Wavelength dependency and threshold measurements for nanoparticle-enhanced laser-induced breakdown spectroscopy

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ABSTRACT

Nanoparticles of zinc monoxide are selected for laser-induced breakdown spectroscopy with 5 ns pulsed 1064 nm, 532 nm, and 355 nm radiation from a Nd:YAG laser device. Fluences of 2 to 20 J/cm² are used, and plasma conditions are determined by recording emission spectra in the temporal window of 1 to 2 μs after optical breakdown initiation. The bulk- versus nano-particle plasma in laboratory air show that the averaged electron density and temperature values are practically identical. Enhanced signals are recorded for nanoparticles in the amount of ×10 to ×120 for 355 nm radiation. The nanoparticles cause lower optical breakdown thresholds and show signal enhancements as evidenced from the analysis of the Zn I line at 481.0 nm. The measured Hα line at 656.3 nm usually occurs in laser-induced plasma experiments in standard ambient temperature and pressure laboratory air, and it is used in the interpretation of the bulk- and nanomaterial results. The theoretical model largely predicts and confirms the excitation wavelength-dependent experimental results.

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1. Introduction

The generation of laser-induced plasma [1–3] requires above-threshold peak irradiance of the order of 100 GW/cm² for standard ambient temperature and pressure (SATP) air. The thresholds are lower by several orders of magnitude for aerosol- and/or nanoparticle-laden laboratory air [4], moreover, can be further reduced for solid materials. The laser-induced plasma at or near the surface emits radiation. In plasma spectroscopy, electron density and temperature are usually determined to describe the plasma conditions [5]. The analysis of the emitted plasma radiation is generally called optical emission spectroscopy (OES), or specifically, laser-induced breakdown spectroscopy (LIBS) [2]. Desired outcomes of LIBS include elemental identification, composition and concentration of the investigated sample [1–3]. For the application of LIBS as an analytical technique, it continues to be desirable to increase the sensitivity to allow one to investigate significantly diluted concentrations with a limit of detection (LOD) of the order of a few parts-per-million [1,6]. In order to improve the LOD one can engage in efforts that decrease the background contributions originating from continuum radiation or from random instrumental noise, or alternatively, one can design methods that increase the signal intensity. A variety of approaches were studied with the objective to enhance the value of LIBS in analytical chemistry including the use of double pulse techniques in collinear and orthogonal arrangements [7,8], and use of ultra-short laser pulses [9] with considerable LOD improvements [6].

The addition of a thin layer of nanomaterial composed of noble elements to a solid material surface can be favorable for measurement of increased signals, as previously recognized [10]. The enhanced emission has been explained qualitatively in terms of the action of the localized surface plasmon resonance (LSPR) [10]. However, the interaction of laser radiation with nanomaterials and corresponding bulkmaterials has been investigated recently. Under otherwise the same experimental arrangements and conditions, extensive systematic experimental works employed OES for different laser parameters and time delays [11–14]. Several conclusions were communicated, including: (1) the enhanced emission from the nanomaterials increases linearly with time delays when compared with bulkmaterial; (2) the enhanced emission increases with decreasing laser fluence; (3) there are no apparent changes of the plasma electron density and temperature; and (4) the enhancement factors that may vary for different experimental conditions can be associated with the relative masses ejected from both targets. Detailed experimental studies by De Giacomo et al. [13,14] indicate that the addition of thin layer of nanomaterial composed of noble elements on a metallic target surface reduces the threshold for plasma generation [3,15].

Previous communications elaborate that the enhanced emission can be attributed to the physical properties offered by the new nanomaterials when irradiated at peak power levels capable of generating optical breakdown [12]. The possibility of more efficient transfer of radiation to the target has been recognized including the application of lower laser fluence for nanomaterial than required for bulkmaterial that is analyzed with LIBS.

In this article, new results of the enhanced emission characteristics are presented. Nanomaterial enhanced LIBS (NELIBS) is explored in...
terms of dependency on the laser wavelengths of 1064 nm, 532 nm, and 355 nm and in terms of the required threshold laser fluence. The experimental work is conducted for the fixed time delay of 1 μs from optical breakdown and for a gate width of 1 μs. In the analysis, a refined threshold equation is introduced to predict the plasma thresholds as function of the excitation wavelength and the nanomaterial particle diameter.

2. Experimental details

The experimental setup is similar to the one described in Refs. [11, 12]. Fig. 1 illustrates the arrangement. It is comprised of a Nd:YAG laser device that delivers a maximum energy of 680 mJ within a 5 ns pulse duration at the fundamental wavelength of 1064 nm.

The pulse energy was attenuated with a set of absorbing sheets that are introduced near the focusing lens. A laser beam spot size of radius $1 \pm 0.1$ mm was used for 1064 nm. The other two harmonics at the wavelengths of 532 nm and 355 nm were operated at the maximum output energies of 180 and 95 mJ per 5 ns pulse and were focused to spot sizes of equal radii of $0.55 \pm 0.07$ mm in order to obtain the same range for the laser fluences.

In the experiment, the laser spot sizes for the three laser wavelengths are measured using thermal paper supplied by Quantel R for the different harmonics. In order to reach constant fluence conditions, the laser focusing lens position was carefully adjusted. A quartz beam splitter was utilized to monitor the incident laser peak irradiance. The beam splitter reflects 4% and absorbs 4% of radiation as recorded with the use of an absolutely calibrated power-meter (Ophir model 1Z02165). The emitted radiation from the nano- and bulkmaterials was collected with an optical fiber of inner diameter of 25 μm that was placed at a distance of 15 mm from the plasma expansion axis. Spectra were recorded with an Echelle type spectrograph (SE200 from Catalina) in conjunction with a time-gated ICCD camera (Andor- iStar- model DH734-18F). The gate-open time and the time delay from the laser-induced plasma were adjusted to 1 μs using the control software KestrelSpec 3.9.

The absolute sensitivity calibration of the spectrograph-camera system in the wavelength range from 300 to 900 nm was accomplished with a standard Deuterium-Halogen lamp (Ocean optics R-DH2000-CAL). The wavelength calibration and spectrograph bandwidth in the amount of 0.12 nm were measured using a low pressure Hg lamp (Ocean optics model HGI). The nano- and bulk-ZnO target materials were pressed into shapes of tablets. The supplied bulktarget consisted of irregularly shaped crystals with sizes of the order of a few mm. The crystals were put into a mold and compressed into cylindrical shape of the same thickness as the compressed nano targets. A primarily solid structure resulted for the compressed crystals, referred to as “bulk” material, and a relatively dense but loosely-packed structure was achieved for the nanoparticles, referred to as “nano” material. The targets were prepared in standard ambient temperature and pressure laboratory air, thereby possibly trapping air moisture as well. While hydrogen lines are typically observed in micro-plasma generated with nanosecond laser radiation in air, trapped moisture could contribute to the observed hydrogen alpha line over and above the contributions from the air. Careful future investigations are expected to address this extra source for the appearance of the hydrogen alpha line. A so-called xy-ϕ-holder was used to mount and move the targets and to ensure a fresh target area for each laser shot. The strongest neutral Zn I line at the wavelength of 481.01 nm was selected to monitor the plasma emissions for the different wavelengths and especially for lower fluences of the order of a few J/cm². Typically, the ZnO (MKNANO-ZnO-030) materials of almost spherically shaped powder samples of diameter $D=30$ nm were purchased from “MKNANO®, and were used in the studies without further purification or applying heat treatments.

3. Results and discussion

The analyses of the recorded data from nano- and bulkmaterials are geared towards evaluation of the temperature, electron density and ground state population ratios from the recorded spectra. Results for the threshold values are presented after the basic elements for the modeling are introduced.

3.1. Relative plasma parameters

In order to determine which one or possibly more of the plasma parameters are likely causing enhanced emission signals, electron density, $n_e$, and temperature, $T_e$, as well as particle density, $N_0$, are measured. More specifically, direct measurements were performed of the relative plasma parameters $T_e^B/T_e^N$, $n_e^N/n_e^B$ and $N_0^N/N_0^B$, where the superscripts $N$ and $B$ denote nano- and bulkmaterial, respectively.

Fig. 2 illustrates an overview of typical results that were recorded for various experimental conditions. The plasma emission was monitored using the Zn I line at 481 nm. Enhanced emissions occur for shorter laser wavelengths and show an up to $\times 120$ increase at a laser fluence of 2 J/cm², and larger enhancements occur for the smaller plasma initiation wavelengths.

Relative electron temperature

Measurement of the electron temperatures and hence the ratio $T_e^B/T_e^N$ can be accomplished by constructing a multi-element Boltzmann plot. Spectral intensities of the observed Zn I lines from both nano- and
bulk-plasmas are utilized [12] after correcting the recorded spectral line intensities for self-absorption effects. Self-absorption of the Zn I line occurs because of primarily two reasons, namely (a) zinc material is the major element of the target material and (b) the strong emissions of the Zn I lines at 481 nm as indicated in Fig. 2. Self-absorption correction was required in previous experimental studies [11, 12].

The optically thin H$_\alpha$ line appears in the recorded spectra as indicated in Fig. 3, and for plasma in local thermodynamic equilibrium (LTE) one finds from the relative spectral intensities the temperature ratio

$$T_e^N/T_e^B = 1 + T_e^N \ln \left\{ \frac{I_0^N}{I_0^B} \right\} = 1 + \frac{\ln \left\{ \frac{I_0^N}{I_0^B} \right\}}{12.08}. \quad (1)$$

For the experimental conditions described by laser energy, wavelength, pulse duration and temporal measurement window, the plasma temperatures are of the order of 1 eV; therefore, $T_e^N = 1$ eV [12]. In other words, measurement of the relative plasma electron temperature is accomplished by evaluating the relative intensities of the H$_\alpha$ lines. Fig. 3 shows the spectral radiance of the H$_\alpha$ line that is recorded from both nano- and bulk-plasmas.

From Fig. 3, the ratio $I_0^N/I_0^B = 1$, consequently, the logarithm of the ratio is zero, $\ln \left\{ I_0^N/I_0^B \right\} = 0$, and hence $T_e^N/T_e^B \approx 1$. This result was also documented previously in several communications [11–14]. A unit temperature ratio implies within the LTE conditions, that the electron temperatures for both nano- and bulk-plasmas are practically identical.

Relative concentrations

The determination of the relative concentration, i.e., ratio of population density of the ground states $N_0^N/N_0^B$, from either plasma can be accomplished by applying the multi-elemental Boltzmann plot method [12]. For the zinc experiments, the ratio $N_0^N/Zn/N_0^B/Zn$ can be expressed in terms of the relative spectral intensities of the Zn I line, $I_0^N/Zn/I_0^B/Zn$, and from the temperature ratio, $T_e^N/T_e^B$.

$$\frac{N_0^N}{N_0^{Zn}} = \frac{I_0^N}{I_0^{Zn}} \exp \left\{ - \frac{E_i}{T_e^N} \left( 1 - \frac{T_e^N}{T_e^B} \right) \right\} \frac{I_0^N}{I_0^{Zn}}. \quad (2)$$

The indicated approximate result is obtained by inserting the unit plasma temperature ratio in Eq. (1), i.e., $T_e^N/T_e^B \approx 1$; therefore,
The result for the relative concentrations being equal to the Zn I line ratio, see Eq. (2), was previously predicted when adopting a collisional-radiative model for plasmas with similar temperatures and densities [12]. However, Eq. (2) needs to include the effects of self-absorption of the Zn I spectral lines. This is accomplished by replacing the last term with \( (n_{\text{Zn}B}^0 / n_{\text{Zn}N}^0)(SA_{\text{Zn}B} / SA_{\text{Zn}N}) ) \). It is worth noting that the self-absorption ratio \( SA_{\text{Zn}B} / SA_{\text{Zn}N} \gtrsim 1 \). This implies that the enhanced emissions, and consequently the relative concentration or removed mass from targets, are actually larger than the experimentally recorded values. Within acceptable approximations, a ratio of unity, \( SA_{\text{Zn}B} / SA_{\text{Zn}N} \approx 1 \), can be used indicating that the same spectral line is subjected to almost the identical amount of absorption. The determination of the indicated bulk- vs. nanomaterial self-absorption ratio is further elaborated. First, the amount of bulkmaterial plasma self-absorption of the Zn I line at 481 nm can be expressed by comparison to the H\(\alpha\)-line, as determined from the measured FWHM of the 481 nm line, \( \Delta \lambda_{\alpha-481\text{nm}} \), by fitting the line to a Voigt profile and by applying the formula

\[
\frac{n_{\text{e-481nm}}^\beta}{\omega_{\text{e-481nm}}} \sim \frac{\Delta \lambda_{\alpha-481\text{nm}}}{\omega_{\text{e-481nm}}},
\]

with the Stark broadening parameter, \( \omega_{\text{e-481nm}} \), listed in Stark tables [16]. For instance, an FWHM of 0.1 nm for the zinc line in laser plasma at a temperature of 13,600 K would yield an electron density of \( 10^{17} \text{ cm}^{-3} \); however, primarily the ratio of electron densities for bulk- and nanomaterial is of interest. The electron density from the hydrogen alpha line for the bulkmaterial, \( n_{\text{e-481nm}}^\beta \), is evaluated using hydrogen Stark tables [17]. The same approach is used for the evaluation of the self-absorption for the nanomaterial, using corresponding terms for the variables,

\[
SA_{481\text{nm}}^\beta = \left( \frac{n_{\text{e-481nm}}^\beta}{n_{\text{e-481nm}}^\alpha} \right)^{-1.79},
\]

\[
SA_{481\text{nm}}^N = \left( \frac{n_{\text{e-481nm}}^N}{n_{\text{e-481nm}}^\alpha} \right)^{-1.79},
\]

where \( n_{\text{e-481nm}}^\alpha \) denotes the electron density that was deduced from the 481 nm line of the bulk-ZnO plasma. The value for \( n_{\text{e-481nm}}^\beta \) is

![Fig. 3. Spectral intensities of the H\(\alpha\)-line for the indicated wavelengths and fluences.](image-url)
Subsequently, taking the ratio of the bulk- and of the nanomaterial self-absorption values in Eqs. (3) and (5),

$$\frac{S_{\text{A}181\text{nm}}}{S_{\text{A}481\text{nm}}} = \left(\frac{n_e^{\text{fl}} - H_n}{n_e^{\text{fl}} - H_n}\right)^{-1.79}$$

and inserting \(n_e^{\text{fl}} \approx 1\), as inferred from Fig. 3, yields

$$\frac{S_{\text{A}181\text{nm}}}{S_{\text{A}481\text{nm}}} = \left(\frac{\Delta \lambda_{\text{Stark}} - 481\text{nm}}{\Delta \lambda_{\text{Stark}} - 481\text{nm}}\right)^{-1.79}. \tag{7}$$

or in terms of the FWHM of the measured Stark broadening

$$\frac{S_{\text{A}181\text{nm}}}{S_{\text{A}481\text{nm}}} = \left(\frac{\lambda_{\text{FWHM}}}{\lambda_{\text{FWHM}}}ight)^{-1.79}. \tag{8}$$

The experimental results for nano- and bulkmaterial indicate nearly the same values for the FWHM of the Stark-broadened lines. For instance, at a fluence of 4.2 J/cm² and for 1064 nm radiation, the values of 2.2 nm and 2.3 for nano- and bulkmaterials are obtained, respectively. Similarly, for a fluence of 19 J/cm² the values are 0.72 nm and 0.6 nm. And for fluence levels of 2 J/cm² for 532 nm laser radiation, one finds 0.21 nm and 0.2 nm for nano- and bulkmaterial, respectively. Similarly, for fluence levels of 4.2 J/cm², the experiments show 0.18 nm and 0.16 nm. Consequently, \(\frac{S_{\text{A}181\text{nm}}}{S_{\text{A}481\text{nm}}} \approx 1\).

Relative electron density

The relative electron densities can be directly determined from measurement of the relative Stark broadening of an optically thin spectral, e.g., the H\(_\alpha\) line,

$$\frac{n_e^{\text{fl}} - H_n}{n_e^{\text{fl}} - H_n} \approx \frac{\Delta \lambda_{\text{Stark}} - H_n}{\Delta \lambda_{\text{Stark}} - H_n}. \tag{9}$$

In the analysis presented here, it is acceptable to use the relative Lorentzian spectral line width of the H\(_\alpha\) lines as a measure of relative electron density. The recorded spectra indicate that the Stark widths of the H\(_\alpha\) lines are approximately identical for both nano- and bulkmaterials, see Fig. 3. For that reason, one can infer a ratio of unity, \(n_e^{\text{fl}}/n_e^\text{n} \approx 1\). This result was also recognized previously [12].

3.2. Threshold of laser-induced plasma

The threshold fluence denotes the required minimum laser flux (energy/unit area) to initiate plasma at the target material surface [3,13,15]. Phenomenologically, this threshold is expected to depend on several factors including laser parameters, i.e., wavelength and irradiance, and target ambient conditions. For instance, the laser irradiation occurs in laboratory air or it may occur within a shroud gas at some pressure or it may occur in a vacuum environment. Of course, the threshold fluence may also be a function of the physical properties of the target material, e.g., density or thermal and electric conductivities or specific and latent heats or work function or quantities at the atomic scale such as the ionization energy.

The classical solution to the heat transport equation [18] leads to material-dependent values of the thermal diffusion length, \(\ell_T(m)\), \(\ell_T = \sqrt{\kappa_T/T_{\text{laser}}/P}\). This length describes the distance over which the absorbed thermal energy is diffused or relaxed to the surrounding area during laser irradiation time, \(T_{\text{laser}}\).

The thermal conductivity of the material \(\kappa_T = 111 \text{ W/(m K)}\), laser pulse duration \(T_{\text{laser}} = 5 \text{ ns}\), density \(\rho = 7133\text{ kg/m}^3\), and the specific heat of \(C_p = 383 \text{ J/(kg K)}\), are used to find \(\ell_T = 450 \text{ nm}\).

At the threshold fluence, \(\varphi_{\text{th}}(J/m^2)\), the target materials commence to vaporize in the active interaction volume [3,15]. In terms of the latent heat of vaporization, \(L_V\), of the target material, density and thermal conduction length, \(\varphi_{\text{th}}(J/m^2) = \rho_L \ell_T\) [15]. The use of the latent heat of vaporization only as the minimum required energy to ignite plasma must be extended to include a laser term to obtain a functional dependence on wavelength and on irradiance. Vaporization of the target material is necessary but not sufficient to generate the plasma because the plasma state is not simply a vaporized gas. At least some fraction of the vapor needs to be ionized to initiate plasma.

In this work, the addition of a complementary laser-dependent part is suggested, starting from the energy density threshold, \(u_{\text{th}}(J/m^3)\). The modified threshold fluence, \(\varphi_{\text{th}}\), contains over and above the basic evaporation term, \(\rho_L\ell_T\), the radiation energy term as follows,

$$\varphi_{\text{th}} = (\rho_L \ell_T + u_{\text{th}}) \ell_T. \tag{10}$$

The energy density term, \(u_{\text{th}}\), can be replaced by the threshold laser irradiance \((W/m^2)\), i.e., \(u_{\text{th}} = \frac{1}{2} I_{\text{th}} (\text{Watt/cm}^2)\), where \(c\) is the speed of light.

The laser irradiance for linear polarization, \(I\), is connected to the time-averaged ponderomotive energy \([19,20]\), \(\langle U_p \rangle\), gained by a free electron from the time-averaged electromagnetic field of the incident laser radiation at wavelength \(\lambda\),

$$\langle U_p \rangle = \frac{e^2}{8\pi^2 \varepsilon_0 m_e c^2} \lambda^2 I. \tag{11}$$

For a laser irradiance at the threshold value, \(I_{\text{th}}\), the ponderomotive energy indicates the amount of energy required to initiate ionization, i.e., \(\langle U_p \rangle = E\), where the ionization energy is denoted by \(E\). The threshold irradiance equals \(I_{\text{th}} = \frac{8\pi^2 \varepsilon_0 m_e c^2 e^2}{E \lambda^2}\), where \(m_e\) is the electron mass, \(e\) the elementary charge, and \(\varepsilon_0\) is the permittivity of free space. Therefore, Eq. (10) can be written as

$$\varphi_{\text{th}} = (\rho_L \ell_T + \frac{8\pi^2 \varepsilon_0 m_e c^2 e^2}{E \lambda^2}) \ell_T = (\rho_L \ell_T + 2.235 \times 10^{15} \frac{E}{\lambda^2}) \ell_T. \tag{12}$$

The laser threshold fluence depends inversely on the laser wavelength squared, \(1/\lambda^2\), and on the ionization energy, \(E\), in addition to the relevant thermal quantities of the bulk target material. For the same material, the threshold fluence shows larger values at shorter laser wavelength, and vice versa.

Free electrons may already exist in the vicinity of the target material, or are generated during the irradiation with laser pulses of width \(T_{\text{laser}}\). Subsequently, an avalanche breakdown is likely to occur as electron impact ionization [21]. In other words, free electrons absorb laser energy due to inverse bremsstrahlung and, as usual, the nanosecond plasma is generated and studied with LIBS. However, other experimental factors are omitted in Eq. (12), e.g., melting and boiling points [3], the ambient conditions around target, the composition of the target, purity of the material, type of oxide material, solid or powder, electrical properties, to name a few. The inclusion of more terms in the threshold fluence equation, Eq. (10), would necessitate further theoretical and experimental investigations.

Fig. 4 illustrates measured signal-to-noise (S/N) ratio of the Zn I line at 481 nm for bulk-ZnO material as a function of the three laser wavevolumes \([3,15]\). The data show that the threshold values are listed in Table 1. Fig. 4 further shows that the threshold fluence to produce plasma at the surface of the bulkmaterial depends on the laser wavelength according to \(1/\lambda^2\). This behavior is also reflected in the additional term in Eq. (12), i.e., the threshold fluence is relatively large at short laser wavelengths but decreases towards longer wavelengths. Fig. 4 also indicates
that laser-induced plasma is more readily generated with IR in comparison with UV laser radiation. Moreover, the saturation laser fluences are 19, 5.5 and 3.5 J/cm² at laser wavelengths of 355, 532 and 1064 nm, respectively.

The fluence threshold values for bulk zinc [3], for a zinc ionization energy $E_\text{f} = 9.4$ eV, for a latent heat of vaporization of zinc $L_V = 1.75 \times 10^6$ J/K, and for a thermal conduction length $\kappa = 450$ nm, the first “vaporization” term in Eq. (12) yields the value of $\rho_L v_1 \tau_t = 0.56$ J/cm², while the second “laser term” yields for a laser wavelength of $\lambda = 532$ nm the value of $\left(\frac{1}{\sqrt{2\pi\tau\sigma}}\right) \rho_L v_1 \tau_t = 2.235 \times 10^5 E_\lambda^2$ $\tau_t = 0.53$ J/cm². The repeated application of Eq. (12) for the three laser wavelengths allows one to evaluate the estimates of the threshold fluences as summarized in Table 1 together with the values obtained from the experimental thresholds determined from the results displayed in Fig. 3.

The “laser term” varies as $1/\lambda^2$, and will yield a factor of 4 lower value for 1064 nm and factor of 2.25 higher value for 355 nm than for 532 nm. The overall threshold fluence, or the sum of the vaporization and laser terms, amounts to $\psi_{\text{th}} = 1.096$ J/cm² for a laser wavelength of 532 nm. This calculated overall threshold agrees within ~20% of the experimental value of 0.91 J/cm² given in Ref. [3] under nearly the same conditions.

Comparisons between bulk- and nanomaterial experimental results indicate threshold reductions for the generation of plasma. Fig. 5 portrays the recorded signal-to-noise ratios for both bulk- and nanomaterial. Detailed reviews of the effects due to the reduction of size from bulkmaterial to nanomaterials show that the thermal properties are significantly reduced. A decrease in thermal conductivity and increase of heat capacity occur and hence one would expect a reduction in the classical thermal conduction length $\kappa = \frac{\sqrt{\kappa_\text{bulk}}}{\sqrt{\kappa_\text{nanom}}}$ from the classical bulk value of 450 nm to nanoparticle material dimensions that amount to $D \approx 30$ nm in the experimental studies. For that reason, one would modify Eq. (12) by restricting the thermal conduction length to the diameter of the nanoparticles,

$$\psi_{\text{th}}^{\text{Nano}} \approx \left(\rho N_{\text{Nano}} L_V^{\text{Nano}} + 2.235 \times 10^{15} E_\lambda^2\right) D.$$  

When using the nanoparticle diameter instead of the classical bulk thermal conduction length, the laser fluence threshold would be reduced by a factor of 15, with a further reduction due to the expected changes to the values of latent heat of vaporization. The experimentally measured thresholds using the nanomaterial instead of bulk are shown in Fig. 5 using a backward extrapolation method which yields the thresholds $\psi_{\text{Exp}}^{\text{Nano}} \leq 0.03, 0.07, 0.004$ J/cm² for 1064 nm, 532 nm, 355 nm wavelengths, respectively.

In the computation of the nanoparticle structured ZnO target, the restriction of the thermal conduction length will be the size of the nanoparticle, $D = 30$ nm. The absorbed laser energy is supposed to not relax to the surroundings. However, we kept the value for the latent heat, $L_{\text{Vnano}} = 1.75 \times 10^6$ J/K, due to lack of available data for nanoparticles. We also use the same value for the density, $\rho_{\text{nano}} = 7133$ kg/m³. With these data, one obtains the thresholds listed in Table 2. The experimental values are obtained from Fig. 5 and indicated in the 5th column. The apparent disjoint values for experiment and theory, especially for the UV wavelength of 355 nm, are most likely associated with a variation of the latent heat for the nanoparticles and to a lesser degree are due to the value of the density for our compressed nanomaterial for which we used the classical bulkmaterial value. The low value for the experimental threshold at the laser wavelength of 355 nm is indicated.

**Table 1**

<table>
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<tr>
<th>Wavelength (nm)</th>
<th>Thermal term (J/cm²)</th>
<th>Laser term (J/cm²)</th>
<th>Threshold (J/cm²)</th>
<th>Experiment (J/cm²)</th>
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<td>0.695</td>
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</table>

![Fig. 4](image)

Fig. 4. Signal-to-noise ratio of the Zn I line at 481 nm versus laser fluence recorded from bulk ZnO material for the laser wavelengths 355 nm (circles), 532 nm (squares) and 1064 nm (triangles). The arrows indicate the threshold fluences.
in brackets in Table 2. Further exploration of the experimental threshold values for nanomaterials is of interest in future work.

A further decrease in the threshold values for plasma initiation was observed via modifying the target material through addition of thin layer of nanomaterial to the surface of the irradiated target [10,13,14]. The reduction of the laser threshold fluence was qualitatively explained with the assumption of strong enhancement in the local electric field at the interface between the added nanoparticle external surface and the conductive target material surface. The local enhancement amounts to up to a three orders of magnitude increase in electric field [13,23] or up to six order of magnitude increase in laser local irradiance, which may lead to a sudden transition from multi-photon ionization to strong field, tunneling ionization [14,22,23]. In qualitative reasoning, a 6 order of magnitude increase in electric field for nanomaterial [14] can only occur at the interface between nanoparticles and a metallic surface by means of a collective electron or plasmon resonance, yet this describes a different experimental region compared to our work.

The application of Eq. (13) leads to the predicted values $\phi_{\text{exp}}^{\text{nano}} \leq 0.03, 0.07, 0.11 \text{ J/cm}^2$ for 1064 nm, 532 nm, and 355 nm wavelengths, respectively. The threshold fluence for the nanomaterial ZnO target is significantly over-predicted for 355 nm irradiation. Although there is lack of experimental data of the thermal quantities $(\Delta k_{\text{nano}}, K_{\text{nano}}, C_p^{\text{nano}}, \Delta k_{\text{bulk}})$ for the nano-ZnO component, and for radii of few tenths of nanometers, one can use Eq. (13) to estimate the experimentally measured thresholds.

Fig. 6 indicates quite a different S/N increase with laser fluence from the bulk- to nano-induced plasmas. This difference leads to a decreasing trend [11,12] of the enhancement factors with laser fluence. Fig. 6 illustrates the enhancement factors versus laser fluence; however, it would be desirable to further augment the theoretical model to explain the indicated trends. Equally, there appear to be different saturation tendencies as previously indicated in Ref. [3].

Fig. 7 displays enhanced emission dependencies on the laser irradiation wavelength for several fluences. The enhancements appear to increase towards the shorter laser wavelength for a fluence of 2 J/cm$^2$ (blue circles). This is consistent with the general trend of the absorption characteristics of nano-ZnO with relatively strong absorption in the UV region that peaks near 330 nm.

In a further discussion of the plasma generation phenomena, one can use the so-called Keldysh parameter, $\gamma$, that describes the ratio of the ionization energy or work function of the target material to the ponderomotive energy [24,25].

$$\gamma = \sqrt{E_i / 2U_p},$$  \hspace{1cm} (14)

where $U_p$ depends on the peak irradiance, $I_{\text{peak}}$. Using $I_{\text{peak}} = \phi / \tau_{\text{laser}}$, the Keldysh parameter amounts to

$$\gamma = 1\lambda \sqrt{8\pi^2 \hbar \omega \mu_0 E_i \tau_{\text{laser}} / e^2} = 1.036 \times 10^5 \frac{E_i (eV) \tau_{\text{laser}} (\text{fs})}{q (J/cm^2)}.$$  \hspace{1cm} (15)

The Keldysh parameter, $\gamma$, is independent of the nature of the material target, but it depends on the ionization energy, $E_i$, of target material and on the inverse of the wavelength, $1/\lambda$. It is estimated that possibly a threshold reduction by 30% can occur for nanomaterials of semiconductors, but such reduction remains to be confirmed and is not yet included in the threshold equation for nanomaterials in Eq. (13). Nevertheless, the Keldysh parameter is calculated for only bulkmaterial but it is useful for both bulk- and nanomaterial. The Keldysh parameter can be written as $\gamma = \alpha \tau$, where $\alpha$ is the laser frequency and $\tau$ is the tunneling time through the Coulomb barrier. For $\tau < 1$, the Coulomb barrier appears static and tunneling ionization is more likely to occur, although inclusion of bound electron dynamics by scaling the laser frequency with the classical Kepler frequency [25] may still show the possibility of multi-photon absorption for $\gamma < 1$. For our experimental conditions $\gamma \gg 1$, or $\alpha \tau \gg 1$, the Coulomb barrier appears oscillating to the electron, thereby indicating that ionization is associated with the absorption of photons that of course includes multi-photon absorption leading to ionization.

In the experimental studies, the laser fluences were varied from 2 to 20 J/cm$^2$. The zinc ionization energy equals $E_i = 9.4$ eV, and the laser pulse width was $\tau_{\text{laser}} = 5$ ns. Table 3 shows the Keldysh parameter for increasing fluences and for increasing wavelengths.

The results illustrated in Table 3 would indicate that ionization by absorption of photons is the dominant pre-ionization mechanism to initiate bulk- and nanomaterial plasma. The variation with wavelength reflects the $1/\lambda$ dependence of the Keldysh parameter. Field emission ionization by means of the tunnel effect, viz, $\gamma < 1$ in Eq. (15), may occur for peak laser irradiances and peak electric fields that are respectively 4 and 8 orders of magnitude larger than available in our experiment. Without current experimental evidence of local field enhancements, we can only

### Table 2

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Thermal Fluence (J/cm$^2$)</th>
<th>Laser Fluence (J/cm$^2$)</th>
<th>Threshold Fluence (J/cm$^2$)</th>
<th>Experiment Fluence (J/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>0.037</td>
<td>0.08</td>
<td>0.117</td>
<td>0.0459 (0.004)</td>
</tr>
<tr>
<td>532</td>
<td>0.037</td>
<td>0.0356</td>
<td>0.0726</td>
<td>0.07</td>
</tr>
<tr>
<td>1064</td>
<td>0.037</td>
<td>0.0089</td>
<td>0.0459</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Fluence (J/cm$^2$)</th>
<th>Keldysh Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>2 → 20</td>
<td>1420 → 450</td>
</tr>
<tr>
<td>532</td>
<td>2 → 20</td>
<td>944 → 300</td>
</tr>
<tr>
<td>1064</td>
<td>2 → 20</td>
<td>472 → 150</td>
</tr>
</tbody>
</table>
infer the role of multi-photon ionization for the initial stages of plasma generation followed by electron impact ionization usually encountered in micro-plasma generated with focused nanosecond laser radiation in standard ambient temperature and pressure conditions of laboratory air. Enhancements of the local fields may however occur for different experimental arrangements in investigations of phenomena at interfaces of metallic nanoparticles, e.g., for gold or silver nanoparticles.

4. Conclusions

The reported experimental studies with laser radiation at the three wavelengths of 1064 nm, 532 nm and 355 nm show larger recorded signals from ZnO nanomaterial than from bulk material. The suggested model allows one to predict enhancements along with the reduction of the laser fluence thresholds. Specifically, (1) there is strong reduction of the threshold laser fluence in the presence of nanomaterial target due to the reduction of the classical, bulk thermal conduction length to the size of the nanoparticles in the nanomaterial, and (2) the shorter the laser wavelength the larger the threshold fluence for the bulk materials, and vice versa. The laser radiation dependent threshold fluence varies with wavelength as $1/\lambda^2$. The specific mechanism for the generation of laser-induced plasma is associated with the initial multi-photon ionization followed by the typical avalanche process that occurs with electron impact ionization. In future studies, local field enhancements at or near nanoparticles will be of interest in the investigation of the observed nano–versus bulk material signal enhancements.

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References