

Synthesis of Cinnamon Nanoparticles by Using Laser Ablation Technique

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Abstract

The natural polyphenolic compound that cinnamon contains has a vast range of pharmacological and medicinal properties which are well known for their diverse biological activities. Diverse biomedical and pharmacological applications benefit arise from organic nanoparticles with regulated properties. Cinnamon nanoparticles (CNPs) are bioactive and non-toxic, They can be effective as antibacterial agents. Driven by this notion, pulse laser ablation in liquid technique (PLAL) was used to prepare spherical cinnamon NPs. Using Q-switched Nd:YAG with a wavelength of 1064 nm pulse laser of constant energy 500 mJ, with different number of laser pulses (250, 500, 750, 1000) pulse /sec. Morphology and optical properties of the synthesized CNPs of differing laser fluence were determined. Samples were described through FESEM, UV-Vis and FTIR. The synergy between ethanol as a liquid growth media and fundamental laser wavelength has been the cause of certain distinctive characteristics of CNPs. The spherical CNPs achieved in the suspension of ethanol have been established to be helpful for antioxidant purposes.

Key words

PLAL, cinnamon, nanoparticles, ethanol.

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تحضير جسيمات القرفة النانوية باستخدام تقنية الاستئصال بالليزر

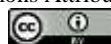
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الخلاصة

يحتوي مركب البوليفينوليك الطبيعي الذي تحتويه القرفة على مجموعة واسعة من الخصائص الدوائية والطبية المعروفة بنشاطاتها البيولوجية المتنوعة، تأتي فوائد التطبيقات الطبية الحيوية والصيدلانية المتنوعة من الأجزاء النانوية العضوية ذات الخصائص المنظمة. جزيئات القرفة النانوية (CNPs) نشطة بيولوجيًا وغير سامة، ويمكن أن تكون عوامل فعالة مضادة للبكتيريا، بناءً على هذه الفكرة، تم استخدام تقنية الاستئصال بالليزر النبضي في السائل (PLAL) لتحضير جسيمات القرفة النانوية. باستخدام ليزر نبضي Q-switched Nd:YAG بطول موجة 1064 نانومتر بطاقة ثابتة 500 مللي جول، مع نبضات ليزر مختلفة (250، 500، 750، 1000) نبضة / ثانية، تم تحديد الخصائص المورفولوجية والبصرية للـ CNPs ذات تأثير الليزر المختلف. تم وصف العينات من خلال FESEM و UV-Vis و FTIR، وقد كان التأزر بين الإيثانول كوسط نمو سائل وطول موجة الليزر الأساسي سبب بعض الخصائص المميزة لـ CNPs. تم تحضير CNPs الكروية المعلقة في الإيثانول لتكون مفيدة لأغراض مضادات الأكسدة.



Introduction

Nanotechnology has the potential to change every aspect of life in the coming decades. Forecasts for what will happen, when, and how this will happen vary widely, but everyone agrees that there is a tremendous potential for nanotechnology, especially in the biological and medical fields. Therefore, nanoscience has now become a landmark in many modern sciences [1, 2]. In previous years, there has been a growing interest in organic materials from plant herbs in many biomedical applications due to their biocompatibility besides being safe and are relatively inexpensive [3, 2]. Organic nanoparticles made from cinnamon and other herbal substances are being made and used as antimicrobial agents and cosmetics. Also, it can be used in the biological field as antimicrobial agents. [2] What distinguishes cinnamon is that it contains a large percentage (of up to (86%) of its composition) of cinnaldehyde and polyphenols which are well known for their biological activities. [4] Koppikar et al. [5]. Have demonstrated the effectiveness of, cinnamon extract against cervical cancerous tumor activity by impairing the potentials of the mitochondrial membrane. It has been shown that the watery cinnamon extract changes the movement of cell growth and works is about cervical cancer only. [5] It is necessary that the size of nanoparticles be less than (100 nm) to be used in a biological field [5]. There are many methods, chemical and physical, to obtain the nanoscale size, The pulse laser ablation in liquid (PLAL) technique has been used in this work because it has many useful features including low cost and the easy control of Laser parameters such as (pulse number, wavelength, intensity, and rate of repetition) to obtain the desired and appropriate nanoscale particles [6-8]. The PLAL technique is considered a successful technology for the development of top-to-bottom liquids NP, a modular technique for the preparation of various forms of nanoparticles, such as metals and alloys. [9] Organic [2] and oxidation [10]. In this technique, nanoparticles can be cultured with liquid, when a laser beam is shed onto a target immersed in a liquid, Type of the liquid can be controlled (water or organic solvents). Laser parameters have shown to play a significant role in regulating the morphology of the produced nanoparticles by monitoring the thermodynamic conditions during the growth and eradication phase of nanoparticles [11, 12].

Experimental work

1. Materials used and preparation

Cinnamon sticks with lengths (7 mm x 20 mm x 2 mm) were used. Analytical grade ethanol (C_2H_5OH , 96% purity from Sigma Aldrich) was used as liquid media to expand the CNPs. Cinnamon sticks were diced (20 x 10 x 2) mm in size and washed by ultrasonic bath of acetone solvent for 1 hour in order to eliminate all organic impurities. Finally, they were washed three times with purified water to remove any pollutants.

2. Synthesis cinnamon nanoparticles (CNPs)

CNPs were synthesized using PLAL technique. A Q-switched Nd:YAG laser with the following parameters was used: wavelength: 1064 nm; pulse repetition rate: 1 Hz, pulse width: 10 ns and spot size: 2 mm). A Q-switched Nd: YAG laser has a constant ablation energy (500 mJ) with varying pulses requirements (250, 500, 750, and 1000) pulse/sec and the laser fluence was ($15.92 J/cm^2$). Cinnamon stick was used the target material. $27cm^3$ of cinnamon was placed in the bottom of a beaker filled with 5ml ethanol which acts as the suspension medium, such that it is 5mm above the cinnamon target. A pulsed laser radiation was applied to the cinnamon target at 10 cm of focal

distance [13]. The beaker containing the targeted cinnamon was rotated at 6 rpm rotational speed to prevent the accumulation of diffusion material on the surface of the produced nanoparticles. Fig.1 shows a schematic diagram of the PLAL process for the CNPs synthesis. During the PLAL phase the produced hot plasma plume is expelled from the target surface within the ethanol solution due to the interaction of the laser [14]. The laser induced plasma rapidly expands at a supersonic speed and produces a shockwave under the sequestration of the ethanol medium. The shockwave subsequently moves the laser plasma and converts it into higher temperature, pressure and thermodynamic non-equilibrium state [2].

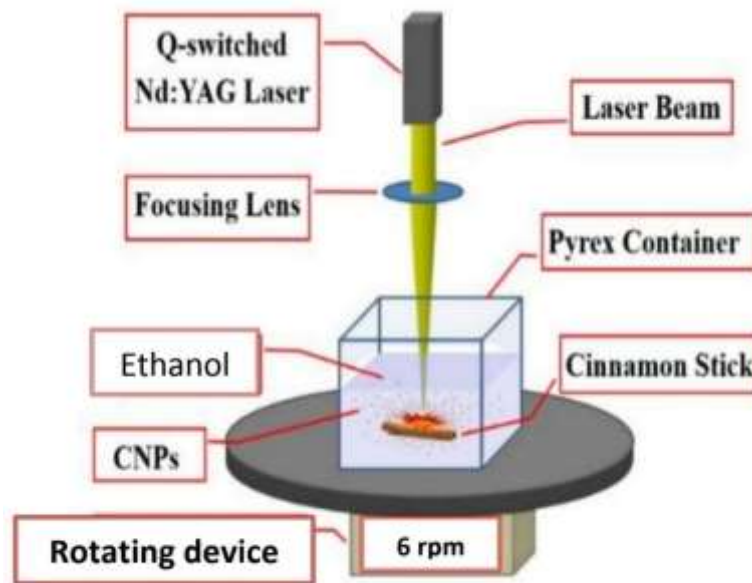


Fig 1: Schematic diagram of the "pulsed laser ablation in Liquid system" (PLAL).

Results and discussion

Fig.2 (a) shows the FESEM image of the sample which was prepared at 1000 pulse/sec and 500 mJ pulse energy shows that the size of the obtained nanoparticles ranged from 7.49 nm to 43.21 nm with an average diameter of 17.32 nm approximately. The nanoparticles have spherical and semispherical shapes. On the other hand, the size of the nanoparticles prepared at (250) pulse /sec and 500 mJ pulse energy ranged from 8.24 nm to 42.64 nm with an average diameter around 21.78 nm (as seen in Fig.2(c)).

The study of the absorption spectra of the colloidal solution of cinnamon nanoparticles (CNP) by means of ultraviolet - visible spectrophotometer (UV-Vis.) for different number of laser pulses (1000, 750, 500, 250) pulse/sec, and a fixed eradication card of (500) mJ. Fig.3(a) shows two distinct bands for absorption obtained within the wavelength range (227-318) nm This is due to the presence of "phenolic acids" and their derivatives ("flavanols, cinnamal- dehyde, phenyl- ropenes and eugenol"), as indicated by previous studies [4, 15]. Fig.3 (a) the first range of absorbance is within the range (227-231) nanometers depending on the number of pulses .The weak absorption peak is due to the presence of "aromatic amino acids" in the structure of proteins. This peak is also due to the effects of tyrosine residues in the protein and the release of protein into the ethanol solution by means of cinnamon, and its potentially significant effect is to investigate the stability of the solution of cinnamon nanoparticles (CNPs) [8, 16] Fig.3(c) the second absorbance peak is

prominent within the range of wavelengths (300-318) nm was obtained gradually. With increasing the number of pulses, a higher absorbance was noticed, in addition to the shifting of the peaks towards longer wavelengths. This is due to the effects of the size of the cinnamon nanoparticles (CNP) [2, 17]. Table1 shows the optical properties CNPs.

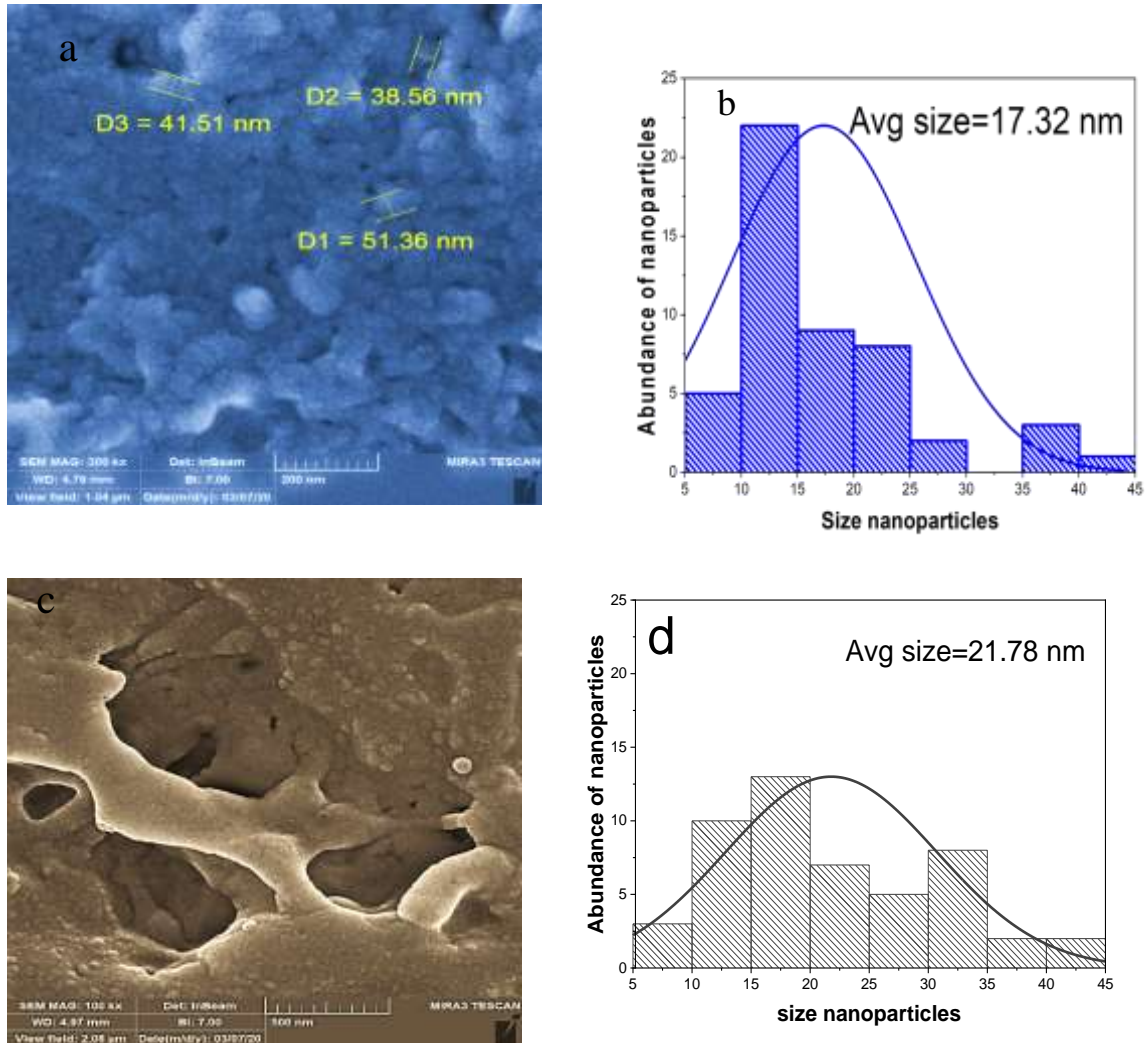


Fig. 2 : CNPs synthesized with optimum pulses laser in ethanol (a) FESEM image of the synthesized sample at (1000)Pulse / sec (b) Distribution of the scale of CNPs relating to (a), (c) FESEM image of the optimum sample at (500)Pulse/sec (d) Distribution of the scale of CNPs relating to (c).

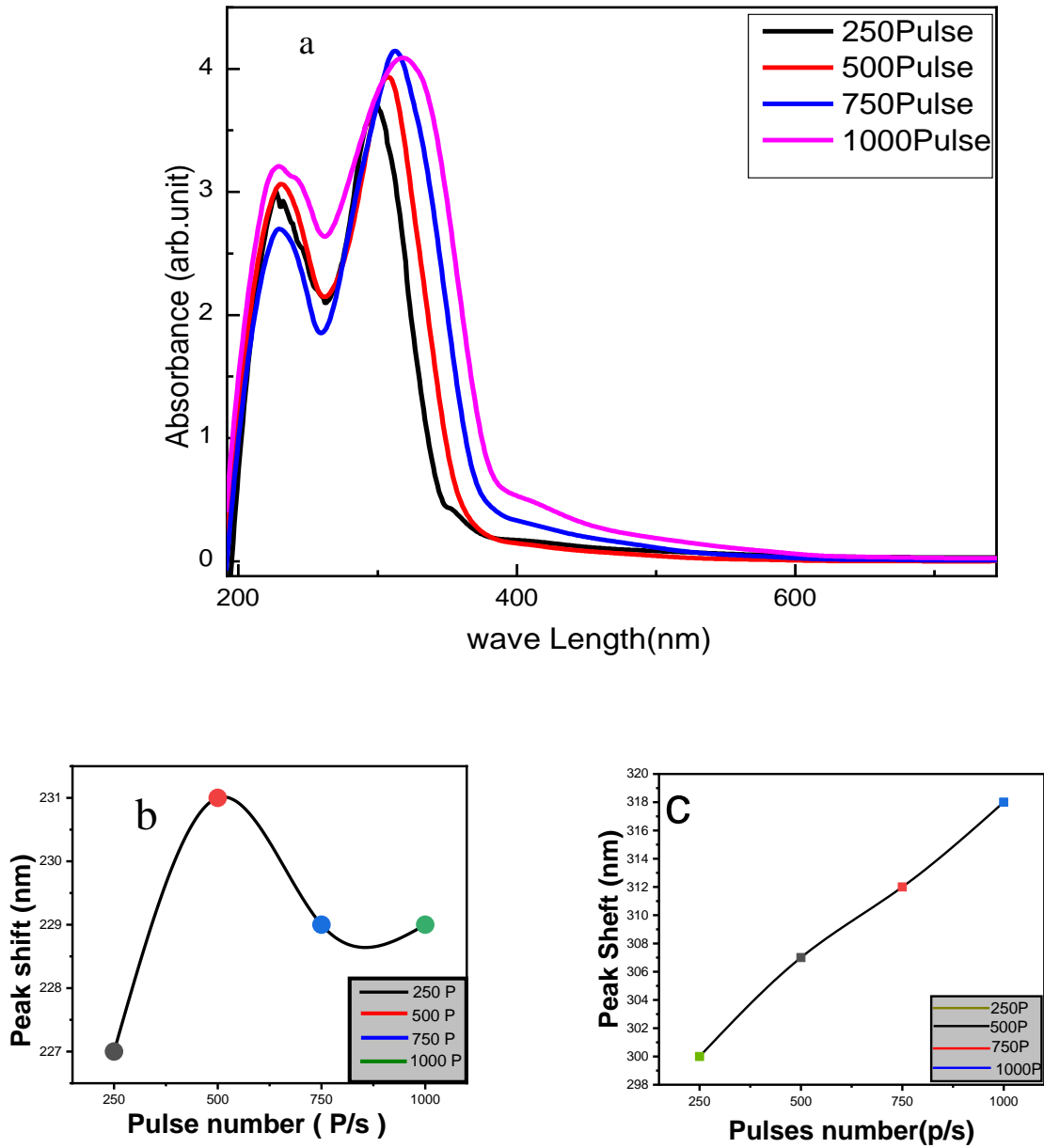


Fig.3: (a) CNP optical absorption spectrum prepared in an ethanol medium with multiple laser pulses (b) peak (minor) shift (c) peak (prominent) shift.

Table 1: The optical properties of CNPs.

Number pulses Pulse/sec	Ablation energy (mJ)	Abs(a.u) (1)	Abs(a.u) (2)	Peak shift (1)	Peak shift (2)
250	500	3.009	3.695	227	300
500	500	3.064	3.933	231	307
750	500	2.698	4.146	229	312
1000	500	3.209	4.0901	229	318

Fig.4 displays the FTIR spectra of all samples in pure structure groups comprising of separate functional groups CNPs. It displays the locations and intensities of the absorption bands for CNPs for samples are prepared using different number of pulses with constant ablation energy. The absorption band was at 881.46 cm^{-1} . This band arose from the C-H bending vibration of alkyl halides and alkynes, indicating their role in the development of CNPs. The existence of these peaks supported the coverage of CNP with functional groups such as ketone, carboxylic acid by plant secondary metabolites such as flavonoids, terpenoids, aldehydes, glycosides, phenols, tannins [8, 18]. The 1064 cm^{-1} absorption lines, which are due to the existence of C-O stretching of aliphatic amines are caused by moving to higher wave numbers with increased intensity and indicated the consumption of ethanol due to the oxidation [18]. The 1409 cm^{-1} band is assigned to the bending of the C-OH vibration alkane [19]. The band located at 1662 cm^{-1} exhibited a nonlinear rise in the amplitude suggesting a heavy tensile vibration of "aldehyde carbonyl" C = O groups of "alkenes" [18, 19]. The 2353 cm^{-1} absorption band indicates the occurrence of -C \equiv C- the "aldehyde and alkyne" group stretch displacement bands.[8,20] The peak located at 2899.01 and 2970.7 cm^{-1} Alkane vibration was allocated to carbon hydroxyl (CH₃ and CH₂) stretching [2, 21]. The incidence of a large and broad CNP absorption band at 3377.35 cm^{-1} was assigned to the hydroxyl group (O-H) stretching vibration [15, 21]. As shown in Table 2.

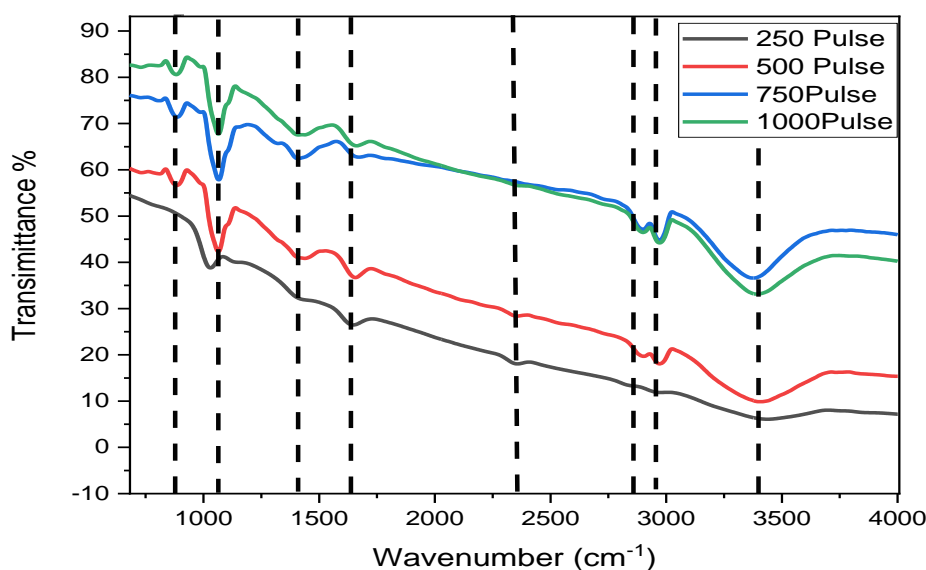


Fig. 4: FTIR spectrum, depending on the change in the number of pulses.

Table 2: FTIR band positions and assignments of CNPs.

Wavenumber (cm ⁻¹)	Vibrational band assignments	Vibrationmodes
881.46 - 885.32	C-H bending	Alkyl halides and alkynes
1029.98 - 1066.63	C-O stretching	aliphatic amines
1408 - 1438.89	C-OH stretch	Alkane
1647- 1672.28	C = O stretching	aldehyde carbonyl
2353.15 - 2357.01	-C \equiv C- stretch	aldehyde and alkyne
2899.01 - 2902	CH ₃	carbon hydroxyl
2970.3974.23	CH ₂	Alkane
3377.35 - 3437.15	O-H stretching	Hydroxyl

Conclusions

CNPs in ethanol are synthesized using the PLAL technique. The sensitivity of the Nd:YAG laser (1064 nm) and ethanol media to the morphology, and study optical properties of CNP was assessed. The structure and morphology of CNP has been shown to be governed by the intelligent selection of the correct liquid media and laser parameters, particularly number of pulses and the wave length. FESEM image diameters scale acquisition of less than 50 nm CNPs with of distributions of Gaussian magnitude. Good CNP absorption in the UV area demonstrated their efficacy for biomedical (antioxidant and antibacterial) applications. The quantum scale effects of CNPs have been due to the expansion and change between the absorption and emission peaks. The bonding motions of stable and pure composite CNPs have clearly demonstrated the existence of many functional groups in the FTIR spectrum. Certain green CNPs with the desired properties and chemical structure have been recognized to be useful in biomedicine.

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