2mg/ml).

FESEM analysis :

Figure (2) shows the field emission electron microscope (FESEM-ZIESS) surface morphology of CNT's the produced using $NiSO_4.6H_2O$ solution catalyst at concentration of 5 mg/ml spin coated on silicon (100) substrate. The coated substrate was irradiated with Nd-YAG Q-switched laser (wavelength=532nm, 1064nm and pulse duration 7 ns) to break the $NiSO_4$ film into nanoparticles at room temperature . Figure (2a) is shown that large area, with high density, homogenous carbon nanotubes grown out of the silicon substrate with noodle shape .This suggest new structure is called noodles –like carbon nanotubs . Figure (2b) show higher magnification (30.0 KX) of CNT's with average diameters around 47 nm. The length of CNT's was rather long; therefore it could not be accurately measured due to the randomly structured. However, it was obviously larger than one micron a small bright catalyst particles were detected in Figure (2c) at the tip of the tubes for Ni metal. This suggests that the tip growth mechanism is likely to be responsible for MWCNT's synthesized under the present conditions. These results are confirmed by other workers [23]. The FESEM and TEM analysis are confirm the shape of the tubes which has been investigated by optical microscope as shown previously in Figure (1a and b) at the same concentration.





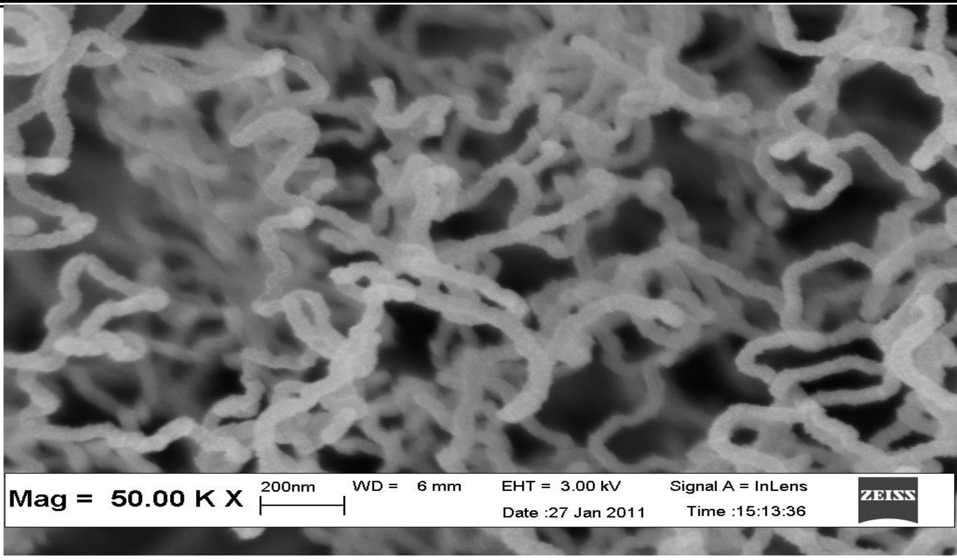
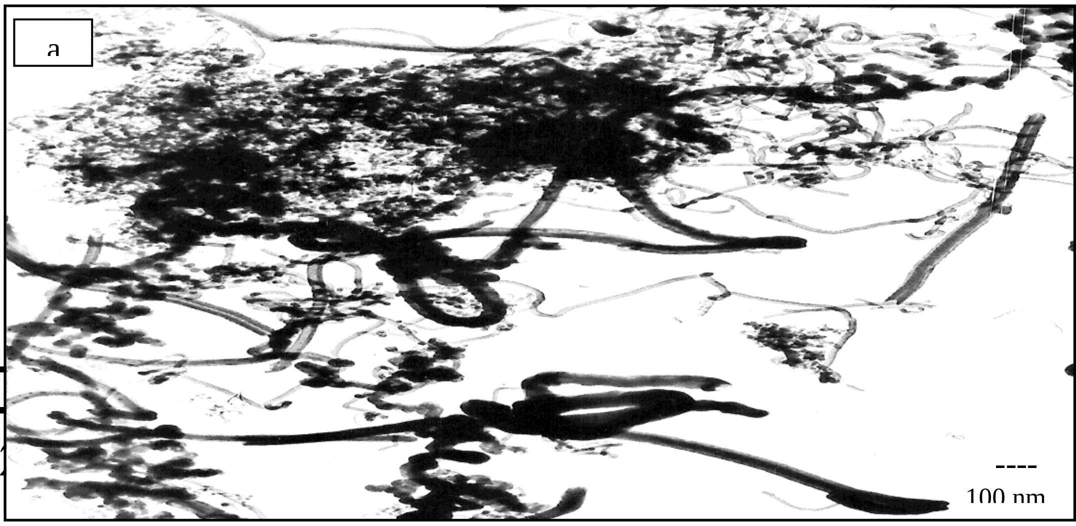


Figure (2): FESEM micrographs at different magnifications (of the grown CNT’s using CVD method with 5 mg/ml of $NiSO_4.6H_2O$ catalyst solution spin coated on Si (100).

TEM Analysis:

The morphology of the produced CNT's was investigated using transmission electron microscope (TEM –Philips-CM12) working at (80) kV accelerating voltage. The grown CNT’s on silicon substrate was scraped and fixed on 3.05 mm copper grid for TEM investigation. Figure (3) shows carbon nanotubes grown for dip coated silicon substrate (100) with 2 mg/ml solution of $NiSO_4.6H_2O$ catalyst. The catalytic substrate was also irradiated with Nd-YAG Q-switched laser (wavelength=532nm, 1064 nm and pulse duration 7 ns) to break the $NiSO_4$ film into nanoparticles at room temperature . Figure (3a) shows the effect of laser irradiation on the growth area. The morphology of CNT's with diameters ranging between 20-70nm. CNT's after irradiation with laser at 6 J/cm^{2}using 30 pulses. Long tube with large diameter (70 nm) grown from large catalyst size with small tube size (20 nm) diameter grown at the outer surface of the catalyst. The large and small CNTs sizes due to different Ni catalyst sizes. These can clearly observed through the inset of Figure 3b which also shows the tip growth mode for CNT's catalyst particles.



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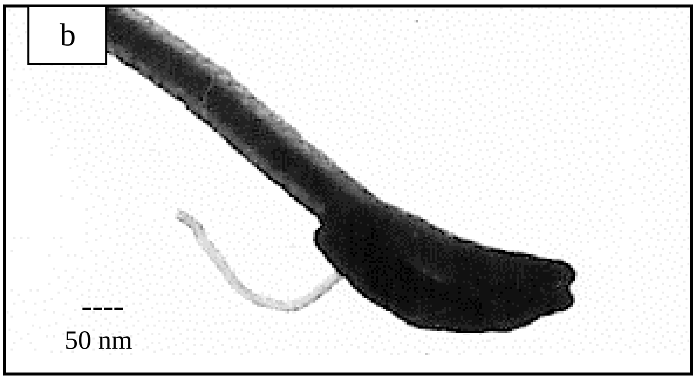

Figure 3: (a) Typical TEM images of carbon nanotubes grown from catalyst prepared dip coating 2 mg/ml. (b)CNT with Tip catalyst.

CONCLUSION :

Chemical vapor deposition (CVD) was used to grow CNT's on silicon (100) substrate coat
th $NiSO_4.6H_2O$ solution as catalyst by dipping and spinning methods. Catalyst nanoparticles were successfully produced using Nd- YAG pulsed laser irradiation technique to break clusters. The CNT's synthesized were dependent on the size and shape of the catalyst used after irradiated with laser. The results were characterized using optical microscope with CCD camera, FESEM and TEM. CNT's produced were relatively small size diameters (20-70 nm),long , randomly oriented ,high density and new shape called noodle like suggested .This study proved that carbon nanotubes growth can successfully be achieved using $NiSO_4$ as a nanocatalyst using Nd-YAG laser pulses technique .

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النمو المحفز لآنابيب الكاربون النانوية على جسيمات النيكل النانوية المحضرة باستخدام ليزر الياك النبضي

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الخلاصة:

تم تحضير ودراسة انابيب الكاربون النانوية باستعمال محفز كبريتات النيكل المائية المشعة بليزر الياك النبضي. تم تحضير محلول كبريتات النيكل بالماء المقطر وبتراكيز مختلفة(2–5)ملغم/مل. تم طلاء قواعد السيلكون (المانح) النظيفة بمحلول كبريتات النيكل المائية باستعمال تقنيات الطلاء بالغمر والطلاء المغزلي بالتعاقب، بعدها شععت النماذج بمعلمات مختلفة من ليزر الياك النبضي في الظروف الاعتيادية لانتاج جسيمات نانوية محفزة. تم ادخال نموذج السيلكون المشعع في وسط انبوب من الكوارتزموضوع في داخل الفرن. تنمية انابيب الكاربون النانوية بدرجة حرارة750 درجة مئوية باستعمال غازات الاستيلين والاركون ولمدة عشرين دقيقة تقريباً. شخصت النتائج بالمجهر البصري والمجهر الالكتروني الماسح ذات الانبعاث المجالي (FESEM) والمجهر الالكتروني النافذ (TEM). بينت الدراسة نمو انابيب الكاربون النانوية نوع ذات الجدران المتعددة باقطار من (20–70)نانومتر. وتم التحقيق بنجاح بوجود المحفز النانوي لكبريتات النيكل المائية مستعملاً ليزر الياك النبضي كاداة تهشيم. تبين من خلال صور المجهر الالكتروني الماسح تركيب جديد لانابيب الكاربون النانوية والتي يكون شكلها متعرج