Nano-particle enhancement of diagnosis with Laser-Induced plasma spectroscopy

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Abstract. This work discusses nano-particle augmentation of signals in laser-induced plasma spectroscopy. Radiation from a Nd: YAG laser device generates optical breakdown at nano-structured target materials. Extensive scientific investigations of different types of nanomaterial explore dependencies on nanoparticle size, laser wavelength and fluence, and time delay to obtain stronger signals from nano-material than from corresponding solid bulk matter. Modelling of the measurements interprets the occurrence of enhanced detectability of atomic species. Opportunities present themselves for biological and spectrochemical synthesis.

1. Introduction

Diagnosis of species composition leads to fundamental understanding of gaseous, liquid, or solid materials. Analytical chemistry utilizes electrical discharges [1] amongst several other techniques for synthesis of materials. Application of discharges effectively vaporizes or atomizes substances, and optical spectroscopy determines the composition. Application of pulsed, focused laser radiation however can induce optical breakdown and generate micro-plasma at or near targets of interest with an area precision of a few dozen of micrometre-squared. Determination of time-resolved temperature and species distributions, including high-speed imaging and spectral mapping, is fundamental to research into chemical or biological materials and surrogates.

Historically in 1959-1960 [2], the first working optical oscillator with an embedded amplifier demonstrates the ability to manufacture devices that show qualities such as directionality and focusability over and above scientific aspects of coherent radiation. On December 29, 1959, Richard Feynman [3] presents a lecture “There’s Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics” that stimulates engagement in the study and manipulation of individual atoms. On may construe Feynman’s lecture as an invitation to the nano-world. Various detection schemata utilize nano-particles for enhancement of signals, e.g., surface-enhanced Raman spectroscopy [4], make use of broad resonances of metallic nano-particles for signal augmentation, apply saturation properties for development of nano-particle induced optical switches [5], etc. Recently, laser plasma induced by high peak irradiance on a leaf and in presence of a layer of silver nanoparticles reveals remarkable signal improvements [6].
From a physics point of view, the laser-induced plasma needs to be characterized by measuring electron density and temperature over and above species composition. The plasma parameters are traditionally determined by analysing the emitted light using passive optical emission spectroscopy (OES) [7, 8] in contrast to laser atomic absorption spectroscopy (LAAS) [9]. A variety of techniques produce plasma for analytical purpose, e.g., inductively coupled plasma [10].

In this work, laser beams are focused to high peak powers of the order of $10^8$ to $10^9$ W/cm$^2$ for generation of laser-induced plasma [11]. Irradiance of the order of $10^8$ Watt/cm$^2$ can produce instant vaporization and ionization of the target material, viz. laser induced plasma (LIP) and laser-induced breakdown (LIB). The analysis of the emitted light for spectrochemical identification purposes utilizes laser-induced breakdown spectroscopy (LIBS) [12]. However, study of the plasma fundamentals from the emitted light is also known as laser induced plasma spectroscopy (LIPS). Addition of metallic nanoparticles to target surfaces causes enhanced emission and improves the limit of the detection of some elements using so-called nano-particle enhanced laser-induced breakdown spectroscopy (NELIBS) [6]. However, recent research of nano-particle enhanced laser-induced plasma spectroscopy (NELIPS) [13] explores OES enhancements due to generation of plasma from nanoparticles themselves.

2. Characteristics of laser plasma spectroscopy

Fundamentals of plasma spectroscopy are elaborated in various monographs and textbooks [7, 8, 14-16]. Different experimental and theoretical approaches in plasma spectroscopy recommend various methods for the measurement of plasma electron density and temperature distributions. In laser-induced plasma, high peak-irradiance in the focal volume is capable to initiate plasma, subsequently, to form a plume [11] that expands adiabatically [17] and normal to the target surface. Expansion against ambient pressure causes a decrease of the energy, leading to plasma cooling. The plasma emits radiation via different recombination schemes [11].

At early time delays, the plasma emits continuum radiation that originates from the slowdown of electrons (Bremsstrahlung) in the electromagnetic fields of atoms and ions. The kinetic energy gradually decreases and emission of radiation occurs over broad wavelength region. Measurement of strong continuum radiation indicates relatively large plasma density of the order of a few amagat and temperature of the order of several eV [11].

For early time delays, the plasma is almost in a state called complete thermodynamic equilibrium (CTE), i.e., complete equilibrium between temperature of the different plasma species such as atoms, ions, electron and radiation [7, 8, 11]. Electron density and temperature can be measured from the spectral continuum emission by absolute calibration and comparison to Planck’s distribution law at a specific radiation temperature [11]. Fig. 1 displays temperatures up in excess of 10 eV (116,000 K) and electron densities as high as $5 \times 10^{19}$ cm$^{-3}$ ($\approx$ 2 amagat) during the first dozen of nanosecond after laser pulse cessation.

Experimentally measured spectral lines shapes may indicate distortions due to re-absorption along the line of sight, viz. self-absorption [18], or line-reversal, viz. self-reversal [19]. Inhomogeneous plasma plume features may be caused due to the focusing of the laser beam, leading to gradients of plasma parameters from center to peripheries [18, 19]. Cooler plasma peripheries can re-absorb plasma radiation [18, 19].

After several microseconds, lower atomic states may cease to be in thermodynamic equilibrium with the surrounding plasma species because of the relatively large values of transition probability in comparison to the electron atom collision frequency [7], but the plasma is in partial thermodynamic equilibrium (PLTE). For PLTE, principles of electron density and temperature measurements can be applied. However, lower atomic states are best avoided in favor of higher state that is still in thermodynamic equilibrium with plasma species [7, 8]. For larger time delays, accompanied with further decrease in electron density (much lower collision frequency comparable with transition probability of atomic states) the radiative processes dominate collisional processes. The system is completely out of equilibrium and collisional radiative modeling is preferred [7].
3. Laser plasma from nanomaterial

Advanced technology enables one to fabricate a new class of materials of less than 100-nm size [20]. A substantial change in the physical properties of these class of particles are identified, e.g., mechanical [21], electric [22], magnetic [23], optical [24], and thermal [25] properties. The large percentage of surface area to volume favors that quantum mechanical properties are well-pronounced. From the point of view of plasma spectroscopy, one can anticipate that such changes in the properties of matter should manifest themselves during interaction with laser beams of high peak irradiance.

Enhancement of the optical signal has been reported by Ohta et al. [6] when a thin layer of silver nanoparticle are added to plant leaf during routine procedures of spectro-chemical analysis of its ingredients. At that time, the enhanced emission was attributed to the effect of the localized surface plasmon resonance (LSPR) and causes strong coupling of the incident laser beam when the wavelength (520 nm) matches the plasmon resonance of silver nanoparticles on the leaf [6].

Systematic experimental studies are necessary to explore the apparent advantages of nanoparticles. To this end, two typical targets are used under otherwise identical experimental conditions. One target is composed of pure nanoparticles, and the other target is the corresponding solid bulk material. Both targets are irradiated by Q-switched Nd: YAG radiation. The recorded plasma signals are compared following a relative measurement technique [26].

![Figure 1](image.png)

**Figure 1.** Experimental setup used for NELIPS experiments.

In order to carry a controlled experiment, the Laboratory of Laser and New Materials experimental facilities at Cairo University are utilized as illustrated in Figure 1. For the plasma generation, a Q-switched Nd: YAG laser is employed at wavelength of 1064 nm, 532 nm, and 355 nm. The laser energy controlled by using set of neutral density filters, and the spot size at the target surface was controlled by changing the distance from the laser focusing lens to the target surface as well as the gate and time delay of the intensified array detector. The emitted light from plasmas were analyzed and recorded using an SE200 Echelle spectrograph (resolution of 2500) equipped with Andor ICCD camera with resolution of 0.02 nm/pix. The whole experiment was synchronized using supplied software KestrelSpec® 9.6. The data as given in arbitrary units versus wavelength is processes using homemade software based on MATLAB station.

Figure 2 illustrates preliminary results of plasma emission from different types of nanomaterials-based targets. Figure 2 also compares the signal with the ones obtained from the corresponding bulk material. Enhanced emissions occur for neutral zinc, silver, silicon, titanium, aluminum, and iron spectral lines.
Figure 2. Spectroscopy signals are larger for nanomaterial than those for bulk material. (a) zinc, (b) silicon, (c) aluminum, (d) titanium, (e) silver, (f) iron spectra of neutral atomic species.

The series of experiments for pure nanomaterial plasma at different time delays [26], for different nanoparticle composition, laser parameters in terms of fluence and wavelength [27] and for different sizes of the nanomaterial [28] indicate the following results:
i. There are stronger signals from the plasma created at surface of nanomaterial-based targets than for the corresponding solid bulk matter [13, 26-28].

ii. The plasma ignition threshold depends on the material, the inverse square of laser wavelength [27] and linearly on the size (diameter) of the nanoparticles [28].

iii. The enhancement coefficients differ for emitted wavelengths [13].

iv. The enhancement factor decreases monotonically with laser fluence [29].

v. Enhancement factors increase linearly up to an optimum time delay [26].

3.1. Effect of the time delay

At fixed level of laser fluence of 9.5 J/cm², camera gate time at 2 µs and wavelength at the 1064 nm, the plasma emission was monitored versus time delay. The strongest lines are picked for each material, e.g., Ag I at 768.7 nm, Al I at 396.2 nm, Ti I at 498.2 nm.

Figure 3 shows examples of the variation of spectral line intensity for the Ag I line at 768.7 nm with time delay from the nano-based silver (upper open circles) and for bulk-based target (lower red squares). Similar trends are observed from different nanomaterials subjected to this study. One can notice the different decreasing rates of the spectral line intensity with delay; which means that there will be an increase of enhancement factors Enh. = I_{nano}/I_{bulk} with time delay. Figure 3 also shows enhancement factors for different nanomaterials.

![Figure 3](attachment:image.png)

**Figure 3.** (a) The rate of decrease of signal height of the Ag I line at 768.7 nm from nano silver in comparison to bulk, (b) the result of rate of enhancement factor variation with delay time using different nanomaterials (Ag open circles, Al open red squares, Ti green triangles)

3.2. Effect of the laser fluence

Two pure nanomaterials (silver of size 95 nm and Zinc of size 30 nm) were subjected to quantitative study of the enhancement factor with laser fluence [26, 30]. At a fixed delay and gate times of 1 µs, and laser wavelength at 355 nm with maximum delivered energy of 95 mJ at duration time of 5 ns. The laser energy was decreased using a set of neutral density filters and the spot size was carefully measured at the target surface and found to be 0.5 mm as measured using a special supplied thermal paper from Quantel®.

The optical signal to noise ratio from plasmas were recorded using the prominent lines arises from silver Ag I line at wavelength 546.2 and from zinc Zn I line at 481 nm. Figure 4 illustrates the signal-to-noise variation with laser fluence (from nano-based silver target was compared to that from the corresponding bulk one and from the Zinc nanomaterial). Figure 4 also shows the enhancement factors of up to two orders of magnitude at fairly low laser fluence values.
The variation of signal-to-noise, S/N ratio with laser fluence (using laser at 355 nm, gate and time delay: 1 µs) and threshold fluence. (a) zinc nano-particles in comparison to bulk, (b) silver nanomaterial. Signal enhancement factors for (c) nano zinc and (d) nano silver.

The minimum laser fluence required for plasma initiation is called plasma ignition threshold and was measured using these figures via the backward extrapolation technique until the point of intersection with the vertical axis at a point corresponding to S/N = 3 [26-28] as shown for both nano and bulk materials. In that case one should assume that there is linear regression of the signal to noise ratio at small laser fluence [31]. The zinc nanoparticle target shows thresholds of approximately 0.003 J/ cm², while nano-silver shows 0.45 J/cm². For bulk zinc and silver, the threshold are 1.6 J/ cm² and 4.3 J/ cm², respectively.

3.3. Effect of the laser wavelength.
The wavelength dependency is investigated using available laser harmonics at 1064, 532 and 355 nm. The laser fluence was adjusted in the range of interest (for zinc and silver) by suitable change of the distance.
from laser focusing lens to the target surface. For example, the focal spot radii were amounted to 1±0.1, 0.7±0.05 and 0.5±0.03 mm for the case of using zinc nanoparticles and 0.5±0.05, 0.44±0.05, 0.27±0.03 mm for the case of silver nanoparticles [26, 27, 30]. In order to measure the laser threshold fluence at different laser wavelengths, the laser energy was detuned to the lower possible energy by a set of calibrated neutral density filters while the S/N ratio was recorded at each value of laser fluence from the nano-based target and from the corresponding bulk-based target. A plot of the S/N at each laser fluence shows similar results as displayed in Figure 4 (a) and (b) [26-31]. A backward extrapolation technique was adopted until the threshold of plasma ignition is obtained at S/N ~ 3.

Three outcomes are identified:
(i) From bulk to nano-scaled material, there is strong reduction in the plasma ignition threshold,
(ii) The thresholds scales as the inverse square of the exciting laser wavelength, and
(iii) The amount of enhanced emission and the threshold depends on the type of the material used.

The measured dependence of the laser-plasma ignition threshold on laser wavelength can be extracted from Figure 5. For zinc (Fig. 5a) [26-28] and silver (Fig. 5b) [31] nanomaterials, the threshold scales linearly with inverse square of laser wavelengths [26, 30].

Figure 5. Variation of threshold with laser wavelength for (a) zinc and (b) silver; red for 1064 nm, green or 532 nm and blue for 355nm. Symbols N and B indicate nanoparticle and bulk targets, respectively.

3.4. Effect of the nanoparticle size.
The availability of the ZnO at different sizes encouraged us to investigate the effect of the nanoparticle-size on the plasma ignition threshold [28]. Four sizes of diameters of 20, 40, 70 and 100 nm were put on the form of small tablet target and exposed to IR laser at 1064 nm. Plasma was monitored using the strong 481 nm Zn I line and fluence was changed down to 3 J/cm². Figure 6 depicts the variation and linear regression of the ignition threshold with size diameter of the nanoparticle-based target plasma.
4. Thresholds for laser plasma generation

From the previous sections one can conclude the following: There is strong enhanced emission from the plasma created at surface of nanomaterial-based targets with respect to the corresponding bulk one [26-31]. The nano-particle plasma ignition threshold depends on material parameters, on the inverse square of the laser wavelength [27], and it depends linearly on the diameter of the nanoparticles [28] in place of the usual thermal diffusion length for solid bulk matter. This enhancement factor decreases in a monotonic way as the laser fluence increases [26-31], and finally, enhancement factors increase linearly with delay time [26]. The previously communicated laser plasma ignition threshold \( \phi_{th} \) [27,28,31] for bulk material having density \( \rho \), latent heat of vaporization \( L_v \), coefficient of thermal conductivity \( \kappa_T \) and specific heat at constant pressure \( C_P \), ionization energy \( \varepsilon_i \), with thermal conduction length \( \ell_T = \sqrt{\kappa_T / \rho C_P} \) and irradiated by a laser having pulse duration time \( \tau_L \) and wavelength \( \lambda_L \) can be given by:

\[
\phi_{th} = \left( \rho L_v + 2.25 \times 10^{15} \frac{\varepsilon_i}{\lambda_L^2} \right) \ell_T, \quad \text{and for pure nanomaterial we can replace this relation by:}
\]

\[
\phi_{th}^{Nano} = \left( \rho^{Nano} L_v^{Nano} + 2.25 \times 10^{15} \frac{\varepsilon_i}{\lambda_L^2} \right) D^{Nano}.
\]

Both relations can be used for:

(i) Demarcation of laser ablation (ejection of particles and vapor from the target upon laser irradiation at maximum fluence of \( \phi_{max}^{Ablation} = \rho L_v / \ell_T \)) and the plasma state (in which the laser ionization term should be added)

(ii) Characteristics of the target material at fixed laser parameters of wavelength and pulse-duration, \( \lambda_L \) & \( \tau_L \), namely; \( \varepsilon_i = \frac{\lambda_L^2}{2.25 \times 10^{15}} \left( \frac{\phi_{th}}{\ell_T} - \rho L_v \right) \), via measurement of ionization energy as examined for different materials used as targets [31].

(iii) Novel method for the determination of the size of the nanoparticles (see Fig. 6b), using \( D^{Nano} = \ell_T \left( \frac{\phi_{th}^{Nano}}{\phi_{th}^{Bulk}} \right) \); the ratio \( \frac{\phi_{th}^{Nano}}{\phi_{th}^{Bulk}} \) can be measured and the thermal conduction length can be calculated using the classical constants (thermal conductivity, isobaric heat capacity, density and the laser irradiation time). In that case, we have to assume that the energy density per unit volume need for vaporization \( \rho L_v (\ell / \omega) \) is not changed from the bulk to the nano sized materials, i.e.,

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**Figure 6.** experimentally measured thresholds at different nano size diameters (circles with error bars) [28].
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\[ \rho_{\text{nano}} L_{\text{Nano}} = \rho_{\text{Bulk}} L_{\text{Bulk}} \] at fixed irradiation wavelength. Consequently, one can predict for the nanomaterials that \[ \rho_{\text{nano}} \propto \frac{1}{L_{\text{Nano}}} \]. Future experiments can be carried to verify this assumption.

5. Discussion of applications and conclusions

The thermodynamical modelling of nanoparticle enhanced laser plasma spectroscopy relies on the knowledge of the thermal nano-material parameters. These parameters (density \( \rho_{\text{nano}} \), latent heat of vaporization \( L_{\text{Nano}} \), coefficient of thermal conductivity \( \kappa_{\text{Nano}} \) and specific heat at constant pressure \( C_{\text{P Nano}} \)) are not necessarily identical to the bulk properties. However, thresholds have been successfully predicted by replacing the thermal conduction length \( \ell_{T} \) with the nanoparticle diameter \( D_{\text{Nano}} \).

Applications include improvements of laser-induced breakdown spectroscopy, utilizing the results from the nanoparticle laser plasma investigations. Extensions of the experimental work, of course, would be to apply results from pure nanomaterial to the understanding of adding a layer of nanomaterial.

For these extensions, results of two nano-particle enhanced LIBS (or NELIBS) experiments are communicated. In the first experiment, a thin layer of titanium nanoparticles of 30-nm size is added, and in the second experiment, a thin layer of 20-nm gold nanoparticles was added to a titanium bulk material. A comparative study between plasma emissions from the pure titanium bulk and the sample covered with nano titanium layer was conducted using 1064-nm laser radiation with a fluence of 1.9 J/cm², both time delay and gate width are fixed at level of 1 µs. The result of enhanced emission from both samples is shown in figure 7 (a). While the sample covered with gold covered titanium in comparison with pure titanium is shown in figure 7 (b).

The same technique is used as before: The incident laser fluence is decreased from 7 down to 1.5 J/cm². The plasma was monitored using the prominent Ti I-line at 498.18 nm at different laser fluencies. Figure 7 (c) displays S/N vs. laser fluence. Under similar conditions, but with the use of nano gold covered bulk titanium, the variation of the laser fluence from 11 down to 7 J/cm² is shown in figure 7 (d). Figures 7 (c) and (d) allow one to infer the threshold of the laser-induced plasma from the bulk titanium, 0.93± 0.1 J/cm². This threshold value is clearly reduced to 0.12 J/cm² upon the addition of nano titanium particles of size 30 nm to the surface of pure titanium. This threshold is further reduced to 0.025 J/cm² with the use of nano gold layer to the same surface.

From the material parameters of titanium (density 4500 Kg/m³, latent heat of vaporization 8.88 KJ/Kg, thermal conductivity 21.9 W/m K, heat capacity 5.23 J/Kg K and ionization energy of 6.83 eV), and the threshold, \( \phi_{\text{th}} = \frac{\rho L_{\nu}}{2.25 \times 10^{15} E_{i}^{3/2}} \ell_{T} \), the following can be predicted: Thermal conduction length, \( \ell_{T} = 213 \text{nm} \); threshold for pure titanium material \( \phi_{\text{th Bulk-Ti}} = 0.908 \text{J/cm}^{2} \); titanium 30-nm nanomaterial threshold, \( \phi_{\text{th Nano-Ti}} = 0.126 \text{J/cm}^{2} \). Consequently, the threshold is reduced by the same ratio \( \left( D_{\text{Nano}} / \ell_{T} \right) \) as predicted by the model.

For the 20-nm gold nanoparticle experiment, a similar approach is applied. First, assume that there is no change in the energy density/unit volume from the bulk to nanomaterial, \( \rho_{\text{Nano}} L_{\text{Nano}} = \rho_{\text{Bulk}} L_{\text{Bulk}} \). Second, use the properties of bulk gold material (density 1932 Kg/m³, latent heat of vaporization 1577 KJ/Kg, thermal conductivity 310 W/m K, heat capacity 129 J/Kg K and ionization energy of 9.22 eV). Third, take into account the 20-nm diameter of the gold nanoparticles. And fourth, calculate the threshold
for the nanogold from:

$$\phi_{th}^{\text{nano-gold}} = \left( \rho_{\text{gold}} L_{\nu_{\text{gold}}} \frac{2.25 \times 10^{15}}{\lambda_{L}^{2}} \right) D^{\text{nano-gold}}.$$

The result for 20-nm gold nanoparticles is: \( \phi_{th}^{\text{nano-gold}} = 0.012 \, J/cm^2 \). However, the predicted value differs by a factor of two from the experimentally measured threshold value of 0.025 ± 0.05 J/cm². For an explanation of this discrepancy, further theory efforts are recommended. Deviation of the measured from predicted thresholds may possibly increase for smaller nano-particles.

In conclusion, upon addition of nano particles of certain diameter as a thin sheet to cover the analysed material, the threshold is strongly reduced to values that can be predicted from

$$\phi_{th}^{\text{nano}} = \left( \rho_{\text{Bulk}} L_{\nu}^{\text{Bulk}} \frac{2.25 \times 10^{15}}{\lambda_{L}^{2}} \right) D^{\text{nano}} [27-31].$$

Figure 7: Enhanced emission from (a) nano-titanium covered sample, (b) nano gold covered sample, (c) S/N versus laser fluence using the Ti I line at 498.17 nm for nano titanium covered sample, and (d) nano-gold covered sample.
Furthermore, the model for the threshold which is based on thermodynamic heat transfer from laser to nanomaterial may explain the reason of strongly enhanced emission at low laser fluence as usually applied in NELIBS. However, for explanations of the detailed mechanisms for the very early creation of plasma at or near nanomaterials covered bulk materials, further theory efforts would be recommended, especially for nanoparticles of the order of 20 nm.

The use of nanoparticles in medicine is quite extensive. For example, iron-oxide nanoparticles are used to enhance sensitivity of Magnetic-Resonance-Imaging, but nanoparticles can also be utilized to transport medicine. For diagnostic purposes, nanoparticles can be instrumental to enhancement of photoacoustic diagnostics and possibly to achievement of therapeutic goals by favourable interaction with short-pulsed laser radiation to induce localized cell necrosis.

Applications of nanomaterials extend to assessment of pharmaceutical products. The quality of the pharmaceutical products depend not only the basic ingredients but also on the concentration of the unwanted elements or ingredients. The minority concentrations can be detected using normal LIBS technique, but it will be rather sensitive after addition of the thin layer of nanoparticles to the analysed arbitrary sample [6]. Moreover, this sensitivity can be used to possibly identify flawed or untrustworthy products that are circulated.

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