Optical and structure characterization of cinnamon nanoparticles synthesized by pulse laser ablation in liquid (PLAL)

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Abstract. Organic nanoparticles development is under exploration due to its beneficial applications in nanobiomedical and research interests. PLAL technique of Q-switched 1064-Nd: YAG (10 ns pulse duration, repetition rate 1 Hz and laser energy 20-100 mJ) has inherent advantages and rapid growth of nanoparticles when compared to conventional methods because of the controlled fabricated nanoparticles, stability, and purity. Cinnamon sticks as a target are immersed in 5 ml ethanol medium and irradiated by a laser beam for the growth process. The morphology, optical characteristic, and bonding structure of cinnamon nanoparticles (CNPs) are determined and evaluated by transmission electron microscope (TEM), UV-Visible spectroscopy and Fourier transform infrared spectroscopy (FTIR). Spherical, homogenous and high crystallinity CNPs was revealed within the particle size range of 2 - 28 nm. The absorption band was found in the ultraviolet region around 259 nm and 319 nm. The present of FTIR spectra confirmed that the nanoparticles were covered by plant secondary metabolites. The experimental findings revealed that the synthesize CNPs in ethanol has a potential for nanomedicine applications.

1. Introduction
Nanotechnology is a multidisciplinary field and fast grown, especially in biotechnology [1]. the advanced synthesized and analytical tools of nanoscience in the chemical, physical, biphotonic, biological and electronic can be controlled at the nano-scale due to their distinctive structures and unique properties form [2]. Indeed, nanomaterials are under investigation due to wide-scale usages in the nanobiomedicine, biphotonic applications and research interest in nanoscience; of great systematic interest as they bridge the gap between bulk materials and molecular structures. Other paragraphs are indented (BodytextIndented style).

Recently, there is a growing interest in the organic material of systems at the nanoscale because lots of materials have diverse unique properties when compared to bulk counterpart. Therefore, intensive studies using organic nanoparticles suspended in surfactant solutions have been assumed because of their size-dependent, morphology and characteristic properties [3]. Earlier, several
development techniques are applied for the synthesis of nanoparticles having diverse morphologies such as nanowire, nanoflower, nanoprolate, nanotube, nanospheres, nanorods, etc. [4,5]. These approaches techniques are employed for multidisciplinary research area synthesis of nanoparticles including laser ablation, ball milling, precipitation, chemical etching, sputtering, phase transport, sol-gel, vapor deposition, molecular condensation, enzymes and microorganism [5,6]. However, pulse laser ablation in liquid (PLAL) became recently widespread methods to the development of organic nanoparticles and overcome on many other techniques due to its interesting attributes such as simplicity, growth controlled, variability, economic and free of impurities. It has a promising advantage to control the size, shape, and crystallinity of the nanoparticles by changing the laser parameters such as laser fluence, repulsion rate, wavelength, pulse number and solvent [6,7].

Natural plant parts appeared as a prospective contender for a broad range of biomedicine applications due to their biocompatibility, variability low cultivation cost, effortless, abundance, short production, these are favored over metal nanoparticles [8]. Therefore, cinnamon parts are attentionally attractive the researchers because of its wide range of beneficial usages and considering as one of the traditional herbal medicine in Asia due to the presence of the natural major compound in cinnamon such as polyphenols and cinnamaldehyde [9].

In this novel report, we produced CNPs immersed in ethanol liquid medium accompanying by different laser ablation energy of 20 mJ up to 120 mJ using PLAL technique. The effect of various laser ablation energy on morphology, absorption properties and chemical bonding structural of CNPs was determined and observed by TEM, UV–Vis and FTIR measurements.

2. Methodology

2.1. Experiment Materials and Sample Preparation
Cinnamon sticks with dimension (80 mm × 20 mm × 2 mm) were purchased from the local supermarket (Aeon, Kuala Lumpur, Malaysia). Analytical grade ethanol (C2H5OH, 96% purity from Sigma Aldrich) was used as liquid media to grow the CNPs. Cinnamon sticks were chopped at a dimension of (20 × 10 × 3) mm and cleaned using ultrasonic bath with acetone solvent, thereafter, each small cinnamon stick washed with purified water to eliminate the presence of any contaminants.

2.2. Synthesis CNPs
Cinnamon nanoparticles grown in ethanol liquid medium was synthesized using PLAL technique. A Q-switched 1064-Nd: YAG laser (10 ns pulse duration, repetition rate 1 Hz and varying laser energy 20-100 mJ) was applied. First, the cinnamon stick as a target material was immersed at the 27 cm³ cubic container bottom with 5 ml liquid ethanol as growth solution. the schematic diagram of the experimental setup of CNPs displayed in the Figure 1. The laser irradiation was directly focused on the surface of the target through a lens of focal length 80 mm. The distance between the laser lens and cinnamon surface target was positioned at 17 mm because of the refraction of the light phenomenon as reported earlier [10].
2.3. Characterizations of CNPs
The morphology (size and shape) and fast Fourier transform (FFT) pattern of CNPs were examined via Biological Transmission Electron Microscope (model, BIO-TEM from Hitachi HT7700, Universiti Teknologi Malaysia (UTM)). Absorption spectra of CNPs were measured using a UV-Vis spectrophotometer (PerkinElmer Lambda 25 Spectrometer, UTM). FTIR absorption spectra of the CNPs samples in the wave number range of 500-4000 cm$^{-1}$ was recorded on a PerkinElmer Frontier$^\text{TM}$ Spectrometer, UTM using KBr pellets techniques. In this process, a small drop (~0.5 ml) of the sample was poured on one of the KBr pellet surfaces using a Pasteur pipette and the second pellet was placed on the top of the drop with a quarter turn.

3. Results and Discussion

3.1. Morphology of CNPs
Figure 2(a) and (b) show the TEM image, FFT pattern and size distribution of CNPs grown at the optimum laser ablation energy of 80 mJ respectively. The TEM image in Figure 2(a) shows the morphology of the CNPs which was found to be predominantly spherical in shape, homogenous, and small particle diameter. This morphology of CNPs was attributed to the generated atoms that were trapped by the existing nuclei during the diffusion-controlled growth process. The inset in Figure 2(a) depicts the crystallinity phase of CNP. The corresponding (Figure 2 (a)) CNPs size distribution is revealed in Figure 2(b) where the average size was ascertained to be $\approx 9.14$ nm.
3.2. UV-Vis Absorption Bands

Figure 3 illustrates the absorption bands spectra of all prepared samples as a function of laser ablation energy. The CNPs containing solution color and the intensities as well as absorption peak positions was changed which indicating the difference growth in the CNPs morphology (size and shapes) and crystallinity. This observation agreed well with the findings of the previous report [11]. The inset in Figure 3 shows the laser ablation energy dependent size variation of CNPs, the color gradually changed from colorless (ethanol liquid medium) into brown in short time intervals, which was confirms the growth of CNPs. In the meantime, the ethanol medium containing CNPs revealed an enhancement in the percentage of absorption intensity with increasing the laser ablation energy (Figure 3). This suggested that the NPs number density, shape and size was indeed influenced by the laser ablation energy. It is value noting that this mechanism of CNPs formation is quite different than other growth methods i.e. vacuum pulse laser deposition technique, where the number and sizes of formed nanoparticles are obvious by the concentration of laser ablated plasma plume on the target surface.

Irrespective of the laser ablation energy, two characteristic bands were evidenced centered around 259 nm and 323 nm (Figure 3). The broadening of these absorption bands verified the size dispersion of nanoparticles grown in the ethanol medium. The intense absorption band was allocated to the phenolic acids and their derivatives (flavanols, cinnamaldehyde, phenylpropenes, and eugenol). The weak absorption peak (Figure 3) revealed a slight broadening accompanied by a tiny redshift. The occurrence of this weak peak was assigned to the presence of the ring of benzoyl and cinnamoyl system in the nucleated CNPs. Furthermore, it is known that the absorption band in the range of 259-263 nm arises due to the present of polyphenols compounds and the protein of plants. This observation indicated the exited of protein into the ethanol solution by cinnamon compound and acted as a probable mechanism for stabilization of CNPs solution. While, the intensity of the prominent absorption bands in the range of 323-327 nm was progressively increased. This observation was ascribed to the quantum size effects of CNPs as the report earlier [11,12].

Figure 2. Cinnamon nanoparticles synthesized with optimum laser ablation energy of 80 mJ (a) TEM morphology (Inset: the FFT pattern) (b) size distribution of CNPs corresponding to (a).
3.3. FTIR Absorption Bands

Figure 4 shows the spectra of all samples in the presence of various functional groups. The structure of compound present in the CNPs and the purity of the liquid medium (ethanol) was analyzed in terms of wavenumbers. The FTIR positions of absorption band spectra of CNPs samples exhibited a slight shift with a change in the absorption band intensity. The appearance of a broad and strong absorption band of CNPs around 3352 cm$^{-1}$ was assigned to the stretching vibration of (O-H) of alcohols and phenols. Whereas, the absorption band located at 2877 cm$^{-1}$ was corresponded to the stretching vibration of (C-H) alkane groups [11]. The absorption band at 2510 cm$^{-1}$ and 1910 cm$^{-1}$ showing the occurrence of -C≡C- the stretch vibration bands of aldehydes and alkynes groups. The gradual decrease in the absorption intensity of the band around 1910 cm$^{-1}$ was due to the ethanol oxidation and subsequent formation of CNPs. The band at 1651 cm$^{-1}$ showed a nonlinear increase in the intensity which was related with the stretching vibration of C=O groups of alkenes [12]. Herein, the growth of CNPs confirmed and supported by the observed broadening and shift in UV-Vis peaks (Figure 3). The dominant peak as showed in Figure 3 corresponded to the presence of major compound in the cinnamon (cinnamaldehyde, flavonoids and aldehydes) [9,11]. The band at 1408 cm$^{-1}$ was allocated to the bending of C-OH vibration alkane. The revealed of absorption bands at 1025 cm$^{-1}$ which was attributes to the presence of C-O stretching of aliphatic amines caused by shifted to the higher wavenumber with the increase in intensity Besides, the absorption band at 857 cm$^{-1}$ was shifted and the intensity was enhanced with increasing ablation energy. The occurrence of this band was assigned to the alkynes and alkyl halides in the located absorption band of C-H bending suggesting their contribution in the CNPs growth. FTIR spectra peaks as shown in Figure 4 established that the CNPs were covered by plant minor metabolites such as flavonoids, glycosides, phenols, terpenoids, tannins, carboxylic acid, aldehyde and ketone [12-14].

Figure 3. Laser ablation energy dependent optical absorption spectra of CNPs (Inset: particle size dependent color change).
Conclusion
A novel report was to synthesize CNPs immersed in ethanol liquid medium accompany varying laser ablation energy using PLAL technique. The morphology, structure and optical properties of such CNPs were found to be sensitive to the variation of laser ablation energy. UV-Vis spectra revealed two characteristic bands in the range of 259 and 323 nm. The optimum stability of CNPs was attained at laser ablation energy of 80 mJ. Furthermore, the functional groups of CNPs samples are clearly obtained in the range of 900-1700 cm$^{-1}$ due to the presence of aromatic plants and portions in the nanoparticles. It was established that the proposed natural CNPs may be significantly prospective for the medicine application.

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