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Carbon Nanotube Prepared by Pulse Laser Ablation of Graphite Target in Iso-Propanol solution

Dr. Khawla S. khashan
Applied Sciences Department, University of Technology / Baghdad
Email: Khawla_ salah@ yahoo.com
Mayyadah H. Mohsin
Applied Sciences Department, University of Technology / Baghdad

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ABSTRACT

In this work carbon nanotube was synthesis by pulse laser ablation of graphite target in Iso-propanol solution. Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectrophotometer and Transmission Electron Microscopy (TEM) were used to study chemical bonding, optical absorption, particle size, structure and morphology of the carbon nanotube. The FTIR absorption peak at 2335.6, 1647.1 cm^{-1}& 1269.1 cm^{-1} stretching vibration bond, it is inferred that the $C \equiv C$, $C = C$ and C-C, respectively. Bonds suggests the formation carbon nanoparticles suspend in this solvent, UV absorption peaks coincide with the electronic transitions corresponding to linear hydrogen – capped polyyne ($C_{n+1}H_2$), polyynes are important precursor molecular components in the formation of carbon nanotubes. The TEM show the aggregation of the carbon nanoparticles with size ranges from (1.66 to 41.6 nm), the structure and morphology of the CNT's with diameter at range 11.1 – 46.15 nm and length at range 261.1 - 592.3 nm.

Keywords: Polyyne, Carbon Nanotube, Laser Ablation in Liquid, Nanostructure

تحضير انابيب الكاربون النانوية بواسطة تقنية الاستئصال بالليزر النبضي للكرافيت في محلول الايزو-بروبانول

الخلاصة

تم في هذا البحث تحضير انابيب الكاربون النانوية بواسطة تقنية الاستئصال بالليزر النبضي للكرافيت المغمور بمحلول الايزو-بروبانول , وتم استخدام الاشعة الحمراء و طيف الاشعة الفوق البنفسجية –المرئية و المجهر الالكتروني النافذ لدراسة الاواصر الكيميائية , اطياف الامتصاص, حجم الجسيمات , هيكل وتشكل انابيب الكاربون النانوية داخل السائل. قمم الامتصاص للاشعةالحمراء عند 2335.6, 1647.1 cm^{-1}& 1269.1 cm^{-1} تدل على C-C ,C═C , C≡C على التوالي . شكلت الاواصر جسيمات الكاربون النانوية العالقة داخل المذيب. قمم امتصاص الاشعة فوق البنفسجية تشير الى وجود سلاسل الكاربون النانوية والتي تعتبر المفتاح او السلائف الجزيئية في تكوين وتشكيل انابيب الكاربون النانوية. المجهر الالكتروني النافذ يظهر لنا التكتل الحاصل لجسيمات الكاربون النانوية مع مديات الحجوم لهذه الجسيمات الذي يتراوح مابين (١،٦٦-

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

٤١،٦ نانوميتر) وايضا تركيب و طوبغرافية انابيب الكاربون النانوية التي يتراوح اقطارها ما بين (11.1 – 46.15 nm) واطوالها مابين (261.1 - 592.3 nm)

INTRODUCTION

Carbon Nanotubes (CNTs) can contain a variety of foreign molecules. Experimentally, it has been found that Single-Walled Carbon Nanotubes (SWNTs) can contain pure and endohedral fullerenes; SWNTs containing water [1], organic [2], and polyyne [3]. Although polyynes (C_mH_2), carbon linear chains terminated by hydrogen atoms, have high reactivates, they are stabilized up to 450 c° inside CNTs [4]. Linear carbon chains (C-chains), which consist of sp-hybridized carbon atoms, have attracted interest in recent years within the context of a wide range of topics such as interstellar molecules [5], and carbon nanowires as the so-called fourth allotrope of carbon [6] after diamond, graphite (graphene), and fullerenes together with carbon nanotubes [7]. Considering the degeneracy of orbitals of each carbon atom, two forms of infinite carbon chains have been hypothesized. An infinitely long C-chain, sometimes called carbine (polyyne), is an ultimate nanowire only one atom wide and therefore is a real one-dimensional (1D) nanomaterial, which is one of the most ideal model systems for exploring chemical and physical nanowire of 1D nanostructure [8].

When a graphite target is irradiated in liquid phase, Polyynes, linear carbon chains with alternating triple and single sp - hybridized C–C bonds terminated by atoms or groups (conventionally polyynes represent the class of molecules $H(–C\equiv C–)_mH$, with (integer m), have attracted considerable interest in astrophysics and nanoscience [9], and are important precursor molecular components in the formation of fullerenes and carbon nanotubes [10]. Including Nano- wires with controllable conductivity. Recently, hybrid Nano-materials have been developed in which polyynes have been inserted into single wall carbon nanotubes [4]. And Zhao et al reported the experimental fabrication of monatomic carbon linear chain which was shown to be inside double-walled carbon nanotubes of 0.7 nm in diameter [11], and their one-dimensional electronic structures have attracted considerable attention due to its size-dependent band gap [12], and nonlinear optical properties. In addition, CNTs have been intensively studied due to their potential technical applications, including field emission displays, hydrogen storage media, sensors, nanometer-sized semiconductor devices, and so on [13]. Laser ablation in liquid phase is a very unique approach for the nanostructure formation of refractory materials [14]. Carbon materials can be evaporated easily by laser ablation, since the energy densities of pulsed laser beam are high in small area and short time. The evaporated carbon particles form ablation plumes of the plasma state. The plume interacts with the background while diffusing, which is explained by Shock model or Drag model [15]. In gas phases, the evaporated particles are condensed, and Nano-particles, such as fullerenes C60, are synthesized [16]. In liquid phases, diffusions of the evaporated particles are intercepted therefore; the densities at the shock front are very high. Then, it was considered that larger particles would be formed by laser ablation in the liquid with the high solubility.

Liquid-phase laser ablation has been used to produce CNTs & polyynes; this method has some advantages. The cost is comparatively low, because expensive instruments such as a vacuum apparatus are unnecessary. The recovery of the product is higher than that of laser ablation in the gas phase. Moreover, ablation surroundings can be easily changed by replacing solvent. This technique is not yet adequate for industrial application, but provides an alternative method to produce CNTs. It has been found that the synthesis in liquid phase bears excellent chemical flexibility and synthetic tenability at normal pressure.

The purpose of the present use a new method to prepare long chain carbines and CNTs is reported under normal temperature and pressure by pulsed laser ablation of a graphite target in Iso-propanol solution at 1064 nm and study the effect of laser energy and number of laser pulse on CNTs & polyyne production by using FTIR spectroscopy, UV-Vis spectrophotometer, respectively and characterize the particle size, structure and morphology of the CNT’s by using TEM.

EXPERIMENTAL

Linear-chain polyyne molecules and carbon nanotube were produced by laser ablation of a pure graphite pellet that was cut from a graphite rod (99.9 % from national spectroscopic electrodes co. diameter = 5 mm) was used in a glass Petri dish container filled with 5 ml of pure Iso-propanol. The Petri dish was rinsed with ethanol cleaner prior to preparation. The target was immersed in Iso-propanol solution to a depth of around 2 mm below the Iso-propanol's surface during laser ablation. The target was rotated constantly during laser ablation for uniform ablation, ensuring that the nanoparticles that formed dispersed uniformly into the Iso-propanol and minimize the target aging effect and to give some stirring effect. The graphite target was irradiated vertically by a Nd: YAG laser (system type HUAFEI) operating at a wavelength of 1064 nm was used to ablate the target as depicted in Figure (1). The repetition rate was 1 Hz. The laser energy used in this experiment at range from (20 to 200 mJ/pulse), and the laser pulse ranged from (25-100).the laser beam was loosely focused using lens with focal length of 12 mm.

The optical properties of the nascent polyynes suspension were examined at room temperature in a quartz cell with 1 cm optical path. By a UV-Vis absorption spectrophotometer (SHIMADZU) operating in the wavelength range of (200-400 nm), the chemical bonding studied by Fourier Transform Infrared Spectroscopy (FTIR) (8400S, SHIMADZU) were also taken by drying drops of CNPs colloids on NaOH cell and Transmission electron microscopy (TEM) (type CM10 pw6020, Philips-Germany) were used to study the particle size and the morphology, by depositing the CNPs colloids onto copper mesh coated with an amorphous carbon film.

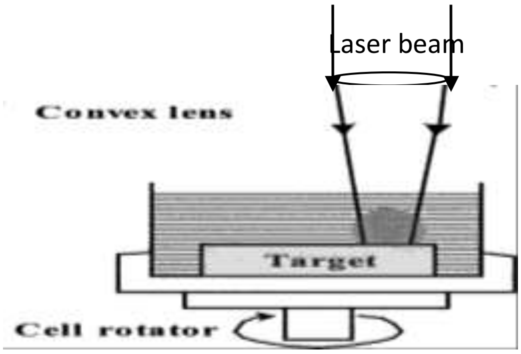

Figure (1) Experimental setup for Synthesis carbon Nanoparticles in Iso-propanol by laser ablation.

RESULTS AND DISCUSSION

A carbon nanoparticle is dominated by sp^2 carbon atoms, so there should be chemical bonds on its suspensions and it should be very reactive. As indicated by the FTIR spectrum shown in Figure (2), shows the FTIR spectrum of carbon nanoparticles suspensions prepared by laser ablation of graphite target in Iso-propanol with laser energy (20, 80 and 200 mJ/pulse) with 25 laser pulse.

From all figures , one can notice that the bond for all suspensions is between (3000 to 3500 cm^{-1}) is due to the O – H stretching vibration, and a peak between (3000 to 2800 cm^{-1}) is due to the C – H stretching vibration bond; asymmetric C – H stretching occurs at 2887.2 cm^{-1} , 2885.3 cm^{-1}, 2860.2 cm^{-1} and 2856.4 cm^{-1}, while symmetric C – H stretching occurs at 2977.2 cm^{-1} , 2972.0 cm^{-1} and 2923.9 cm^{-1}. The peak at 2335.6 cm^{-1} is due to the C ≡ C stretching vibration bond, while C = C stretching vibration bond appear at ~ 1647.1 cm^{-1}, suggests the formation carbon nanoparticles suspend in this solvent. the peak between (1250 – 1500 cm^{-1}) is due to the symmetrical C – H stretching bonded also appear around the 881.4 cm^{-1}, while peak at ~ 1049.2 cm^{-1} is due to the C – O stretching bonds and peak around 1269.1 cm^{-1} is due to the C-C stretching vibration bond.

According to the results of figure, the relative intensity of FTIR absorption peak is change with change laser energy while the positions and width of observed peak are well constant for the most part in each spectrum, it is inferred that the C ≡ C and C = C bonds was formed by laser ablation of graphite in ethanol which referred to formation carbon nanoparticles suspend in this solvent. These result was agree with reference [17, 18]**.** Figure (3) shows the FTIR spectra of carbon nanoparticles suspension preparation at laser energy (80 mJ) with different laser pulse (25 – 100). Also the same vibration bonded of C≡C and C=C stretching vibration while the peak absorption of carbon suspension prepared for 100 laser pulse higher than peak absorption at 25 pulse, this due to increased carbon nanoparticles concentration ,which cues scattering of laser light and reduce the absorption of solution and increased the transmission spectrum.

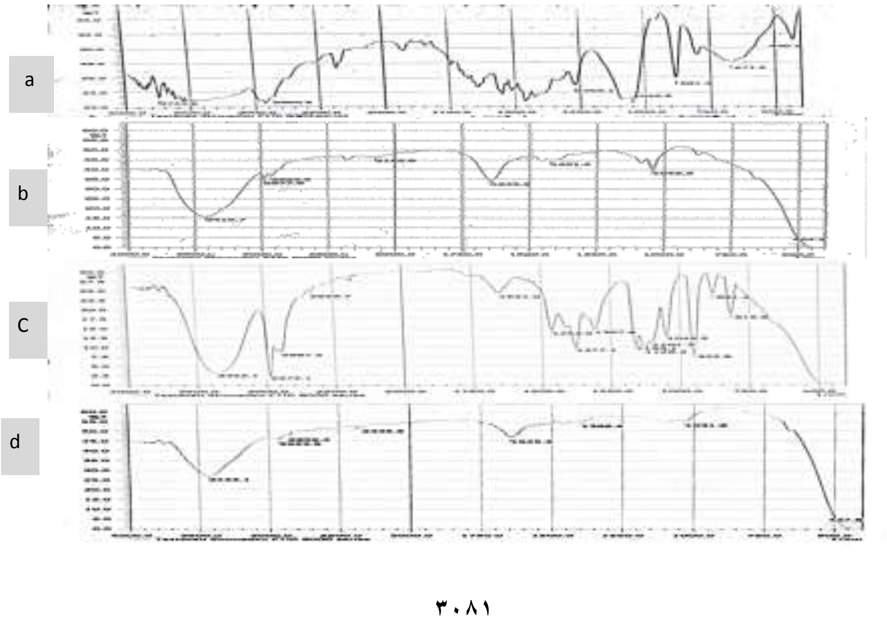

Figure (2) FTIR spectrum of CNPs suspensions whit different laser energy a) Iso-propanol solvent b) CNPs at 20 mJ c) CNPs at 80 mJ d) CNPs at 200 mJ.

Production of polyynes can be confirmed most easily by UV-Vis absorption spectroscopy through the assignment of the characteristic absorption peaks which reflect the lengths of polyynes. The effect the number of laser pulse on the formation of carbon nanoparticles is very important, Figure (4) shown UV-Visible absorption spectra of suspensions of CNPs prepared by laser ablation of a graphite target in Iso-propanol solution at different laser pulse at range from (25 to 100pulse) and 80mJ, These spectra commonly exhibit many sharp bands in the UV region. The three sample spectrums show almost similar peaks, The peak at 235 nm belongs to C6H2; the peak at 205.0 nm represents C8H2; the peak at 237.6 nm represents C10H2; the peak at 233.0 nm represents C11H2; the peak at 275.0 nm represents C12H2; the peak at 245.0 nm represents C13H2; the peak at 253.0 nm represents to C14H2, the peak at 281.0 nm represents C16H2 [19, 20], but each line has different absorbance value in each point of the wavelength. This indicates that the carbon nanoparticles produced have different size of distribution. Small polyynes (n< 6) are difficult to observe due to the weak intensity of the absorption peak at 200.0 nm. The absorption behavior as a function of polyyne length is obtained by semi-empirical calculations of the electronic absorption of H-polyynes and dicyanopolyynes [21].

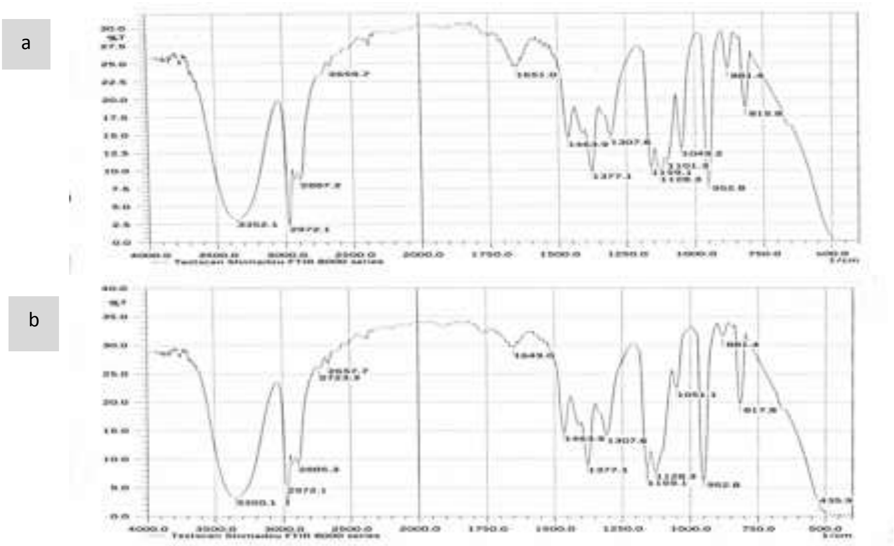

Figure (3) FTIR spectrum of CNPs suspensions with different no. Of Laser pulses a) 25 pulse b) 100 pulse.

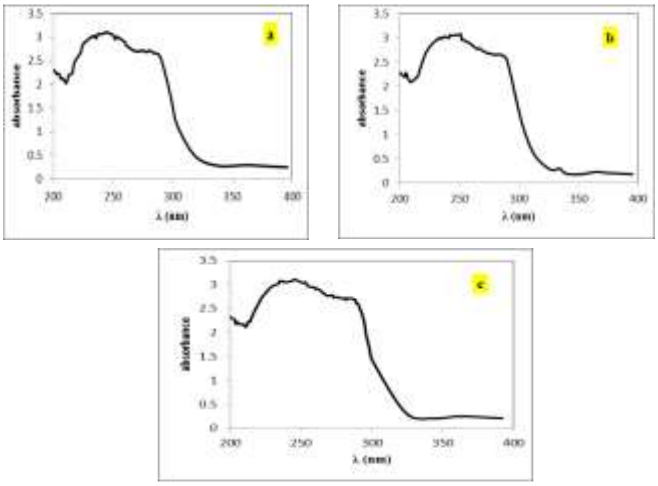

Figure (4) UV absorption spectrum of CNPs suspensions formed by liquid laser ablation of graphite target in Iso-propanol at 1064 nm, 80 mJ/pulse, and different laser pulse a) 25 pulse b) 75 Pulse c) 100 pulse.

The effects of no. of laser pulse on the peak intensities of polyyne at wavelengths are displayed in Figure (5), which reflects the concentration of (C_8H_2) in suspension. The absorbance of polyynes (more strictly, polyyne plus other carbon contaminants) increase with increased number of laser pulse but the absorbance was drastically reduced after 25 pulses and then increases. This peak shifts is due to the fact that strong scattering of light occurs when vapor nano-bubbles were formed at the time of leading edge of laser pulse and increase the concentration of CNPs. It is observed that the optical absorbance of polyynes (C_nH_2) at wavelengths increases slightly with increasing the number of laser pulse .this spectral change indicates that the abundance of CNPs is enhanced more under irradiation of laser.

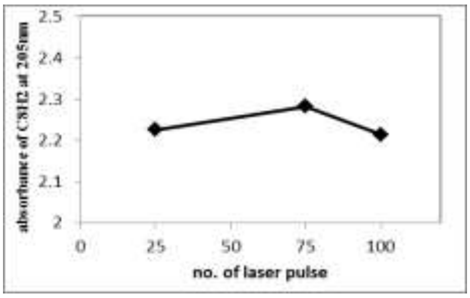

Figure (5) the effects of number of laser pulse on the peak Intensities of polyyne (C_8H_2) at wavelength 205 nm.

Figure (6) demonstrates the influence of the number of laser pulse on nanoparticle concentration generation by laser ablation of graphite target in Iso-propanol solution, using a 2 mm liquid layer, laser energy at 80 mJ and laser pulse at range from 25 to 100. It was clearly observed that the increase number of laser pulse between 25 and 100 Allows higher particle concentration because of the ablation rates is a constant. Increase productivity (concentration) of the Carbon nanoparticles in the case of laser ablation in a liquid is related to increased radiation absorbed by the material due to increased beam absorption in the pre machined spot area, where as in nanosecond ablation thermal effects play an important role. As expected, the material removal rate, thus nanoparticle productivity, strongly depends on number of laser pulse. When increase the number of pulses these lead to increase the overlapping between pulses when the target rotator during the process and then lead to increase in a local temperature. We assume that two effects tend to affect Nano particulate production efficiency in the case of increase number of laser pulse. First, in the high overlap between pulses, interaction of the laser beam with the previously ablated nanoparticles and the previously generated cavitation bubble could be the principal mechanism preventing the material from higher ablation. Referring to the literature, laser ablation in liquids generates a cavitation gas bubble [22-23] that lasts around 300 μs using Nd: YAG nanosecond laser irradiation of (36 J/cm^2) laser fluence. [24, 23] This cavitation bubble contains primary nanoparticles of extremely high local concentration that can scatter, reflect, or absorb the subsequent laser pulse.

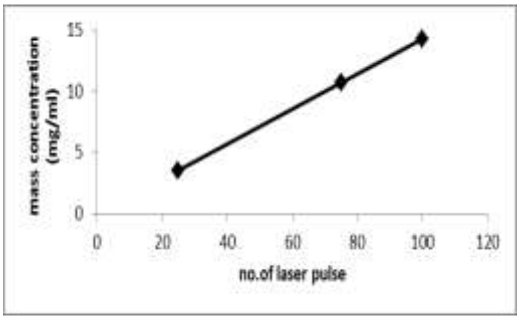

Figure (6) Carbon nanoparticles concentration as a function of the number of laser pulse.

Another parameter having an important effect on the formation of carbon nanoparticles is the laser energy Figure (7) shows UV-Visible absorption spectra of suspensions of CNPs prepared with different laser energy range from (20 ,80 and 200 mJ/pulse) with 25 laser pulse, these spectra commonly exhibit many sharp bands in the UV region. The observed bands coincide well with those of a series of hydrogen – capped polyynes. We conclude that the suspensions contain polyynes with n= 6, 8, 10, 11,12,13,14 and 16 [25]. As can be seen in Figure (7), we measure sensible increase in the absorption intensity, accompanied by a slight change in band width and maximum wavelength, when increasing in the laser energy. This enhancement in intensity can be explained by the increase in the concentration of carbon nanoparticles formed in solution during the ablation process. The height and width of the absorption spectra were found also to be dependent upon the laser energy.

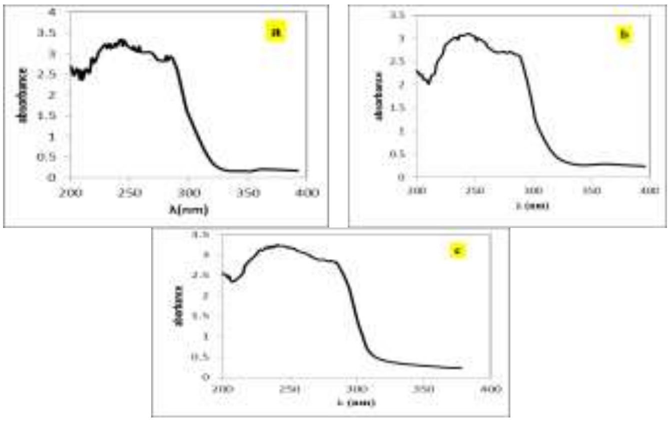

Figure (7) UV-Visible absorption spectrum of CNPs suspensions formed by liquid laser ablation of graphite target in Iso-propanol at 1064 nm, 25 laser pulse, and different laser energy a) 20 mJ b) 80 mJ c) 200 mJ.

The three sample spectrums show almost similar peaks, The peak at 235 nm belongs to C6H2; the peak at 205.0 nm represents C8H2; the peak at 237.6 nm represents C10H2; the peak at 233.0 nm represents C11H2; the peak at 275.0 nm represents C12H2; the peak at 245.0 nm represents C13H2; the peak at 253.0 nm represents to C14H2, the peak at 281.0 nm represents to C16H2, But each line has different absorbance value in each point of the wavelength. This indicates that the carbon nanoparticles produced have different size of distribution. The narrower the spectrum of peak indicates the more homogenous size distribution. If the height of the peak is calculated from the based line of spectrum, spectrum (80 and 200mJ) shows highest absorbance, which indicates the highest number of CNPs in solution. Spectrum (20 mJ) show lower absorbance most probably that is because the spectrum has more number of big particles in the solution that reflect much more light than the spectrum (80 and 200 mJ).

The effects of laser energy on the peak intensities of polyynes at wavelengths are displayed in Figure (8), which reflects the concentration of (C_8H_2) in suspension. The absorbance of polyynes (more strictly, polyyne plus other carbon contaminants) increase with increase laser energy .illustrates the relative concentration of polyynes (2), (C_8H_2), which were estimated from the absorbance data at wavelengths, as a function of laser energy. At first glance, polyynes show turned in this absorption intensity as laser energy increases. Nerveless, the slight difference in the slop may possibly imply that polyynes are preferably produced at higher laser energies, this in line with the result of Figure (7) ,which shows the effect of laser energy on growth of large polyynes.

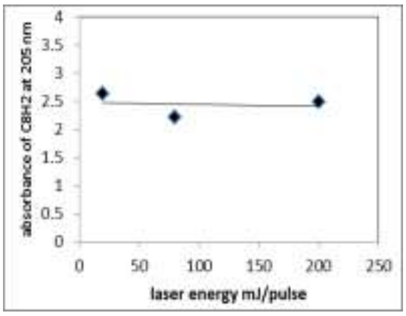

Figure (8) The effects of laser energy on the peak intensities of polyyne (C_8H_2) at wavelengths 205 nm..

Figure (9) demonstrates the influence of the laser pulse energy on nanoparticle concentration generation by laser ablation of graphite target in Iso-propanol solution, using a 2 mm liquid layer, laser energy at range from (20, 80 and 200 mJ) with 25 laser pulse. In the range 20-200 mJ nanoparticle concentration increased almost linearly with pulse energy.

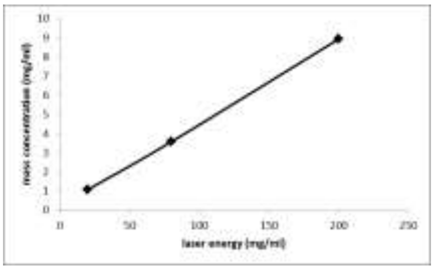

Figure (9) Carbon nanoparticles concentration as a function of the applied laser pulse energy.

A typical TEM image of the carbon nanoparticles is presented in Fig. 10. The nanoparticles where strongly aggregated due to a small electrostatic repulsive force between them, since the absolute value of the potential was small. The size of the nanoparticles ranges from 1.7 to 25 nm in Figure (10 a, c) with few individual nanoparticles larger than 41.6 nm found in the Figure (10 a). It is suggested that the liquid environment favored growth of the carbon nanoparticles during laser ablation [26]. The plasma species produced during laser ablation are quenched by heated vapor under very high pressures. The kinetic energy of carbon atoms is reduced by multiple collisions with the surrounding molecules and atoms through expansion. The liquid media induce quick nucleation followed by rapid growth of the nanoparticles.

The laser energy is a very important parameter influencing the synthesis of high-quality CNTs. Serial laser energy was tried to ablate the graphite target in the experiment. It is found that CNTs were acquired when the laser energy was in 200mJ/pulse and few CNTs were obtained outside this range. Transmission electron microscopy (TEM) characterization of the sample Figure (11) show most of the obtained CNTs are not very straight (spiral helicine) with 30.76–46.15 nm in diameter and a 592.3 nm in length in Figure (11 a), Some carbon nanoparticles with spherical geometry (indicated by solid arrows) are contained in the middle of these spiral helicine CNTs. while in Figure (11 B) represent a few nanotubes can be observed formed on the same sample with diameters 11.1 nm and a 261.1 nm in length. These results agree with Chen [27].

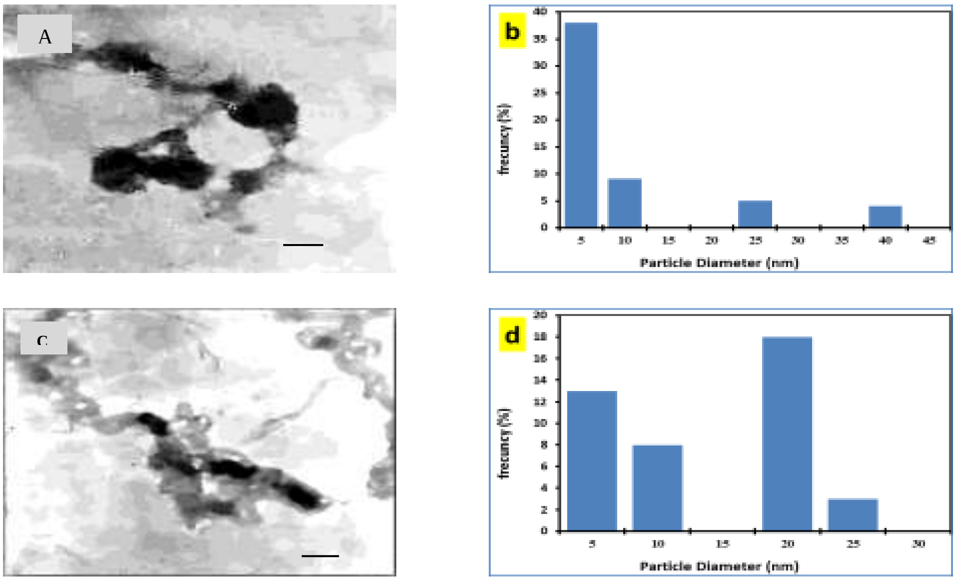

Figure (10) A, C) TEM image shows the morphology of CNPs (Aggregation of carbon nanoparticles and elongated particle like double walled nanotubes can be observed) suspend in Iso-propanol at laser irradiation with 25 pulses and energy of 80mJ/pulse b, d) the size distribution of CNPs.

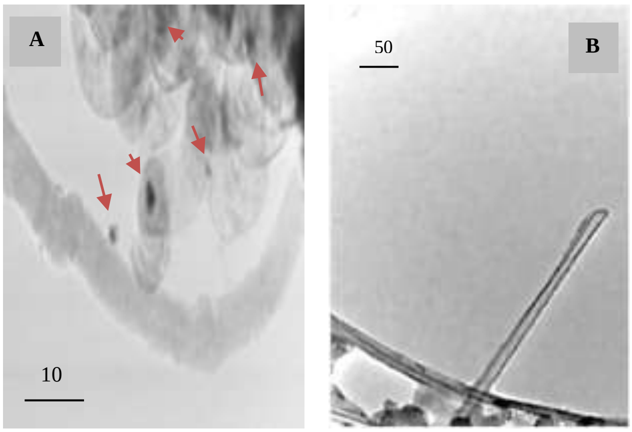

Figure (11) TEM image of CNTs prepared by pulsed-laser ablation of graphite target at solid–liquid interface (Iso- propanol) at laser irradiation

with 25 pulses and energy of 200mJ/pulse. (A) Spiral helicine CNTs (B) straight CNTs.

CONCLUSIONS

CNTs were synthesize at solid–liquid interface by pulsed laser ablation of graphite target in pure Iso-propanol was developed. This method not only synthesizes the CNTs under the normal temperature and pressure but also realizes the modification of the CNTs at the same time. It provides a novel approach to synthesize the CNTs and has a vast research prospect. And formation of linear-chain polyynes (C_nH_2: n = 6-16) has been observed ensures a very simple and effective method to produce polyynes in solution and the polyyne insert CNTs. The results of FTIR absorption peak which referred to formation carbon nanoparticles suspend in this solvent. UV absorption peaks coincide with the electronic transitions corresponding to linear-chain polyynes the peak intensities increased when polyynes were produced different laser energy and the formation rats of polyynes increased with increased number of laser pulse. We have shown that the irradiation at 80 mJ and 25 laser pulse lead to formation of CNPs with nanoparticles ranging from 1.7 to 41.6 nm and we have shown that the irradiation at 200 mJ and 25 laser pulse lead to formation of CNTs with diameter at range 11.1 – 46.15 nm and length at range 261.1 - 592.3 nm were observed by TEM.

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