Synthesis of polyynes by laser ablation of graphite in ethanol

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Abstract

In this work Polyynes was synthesized by pulse laser ablation of graphite target in ethanol solution. UV-Visible Spectrophotometer, Fourier Transform Infrared Spectroscopy (FTIR) and Transmission electron microscopy (TEM) were used to study the optical absorption, chemical bonding, particle size and the morphology. UV absorption peaks coincide with the electronic transitions corresponding to linear hydrogen – capped polyyne ($C_{n+1}H_2$), the absorption peaks intensity increased when the polyynes were produced at different laser energies and the formation rats of polyynes increased with the increasing of laser pulse number. The FTIR absorption peak at 2368.4 $cm^{-1,}$ 1640.0 cm^{-1} and 1276.8 cm^{-1} stretching vibration bond, were refer to the C ≡ C, C = C and C-C, respectively. A bond suggests the formation carbon nanoparticles suspend in this solvent and the TEM show the formation of spherical nanoparticles with size ranges from (1.2 to 105.9 nm) and aggregation of the carbon nanoparticles.

Key words
carbon nanoparticles,
polyynes,
optical properties of CNP.

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انتاج البولين بواسطة الأستئصال بالليزر للكرافيت في الايثانول

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الخلاصة

تم انتاج Polyynes بواسطة الاستئصال بالليزر للكرافيت في سائل الايثانول. استخدم مطياف طيف مرئي – فوق البنفسجية UV و مطياف تحويل فوريبه لآشعة تحت الحمراء(FTIR) و المجهر الالكتروني النافذ (TEM) لدراسة الامتصاص البصري و الاواصر الكيميائية وحجم الجسيمات وطبيعة السطح. تمثل قمم امتصاص الاشعة فوق البنفسجية والمتزامنة مع الانتقالات الالكترونية للهيدروجين الخطية – وتوج Polyyne ($C_{n+1}H_2$) تزداد شدة القمم للبولين المتولد بأختلاف طاقات الليزر و يزدادمعدل تشكيل البولين بزيادةعدد نبضات الليزر. قمم امتصاصFTIR عند 2368.4 cm^{-1} و 1640.0 cm^{-1} و 1276.8 cm^{-1} الأهتزازية تدل على وجود C≡C و C=C و C-C على التوالي. شكلت الاواصر جسيمات الكاربون النانوية العالقة في المحلول ، يظهر المجهر الالكتروني تشكيل جسيمات كروية يتراوح حجمها من 1.2 – 105.9 وتكتل جسيمات الكاربون النانوية.

Introduction

Increasing interest has been found in the formation mechanism of sp-hybridized linear carbon chain molecules under laser ablation of carbon species [1]. Laser ablation of a solid graphite target has been a topic of utmost research interest since the advent of lasers in 1960s [2]. Carbon clusters of various sizes were formed simply by irradiating Graphite surface in vacuum or gas-phase and remained highly stable due to their high binding energies [3]. Accordingly, laser ablation of graphite has been widely employed as an effective tool for the synthesis of carbon clusters and it has ultimately brought about the discovery of fullerenes C60.

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 $H(-C\equiv C-)_m H$, with (integer m), have attracted considerable interest in astrophysics and nanoscience [4]. These compounds have been detected in interstellar materials [4], and are important precursor molecular components in the formation of fullerenes and carbon nanotubes [5]. Including nano-wires with controllable conductivity [6]. They have been investigated as prototypes of carbyne, a novel sp-bonded allotrope of carbon [7]. Recently, hybrid Nano-materials have been developed in which polyynes have been inserted into single wall carbon nanotubes [8]' 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 [9], and their one-dimensional electronic structures have attracted considerable attention due to its size-dependent band gap [10], and nonlinear optical properties [11]. In addition, the nanostructured carbons are also supported to be utilized for a variety of applications, such as catalysis supports [12], and oil adsorbents[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 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. Tsuji et al. reported on the synthesis of polyynes (C_8H_2, $C_{10}H_2$, $C_{12}H_2$, and $C_{14}H_2$) by the ablation of graphite in hexane, and those ($C_{10}H_2$, $C_{12}H_2$, $C_{14}H_2$, and $C_{16}H_2$) by the same method in benzene and toluene [16]. Moreover, they reported on the synthesis of polyynes up to C = 12 ($C_{12}H_2$) by the ablation of fullerene in hexane [17]. Besides the organic solvents, Giuseppe et al. reported on the synthesis of polyynes by the ablation in pure water [18].

The purpose of the present study is to clarify how long chain carbines are produced in the liquid phase by laser ablation of graphite in ethanol solution at 1064 nm and study the effect of laser energy and no. of lase pulse on polyyne production by using UV-Vis spectroscopy, FTIR spectroscopy, respectively and structure properties by using TEM.

Experimental part

In this work, polyynes 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 ethanol. Both the target and Petri dish were rinsed with ethanol cleaner prior to preparation (Fig.1). The target was immersed in ethanol solution to a depth of around 2 mm below the ethanol'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 ethanol and minimize the target aging effect and to give some stirring effect.

The graphite target was irradiated vertically by an Nd: YAG laser (HUAFEI, λ=1064 nm, 1HZ). 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 (200-1000 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.

Results and Discussion

Fig.2 shows the FTIR spectrum of carbon nanoparticles suspensions prepared by laser ablation of graphite target in ethanol at laser energy (20, 80 and 200 mJ/pulse) with 25 laser pulse. It is notice that, the bond between (3000 to 3500 cm^{-1}) is due to the O – H stretching vibration.

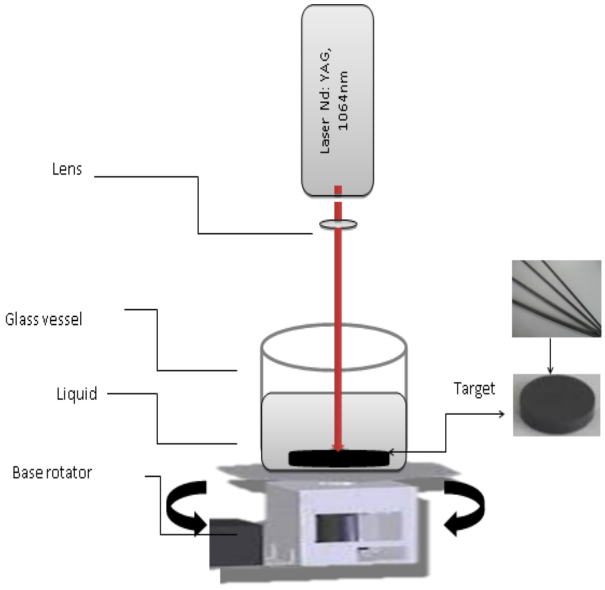

Fig.1: Experimental setup for carbon nanoparticles synthesis.

The 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}, and symmetric C – H stretching occurs at 2974.0 cm^{-1} [19]. A peak at 2368.4 cm^{-1} is due to the C ≡ C stretching vibration bond, while C = C stretching vibration bond appear at ~ 1640.0 cm^{-1}, suggests the formation carbon nanoparticles suspend in this solvent [20]. the peak between (1250 – 1500 cm^{-1}) is due to the symmetrical C – H stretching bonded also appear around the 881.4 cm^{-1}, a peak at ~ 1049.2 cm^{-1} is due to the C – O stretching bonds and peak around 1276.8 cm^{-1} is due to the C-C stretching vibration bond.

According to the results of Fig.2, the relative intensity of FTIR absorption peak is change with change laser energy while the positions and the width of the 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 the formation carbon nanoparticles suspend in this solvent.

Fig.3 shows the FTIR spectra of carbon nanoparticles suspension preparation at laser energy (80 mJ) with different laser pulse (25 & 100). This shows the same vibration bonded of C≡C and C=C stretching vibration, but the peak absorption of carbon suspension prepared at 100 laser pulse higher than peak absorption at 25 pulses, due to increase in the carbon nanoparticles concentration.

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 of the number of laser pulse on the formation of carbon nanoparticles is very important. Fig.4 shows the UV-Visible absorption spectra of suspensions of CNPs prepared by laser ablation of a graphite target in ethanol solution at different laser pulse at range from (25 to 100pulse) and 80 mJ. These spectra commonly exhibit many bands in the UV region [21, 22], show in Table 1, 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 [23].

The effects of number laser pulses on all the peak intensities of polyynes at wavelengths is displayed in Fig.5, which reflects the concentration of (C_8H_2) in suspension. The absorbance of polyynes increases with increased number of laser pulse but it was reduced after 75 pulses. Results of scattering light due to the increased concentration of CNPs.

Fig.6 demonstrates the influence of the number of laser pulse on nanoparticle concentration generation by laser ablation of graphite target in ethanol 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 the number of laser pulse. When the number of pulse was increased the overlapping between pulses was increased and leads 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 [27-28] that lasts around 300 μs using Nd: YAG nanosecond laser irradiation of 36 J/cm^2 laser fluence [29, 28]. This cavitation bubble contains primary nanoparticles of extremely high local concentration that can scatter, reflect, or absorb the subsequent laser pulse.

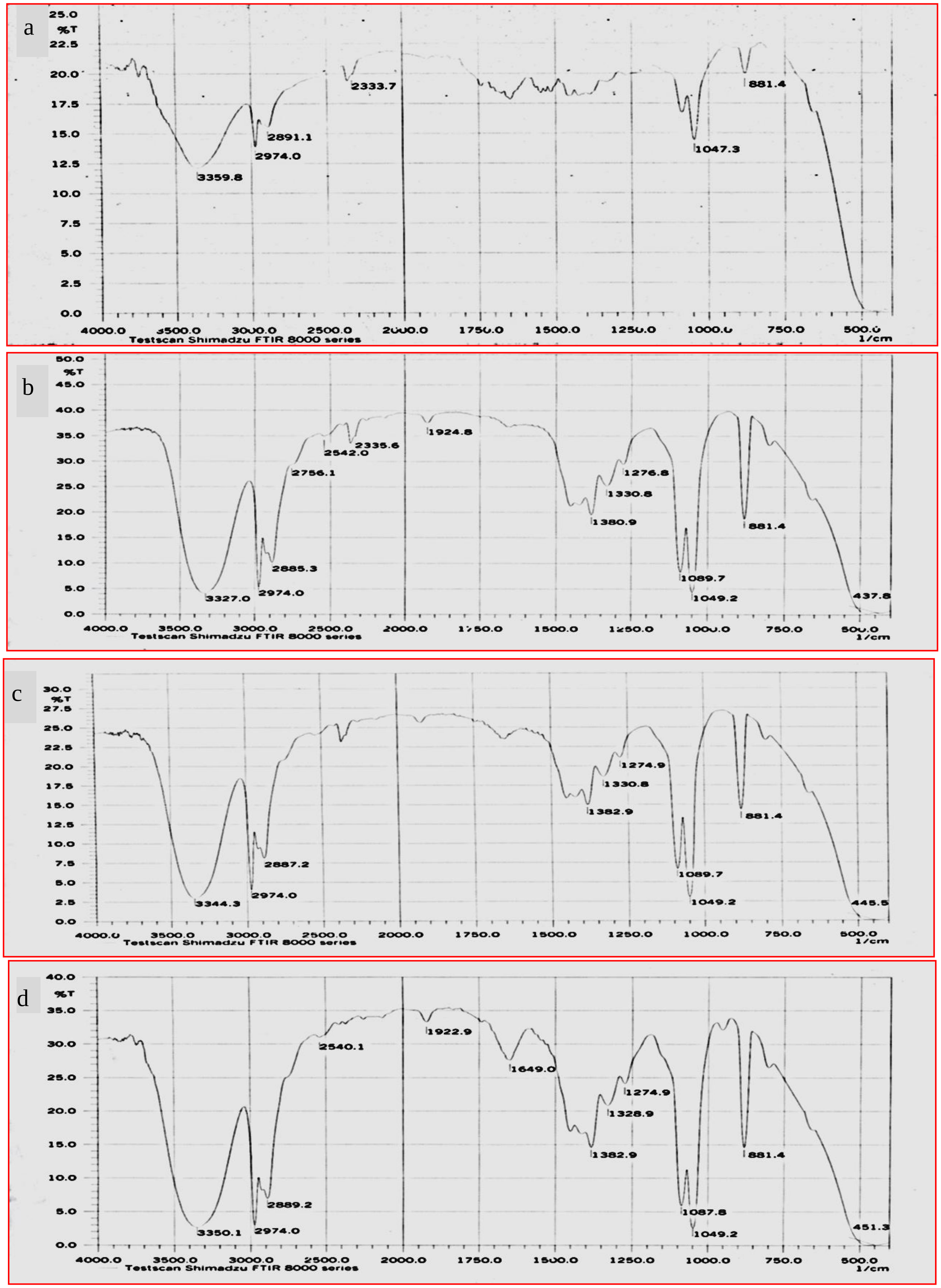

Fig.2: FTIR spectrum of CNPs suspensions produced at different laser energy a) ethanol solvent b) CNPs at 20 mJ c) CNPs at 80 mJ d) CNPs at 200 mJ.

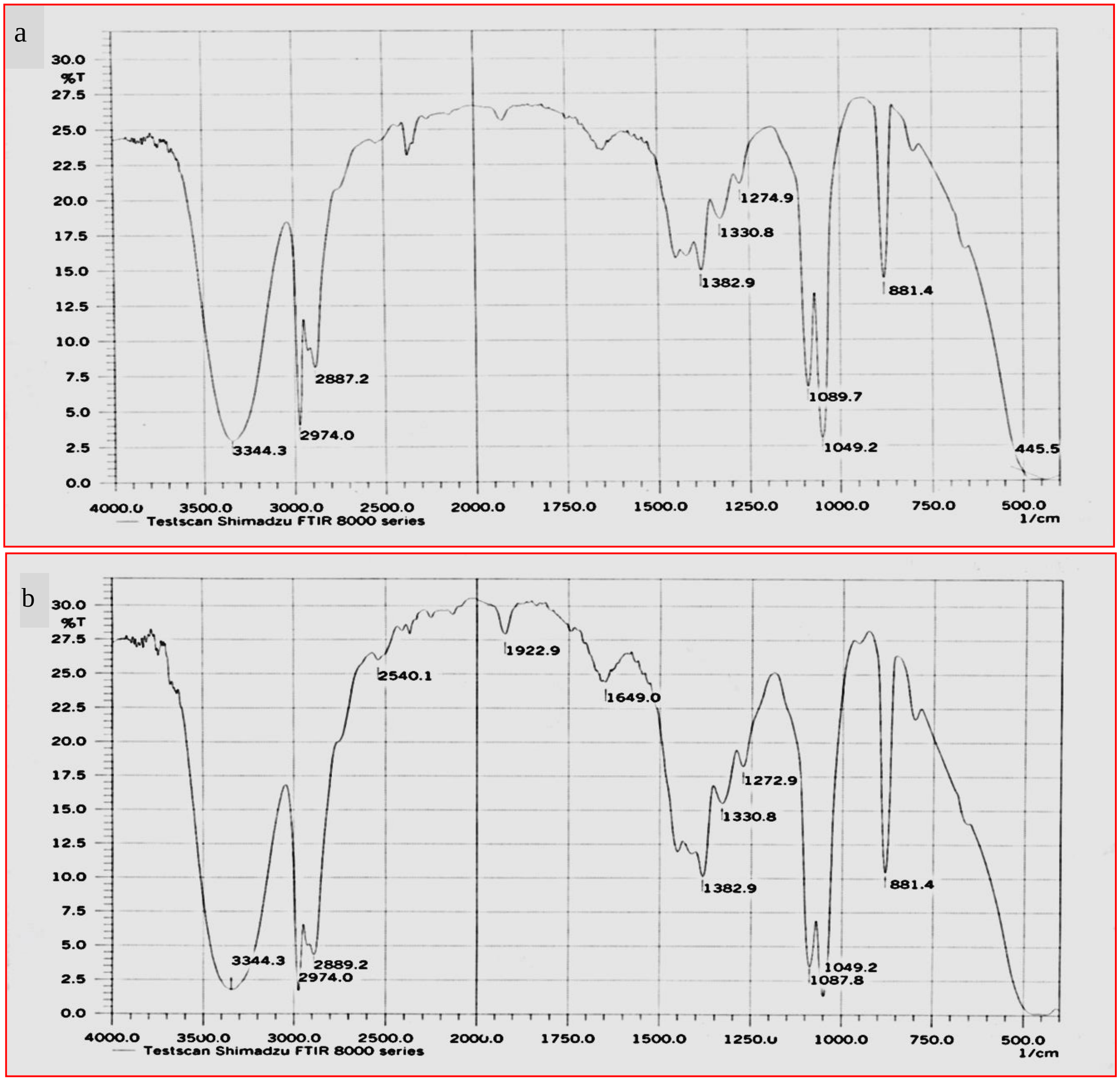

Fig.3: FTIR spectrum of CNPs suspensions at different laser pulse a) 25 pulse/80mJ b) 100 pulse/80mJ.

Table1: The polyynes at ethanol suspension prepared at different laser pulse and different laser energy.

Polyynes	Peak at wavelength (nm)
C_6H_2	228.0
C_8H_2	205.0
$C_{10}H_2$	237.6
$C_{11}H_2$	233.0
$C_{12}H_2$	275.0
$C_{13}H_2$	261.0
$C_{14}H_2$, $C_{16}H_2$	281.0
$C_{18}H_2$	287.0

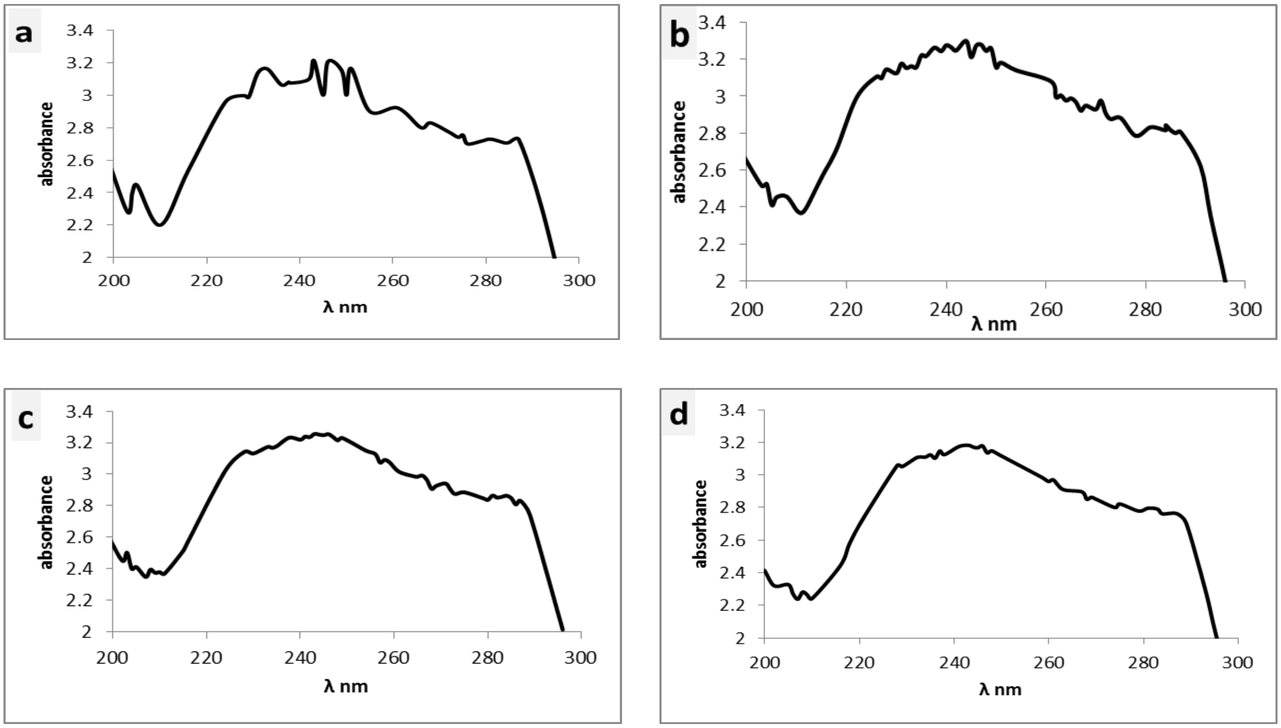

Fig.4: UV absorption spectrum of CNPs suspensions in ethanol at different laser pulse a) 25 pulse b) 50 pulse C) 75 Pulse d) 100 pulse.

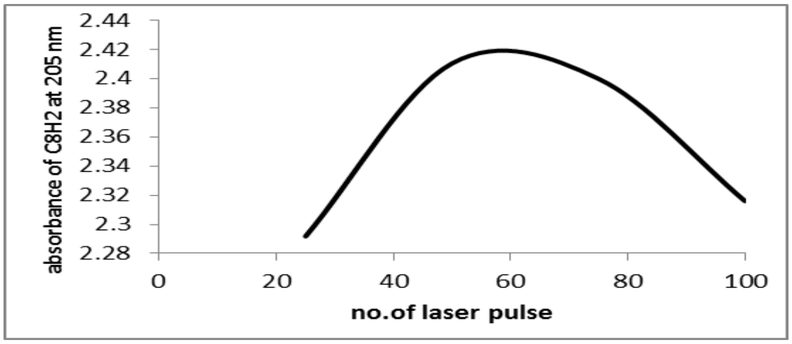

Fig.5: The effects of number of laser pulse on the peak intensities of polyynes (C_8H_2) at 205 nm wavelengths.

Fig.7 shows UV-Visible absorption spectra of suspensions of CNPs prepared at different laser energy range from (20, 80 and 200 mJ/pulse) with 25 laser pulse, these spectra commonly exhibit many 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, 12,13,14,16 and 18 [22], see Fig.4. 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. The all sample spectra show almost similar peaks, shows in Table1, 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, spectrums (80 and 200 mJ) show highest absorbance, which indicates the highest number 0f CNPs in solution. Spectrum (20mJ) 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).

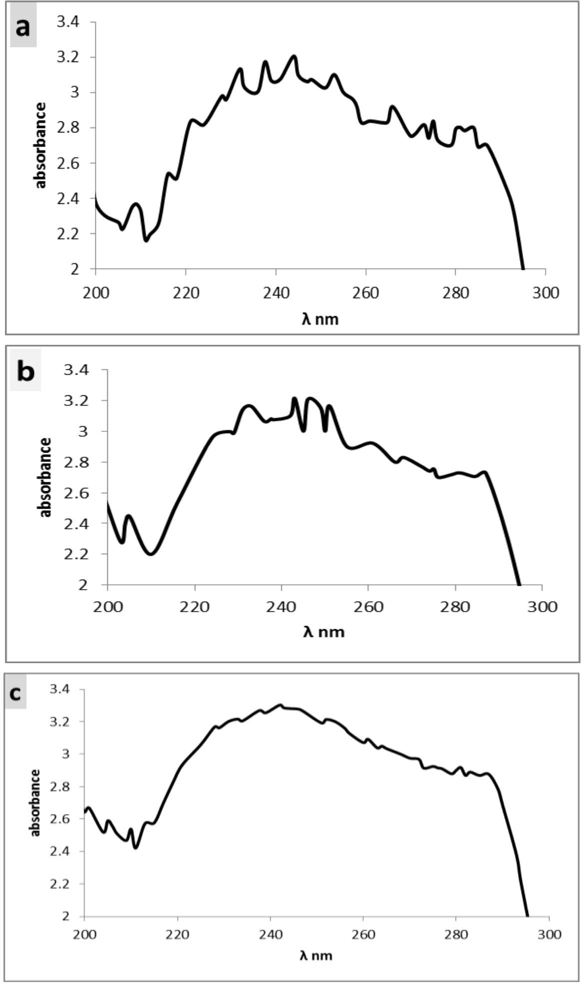

Fig.7: UV-Visible absorption spectrum of CNPs suspensions at different laser energy a) 20 mJ b) 80mJ C) 200mJ.

The effects of laser energy on all the peak intensities of polyynes at wavelengths are displayed in Fig.8, which reflects the concentration of (C_8H_2) in suspension. The absorbance of polyynes increase with increase laser energy .illustrates the relative concentration of polyynes (■), ($C_{n+1}H_2$), 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 Fig.7 which shows the effect of laser energy on growth of large polyynes.

Fig.9 demonstrates the influence of the laser pulse energy on nanoparticle concentration. In the range 20-200 mJ nanoparticle concentration increased almost linearly with pulse energy.

Fig.10a shows TEM image of the carbon nanoparticles. 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 1.2 to 70.5 nm with few individual nanoparticles larger than 70.5 nm found in the image shown in Fig.10b it is suggested that the liquid environment favored growth of the carbon nanoparticles during laser ablation [24]. 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. These results agree with Chen[25].

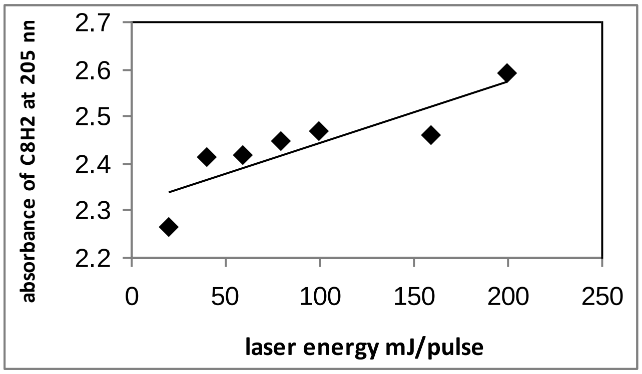

Fig.8: The effects of laser energy on the peak intensities of polyynes (C_8H_2) at 205 nm wavelengths.

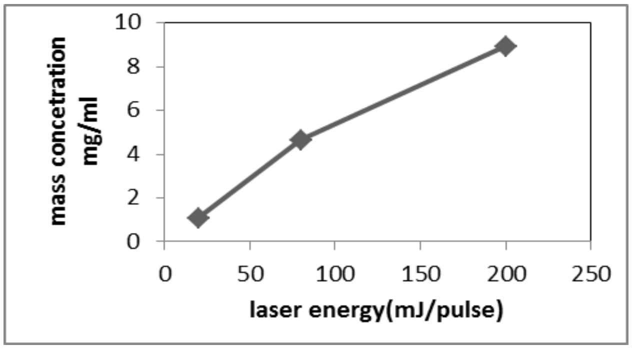

Fig.9: Carbon nanoparticles concentration as a function of the applied laser pulse energy

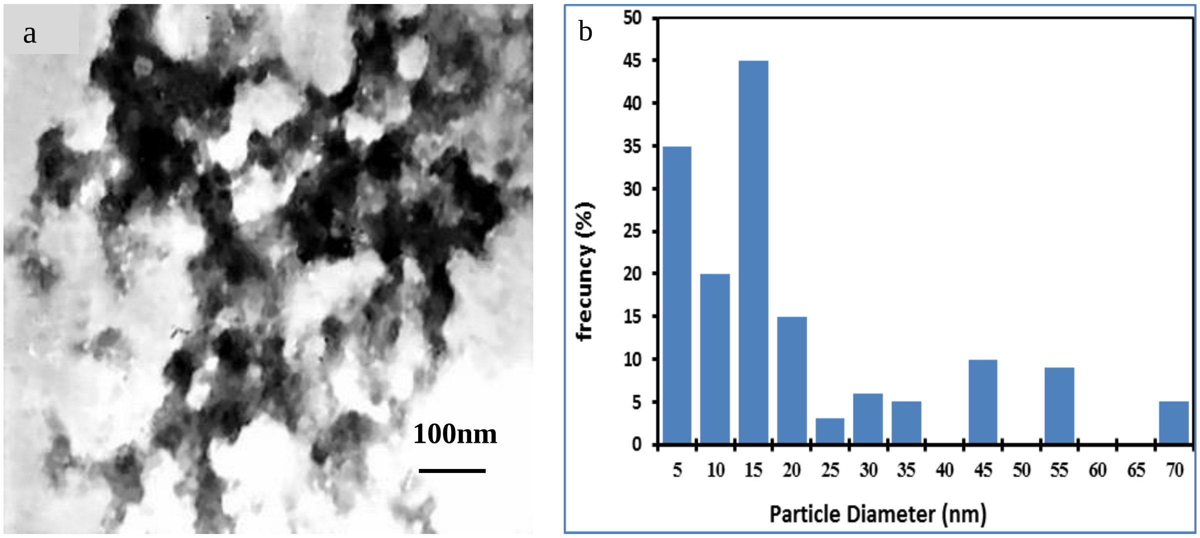

Fig.(10 a): TEM image of carbon nanoparticles obtained by laser ablation of graphite target at 80 mJ/pulse and 25 laser pulse in ethanol, b) The size distribution of CNPs.

Fig.11 displays atypical TEM image of a group of carbon spheres. The carbon spheres produced in the experiments, with range from 35 to 105.9 nm, much smaller than those observed elsewhere [26]. Thus, the particles are sure to have perfect sphere morphology, and other shape can be excluded and Low magnification TEM image of carbon sphere (upper left) at sized 117.6 nm

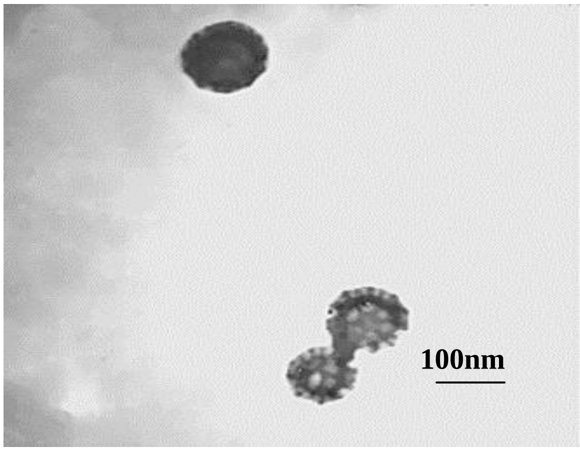

Fig.11: A typical TEM image showing a group of nano-sized carbon particles with prefect spherical geometry.

Conclusions

LP-PLA is a very simple and effective method to produce polyynes in solution. 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. CNPs have spherical geometry with ranging from 1.2 to 105.9 nm were observed by TEM.

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