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Regular Article

Nanosecond laser-induced breakdown assisted by femtosecond laser pre-ionization in air: the effect on spatial resolution and continuous radiation

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Abstract. Laser-induced breakdown spectroscopy (LIBS) is a powerful technique for quantitative diagnostics of gases. The spatial resolution of LIBS, however, is limited by the volume of plasma. Here femtosecond-nanosecond dual-pulsed LIBS was demonstrated. Using this method, the breakdown threshold was reduced by 80%, and decay of continuous radiation was shortened. In addition, the volume of the plasma was shrunk by 85% and hence, the spatial resolution of LIBS was significantly improved.

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is a technique in atomic spectroscopy that uses atomic spectra excited by high laser energy density to retrieve the elemental composition of a sample. Because the setup of LIBS is simple, and the signal intensity is strong enough to tolerate the interference, it has been widely applied to on-line measurements of gases [1,2], liquids [3,4], and solids [5,6]. In recent years, LIBS has been widely used in combustion diagnostics to obtain parameters such as elemental composition and mixture fraction [7–9]. However, the process of laser-induced breakdown is initiated by multiphoton ionization and avalanche ionization. The stochastic variation in the ionization process and reverse bremsstrahlung make the plasma unstable and bring some issues to LIBS [10–12]. Firstly, LIBS is usually considered as a pointwise technique, and the spatial resolution is decided by two parameters: the size of the laser focal region and the process of plasma expansion. The signal of LIBS includes both the signal from the focus region and the signal from the excitation of the surrounding gas. Therefore, the original excitation region is related to the volume of plasma, and the spatial resolution corresponds to the original excitation region. The spatial resolution is a concern in LIBS measurements since its plasma volume is on the order of cubic millimeters [13]. The issue becomes problematic where higher spatial resolution is needed. For example, the scale of flame thickness under atmospheric pressure and the vortices in gas flows are both on the order of tens of micrometers, let alone the practical combustion and gas-flow facilities that often work under much higher pressures. Therefore, it has always been an important task for us to improve the spatial resolution of LIBS to meet the requirement for diagnostics of combustion and flow fields. Secondly, the continuous radiation from the plasma interferes with LIBS measurements, and a standard measure to remove it is by using an appropriate detection delay on the order of microseconds. According to reference [14], the emission of LIBS is dominated by atomic spectra and continuous radiation at the early stage in laser-produced plasmas. Then, as the plasma cools, molecules are formed, and the atomic emission is reduced. Therefore, the LIBS measurement was obviously affected by the detection delay.

In fact, the energy of the laser that induces the breakdown in the air will significantly influence the size of the plasma and the detection delay of LIBS. Therefore, we need to find a way that lower the breakdown threshold to reduce the energy used in air breakdown, and there are two ways according to the references [15,16]. One is seeding gases with a lower breakdown threshold and the other pre-ionization. For the former, noble gases such as argon were seeded, but this intrusive method largely limits its application. For the latter, a nanosecond (ns) UV-laser was used to generate free electrons to lower the breakdown threshold. But there are still some issues to the pre-ionization. When the ns laser energy used to pre-ionize the gases is low, the density of free electrons will be limited and has little effect on the breakdown threshold; when the ns laser energy is high, it may induce air breakdown by itself from time to time. Compared with the ns laser, femtosecond (fs) laser has extremely high peak power and ultrashort pulse duration to avoid the problems faced by using the ns laser. The extremely high peak power can pre-ionize the gas efficiently with a low laser pulse energy, and the ultrashort pulse duration can suppress avalanche ionization to avoid the breakdown during the pre-ionization [17]. Therefore, the fs laser is a better choice for pre-ionization. In recent years, many studies have been performed about the fs-ns dual pulsed LIBS, such as the enhancement of the

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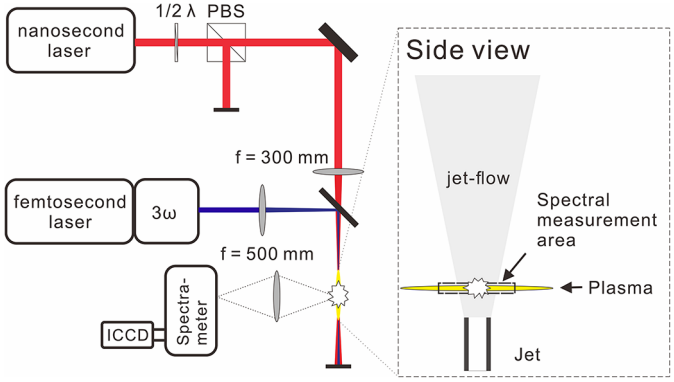


Fig. 1. A schematic of the experimental setup (inset is the side view of the jet).

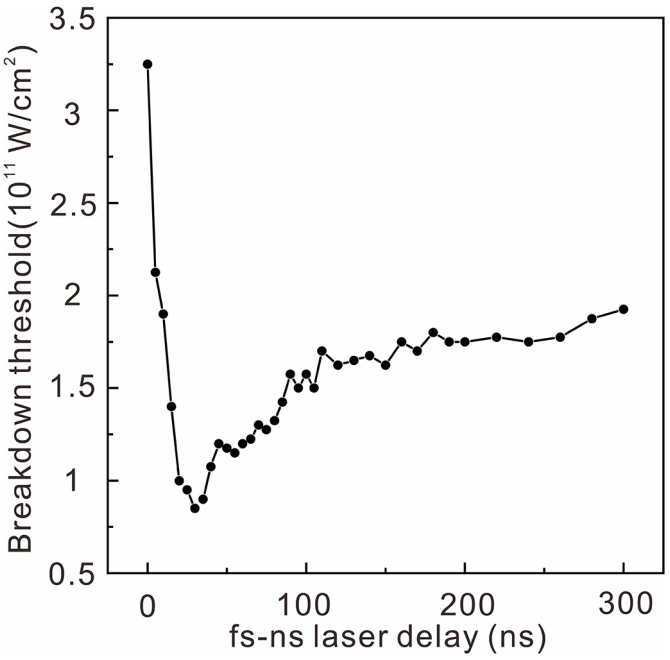


Fig. 2. The relationship between the breakdown threshold and the delay time of the ns laser relative to the fs laser.

breakdown spectra and the reduction of breakdown threshold [18–21]. However, few studies have focused on issues such as the spatial resolution of LIBS measurement and continuous radiation.

In this work, a dual-pulse strategy was used to reduce the breakdown threshold for LIBS measurements with an fs laser to achieve pre-ionization and a following ns laser to induce a breakdown. We studied the breakdown threshold, the plasma geometry, and the spectra (including continuous radiation) during LIBS measurements with and without the pre-ionization process.

2 Setup

Shown in Figure 1 is the experimental setup that includes three parts: light source, flow field generating devices, and signal collecting devices.

The light source consists of two lasers: an fs laser and an ns laser. The fs laser pulse came from a Ti:Sapphire laser system (Spitfire Ace, Spectra-Physics). The third harmonic of the fs laser was adopted, 267 nm in wavelength, ~45 fs in pulse duration, and 150 μJ in pulse energy. Besides, due to the femtosecond laser's self-focusing effect, the spot size of the femtosecond laser depends on laser wavelength, and the diameter of the spot is around 110 μm at the focal point. An Nd:YAG laser (Brilliant b, Quantel) was used to produce nanosecond pulses with a pulse duration of 5 ns at a wavelength of 1064 nm with a maximum pulse energy of 600 mJ. The pulse energy was controlled by a half-wave plate and a polarizer. In addition, the spot diameter of the ns laser is about 130 μm at the focal point. The delay between the two lasers was controlled by a digital pulse/delay generation (DG645).

The gas measurements were performed in a high-speed airflow generated from a jet (2 mm in diameter) with a velocity of 120 m/s. It should be noted that the LIBS measurements were performed in an airflow, i.e., the plasma was generated in the gas. To evaluate the geometry of the laser-induced plasma, we photographed the plasma by an ICCD camera (PI-Max 4, Princeton Instruments) equipped with a glass lens (f = 50 mm, f/1.2, Nikon), and no filter was used in experiments. To evaluate the emission spectra from the LIBS, we measured the plasma with a spectrometer (Acton 2300i, Princeton Instruments): the LIBS signal was zoomed out and imaged on the slit of the spectrometer by a lens (f = 100 mm) to collect the signal (see the inset of Fig. 1); the LIBS signal was diffracted by a grating (300 g/mm) and then captured by another ICCD camera (PI-Max 4, Princeton Instruments) at the exit port.

3 Results & discussion

Firstly, the change in the breakdown threshold was measured over the delay time of the ns laser relative to the fs laser. The breakdown threshold is defined as the laser energy, at which 90% of the laser pulses result in a visible optical breakdown. When only the ns laser is on, the breakdown threshold is about 4.25×10^{11} W/cm^2. When both the fs laser and the ns laser are on, the threshold drops significantly, and it is affected by the delay time of the ns laser relative to the fs laser. The results are shown in Figure 2.

The breakdown threshold sharply decreases and reaches its minimum (8.5×10^{10} W/cm^2) at 30 ns, and afterward, it begins to increase gradually. This phenomenon may be the result of a combination of factors, but based on [24], I propose a hypothesis that plasma refractive index changes play a significant role in the changes of the breakdown threshold. According to references [22–25], the plasma density produced by the fs laser used in this work is about 10^{16} cm^{-3}, and the relationship between the plasma density and the refraction index can be described as follows:

$$\omega_{pe}^2 = 4\pi n_e e^2/m_e \quad (1)$$

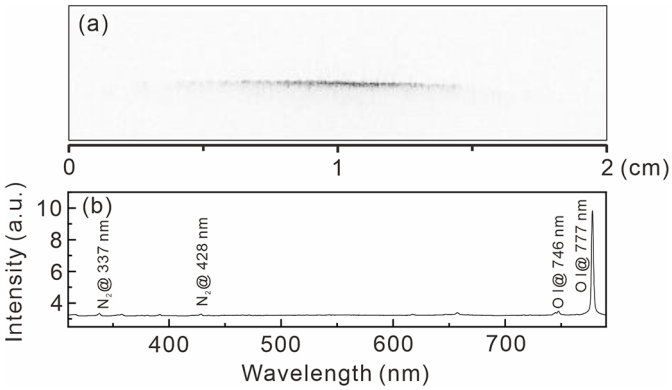


Fig. 3. The emission of the plasma generated from the fs laser: (a) the image of the plasma; (b) the spectra of the plasma.

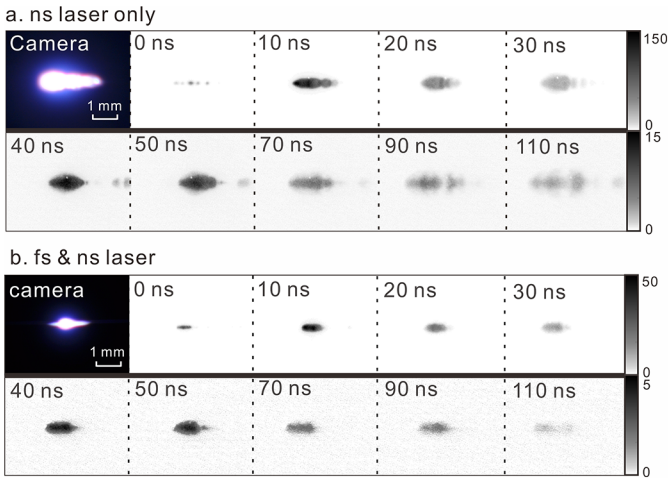


Fig. 4. The development of the plasma's geometry over time: (a) only the ns laser was on; (b) both the ns laser and the fs laser were on.

where ω_{pe} is the electron plasma frequency, n_e is the density of free electrons, m_e is the mass of an electron.

$$\omega^2 = c^2k^2 + \omega_{pe}^2 = v_p^2k^2 \tag{2}$$

$$n = c/v_p = \sqrt{1 - \omega_{pe}^2/\omega^2} < 1 \tag{3}$$

equation (2) is the dispersion relation of plasma, where c is the velocity of light in vacuum, v_p is the phase velocity of light in plasma, n is the plasma refractive index. From equations (1)–(3), we can derive that the plasma refractive index decreases with increasing free electrons density. Therefore, the density of free electrons in plasma has complicated effects on the breakdown threshold. One hand, the free electrons in pre-ionization generated by the fs laser will serve as seeds to enhance the avalanche ionization and, as a consequence, to decrease the breakdown threshold of the ns laser. On the other hand, the free electrons in pre-ionization will defocus the ns laser, which tends to increase the energy of the ns laser needed to induce breakdown. Hence, there is a balance point where the breakdown threshold is the lowest, and it can be seen in Figure 2. In summary, the hypothesis might be a relatively plausible explanation for the change in the breakdown threshold.

The plasma emission generated from the fs laser was also measured, and the results were shown in Figure 3. Due to the fs laser's low pulse energy, the intensity of the plasma emission is very weak. A gate width of 5 ns is not sufficient to complete the recording of plasma evolution. We can only obtain the fs plasma emission at the beginning, and most of the plasma emission comes from O I 777 nm.

Secondly, the photos of the plasma were obtained, and the results are shown in Figure 3. Figure 3a was obtained when only the ns laser was on (ns-only situation), and the pulse energy of the ns laser was kept at about 170 mJ when the focused power density is about $4.25 \times 10^{11}\,\mathrm{W/cm^2}$ at the breakdown threshold. Figure 3b was obtained when both the ns laser and the fs laser were on (fs & ns situation), and the pulse energy was kept at about 150 μJ for the fs laser and about 35 mJ for the ns laser (the focused power density is about $8.5 \times 10^{10}\,\mathrm{W/cm^2}$) for the ns laser. The delay time between the fs laser and the ns laser was kept constant at 30 ns, since the ns laser energy required for a breakdown is the lowest at this point. The two-color photos in Figure 3 were obtained by an SLR camera (Nikon D90) with its gate width of 0.1 s. Other images were shot by the ICCD camera at different timings after the plasma being generated to follow the development of the plasma geometry, and the gate width was kept constant at 5 ns for each shot. Comparing the photo taken by the SLR camera in Figure 3, we find that the pre-ionization process has a significant effect on the shape of the plasma, with a slight extension on both sides of the plasma, the phenomenon was mentioned in reference [26].

Next, The change in the volume of the plasma was evaluated at different conditions. Assuming that the plasma is axisymmetric and concerning that their cross-sections are given in Figure 4, the cross-section of plasma was rotated to obtain a rotating body, and the volume of the rotating body could be considered as the volume of the plasma. then the plasma volume can be easily calculated at each condition. The results can be seen in Figure 5. The volume of the plasma is almost the same in both situations at 0 ns, which means that the volume directly excited by the laser is roughly the same. But the expansion of the plasma over time shows a difference. The expansion velocity of the plasma is much faster in the ns-only situation than the one in the fs & ns situation. The expansion velocity can be estimated from the image, and it reaches the order of $10^6\,\mathrm{cm/s}$ in both situations. It should be noted that electron excitation is the main process of generating signals. During the expansion process, electrons will inevitably excite the surrounding atoms and molecules. Therefore, the volume of the original excitation region is significantly affected by ns-laser energy. Furthermore, due to the reduction of ns-laser energy in fs & ns situation, the volume of the plasma shrinks by 85% compared with the one in the ns-only situation. It indicates that the pre-ionization using the fs

laser can not only lower the breakdown threshold to 20% but also reduce the volume of the plasma to 15%, and the reduction in the plasma size is effectively equivalent to the reduction of the original excitation region. Besides, It should be noted that we performed multiple measurements under the same conditions in order to obtain the volume fluctuations of the plasma, and the fluctuation in the volume of the plasma (see the error bars in Fig. 5) produced by the ns laser only is much bigger than that produced by both the fs and ns lasers. Therefore, the plasma produced in the latter case is more stable than the former. It means that the spatial resolution and the stability of the measurements are both improved.

Thirdly, we followed the development of the plasma spectra over time, and the results are shown in Figure 5.

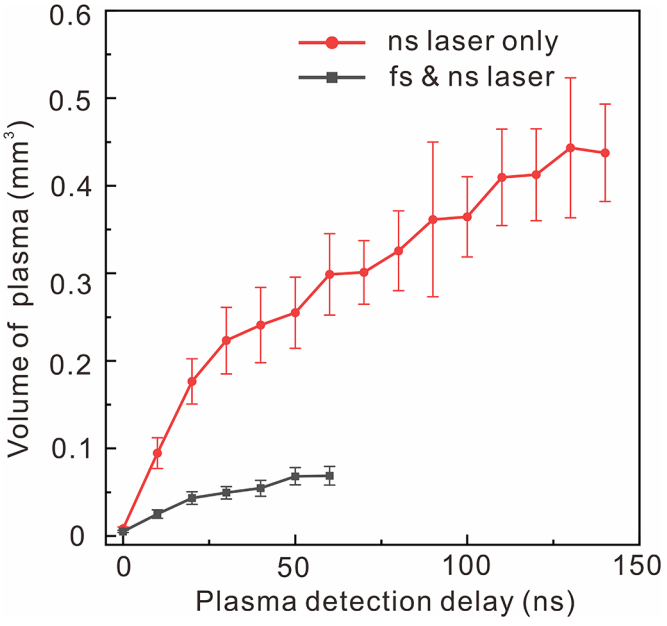


Fig. 5. The development of the plasma's volume over time.

The spectral lines of species are from the NIST database. It should be noted that the spectral lines in Figure 5a present themselves again in Figure 6b. Although the reduction of the ns-laser energy used to induce breakdown makes the signal of the fs & ns situation weaker than that of the ns-only situation, we have not sacrificed any element information.

Next, we focus on the continuous radiation for the two situations, since it is the main interference for LIBS measurements. We noticed in Figure 5 that there is no spectral line of species in the range from 485 to 490 nm, and hence, we consider the signal intensity there as a measure to evaluate the continuous radiation. The decay of the continuous radiation over time was measured, and the results are shown in Figure 6 as symbols (black squares for the fs & ns situation, and red dots for the ns-only situation). The two curves are the exponential fittings of the experiments, and the lifetime for each decay was calculated: the lifetime of the continuous radiation is 11 ns in the fs & ns situation, and it is 25 ns in the ns-only situation. The results indicate that the decay of the continuous radiation becomes faster in the fs & ns situation than that in the ns-only situation.

Furthermore, we studied the signal-to-background ratio (SBR) of the plasma emission for the two situations in Figure 6, where the signal is the contribution from the atomic lines, and the background is mainly from the continuous radiation (see the inset of Fig. 8). The results are shown in Figure 7. The SBRs of N II at 463 nm and N III at 400 nm in both situations increase over time. The reason is that the decay of the continuous radiation is faster than that of the atomic lines (see Fig. 7). It should be noted that we see a 3-fold increase in the SBR when we switch from the ns-only situation to the fs & ns situation. It indicates that the fs & ns situation favors the LIBS measurements in terms of reducing the continuous radiation interference. In other words, to achieve the same level of SBR, a much shorter delay time is needed in the fs & ns situation for LIBS to be measured, which will further improve the spatial resolution of LIBS concerning the plasma's rapid

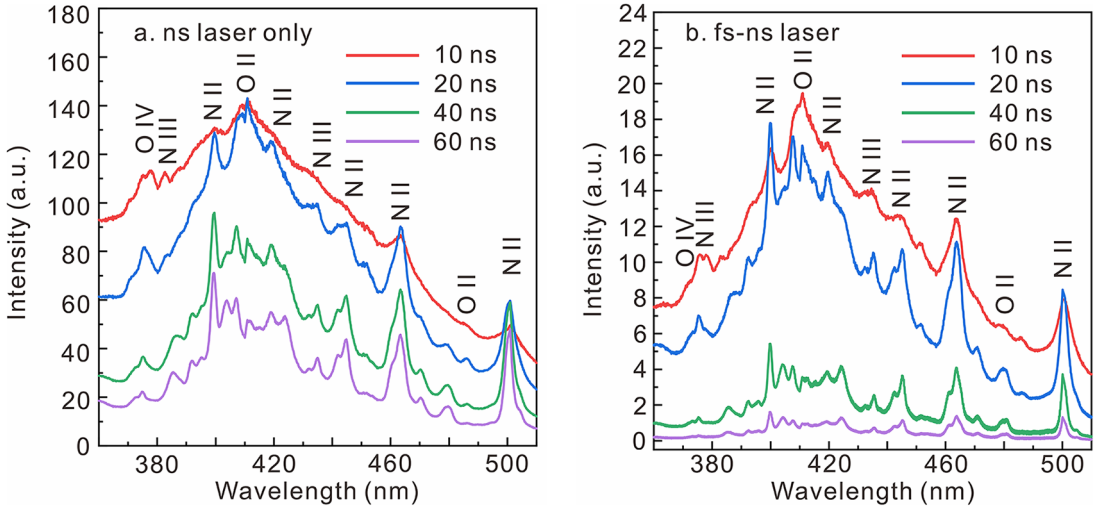


Fig. 6. The development of the plasma's spectra over time: (a) only the ns laser was on; (b) both the ns laser and the fs laser were on.

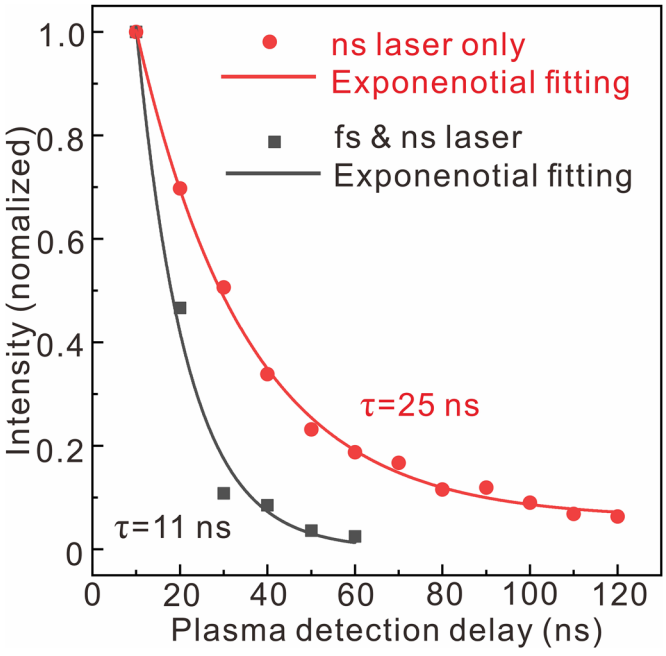


Fig. 7. The development of continuous radiation over time.

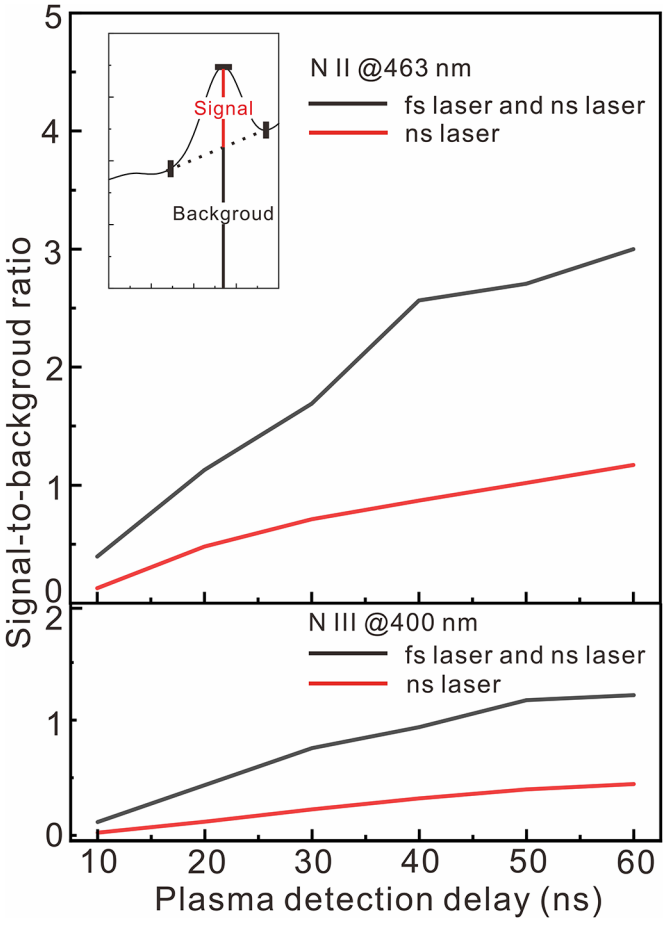


Fig. 8. The changes of the signal-to-background ratios (SBR) over time. a, the SBR of N II at 463 nm; b, the SBR of N III at 400 nm.

expansion. This feature is particularly important when the LIBS is used in a high-speed flow field, such as a supersonic scenario where a shorter delay time is preferred since a longer one will result in a substantial movement of the plasma.

4 Conclusion

In this study, a dual-pulse strategy was used to reduce the breakdown threshold for LIBS measurements in airflows with a femtosecond (fs) laser to achieve pre-ionization and a following nanosecond (ns) laser to induce the breakdown. The reduction of breakdown threshold can be controlled by the delay time of the ns laser relative to the fs laser. Then the breakdown threshold reaches the lowest point at about 35 mJ/pulse when the delay time is 30 ns. Compared with conventional LIBS that using only one ns laser, the breakdown threshold was reduced by 80%.

Further study of the plasma geometry indicates that the reduction of the laser energy used to induce breakdown after fs-laser pre-ionization can significantly reduce the volume of plasma. the results show that the volume of plasma shrinks by 85%, and the original excitation region is related to the volume of the plasma. Therefore, the spatial resolution could be significantly improved by the fs-ns dual-pulse strategy.

Finally, we focused on the time-resolved LIBS spectra, i.e., the development of continuous radiation and atomic spectra over time. The results indicate that the reduction of the ns laser energy used for the breakdown makes the decay of the continuous radiation faster. It indicates that the delay time (to avoid the continuous radiation interference) for LIBS detection can be significantly shortened, and it will also further improve the spatial resolution of LIBS concerning the plasma's rapid expansion. In summary, the fs-ns dual pulse strategy can efficiently improve the spatial resolution and shorten the delay time for LIBS detection.

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Author contribution statement

Bo Li provided the idea of using the femtosecond laser to improve the spatial resolution of the nanosecond laser-induced breakdown in air and wrote the manuscript with inputs from all the authors. Xiaofeng Li performed the experiments and proposed the method for volume calculation. Zhifeng Zhu conducted the processing and analysis of spectra data. Qiang Gao proposed the mechanism of the change in the breakdown threshold.

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