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Environmental-Amiable Pulsed Laser Ablation in Liquid Mediated Growth of Silver/Cinammon Nanocomposites: Absorption Attributes

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ABSTRACT

Inspired by the great prospects of both silver (Ag) and cinnamon (C) nanostructures in the biomedicine applications we prepared some colloidal nanocomposites of Ag-C in the form of nanoparticles (hereafter designated as Ag-CNPs). Very strong reactivity and wide surface area of Ag-CNPs blend made them effective for various biomedical purposes. These Ag-CNPs were grown via green (chemical-free environment) pulsed laser ablation in liquid (PLAL) technique using ethanol as liquid medium at optimum laser fluence. Fourier transform infrared (FTIR) spectra identified the right chemical bonding vibration and confirmed the production of Ag-CNPs dispersed in ethanol. It comprised of several prominent bands assigned to the symmetric and asymmetric stretching of O-H, C=O, C-O, C-OH, and C-H bonds. The occurrence of vibrational modes corresponding to hydroxyl and carboxylic functional groups confirmed the existence of polyphenols compounds and their derivatives including cinnamaldehyde, flavanols and phenylpropenes. Ultraviolet-Visible (UV-Vis) absorption spectra revealed two intense absorption bands at 321 nm and 406 nm, confirming the formation of stable Ag-CNPs. These achieved Ag-CNPs with proven unique structural and absorption attributes were established to be beneficial for widespread usage.

Keywords:
Colloidal Ag-CNPs, PLAL, absorption properties, structure

1. Introduction

In recent times, there is a growing interest in the field of nanomaterials (organic and inorganic) due to their distinctive physical, structural, optical and chemical properties that are not shown by their bulk counterpart [1]. Over the years, top-down and bottom-up approaches have been commonly used to synthesize these nanoparticles (NPs). These techniques include sputtering, chemical etching, mechanical milling, sol-gel, vapor deposition, spray pyrolysis and atomic or

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molecular condensation. However, the produced nanoscale structures by these methods have several limitations involving the purity, morphology (size and shape), structure, requirement of expensive and hazardous chemicals, undesirable properties, and customized morphology [2-4]. For instance, preparation of accurate nanostructures that demands various chemical precursors are very difficult to eliminate during purification phases from the colloids or aqueous containing reactive NPs [3,5]. Gas phase method has been used to produce a microsize NPs which are hardly re-dispersible into aqueous solution or grindable down to the primary particles [6]. Recently, assorted organic, inorganic and colloidal NPs have been examined for numerous applications including bio-photonics, biosensors, solar cells, antibacterial agents, catalysis in biomedicine, cancer treatment, bio-imaging, antiseptic metal ion release, cosmetic, sun lotions, etc. to cite a few. Despite such dedicated efforts diversified biomedical applications of such NPs are still limited [6-9]. Yet, NPs having controlled structures and morphology (size and shape distribution) together with desirable optical, physical, chemical, magnetic and transport properties are greatly demanding [8].

Of late, pulsed laser ablation in liquid (PLAL) technique, due to its environmental friendly traits and better control received intense attention for the production of various NPs with precise structures and morphology. The NPs produced by PLAL method have been demonstrated to be completely free of undesired impurities, devoid of harmful reactants and highly stable [10,11]. It is worth mentioning that for biomedicine applications, use of stabilizer (capping agents) may be effective to tune the chemical reactivity of these NPs surfaces [12]. In the PLAL process, the plasma induced by the laser beam irritated on the target material (Ag rod or cinnamon stick) immersed in ethanol media creates cavitation bubble and a suitable thermodynamic condition that imparts such extra stability to the formed NPs [13,14].

Amongst diverse metallic and nonmetallic nanostructures AgNPs and CNPs displayed great potential towards biomedical field especially as antibacterial agents [15,16]. To date, the biomedical efficacy of colloidal Ag-CNPs has not been investigated. Driven by these facts, we took a fair attempt to prepare colloidal Ag-CNPs (in ethanol as liquid media) with accurate size distribution via PLAL method at optimal laser energy. These as-synthesized Ag-CNPs have subsequently been characterized systematically to evaluate their biomedical effectiveness in terms of structures and absorption features. UV-vis and FTIR spectra were analyzed in-depth to unravel to hidden potency of these NPs for sundry purposes.

2. Materials and Methods

Analytical grade Ag plate (Sigma Aldrich, purity of 99.999%) of thickness 2 mm and natural cinnamon stick (purchased from Aeon supermarket, Malaysia) of dimension (80 mm × 10 mm × 2 mm) were used as target materials to produce NPs. Prior to laser ablation, the silver plate was treated with emery paper sheet to remove surface imperfections and the cinnamon sticks were chopped into small pieces. Analytical grade ethanol (Sigma Aldrich, purity of 96%) was utilized as liquid media. Both targets (Ag and cinnamon) were cleaned using ultrasonic bath with acetone as chemical solvent for the duration of 30 min and then rinsed in distilled water to remove organic impurities.

Figure 1 displays the schematic diagram of the PLAL set up. In the PLAL technique, a Q-switched Nd: YAG laser (532 nm of wavelength) was used to synthesize cinnamon and Ag NPs. First, Ag target was dipped inside a pyrex container filled with 5 ml of liquid ethanol and irradiated by the laser beam with repetition rate of 8 Hz, pulse duration of 8 ns, spot size of 1.8 mm, ablation energy of 180 mJ and pulse time of 8 min. Second, the cinnamon target was immersed inside 5 ml of liquid ethanol in a pyrex container and exposed to laser beam with repetition rate of 1 Hz, pulse duration of 8 ns, spot size of 1.8 mm, ablation energy of 90 mJ and pulse time of 2 min. Both targets surface was placed

inside the liquid at a distance of 17 mm from the lens to optimize the refracted light beam intensity [17]. The container was revolved at the speed of 15 rpm using a magnetic stirrer in order to avoid the diffused materials aggregation onto the surface of NPs. The interaction of the laser energy/pulse with the target surface (Figure 1) caused the material to vaporize, which in turn created a plasma plume from the target on the interface of the confining liquid media and target surface [18]. Intense plasma plume in the liquid surrounding generated appropriate thermodynamic conditions for the growth of the induced plasma species and subsequent nucleation desirable nanostructure inside the ethanol [10]. The liquid absorbed the energy at faster rate than the target and resulted in the removal of material by direct laser ablation [19]. When the quantity of laser energy arrived into the target surface appeared zero, the produced plasma in the ethanol created a cavitation bubble which eventually collapsed followed by an expansion [20].

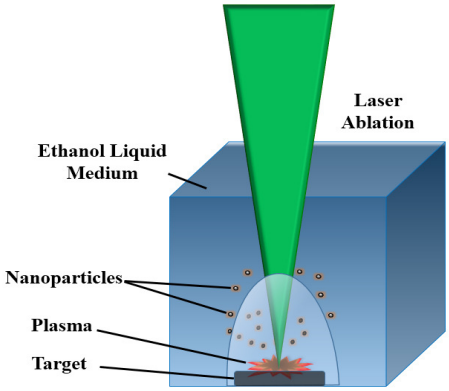

Fig. 1. Schematic diagram of PLAL process with ethanol as liquid medium and the formation of NPs from plasma at the target material surface

The room temperature optical absorption spectra of Ag-CNPs in the wavelength range of 200-500 nm was recorded using a UV-Vis spectrophotometer (PerkinElmer Lambda 25 Spectrometer). A cuvette (quartz) having path-length of 0.5 cm was utilized for the absorption measurements. The room temperature FTIR absorption spectra of the CNPs in the wavenumber range of 700-4000 cm^{-1} was measured on a PerkinElmer Frontier™ Spectrometer using KBr pellets techniques.

3. Results and Discussion

Figure 2 shows the UV-Vis absorption spectrum of synthesized Ag-CNPs in ethanol media. The spectra displayed two significant absorption peaks at 321 nm and 406 nm, confirming the nucleation of Ag-CNPs in the ethanol media. The inset of Figure 2 revealed the change in appearance of the liquid suspension from colorless (pure ethanol) to pale brown (containing sliver and cinnamon NPs), which was attributed to the surface plasmon resonance (SPR) and quantum size effects of Ag-CNPs [16]. This alteration in solution color (optical absorption properties) also verified the formation of NPs with varying structure and morphology (size and shape). The broadening of the absorption band at 406 nm accompanied by a red shift indicated the AgNPs covering and interaction with CNPs, making the composite more stable and uniform with narrow size distribution [21]. The full width at half maximum (FWHM) of this band was measured to be 53 nm, where the broadening was ascribed

to the quantum size effect of CNPs. Furthermore, the presence of an intense and relatively narrower peak (FWHM of 22 nm) at 312 nm was attributed to CNPs or may be due to the amide-based structure, the tryptophan and tyrosine residues in the protein that caused the stabilization of Ag-CNPs [14]. The broadening of this band was ascribed to the varied size distribution of Ag-CNPs and the organic molecules of cinnamon which interacted with ethanol media [14,18]. This strong absorption feature of Ag-CNPs may contribute to the development of the nanobiomedicine.

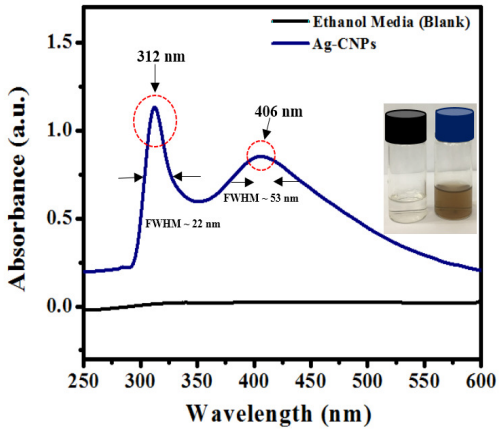

Fig. 2. Absorption spectrum of grown pure ethanol and Ag-CNPs suspended inside ethanol (Inset: Bottle containing pure ethanol liquid (colorless) and ethanol with suspended Ag-CNPs (brown)).

Figure 3 depicts the FTIR spectra of as-prepared colloidal Ag-CNPs suspended inside ethanol. The spectra exhibited several significant IR absorption bands positioned at 3380, 1652, 1058 and 878 cm^{-1} which were assigned to the symmetric and asymmetric stretching vibrations of O-H, C=O, C-O and C-OH bonds [22,14]. The observed peaks at 2967 cm^{-1}, 2533 cm^{-1} and 1919 cm^{-1} were allocated to the stretching modes of alkane carbon (C-H), indicating the absorption of cinnamon molecules on the surface of Ag NPs to form the composite. Besides, the absorption by hydroxyl and carboxylic functional groups on the surface of Ag-CNPs authenticated the presence of polyphenols compounds and their derivatives (cinnamaldehyde, flavanols and phenylpropenes) [23,14]. It was affirmed that uniformly dispersed Ag-CNPs with desired morphology can be achieved by PLAL growth technique by adjusting laser parameters.

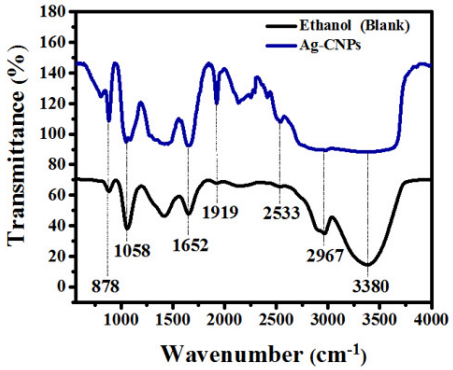

Fig. 3. FTIR spectra of pure liquid ethanol medium (black), and colloidal Ag-CNPs suspended in ethanol media (blue)

4. Conclusion

For the first time, using PLAL technique we synthesized colloidal Ag-CNPs in ethanol liquid medium. The absorption characteristics were determined using FTIR and UV-vis spectral analysis. It was shown that the structure and morphology of Ag-CNPs can be controlled by the selection of liquid media and laser parameters. The emergence of two UV-Vis absorption bands at 312 nm and 406 nm verified the nucleation of Ag-CNPs inside ethanol. The broadening and shift in the absorption peaks were attributed to the quantum size effects of Ag-CNPs. Presence of various functional groups in the FTIR spectra clearly indicated the bonding vibrations (right chemical structures) of composite Ag-CNPs. It was established that such green Ag-CNPs with desired properties and chemical structure could be advantageous in biomedicine.

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