Spectroscopy and Formation of Carbon Nitride by Pulse Laser Ablation in Liquid of Graphite target

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ABSTRACT:

In this work carbon nitride was synthesized by pulsed laser ablation of graphite in ammonium solution. Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectrophotometer and Transmission Electron Microscopy (TEM) were used to study the bonding, absorption, size and morphology of the carbon nitride nanoparticles. The FTIR absorption peak at 2121.6, 1631.7, 1384 cm^{-1} stretching vibration bond, it is inferred that the C ≡ N, C = N and C-N, respectively. Bonds suggested the formation carbon nitride nanoparticles. UV absorption peaks coincide with the electronic transitions corresponding to formation carbon nitride C_3N_4 and monocyanopolyynes. The TEM image showed the aggregation of the carbon nitride nanoparticles with size ranges from (4 to 83.3 nm); the Leaf- like structure is shown in the structure of carbon nitride suspension.

Keywords: carbon nitride, laser ablation in liquid, nanostructure.

مطيافية و انتاج كاربون نترايد C_3N_4 بواسطة الأستئصال بالليزر النبضي لهدف الكرافيت في محلول الامونيوم

الخلاصة:

في هذا البحث تم تحضير كاربون نترايد بواسطة الاستئصال بالليزر النبضي للكرافيت المغمور بمحلول الامونيوم . تم استخدام الاشعة الحمراء و مطياف الاشعة الفوق البنفسجية –المرئية و المجهر الالكتروني النافذ لدراسة الاواصر و الامتصاص و الحجم والطوبوغرافية لجسيمات الكاربون نترايد النانوية. قمم الامتصاص للاشعة تحت الحمراء عند 2121.6 ، 1631.7 و 1384 سم $^{-1}$ للاواصر C≡N ، C=N، C-N على التوالي . تدل هذه الاواصر على تشكل جسيمات الكاربون نترايد النانوية. تشير قمم امتصاص الاشعة فوق البنفسجية الى وجود سلاسل الكاربون النانوية monocyanopolyynes وكاربون نترايد . يظهر المجهر الالكتروني النافذ التكتل الحاصل لجسيمات الكاربون نترايد النانوية مع مديات الحجوم تتراوح مابين (4- 83.3 نانوميتر) و نشاهد تركيب شبه ليفي لعالق الكاربون نترايد.

INTRODUCTION:

Into the forecast by Liu and Cohen in 1989 of carbon nitride solid, intensive worldwide experimental and theoretical analysis efforts is created to synthesize such material. According to unpractical predictions [1–3], C_3N_4 will adopt many various crystalline structures, like α-C_3N_4, β-C_3N_4, *g*-C_3N_4 , *p*-C_3N_4 and *c*-C_3N_4. The β-C_3N_4, relies on the structure of β-Si_3N_4, with C substituted for Si. β-C_3N_4 which more expected to obtain a good band gap

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and high thermal conduction, therefore they have potential applications as an electron emitter, variable semiconductor and as a transparent hard coating [4].

Monocyanopolyynes, H-(C ≡ C) $_n$ - N, where (*n*= 1, 2, 3...), a member of polyyne cluster was detected in the interstellar space since 1970s [5, 6]. Which are formed through rapid solidification of liquid carbon, close to the surface of the coagulated droplets formed upon solidification within the solid type, Monocyanopolyynes have a hardness intermediate between diamond and graphite [7].

Nano scale growth of carbon nitride particles was prepared by using liquid phase pulsed laser ablation (LP-PLA). This method involves focusing a laser beam onto the target that is submerged in a liquid [8]. The species inside the plume collide and react with molecules of the encompassing liquid, manufacturing new compounds containing atoms from every the initial target and additionally the liquid. This technique has some benefits, the cost is relatively low, as a result of expensive instruments like vacuum equipment are unnecessary, also it could be a very unique approach for the nanostructure formation of refractory materials [9-11].

The Purpose is the use of a unique technique to prepare carbon nitride below traditional temperature and pressure by pulsed laser ablation of a graphite target in ammonia solution. Studying the impact of laser flunce and a number of laser pulses on the characterization the particle size was investigated, the Structure and morphology of carbon nitride production were examined by using FTIR Spectroscopy, UV-Vis photometer, and TEM.

Experimental

Carbon nitride and monocyanopolyynes 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 closed stainless steel cell filled with 5 ml of NH_4OH. Both the target and cell were rinsed with ethanol cleaner prior to preparation. The target was immersed in NH_4OH solution to a depth of around 2 mm below the hydroxide ammonium's surface. The target was rotated during laser ablation for ensuring that the nanoparticles formed dispersed uniformly into the ammonia and also minimize the target aging effect. The graphite target was irradiated by an Nd: YAG laser (HUAFEI, λ=1064nm (fundamental), beam diameter = 4.38 mm, 1HZ, pulse duration = 9 ns). The laser flunce used in this experiment at range from (3.32, 13.28 and 33.2 J/cm^2), and the laser pulse ranged from (25-100). This focused by using a lens with focal length of 12 mm. The optical properties of the monocyanopolyynes suspension were examined 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) 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.

Result and Discussion

Figure (1) shows the FTIR spectrum of carbon nitride nanoparticles suspensions prepared by laser ablation of graphite target in hydroxide ammonium at laser flunce (3.32, 13.28 and 33.2 J/cm^2) with 25 laser pulses. From all figures , notice that the bond for all suspensions the symmetrical C – H stretching bonded appeared around the 962.4 cm^{-1} and 929.6 cm^{-1} ,while the peak at ~ 1034 cm^{-1}, 1044 cm^{-1}, 1050 cm^{-1} is due to the C – O stretching bonds, while the peaks at 1002.9 cm^{-1} , 1114.8 cm^{-1} , 1112.9 cm^{-1} and 1384 cm^{-1} correspond to C-N stretching mode. The absorption bounds at 1637.5 cm^{-1}, 1641 cm^{-1} and 1631.7 cm^{-1} is assigned to the stretching vibration mode of C=N. more over a small but clear peak at 2102.3 cm^{-1}, 2098.4 cm^{-1}, 2104.2 cm^{-1} and 2121.6 cm^{-1} can probably be attributed to C≡N bonds, suggested the formation carbon nitrate nanoparticles suspend in this solvent, Although it is much weaker compared with the other stretching modes. Abroad band centered at 3423 cm^{-1} is due to NH group vibrations. According to the results, the intensity of FTIR absorption peak is changed with varying 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 ≡ N and C = N bonds were formed by laser ablation of graphite in ammonia which referred to formation carbon nanoparticles suspend in this solvent, which suggests the formation of crystalline C_3N_4 and monocyanopolyynes. These result was agree with Yang *et al* [12] and sivkov *et al* [13].

Figure (2) shows the FTIR spectra of carbon nitrate nanoparticles suspension preparation at laser energy (80 mJ) with different laser pulse (25 – 100). Also the same vibration bonded of C≡N and C=N stretching vibration, while the peak absorption of carbon nitrate suspension prepared for 100 laser pulse higher than peak absorption at 25 pulses. This is due to increase carbon nitrate nanoparticles concentration, which caused scattering of laser light and reduced the absorption of solution and increased the transmission spectrum.

The effect the number of laser pulse on the formation of carbon nitrate nanoparticles is very important, figure (3) shows UV-Visible absorption spectra of suspensions of CNPS prepared by laser ablation of a graphite target in hydroxide ammonium solution at different laser pulse at range from (25 to 100 pulse) with 80 mJ. These spectra commonly exhibited many sharp bands in the UV region. Hence, The four sample spectrums showed almost similar peaks, the peak at 269.0 nm, 264.0 nm , 266.0 nm and 250.0 nm represent to C_3N_4, It is known that the g- and α-C_3N_4 phases both contain aromatic 1,3,5-triazine rings, which exhibit absorption around 250 nm due to a π-π* electronic transition [14]. Hence, the experimental 266 nm absorption peak could indicate the presence of one or more of these phases of C_3N_4 within the ablated material. Interestingly, this peak is red-shifted with increasing nanocrystals size [15].

While, the four sample spectrums exhibit almost similar peaks for monocyanopolyynes, shown in Table (1) [16-18], these peak represent to formation monocyanopolyynes in suspensions. The absorption behavior as a function of carbon nitride and monocyanopolyynes length is obtained by semi-empirical calculations of the electronic absorption of monocyanopolyynes [14, 19].

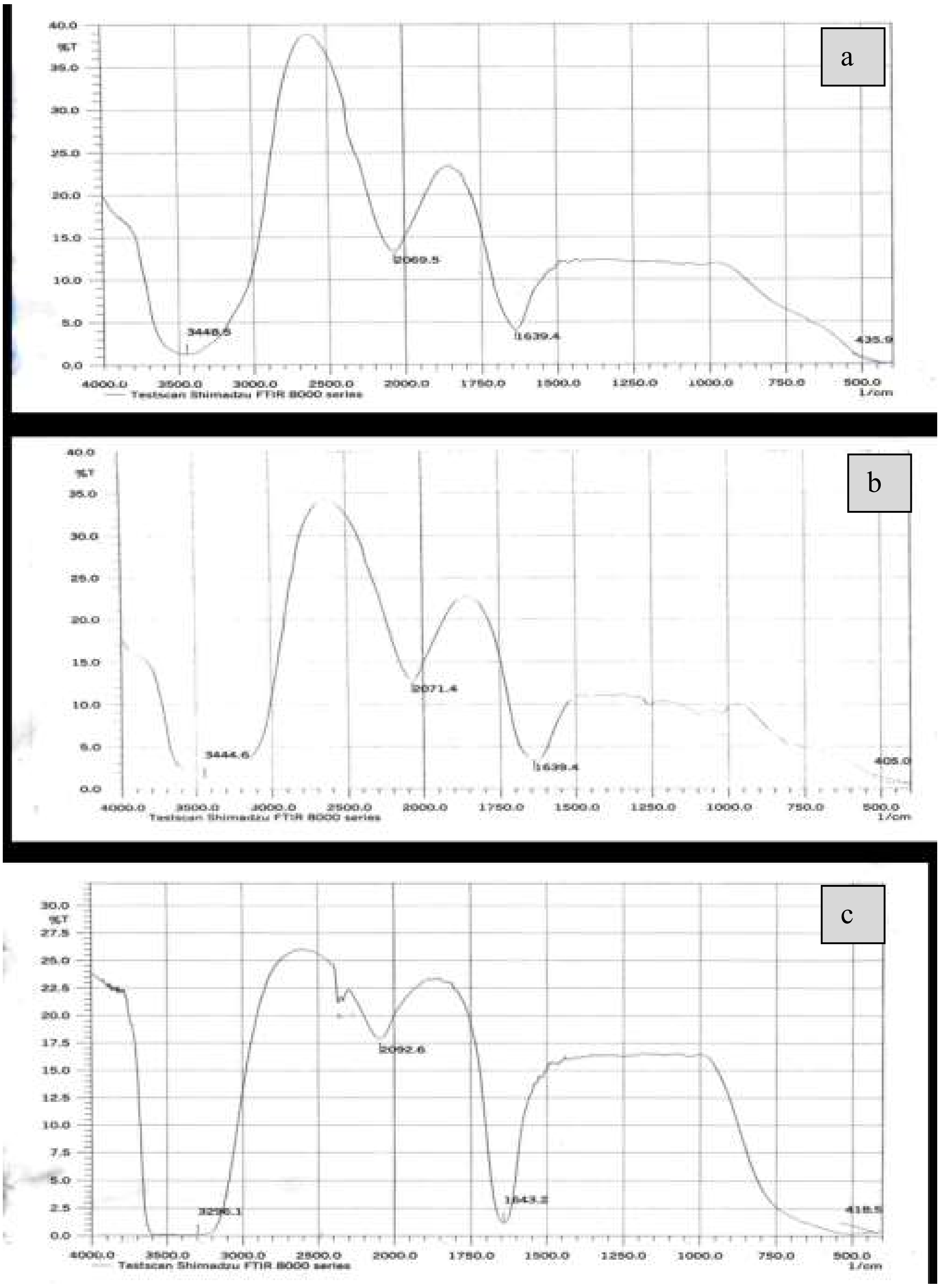


Figure (1) FTIR spectrum of CN NPs suspensions in hydroxide ammonium at different laser flunce a) 3.32 J/cm^2 b) 13.28 J/cm^2 c) 33.2 J/cm^2

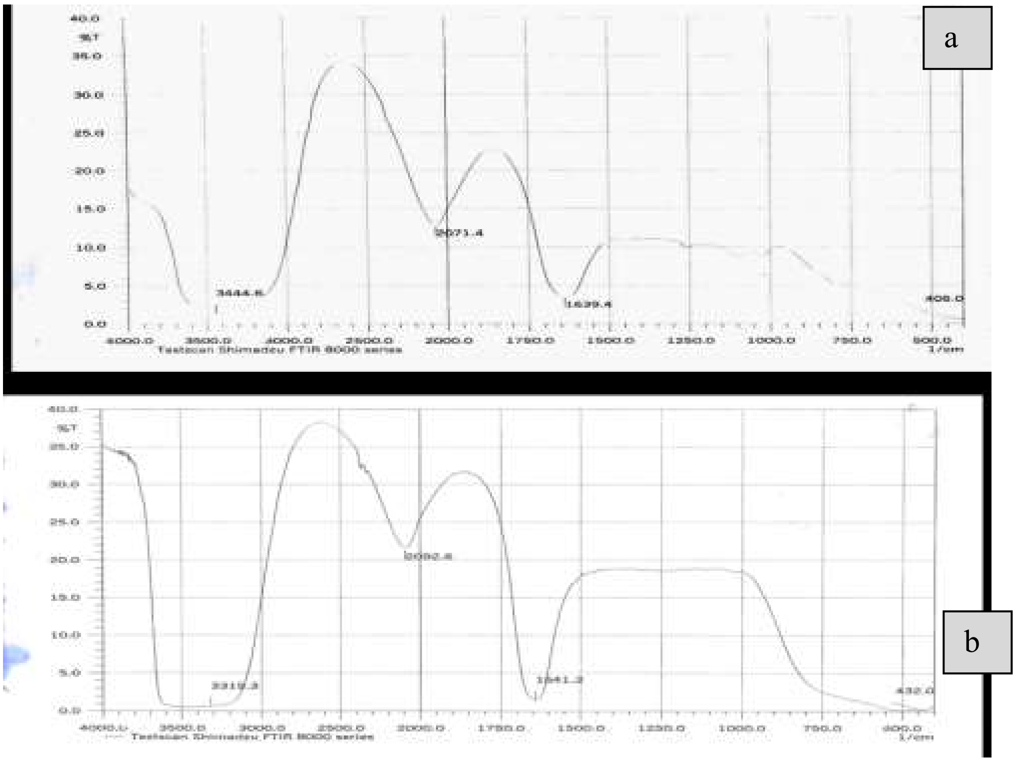


Figure (2) FTIR spectrum of CN NPs suspensions in hydroxide ammonium at different laser pulse a) 25 b) 100.

Table(1): The monocyanopolyyne at ammonia suspension prepared at different laser pulse and different laser flunce.

monocyanopolyynes	Peak at wavelength (nm)
HC_4N	215
HC_6N	208
HC_8N	205
$HC_{10}N$	237.6
$HC_{11}N$	243
$HC_{12}N$	275
$HC_{13}N$	261
$HC_{14}N$	266
$HC_{15}N$	254
$HC_{16}N$	281
$HC_{18}N$	287
$HC_{20}N$	294

The effects of number of laser pulse on the peak intensities of carbon nitride at wavelengths 266nm and monocyanopolyynes at wavelengths 205nm were displayed in figure (4) and (5) respectively. The absorbance of C_3N_4 and HC8N increased with increasing number of laser pulse due to increase the concentration of carbon nitride.

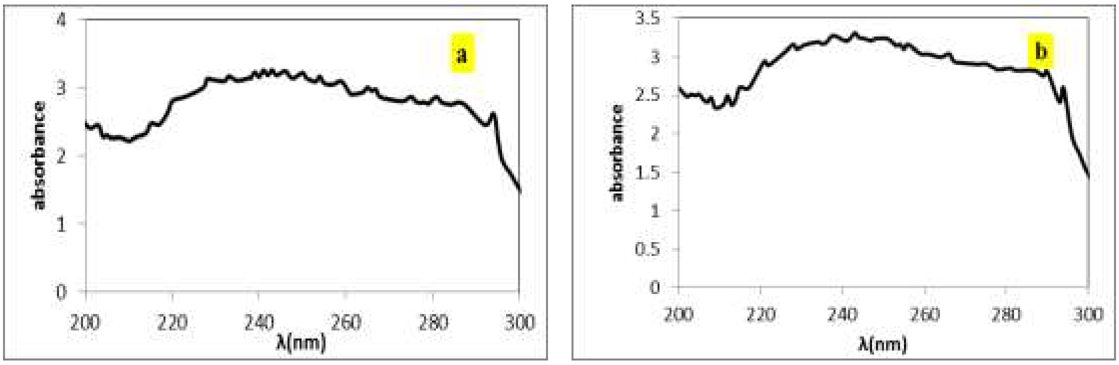
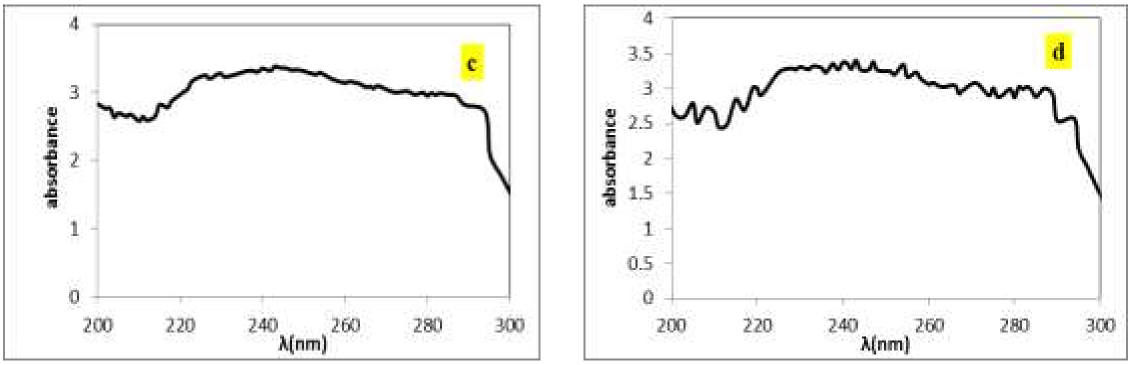


Figure (3) UV absorption spectrum of C_3N_4 suspensions at different laser pulse a) 25 pulse b) 50 Pulse c) 75 pulse d) 100 pulse



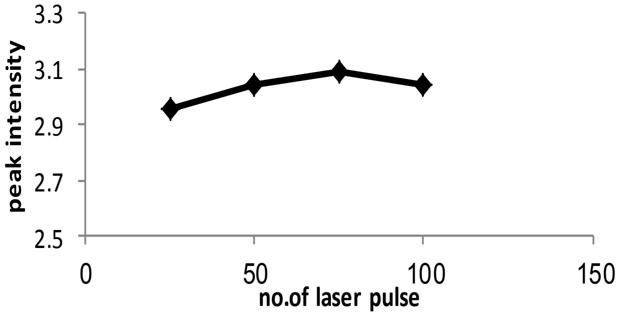


Figure (4) the effects of number of laser pulse on the peak intensities of C_3N_4 at 266 nm.

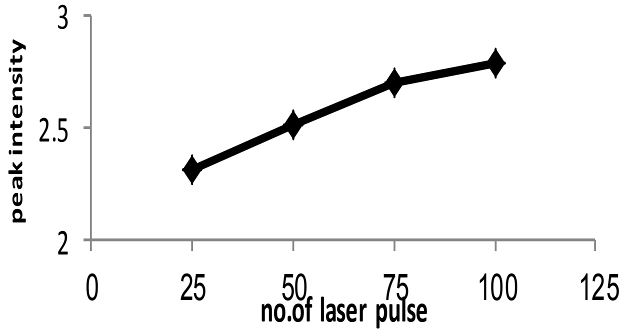


Figure (5) The effects of number of laser pulse on the peak intensities Of HC_8N at 205 nm.

Figure (6) demonstrates the influence of the number of laser pulse on nanoparticle concentration. It was clearly observed that the increase number of laser pulses between 25 and 100 pulse allows higher particle concentration. Increase concentration of the carbon nitrate nanoparticles in the case of laser ablation in a liquid is related to increase radiation absorbed by the material due to increase beam absorption in spot size, where as in nanosecond ablation thermal effects play an important role. As expected, the productivity 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 [20, 21] that lasts around 300 µs using Q-switching Nd: YAG laser irradiation of 36 J/cm^2 laser fluenc [22]. This cavitation bubble contains primary nanoparticles of extremely high local concentration that can scatter, or absorb the subsequent laser pulse.

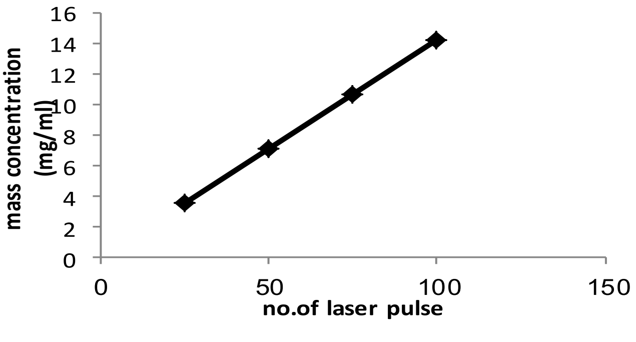


Figure (6) Carbon nitrate nanoparticles concentration as a function of The number of laser pulse.

figure (7) shows UV-Visible absorption spectra of suspensions of CNPs prepared at different laser flunce range from (3.32 , 13.28 and 33.2 J/cm^2) with 25 laser pulse, The spectrums show almost similar peaks, the peak at 269.0 nm, 264.0 nm, 266.0 nm and 250.0 nm represent to

C_3N_4. It indicates the peaks to have approximately the same wavelength with different laser energy. As an increase in laser energy is unlikely to cause a decrease in sp^3 carbon content, the shift in wavelength of the optical absorption edge can be attributed to an increase in particle size [23], and the peak of monocyanopolyynes show in Table (1) This is reasonable, as the higher laser energy may allow ablation of larger graphite particles. Alternatively, the higher pressure and/or effect of laser assisted absorption by the plasma, may cause further material reaction and growth to produce larger nanostructures. There is a trend for higher laser flunce to have higher UV-Vis absorbance peaks, and hence produce more material. This may be due to higher plasma pressure causing further ablation, material reaction with the liquid phase and/or nanostructure growth. The latter two points could also be a result of greater laser-assisted plasma absorption via higher laser energy. The effects of laser energy on the peak intensities of C_3N_4 at 266 nm are displayed in figure (8), the intensity increase with increasing laser energy. Also figure (9) show the same behavior of effects of laser energy on the peak intensities of HC_8N at 205 nm.

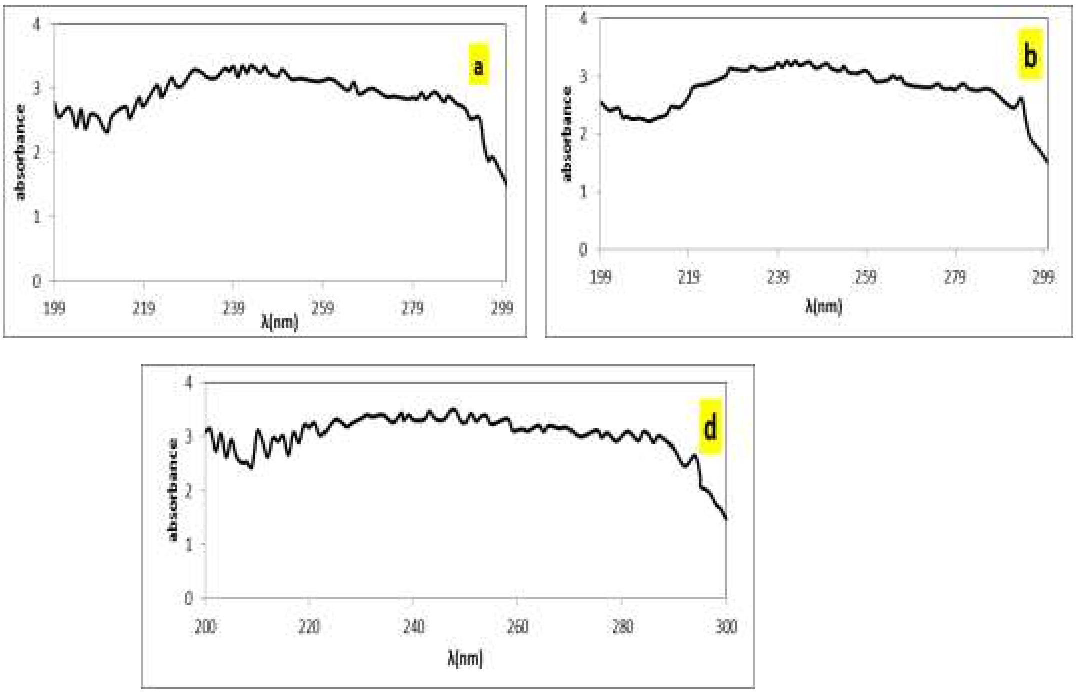


Figure (7) UV-Visible absorption spectrum of CNPS suspensions at different laser energy a) 3.32 J/cm^2 b) 13.28 J/cm^2 C) 33.2 J/cm^2

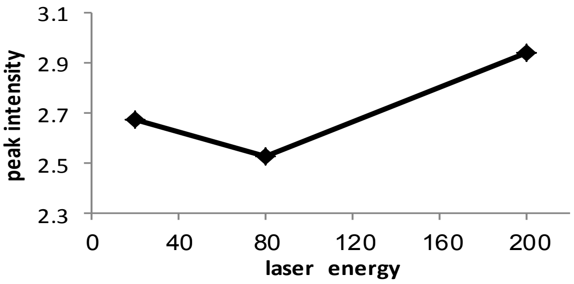


Figure (8) the effects of laser flunce on the peak intensitiesOf C_3N_4 at 266nm.

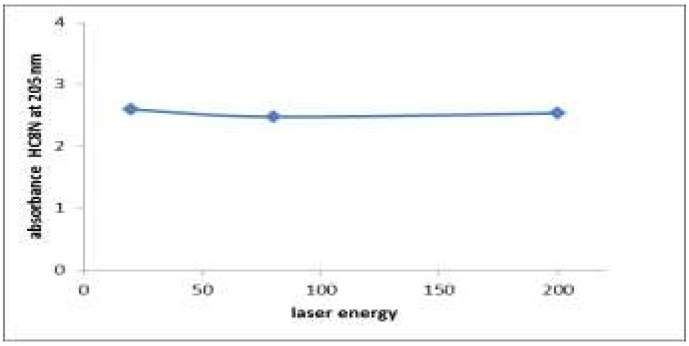
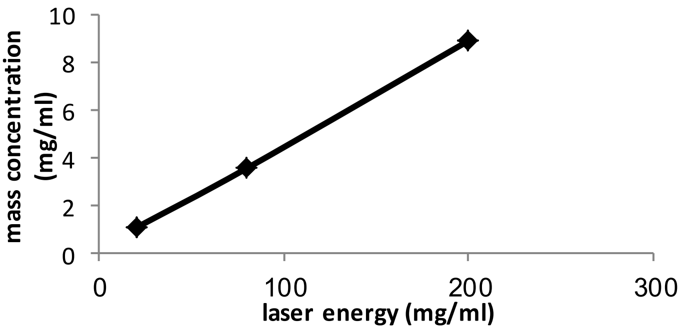


Figure (9) the effects of laser flunce on the peak intensitiesof HC_8N at 205 nm.

Figure (10) demonstrates the influence of the laser pulse energy on nanoparticle concentration, in the range 20, 80 and 200 mJ nanoparticle concentrations increased linearlywith increase pulse energy.



Figure(10) Carbon nitrate nanoparticles concentration as A function of laser pulse energy.

Figure (11) shows the carbon nitrate nanoparticles formation, the spherical particles and rod shape were notice in figure (11a) the leaf – like structure are formed after only short ablation times. Fig (11b & d) histograms of the diameter distributions for the carbon nitrate nanoparticles with an asymmetrical distribution of size ranging from approximately 4 – 83.3 nm for image (a) and size ranging from approximately 8.8 – 44.5 nm for image (c). The TEM results suggest a critical dependence of the surrounding liquid medium on the shape and size of the synthesized nanoparticles. According to the formation mechanism, there are two mechanisms contributing to the nucleation process during laser ablation of nanoparticles [24]. The first is direct nucleation of atoms in the condense plume and the second is nanoparticles as growing centers for the incoming species. When both mechanisms are growth of particles, the electrostatic repulsive force due to overlapping of electrical double layers of the nuclei and species in the plume prevent further growth, aggregation and precipitation [25]. Finally, nanocrystals of carbon nitride are produced when the plasma plume quenching in the confining liquid, a broad size distribution is expected.

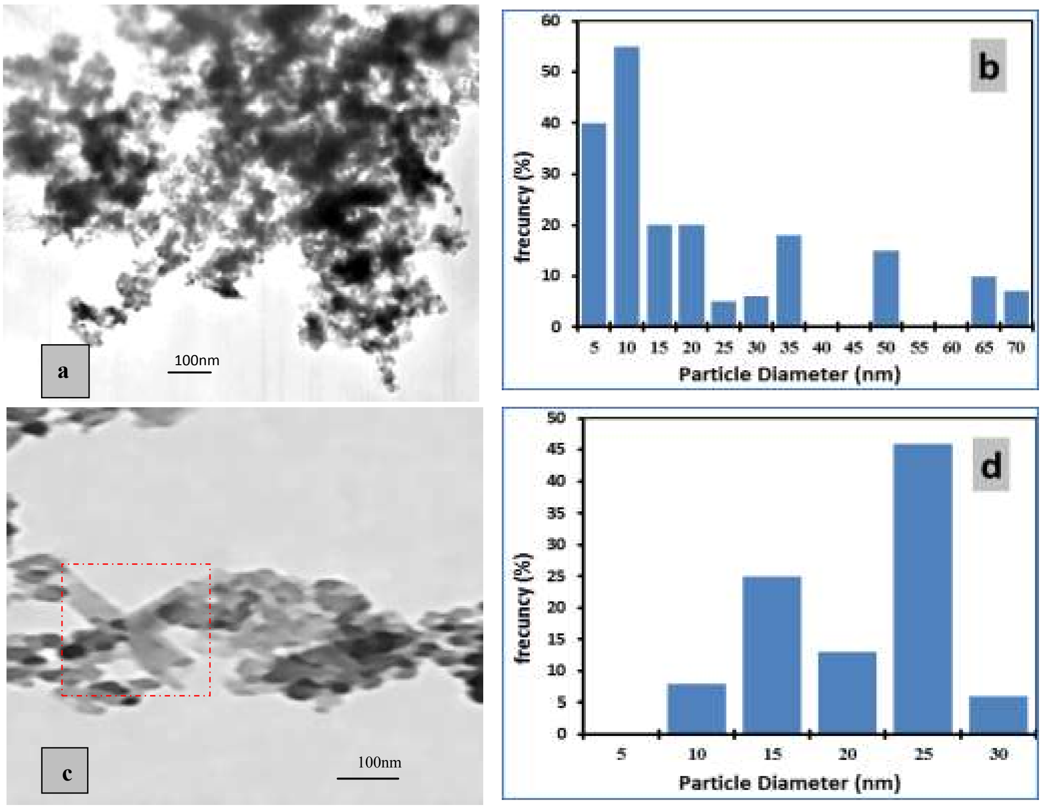


Figure (11) TEM image of carbon nitrate nanoparticles a&c (contain the leaf-like structure of carbon nitride), b & d) the size distribution of CNPs.

CONCLUSION:

The formation of carbon nitride C3N4 and monocyanopolyynes have been observed in the laser ablation of graphite target in hydroxide ammonium solution. LP-PLA ensures a very simple and effective method to produce C_3N_4 and HC_nN in solution. The results of FTIR absorption peak referred to formation of carbon nitride and monocyanopolyyne suspension. UV absorption peaks coincide with the electronic transitions corresponding to C_3N_4 due to a $\pi - \pi^*$ electronic transition, the peak intensities increased when C_3N_4 were produced with different laser energy, also the formation rates were increased with increased number of laser pulse. It has spherical geometry with ranging from (4 - 83.3 nm) and the Leaf- like structure was observed by TEM.

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