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Material Dependence of Laser-induced Breakdown of Colloidal Particles in Water

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Laser-induced breakdown of colloidal suspensions, such as polystyrene, ZrO_2, and SiO_2 particles in diameters of 100-400 nm in water is investigated by nanosecond flash-pumped Nd:YAG laser pulses operating at a wavelength λ = 532 nm. The breakdown threshold intensity is examined in terms of breakdown probability as a function of laser pulse energy. The threshold intensity for SiO_2 particles (1.27×10^{11} W/cm^2) with a size of 100 nm is higher than those for polystyrene and ZrO_2 particles with the same size, namely 5.7×10^{10} and 5.5×10^{10} W/cm^2, respectively. Results indicate that the absorption of five photons is required to induce ionization of SiO_2 particles, whereas the other particles necessitate four-photon absorption. These breakdown thresholds are compared with those measured by nanosecond pulses from a diode-pumped Nd:YAG laser having a different focusing geometry.

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I. INTRODUCTION

Laser-induced breakdown (LIB) refers to the plasma formation by focusing an intense pulsed laser beam into substances. LIB is a complex phenomenon with various optical, electronic, thermal and mechanical effects. Over the last decades, considerable effort has been extended to understand the LIB phenomenon in various phases [1-6]. The physical effects associated with optical breakdown are visible plasma emission, acoustic shock wave, and cavitation bubble formation. Experimentally, these observable signals after plasma formation define optical breakdown in aqueous media and are used for the determination of the LIB threshold intensity. The threshold intensity required for LIB is a function of both the medium characteristics (ionization potential, impurity level) and the beam characteristics (wavelength, pulse duration, beam waist at focus). The parameter dependence of LIB thresholds is dealt with in greater detail in [7].

It is well known that the threshold intensity (I_{th}) for LIB strongly depends on material properties in the order of I_{th} (solid) < I_{th} (liquid) < I_{th} (gas) [8]. This characteristic is used for particle detection when a laser energy is chosen just below the threshold energy for a liquid. When a particle is suspended in the focal region of laser pulses, a plasma is ignited due to its lower threshold intensity. In the late 1980's, Kitamori *et al.* made an attempt to quantify traceable colloidal contamination in the manufacturing process of semiconductors [9,10]. They made use of the photo-acoustic effect associated with optical breakdown. During the last decade, laser-induced breakdown detection (LIBD) which has been developed extensively by Kim *et al.* [11-13] has attracted increasing interest in a number of applications for characterizing very dilute colloids in aqueous media.

An atom or a molecule with ionization potential I_p can be ionized by the simultaneous absorption of k photons of energy $h\nu$. A typical electron ionization potential of a solid ranges from 6 < I_p < 10 eV [14], and thus k is between 3 and 5 for the nonresonant ionization with visible laser pulses, e.g. 532 nm with a photon energy of $h\nu$ = 2.3 eV. The efficiency of the breakdown process depends on the material properties of a dense solid particle, e.g. ionization potential, as does avalanche ionization by inverse bremsstrahlung and impact processes. Quantification of the colloid number density and the size distribution entails an adequate calibration of the LIBD method. For this purpose, there are only a few reference particles over a wide size range other than polystyrene particles, which are available as well-defined monomodal particles, ranging from 20 to 1000 nm or greater. Hence, an operational relationship of LIBD in connection with the material property of colloids has to be established.

This work aims to determine threshold intensities for breakdown of different monomodal colloids, such as polystyrene, SiO_2, and ZrO_2 particles dispersed in pure water. LIB generated by focusing nanosecond laser pulses is analyzed in terms of an acoustic shock wave and optical emission associated with plasma formation. Results of breakdown thresholds obtained by different laser systems are compared and discussed.

II. EXPERIMENT

The apparatus used in the experiment is illustrated schematically in Fig. 1a). The laser system to perform the experiments is a Q-switched Nd:YAG laser (Continuum Surelite I-20) which delivers 6 ns pulses with energies up to 200 mJ at 532 nm at a repetition rate of 20 Hz in a single transverse mode (TEM_{00}). The divergence of the laser pulse is 0.6 mrad. The linearly polarized laser pulses with a beam diameter of 4 mm are focused with a 40 mm plan-convex focal lens into a quartz cell (Hellma, 45×10×10 mm^3). The pulse duration is measured by a high speed GaAs PIN photodiode (Hamamatsu) and a digital storage oscilloscope (HP/Agilent 54845A Infiniium, 1.5 GHz, 8 GSa/s). The pulse energy is measured using a pyroelectric detector (Newport, 818J-09) calibrated against a thermal head power meter (Ophir, 3AP). For monitoring the incident pulse energy, a small fraction of pulse energy is reflected onto the pyroelectric detector by a thin quartz plate beam splitter. The pulse energy is varied by a pair of Glan-Thomson polarizers (Newport, 10GL08).

The shock wave associated with thermal expansion after plasma formation was detected by a piezoelectric crystal attached to the quartz cell perpendicular to the beam propagation. On the other hand, the plasma emission in the vicinity of the laser focus is imaged onto a monochrome CCD camera (JAI CV M10, 782× 582 pixels) with a magnified macro-microscope (LEICA). The exact position of laser-induced plasma along the beam propagation axis is appraised on a pulse-to-pulse basis for thousands of laser pulses, and thus a spatially resolved distribution of breakdown events is measured. An assembly of a neutral filter and an interference filter with a narrow bandwidth singles out the 532 nm beam from the background emission. The 2-D plasma image from the CCD camera is recorded by a frame grabber card and processed by a software program (Optima 6.1).

The contour lines in Fig. 1(b) represent the isophotes (region of equal laser intensity) of the laser pulse propagated along the Z-axis. The ellipsoid in the central region corresponds to the highest laser intensity. The laser intensity decreases with an increasing distance from the beam waist at Z = 0 along the laser beam axis. The laser pulse is incident from the left, as depicted

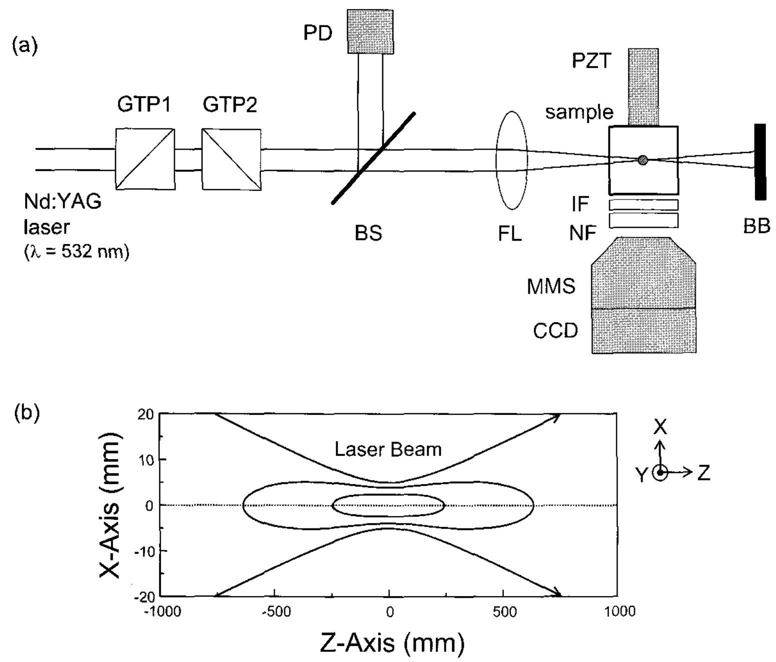

FIG. 1. (a) Experimental setup: GTP: Glas-Thomson polarizer, BS: beam splitter, PD: pyroelectric detector, FL: focusing lens, PZT: piezoelectric transducer, IF: interference filter, NF: neutral filter, MMS: macro-microscope, CCD: charge-coupled device, BB: beam blocker. (b) The hyperbolic lines, so-called isophotes (region of equal laser intensity), in the focus region. The beam direction is from left to right, and the Gaussian focus is at Z = 0.

in Fig. 1(b).

Colloidal suspensions of polystyrene (100, 400 nm, Duke Scientific Corp.), ZrO_2 (100 nm, Alfa Aesar GmbH) and SiO_2 particles (100, 400 nm, Polysciences, Inc.) are prepared in pure water. The particle number density studied in the present work is $\sim 10^7$ particles/cm^3. Prior to each experiment, colloidal particles dispersed in pure water (Millipore, 18.2 MΩcm^{-1}) are ultrasonicated for 30 minutes in order to remove pre-existing micro bubbles. In addition, the outstay of cavitation bubbles at laser focus caused by thermal plasma expansion is suppressed by utilizing a flow-through quartz cell at a flow rate of 1.5 ml/min, since the plasma formation by subsequent laser pulses may be perturbed due to a higher breakdown threshold of micro bubbles remaining in the focus region.

III. RESULTS AND DISCUSSION

3.1 Determination of the beam waist

The threshold for laser-induced breakdown is an intensity threshold, therefore breakdown should occur along the isophotes with $I = I_{th}$ in Fig. 1(b). At a threshold energy E_{th}, breakdown occurs where maximum intensity is encountered, i.e., at the beam waist (Z = 0). With increasing pulse energy, the threshold intensity is exceeded at larger cross sections along the beam path and a larger plasma length is produced. Plasma growth preferentially takes place towards the laser because most of the incident energy is absorbed by the plasma generated before the beam waist. This is particularly true for nanosecond pulses, where only a few fractions of the incident pulse energy are transmitted through the focal region. Such a distributed shielding effectiveness of laser-induced plasma has been discussed in [2,15].

Threshold intensity I_{th} (W/cm^2) is calculated by

$$I_{th} = P_{th}/(\pi\ \omega_0^2) \text{ with } P_{th} = E_{th}/\tau_p, \qquad (1)$$

where P_{th} is the threshold power (W) calculated from the threshold pulse energy (E_{th}) in joules divided by the pulse width (τ_p) in seconds, and ω_0 is the beam radius at the focus. It is worth noting that a measurement of the actual beam waist is very critical in specifying the breakdown intensity thresholds. The beam waist is either measured by the knife edge technique [16] or calculated by the diffraction-limited focusing theory [17]. The spatial profile (beam radius) as a function of distance from the beam waist at Z= 0 is calculated according to

$$\omega^2(Z) = \omega_0^2\{1+[\lambda Z/(\pi\omega_0^2 n)]^2\}, \text{ with } 2\omega_0=(4\lambda/\pi)(f/\#), \qquad (2)$$

where λ is the wavelength, n is the index of refraction (n = 1.336 in water at 532 nm), and the f-number ($f/\#$ = f/D, D: beam diameter before the focusing) expresses the diameter of the entrance pupil in terms of the effective focal length of the lens.

According to Eq. (2), the beam waist $2\omega_0$ also called spot size of the laser beam, is calculated to be 6.8 μm at the 1/e^2 energy level. Additionally, the beam waist is determined to be 7.4 μm at the 1/e^2 level of the radial breakdown distributions on the x-axis of pure water at laser focus, as shown in Fig. 2. The radial distribution of breakdown events of pure water remains unaffected by the variation in incident pulse energy. This indirectly determined beam waist agrees well with that calculated by Eq. (2), and thus the mean value of calculated and measured beam waists (7.1±0.4 μm) is considered the beam waist, unless otherwise stated. However, the discrepancy of beam waist between measurements and calculations which leads to erroneous calculations in intensity calculations of the focal area and thus to inflated intensity calculations is discussed in detail in [4,18].

3.2 Material dependence of LIB threshold intensity

The breakdown curve is obtained in terms of breakdown probability (BP) as a function of incident pulse energy which is defined by counting the number of breakdown events relative to the number of incident laser pulses (if 10 breakdown events occur for 1000 laser pulses, the BP is 1%). The threshold intensity is defined as a point where breakdown probability exceeds 1%. Fig. 3 shows breakdown curves of different colloids as a function of incident laser intensity which is calculated according to Eqs. (1) and (2). As can be seen, the threshold intensity for ZrO_2 particles with a size of 100 nm agrees well with that for polystyrene particles of the same size, whereas the SiO_2 particles require higher laser intensity for LIB.

In the nonresonant Keldysh theory [19], the ionization coefficients depend solely on the ionization potential

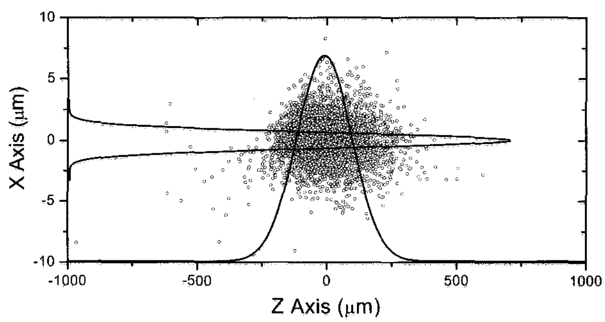

FIG. 2. Two-dimensional distribution of 3000 breakdown events of pure water in the focus region at incident pulse energy of 1 mJ.

and is otherwise independent of the particular level structure of the atom or molecule. For nonresonant ionization of substances with a visible wave of 532 nm ($h\nu = 2.3$ eV), the ionization is a k-order multi-photon ionization (MPI) process (k-order process: number of photons needed for ionization). The ionization potential (I_p) is 7.8 eV for polystyrene [20,21], 8.7 eV for ZrO_2 [22], 11.7 eV for SiO_2 [23], and 12.6 eV for H_2O [14]. The absorption of four photons of $h\nu = 2.3$ eV should be sufficient to induce ionization of ZrO_2 and polystyrene whereas SiO_2 requires the absorption of five photons for ionization and thus higher laser pulse energy by a factor of ~2. The highest threshold intensity is needed for water breakdown due to the 6-photon absorption. The threshold intensity for LIB is correlated well with the ionization potential of materials in the order of $I_p(H_2O) > I_p(SiO_2) > I_p(ZrO_2) > I_p$(polysytrene). The breakdown threshold intensities are dependent on both particle size and material property. A summary of the size and material dependence of LIB is given in Table 1.

3.3 Comparison of threshold intensities

Fig. 4 shows breakdown curves for pure water and SiO_2 particles with sizes of 100 nm and 400 nm as a function of laser pulse energy. The threshold intensities are further measured by using a diode-pumped Nd:YAG laser (BMI-Soliton, DIVA II) with TEM_{00} as light source of an excellent Gaussian beam (>99%). The pulse duration of the laser beam is 7 ns. The only difference between the two laser systems lies in the focusing geometry.

Beam focusing of the diode-pumped Nd:YAG laser is achieved by a Galilean telescope of aspherical lenses. By a f = −50 mm plan-concave lens, the beam is expanded by a factor of 3 and 100 mm behind collimated by a f = +50 mm plan-convex lens, resulting in an effective focal length of ~80 mm. As already mentioned, the critical parameter in determining breakdown threshold is the beam waist, which is measured to be 10 μm in air by knife edge technique and then calculated to be 13.4 μm in water using diffraction-limited focusing [24], compared with 7.1 μm for the flash-pumped Nd:YAG laser. Therefore, the diode-pumped laser system needs higher pulse energy for LIB by a factor of ~4 to reach the laser intensity produced by the flash-pumped laser system. As is apparent in Fig. 4, the ratio of breakdown thresholds of SiO_2 particles relative to that of

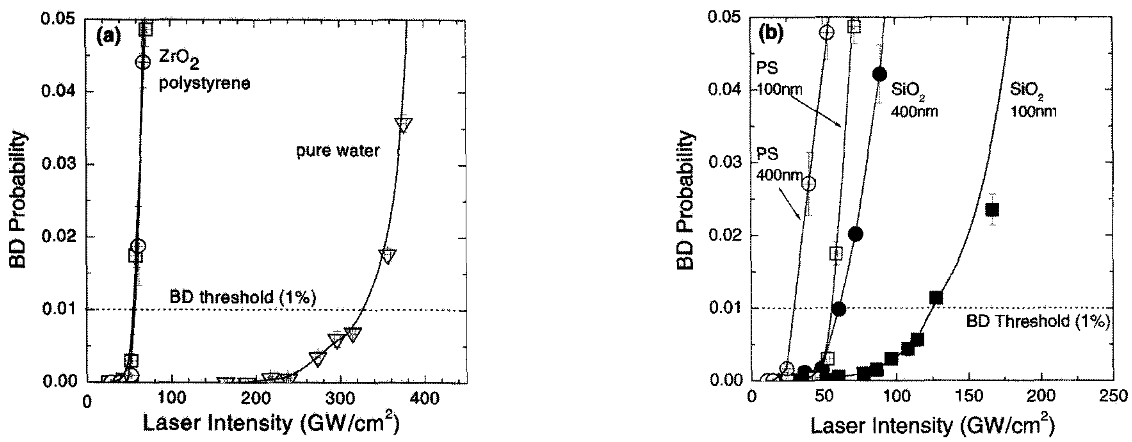

FIG. 3. (a) Breakdown curves of polystyrene particles (□) in diameter of 100 nm, ZrO_2 particles (○) with 100 nm and pure water (▽) as a function of the laser intensity. (b) The effect of breakdown thresholds on the particle size for polystyrene particles of 100 nm (□) and 400 nm (○) and for SiO_2 particles of 100 nm (■) and 400 nm (●).

TABLE 1. Threshold intensity for laser-induced breakdown (LIB) of colloids (particle sizes in the parenthesis measured by scanning electron microscopy (SEM) or photon correlation spectroscopy (PCS)).

	particle		breakdown threshold
material	ionization potential (eV)	size (nm)	I_{th} (GW/cm^2)
polystyrene	7.8 [20,21]	100 (97±3) 400 (404±4)	55 30
ZrO_2	8.7 [22]	100 (96±4)	57
SiO_2	11.7 [23]	100 (100±30) 400 (400±30)	125 60
H_2O	12.6 [14]	-	326

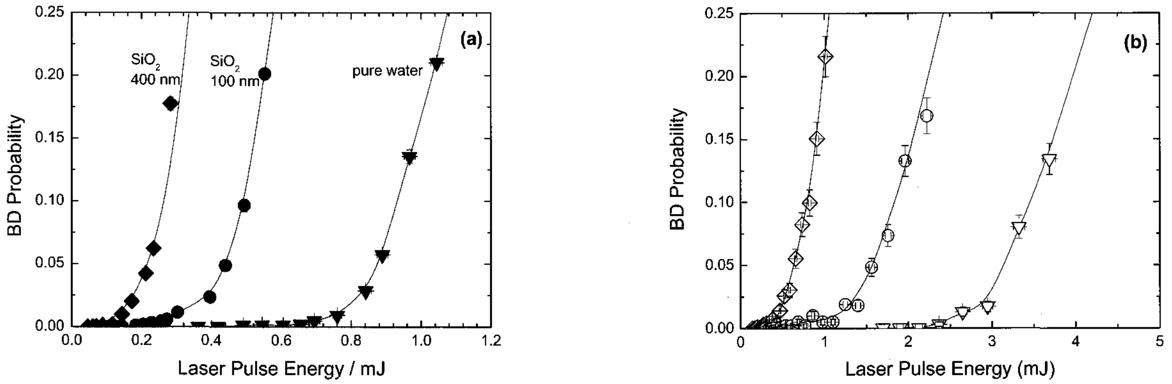

FIG. 4. Breakdown curves of pure water (triangle) and SiO_2 particles with sizes of 100 nm (circle) and 400 nm (rhombs). Filled symbols (a) represent results measured by the flash-pumped Nd:YAG laser, whereas open symbols (b) refer to experimental data obtained by the diode-pumped Nd:YAG laser.

pure water remains almost unchanged at breakdown threshold level, and the size-dependent threshold intensities of SiO_2 particles are within the estimated uncertainty in the calculated beam waist. Summarily, both measurements deliver comparable threshold intensities for SiO_2 particles and pure water, independent of the experimental configurations.

IV. CONCLUSION

The dependence of LIB with the compositional variation of nanoparticles has been investigated. Dielectric laser-induced breakdown shows a threshold-like behavior with a probabilistic nature with particle sizes and material properties. The threshold intensities for breakdown are significantly correlated with ionization potential of materials. Furthermore, the focusing geometry does not exert influence on the LIB characteristics, when the laser beam parameter remains comparable. For the purpose of analyses, the proper calibration of the LIBD method which has been performed with well-defined monodispersed polystyrene particles cannot be applied for all of the colloidal systems, but for the most solid particles which need more or less the absorption of four photons for ionization. Nevertheless, it should be another subject to investigate breakdown behavior of nanoparticles with coating materials or with a mixture of different composites.

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