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Laser–plasma driven green synthesis of size controlled silver nanoparticles in ambient liquid

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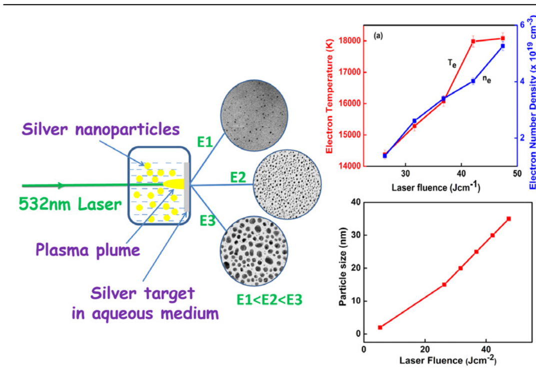
HIGHLIGHTS

- Space resolved optical emission spectroscopy of laser produced silver plasma in liquid media.
- Effects of laser fluence and properties of the ambient medium on silver plasma parameters.
- Laser assisted synthesis of Ag nanoparticles.
- Dependence of laser parameters in nanoparticle size control.
- Optical and morphological characterization of green synthesized Ag nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

This article explores the expansion behavior of laser produced silver plasma in stationary and stirring liquid media using space resolved optical emission spectroscopy and plasma instigated size controlled synthesis of silver nanoparticles via laser ablation. Second harmonics (532 nm) of an Nd:YAG laser was employed for the ablation of a silver target in ambient liquid for plasma formation. Calculation of plasma parameters — electron temperature and electron number density were done for different laser fluences and in various liquid media at room temperature. The Electron temperature (T_e) was measured by exploiting the Boltzmann plot method and the electron number density (n_e) was estimated from Stark broadened profiles of isolated lines from optical emission spectra. UV–Vis spectroscopy, fluorescence spectroscopy and high-resolution transmission electron microscopy further substantiated the optical and morphological characteristics of silver nanoparticles. Obtained novel versatile results pave way for a far-reaching understanding in creation and characterization of silver plasma, in ambient liquid; and provides a methodical green approach towards the synthesis of metallic nanoparticles that can be fine tuned for size and morphology, by varying laser parameters.

1. Introduction

Pulsed laser ablation is used for innumerable applications with expansion of plasma plume into environments, ranging from liquids to high vacuum. Among various analytical applications of laser ablation, laser-induced breakdown spectroscopy (LIBS), laser

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ablation–laser absorption spectroscopy (LA–LAS), laser ablation — inductively coupled plasma mass-spectrometry (LA-ICPMS), etc. are widely used [1]. Since the past few years, laser ablation in liquid medium got a substantial increase in research interest.

When a high intense nanosecond laser pulse interacts with a target material, vaporization take place resulting in plasma production; and it will expand in the form of vapor plume. Inverse bremsstrahlung (IB) absorption happens frequently during the vapor plume expansion process which is considered as heat loss [2]. The key parameters in the evolution of plasma from a material are intensity of incident beam, wavelength, duration of exposure, energy absorption, energy transfer, nature of the target material and distance between the laser and target, environmental conditions etc. [3,4]. Coming in to frame, laser assisted material synthesis and also the interpretation of material formed on the basis of plasma parameters has value-added major research interest in recent years owing to the diverse applications, easy utilization, relative lucidity and high shot-rate potential. Also silver nanoparticles are one of the most versatile products in terms of its application, ranging from air disinfection to bio-medical applications. This has led the scientific community to search for newer approaches for the fabrication of silver nanoparticles on the basis of physical, chemical and biological processes. These processes has some drawbacks including the need for a plethora of chemicals and requirements of multiple washing and heating. In this context, the laser assisted synthesis of silver nanoparticles are highly favorable. Silver nanoparticles produced via laser ablation is basically a top-down method. It is the fastest mode for producing nanoparticles with tunable size, by the modulation of laser and plasma parameters.

There are plenty of spectroscopic studies that have been put forth in the realm of laser ablation in air, dilute gas or vacuum, at different ambient pressures etc. [5–10]. However for laser-induced optical breakdown in a liquid medium, plasma generation happens for locations which surpasses the threshold irradiance for breakdown. Rapid increase in temperature causes accelerated pressure rise within the plasma and results in explosive expansion. This expanding plasma subsequently acts as driving force for shock wave propagation, the dynamic expansion and collapse of cavitation bubbles. When compared with the expansion of plumes in vacuum or gas, the interaction of plume with an ambient liquid involves much more complex dynamic processes. These include deceleration of the ions, thermalization of the ablated species, interpenetration, recombination etc. The current understanding of such processes are very limited and reported studies are mainly restricted for gases, with sole exception of water from liquid domain. Besides this, the diagnostics of plasma plume in liquid is a tedious task in practice.

Both laser induced plasma and cavitation bubbles have significant roles in the ablation process and nanoparticle generation mechanism. In this regard numerous studies and techniques have been already performed [11–20]. Also, so many exciting works were established in laser assisted synthesis, formation mechanism and characterization techniques of various nanostructures, nanocrystals, core shell structures for tailored applications [21–29]. In the case of nanoparticle size control during laser ablation, the photon energy of laser (wavelength) plays an important role. The influence of laser wavelength on particle size can be explained in terms of self-absorption, ablation efficiency, penetration depth of laser beam etc. The mean particle size decreases with decreasing laser wavelength [30]. Our focus of interest is in the behavior of silver plasma with respect to the laser fluence and surrounding medium, and how the laser fluence and in turn the plasma parameters affect nanoparticle growth and size tunability. Here, we present an interplay between the laser–plasma parameters and silver nanoparticle generation.

According to our understanding, laser energy density and its effect on n_e and T_e and the simultaneous process of nanoparticle formation etc. have not been reported yet for silver (Ag) in different liquid environments. Moreover, one of the pronounced advantages of plasma spectroscopy is its modest experimental setup, non-invasiveness and in situ diagnostic method. Herein, our attention falls on the spatial dynamics of silver plasma generated by employing the second harmonic wavelength (532 nm) of an Nd:YAG laser beam, with varying fluences in deionized water and various organic solvents. By scanning the plasma plume along its expansion path, the optical emission can be resolved spatially. We have calculated the T_e, using Boltzmann plot method and n_e, by Stark broadening method [31,32]. Furthermore, we analyzed the variation in T_e and n_e of silver plasma as a function of laser fluence, measurement angle, properties of ambient medium etc. Also we have systematically studied the facets of yellow aqueous solution of silver nanoparticles generated during laser ablation of the silver target using several characterization techniques. Here we detail an overarching view on the effects of laser fluence (laser energy density) and ablation medium on emission and expansion dynamics, electron temperature and electron number density of the plasma plume; and henceforth the tunable optical properties and morphology of silver nanoparticles with a multitude of diagnostic tools.

2. Experimental details

Laser irradiation of a pure silver target by laser ablation technique in deionized water and other organic solvents were performed. It was carried out using laser radiation at 532 nm wavelength with a fluence of 26.3 J cm^{-2} to 47.4 J cm^{-2} in steps of 5.3 J cm^{-2} with a repetition rate of 10 Hz. The plasma parameters were measured using the Optical Emission Spectroscopy. All the possible silver plasma parameters were calculated. Laser irradiation of metallic targets resulted in the production of colloidal solution of metallic nanoparticles. The particle stability and morphology were monitored by UV–Vis absorption spectroscopy and high resolution transmission electron microscopy (HRTEM). Fluorescence spectroscopy was performed conjointly. The experimental conditions favoring formation of size-controlled stable nanoparticles were found.

A pure solid silver target (SIGMA ALDRICH, 99.99% pure trace metal) of thickness 1 mm was properly placed inside a glass cuvette which contained 20 ml of deionized water. A Q-switched Nd–YAG Laser (Litron LPY 674G-10) beam of wavelength of 532 nm, 8 ns pulse width, 10 Hz repetition rate was focused, to a spot size of 0.01 mm, on to the silver target using a plano-convex lens of focal length 15 cm at room temperature. Ablation was performed for different laser energy densities. The laser fluence, varied from 5.3 J cm^{-2} to 47.4 J cm^{-2}, felt within close range to the ignition threshold of plasma, and lead to formation of silver plasma on to the target surface. Spatially integrated emission of silver plasma was conceived onto the fiber optic probe (HR4000CG-UV-NIR), which is thermally resistant. The tip of the probe was positioned at a distance within a maximum of 1 cm from the plasma plume, at an angle from 90^0 to 45^0 to the laser beam. The emission spectrum of the plasma, formed on the silver target surface, was acquired simultaneously by a fiber optic spectrograph (Spectra suite) software system and was stored in PC for consecutive analysis. The signal integration time at the measurement window was fixed as 100 ms for all measurements. The experimental set-up for the optical emission studies is shown in the following Fig. 1.