Optical Opacity of Laser Induced Plasma in Distilled Water with NaCl and TiO$_2$ Nanoparticles Impurities

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ABSTRACT—In this paper, the dynamic behavior of laser induced optical breakdown in impure water was studied by using a pump-probe technique. The plasma was induced by a 1064 nm Nd:YAG laser pulse (with pulse duration ~10 ns) in distilled water with two types of impurities: (I) a solution (highly diluted salt water as a conductor) and (II) a colloidal (TiO$_2$ in colloidal nanoparticle form as a dielectric); and finally the results were compared. The results show that, for both liquids, the probe beam transmission is reduced with pump laser intensity. Our results also show that, impurity size and type of conductivity can influence on plasma time evolution and transmissivity.

KEYWORDS: Highly diluted salt water, Laser induced breakdown, Plasma transmissivity, Pump-probe beam technique, Titanium dioxide nanoparticles.

I. INTRODUCTION

Understanding the laser induced breakdown (LIB) mechanism in transparent dielectrics and conductive solutions, formation of laser plasmas and their time evolution has been of great interest within last five decades because of its various applications. The investigation of the characteristics of LIB is important for many laser applications, including biomedical applications (e.g. plasma-mediated eye and biological tissues surgery) [1], [2], laser induced breakdown spectroscopy (LIBS) [3], inertial confinement fusion (ICF) [4] and laser induced micromachining of transparent dielectrics [5].

When a high intensity pulsed laser beam is focused into a small volume of bulk liquid, a portion of the laser pulse energy is absorbed by the bulk and optical breakdown can be occurred [6]. Essentially, avalanche ionization and multiphoton ionization are two main mechanisms responsible for the ionization of materials. The bound electrons in the valence shell of a dielectric molecule usually have an energy bandgap greater than the incident laser photon energy. However, in room temperature, a small number of free electrons naturally exist in the bulk material. These free electrons provide the required seed electrons for avalanche ionization. These small number of free electrons initially have low kinetic energy but get accelerated through the process of inverse bremsstrahlung. The accelerated electrons gain enough kinetic energy to impact ionize a molecule in collision, resulting in more low energy free electrons. The whole process repeats itself with more electrons gaining higher kinetic energy and exceeding the ionization potential of the bound electrons. By establishing these conditions, they can release bound electrons of other atoms and ionize them via impact ionization. This process leads to formation of plasma by avalanche mechanism. In the multiphoton ionization process, bound electrons may absorb several laser photons simultaneously to overcome their ionization potential [7]. N. Linz et al. showed that in nanosecond LIB, the avalanche ionization is the most responsible mechanism for the electron excitation [8]. In non-distilled water, the seed electrons for avalanche ionization mainly come from...
thermal excitation of the impurities. Consequently, the impurity concentration and type strongly affect the LIB threshold for ns pulses [9].

The study of the LIB inside liquids interested by many researchers because of its application in laser induced breakdown spectroscopy [9]. Furthermore, in synthesis of colloidal nanoparticles by laser ablation, these nanoparticles act as impurities and influence the interaction process in liquid atmosphere. Therefore, it is important to see the effect of these nanoparticles impurities in optical absorption and breakdown processes. When an intense laser pulse with sufficient intensity irradiates the bulk liquid, some phenomena may occur from which plasma formation, electromagnetic radiations originate from laser plasmas, shockwaves, bubble formation and supersonic and sound waves are some examples [10]. Although there are some reports concerning the above issues in different liquids including distilled water [11]–[16], there are not much research reports in studying laser induced breakdown in distilled water which show the influence of impurities. However, the effect of impurities on the reduction of the laser-induced breakdown threshold of air is studied [17].

In a previous work, by using shadowgraphy images, we characterize the refractive index variations in the microsecond time scale in air LIB [18]. Recently, by using a pump- probe beam technique, we studied the dynamics of air breakdown plasma for single pulse and double pulse arrangements [19], [20].

Laser parameters such as wavelength, pulse duration, fluence and the choice of the target material (solid, liquid and gas) can strongly influence the efficiency of conversion of laser energy into plasmas [6]. There are many reports in studying dynamics of optical breakdown process in water as a good dielectric [8], [11]–[16], [21], [22]. However, to our best knowledge there is no report on studying dynamics of optical breakdown process in water as an environment for colloidal nanoparticles. Particularly, the LIB of colloidal nanoparticles has been a key issue in laser induced modification of nanoparticles by post ablation without beam focusing [23], [24]. In the other study, nanoparticles have been used to enhancement of laser induced optical breakdown threshold intensity of the material [25].

Impurities such as ions and nanoparticles play an important role in the process of optical breakdown in distilled water, where they facilitates the initiation of plasma formation [11]. As an example, tap water is an interesting medium for investigating the breakdown threshold with the presence of impurities [14]. In fact, the distilled water characteristics such as dielectric constant can be changed when the impurities are increased. One of the consequences of impurities in water is the variations of dielectric constant which may result in reduction of breakdown threshold intensity. Therefore, it is important to know how the impurities influence the interaction process. We chose NaCl salt as a conductor impurity and TiO₂ nanoparticles as a dielectric impurity in our experiment to see how electrical variations in distilled water can affect its threshold intensity and breakdown dynamics. The present paper, mainly involved to experimentally studying of time evolution of laser induced breakdown plasma in a solution (highly diluted salt water) and a colloidal (TiO₂ in colloidal nanoparticle form). A pump laser beam with sufficient intensity was used to induce the optical breakdown from which its plasma was investigated by a very weak probe laser beam. By analyzing the transmitted probe beam signal, the dynamic behavior (within a time scale of few tens of nanoseconds) of the breakdown can be evaluated.

II. THE EXPERIMENTS

A. Preparation of Solution and Colloidal

The colloidal nanoparticles and highly diluted salt water were prepared by dissolving TiO₂ Nano- powder and high purity NaCl (Merck, Darmstadt, Germany) in distilled water
separately. The colloidal nanoparticles are similar to highly diluted salt water in respect of concentration and differ in terms of particles size and type of conductivity. The characteristic of these impurities are summarized in table 1. It must be noted that, both NaCl impurity and TiO₂ nanoparticles were used with low but similar concentrations in distilled water.

<table>
<thead>
<tr>
<th>Type</th>
<th>Phase</th>
<th>Size (nm)</th>
<th>Concentration (mole/lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Anatase/Rutile</td>
<td>20</td>
<td>1.96×10⁻⁴</td>
</tr>
<tr>
<td>Na⁺, Cl⁻</td>
<td>---</td>
<td>~0.1-0.2</td>
<td>1.96×10⁻⁴</td>
</tr>
</tbody>
</table>

Table 1. Physical characteristics of TiO₂ colloidal nanoparticles and highly diluted salt water.

**B. Transmission Measurement by Pump-Probe Beam Technique**

Dynamics of optical breakdown was studied by using pump-probe beam technique. The dynamics analysis is mainly refer here to time evolution of breakdown process in which the influence of the laser fluence in water and impurities were considered. In this procedure, a small portion of the pump beam was taken by an optical splitter and used as probe beam.

![Schematic diagram of the experimental setup](image)

**C. The Experimental Setup**

The experimental setup of LIB in distilled water with impurities is presented in Fig. 1. The breakdown was induced by a Nd:YAG laser with 1064 nm wavelength, ~10 ns pulse duration and 10 Hz repetition rate.

By beam splitter B.S.1, the expanded Nd:YAG laser beam was divided into two beams. The transmitted and reflected beams were used as the pump and the probe beam respectively. The pump beam was focused into the liquid cell by a doublet lens with focal length of 100 mm (anti reflected at 1064 nm) for creating the optical breakdown. It must be noted that, the beam spot radius at the focal point was ~75 μm. Intensities from 10 to 90 GW/cm² was provided by the pump laser which was used for inducing the breakdown plasma. A beam splitter B.S.2 can split the reflected beam into two parts. The transmitted part of the beam (92%) was send to a pyroelectric energy meter to measure shot to shot laser energy. The reflected part of the beam from B.S.2 was aligned orthogonal to the pump beam, and focused at the central part of the breakdown plasma by using lens L₁ (with focal length of 250 mm). By monitoring the time resolved transmission of the probe beam through the plasma by a silicon fast photodiode, the dynamic behavior of the optical breakdown in liquid was studied. Fine adjustment was also made by inspecting the signal on the oscilloscope to ensure that the probe beam was passed through the most optically dense part of the plasma. The probe beam was collected by lens L₂ (with focal length of 250 mm) and focused on the photodiode.

**III. RESULTS AND DISCUSSION**

Figure 2 shows a typical time-resolved detected probe signal transmitted through the focal region of focusing lens and recorded by oscilloscope. Figures 2(a) and 2(b) show the transmitted probe signal for TiO₂ colloidal in two conditions: when (a) the pump beam is blocked and (b) the probe signal disturbed by optical breakdown induced by the pump laser.
pulse at intensity of $46.0 \text{ GW/cm}^2$. Figures 2(a) and 2(b) are compared in Fig. 2(c).

Fig. 2. (a) Initial probe signal when the pump laser beam is blocked, (b) Transmitted probe beam when the optical breakdown plasma induced (in colloidal TiO$_2$ nanoparticles) at $46.0 \text{ GW/cm}^2$ pump laser intensity, and (c) Comparison of signals (a) and (b).

Figure 2(c) shows that the probe beam is significantly influenced by the breakdown plasma. A key parameter in this research is the behavior of the time resolved probe signal transmitted through the interaction region with and without inducing the plasma. It is well known that plasma generation in liquids or other materials requires laser intensity over a specific threshold [14]. When the pump laser beam is focused into the liquid cell, its laser intensity may become higher than the breakdown threshold intensity of the medium. Consequently, the rapid ionization of the medium leads to the plasma formation. After formation of the plasma in the interaction region, a drastic increase occurs in the material absorption coefficient. Such increase in absorption coefficient leads to a rapid rise in energy transfer from the pump beam to the medium. As shown in Fig. 2(c), the probe beam is not affected significantly within a first few nanoseconds. However, when the pumping laser beam intensity is sufficient to ionize the material, the probe beam is perturbed by the breakdown plasma. As Fig. 2(c) indicates that at this specific time, the probe beam is partially reflected, scattered and absorbed by the breakdown plasma. Therefore, these phenomena results in attenuating the probe beam.

Experimentally, the dynamic behavior of laser induced optical breakdown in liquid can be characterized by detectable effects like plasma emission, bubble formation and release of the shock waves [9]. In this study, we define a threshold time in which the probe beam signal is disturbed. The ratio of time-resolved transmitted probe signals to the original probe signals for TiO$_2$ colloidal nanoparticles (a) and highly diluted salt water (b) for four pump laser intensities are depicted in Fig. 3. The results in Fig. 3 show that, at the first few nanoseconds, the probe beam transmission is almost unity. However, after a short time (and at a specific time), it is reduced with time. This specific time is different for any pump laser intensity which also depends on the impurity.

The variation of the transmission in Fig. 3 can be explained by the dynamics of the laser induced plasma and influence of plasma on the probe beam. In the other words, when the pump laser pulse is focused into a transparent dielectric liquid, its energy is absorbed during a nonlinear absorption process. A highly conductive plasma is formed in the interaction volume.
The plasma electron density is increased dramatically in the first stage of the plasma formation as a result of more absorption of the pump laser energy in the medium. Then, plasma expands in all directions, especially towards the laser beam; consequently, the plasma electron density is decreased in the focal region. Plasma electron density production rate is further reduced within the laser pulse fall time due to reduction of the number of pump pulse photons which interacts with the medium. As the result of the increase in the electron density, plasma can become partially opaque for the probe beam. Therefore, when the probe laser beam propagates through the plasma, it can be disturbed by the plasma.

As described earlier, the free electron density is low within the early stage of the plasma formation; the plasma absorption is negligible for the probe beam. As a result, the probe beam can be transmitted through the breakdown region without significant disturbance at the first few nanoseconds. In the other words, the plasma is transparent to the probe beam at this time interval. As soon as sufficient free electrons are created by the interaction between the pump laser and the liquids, the plasma starts to absorb the probe beam. As the time passes, rising in electron density and consequent plasma absorptivity occurs. Therefore, the plasma absorptivity is increased with time and as a result, the probe transmission is reduced. As Fig. 3 shows, the trend of the transmission versus time for a solution (highly diluted salt water) and a colloidal (TiO\textsubscript{2} in colloidal nanoparticle form) (and four pump laser intensities) are similar, with minor difference for both liquids. Furthermore, the minimum probe transmission also depends on pump laser intensity and the impurity used as the material. As shown in Fig. 3, at a specific time, the reduction of the probe beam transmission is occurred. We define this specific time as the threshold time. In this time, the plasma electron density reaches a critical value in which the probe beam is considerably absorbed by the plasma. It must be noted that, in many studies, this critical value in the plasma electron density is called briefly as the critical density of plasma [6, 29].

The dispersion relation of an electromagnetic wave, with wavenumber \( k \), and angular frequency \( \omega \), in plasma is given by [29]:

\[
\omega^2 = \omega_p^2 + k^2 c^2
\]  

where, \( \omega_p \) is the plasma frequency and \( c \) is the light velocity in vacuum. The plasma refractive index (\( \mu \)) can be described by Eq. (2):

\[
\mu = \left(1 - \frac{\omega_p^2}{\omega^2}\right)^{1/2}
\]  

Since, light (e.g. the probe beam) can propagate only if \( \mu \) is real, hence it is necessary that \( \omega^2 \geq \omega_p^2 \). Since, plasma frequency is proportional to its electron density (and the
electron density of breakdown plasma is a time and space variant function), the condition of \( \omega^2 \geq \omega_p^2 \) implies that the light can penetrate only for times and spatial positions (in plasma) in which the plasma frequency is equal or lower than the light frequency. The density at which \( \omega = \omega_p \) is satisfied, is called the critical density and given by Eq. (3):

\[
n_c = \frac{\omega^2 m_e \varepsilon_0}{e^2}
\]

(3)

where, \( e \) is the electron charge, \( \varepsilon_0 \) is vacuum permittivity, \( m_e \) is the electron mass and \( n_c \) is the critical density [29].

![Fig. 4. Plasma transmissivity as a function of pump laser intensity for NaCl in distilled water and colloidal TiO₂ nanoparticles.](image)

Figure 4 shows the total transmissivity of the plasma (for the probe beam) versus the pump beam intensity. The total transmissivity was calculated by integrating the transmission of the probe beam over time for any specific pump beam intensity. It can be seen that, the total transmissivity of the plasma decreases with increasing the pump laser intensity for any specific impurity. Furthermore, it can be seen that at higher intensities, the transmissivity has low values for two cases. This small transmissivity is due to the increase in the plasma electron density generated by the laser pulse at higher intensities. In the other words, the amount of probe beam energy absorbed by the plasma is closely related to the plasma thermodynamic characteristics (such as electron density, temperature) during the probe pulse time scale. Previous studies show that, the plasma characteristics such as the rate of electron density growth, and temperature together with plasma expansion are time and spatial varying functions which depend on pump laser intensity [29].

A main purpose of this study was to evaluate the effect of impurities on the optical breakdown in water. As depicted in Fig. 4, the reduction of plasma transmissivity also depends on the type of impurity. For pump laser intensity within the range of 20-90 GW/cm², the plasma transmissivity decreases from 0.66 to 0.46 in NaCl solution. While within similar pump intensity range, it is reduced from 0.76 to 0.34 in colloidal TiO₂ nanoparticles, which is larger about twice of that in NaCl solution. Two types of impurities with different physical properties were used in our experiment. Highly diluted salt water is still a good conductive solution and has Nano size particles. The TiO₂ in colloidal nanoparticle form, on the other hand, is a dielectric colloidal with ~5 eV band gap and Nano size particles (~20 nm). According to Fig. 4, for pump laser intensities lower than 28.0 GW/cm², plasma transmissivity for TiO₂ colloidal is higher than that of NaCl solution. However, this figure shows that within the range of 28.0-90 GW/cm², the results are different from those which occur for intensities lower than 28.0 GW/cm². Such results can be explained as follow: The onset of cascade ionization requires the presence of free electrons in the focal volume [11]. In non-distilled water, the seed electrons for avalanche ionization mainly come from thermal excitation of the impurities. Consequently, the impurity size, concentration and material strongly affect the LIB process for ns pulses [9]. It must be noted that, our experiments were performed for both types of impure water with similar concentration. In the case of NaCl solution (which has high electrical conductivity), higher density of free charge carriers facilitate the breakdown process. In fact, the free electrons of Na⁺ and...
Cl\(^-\) ions act as seed electrons in the optical breakdown process. However, in colloidal TiO\(_2\), the pump laser energy must overcome the bandgap of dielectric TiO\(_2\) molecules and ionize them.

The other issue that may affect the breakdown process in colloidal nanoparticles is the nanoparticle size characteristics \[30\]. The absorption of the pump pulse energy by the impurities may differ for particles with different sizes. As a result, the plasma electron density and its time evolution may be different for different particle sizes. The results show that, these two issues must be considered together and the probe beam transmission is influenced by either issues. The results in Fig. 4 show that, the effect of these two subjects may result in a similar plasma transmissivity for both liquids (at 28.0 GW/cm\(^2\) pump laser intensity). Therefore, in our experiment, there are two factors that may affect in the plasma transmissivity: the type of impurities (conductor or dielectric) and the size of impurities. However, for a more detailed description, the breakdown threshold intensity should be considered as well. The breakdown threshold intensity is the minimum energy density required for plasma generation which in colloidal nanoparticles depends on the state of aggregation of the nanoparticles. The threshold intensity is usually high for gases, but has lower values in liquids, and solids \[30\].

The threshold time versus pump laser intensity for two liquids are presented in Fig. 5. As described earlier, it is a time when the plasma electron density is sufficient for considerable absorption of the probe beam. As show in Fig. 5, the trend of the threshold time versus pump beam intensity for highly diluted salt water and TiO\(_2\) in colloidal nanoparticles are similar to trend in Fig. 4. In fact, the characteristic of the impurities such as electrical conductivity and particle size can strongly influence the volume of the plasma and the speed of the plasma growths. Since the population of the free electrons in the plasma considerably depends on different matters such as pump beam intensity and characteristics of the impurities, they can also affect the threshold time.

![Threshold time versus pump laser intensity for laser induced breakdown for NaCl in distilled water (circles) and in colloidal TiO\(_2\) nanoparticles (squares).](image-url)

For visible wavelengths, numerical calculation on the breakdown thresholds by J. Noack and A. Vogel showed that, there is no difference between the breakdown thresholds in pure water and in the presence of impurities \[11\]. A strong influence of impurities was, however, predicted for infrared wavelengths and long pulse durations. For long wavelengths, the creation of the first electron is the prerequisite for the whole breakdown process. Impurities facilitate the generation of the initial electrons and can thus largely change the temporal evolution of the electron density and consequently reduce the threshold time. As shown in Fig. 5, the threshold time values for highly diluted salt water are higher than those of colloidal TiO\(_2\) nanoparticles in the majority of the pump laser intensities. Such results means that higher population of free electrons in conductive salt water can provide the seed electrons which initiate the breakdown process. Finally, the results show that the larger size of the TiO\(_2\) nanoparticles may increase the absorption of pump beam energy.
IV. CONCLUSION
Dynamics of laser induced optical breakdown in liquids strongly depends on physical characteristics of medium and concentration of the impurities. Time-resolved transmission of a probe beam through the breakdown plasma induced in distilled water with colloidal TiO$_2$ nanoparticles and NaCl as impurity was measured. The results show that, both plasma transmissivity and the threshold time was reduced with pump laser intensity for both impurities. From the results, it was concluded that, in comparison with NaCl solution, the plasma transmissivity and the threshold time is lower in colloidal TiO$_2$ nanoparticles. From the results, one can also conclude that the size, concentration, and electrical characteristics of the nanoparticles in colloid (or the concentration of NaCl solution) as impurities influence the probe beam transmission.

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