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Pulsed laser induced microbubble in gold nanorod colloid

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ABSTRACT

The characterization of a pulsed laser induced microbubble (PLIMB) in gold nanorod (GNR) colloid was studied experimentally. The generation of PLIMB is due to the optical breakdown in water. Using an ultrasonic transducer and a probing He–Ne laser associated with a photodetector, the photoacoustic (PA) signals and the bubble formation of the multi-cycled oscillation of a single PLIMB were measured simultaneously. Both results are in agreement to show that the lifetime of PLIMB is reduced as the gold concentration increases. This phenomenon is attributed to the plasmonic light scattering (Faraday–Tyndall effect) in GNR colloid; the energy for optical breakdown is reduced at the focus due to laser-beam defocusing. The effect is particularly pronounced at the longitudinal surface plasmon resonance of GNRs. In addition, the divergence angle of 532-nm CW laser beam through gold nanoparticle (GNP) colloid was measured. Our results show that the divergence angle increases as the concentration of GNP increases. This phenomenon again elucidates Faraday–Tyndall effect.

1. Introduction

The cavitation microbubbles induced by a focused pulsed laser beam in water have been studied using the passive and active ultrasound method to measure the photoacoustic (PA) signals [1,2]. The pulsed laser-induced microbubble (PLIMB) is generated due to the optical breakdown in the focus of laser beam within water. Alternatively, an optical technique of using light beam deflection was proposed to monitor the bubble formation of PLIMB [3,4]. Moreover, an ultrasound method has been used to measure the PA signals of a microbubble in dilute gold colloids of different concentrations (2–10 ppm) [5]. In addition, the lifetime of a PLIMB was characterized at different wavelengths by using this ultrasound measurement [5]. Because of the surface plasmon resonance (SPR) of gold nanoparticle (GNP), a strong light scattering, the so-called the Faraday–Tyndall effect, is caused for a laser beam through a GNP colloid. The SPR is due to the collective motion (oscillation) of electrons in a single GNP. As a result, a slight defocusing of the Gaussian beam in GNP colloid was found to reduce the size of the PLIMB. The Faraday–Tyndall effect is particularly significant, when Nd: YAG laser of 532 nm is used. This is because that the SPR of GNP is at 530 nm. Recently, gold nanorods (GNRs) have been synthesized [6,7]. The advantage of GNRs is that their longitudinal SPRs are tunable by adjusting the aspect ratio and size. Normally, the larger the aspect ratio, the more red-shifted the longitudinal SPR is. In the past decade, a lot of researches have been conducted and proven the applicability of GNRs for biomedical imaging and therapy in the near infrared (NIR) regime [8–14]. For example, GNRs can be utilized as therapeutic agent for photothermal therapy [11], and as contrast agent for the PA imaging [12,13]. Recently, a few of fundamental researches related to PA behavior of plasmonic nanobubbles in GNP or GNR colloids irradiated by a pulsed laser have been reported [15–17]. The major difference in mechanisms of PLIMB and plasmonic nanobubbles is that the former is caused by the optical breakdown of water and the latter by the plasmonic heating of metallic nanoparticles.

In this paper, we propose a measurement system including an ultrasonic transducer (UT) to detect the PA signals of the PLIMB and a probing laser with a photodetector (PD) to monitor the bubble formation. Combining the two measurements, we can analyze the lifetimes of multi-cycled PLIMB to characterize the Faraday–Tyndall effect of GNR colloid in more detail. This method has more advantages in the identification of multi-cycles, compared to the previous PA method we used for PLIBM [5]. In addition, we measure the divergence angle of laser beam through GNP colloid to study the plasmonic light scattering effect of GNPs (Faraday–

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Tyndall effect). The increased divergence angle of a Gaussian beam through GNP colloids of different concentrations can demonstrate this effect quantitatively, particularly at the SPR wavelength.

2. Material and methods

Fig. 1 shows the configuration of our photoacoustic spectroscopy system. A pulsed Nd: YAG laser of 532 nm with an optical parametric oscillator (OPO) is used to generate a pulsed laser beam of different wavelengths [5]. The duration time of each pulse is 10 ns. The probing laser, a stabilized He–Ne laser of 633 nm, associated and a PD (ET-2020, a biased silicon detector with cutoff frequency > 200 MHz, risetime and falltime: 1.5 ns) are used for monitoring the transient bubble formation of PLIMB. Once there is a bubble formed, the intensity of probing beam detected by PD is reduced to indicate the dimension of bubble. A long-working distance (6 mm) objective lens of 20× was used to focus Nd: YAG laser beam into a cuvette (1 cm × 1 cm × 4.5 cm) containing GNR colloid. Additionally, an UT of a focal length of 1/4″ with a bandwidth of 25-MHz is inserted in the cuvette for the detection of the PA signals generated from the cavitation of a LIMB at the focus. An ultrasound Pulser/Receiver (DPR300, JSR) is used for the UT signal amplification and filtering. Through an oscilloscope, these PA and PD signals are acquired and digitalized. In addition, a power meter is used to measure the pulse energy. For our experiment, the degassed water and colloids were used for avoiding the solved gas in water to form permanent bubbles. To investigate these behaviors of PLIMB, we used the system, as shown in Fig. 1, to measure the bubble formation and the accompanying acoustic signal simultaneously. The former is monitored by a probing laser and PD, and the latter detected by UT. A digital storage oscilloscope (GWINSTEK GDS-3504) of 8-bits digitization was used for data acquisition; the bandwidth is 500 MHz and maximum sampling rate is 4 GHz. The sampling rate we used for PA and PD is 250 MHz.

The transient formation of PLIMB can be simply described by the Rayleigh model; the dynamic radius $R(t)$ of bubble is a function of time [1,3,5],

$$\left(\frac{dR}{dt}\right)^2 = \frac{2P_0}{3\rho}\left(\frac{R_{max}^3}{R^3} - 1\right) \tag{1}$$

where P_0 is the atmosphere pressure and ρ the liquid density. Here the maximum radius R_{max} is proportional to the cube root of the optical breakdown energy [1,5],

$$R_{max} = \sqrt[3]{\frac{3E_B}{4\pi P_0}} \tag{2}$$

where E_B is the internal energy of bubble. In addition, the lifetime t_L of a transient bubble is related to the maximum radius,

$$t_L = 1.83\sqrt{\frac{\rho}{P_0}}R_{max} \tag{3}$$

From Eq. (1), the bubble wall velocity is a function of its radius (R) [4],

$$V_B = \sqrt{\frac{2P_0}{3\rho}\left[\left(\frac{R_{max}}{R}\right)^3 - 1\right]} \tag{4}$$

According to Eq. (4), the wall velocities of bubble are much higher than the sound speed at the beginning of bubble growth and the end of shrinkage; i.e. as $R = 0$, $V_B \to \infty$. As a consequence, the supersonic-speed movement produces a sonic boom of the shock wave, which is the cause of PA signal. Therefore, there are two pulses in PA signal associated with each oscillation of a bubble, where the time difference is bubble's lifetime. The PA signal of PLIMB can be detected by UT to characterize the multi-cycle oscillation. Alternatively, the dynamic bubble formation can be real-time monitored by the optical deflection of the probing laser beam (He–Ne laser) in our experiment.

Moreover, we designed a simple experiment to measure the divergence angle of a 532-nm CW laser beam through GNP colloid to verify the plasmonic light scattering (Faraday–Tyndall effect) of GNPs quantitatively. The schematic is shown in Fig. 2, where a beam profiler is used to measure the width of Gaussian beam. After measurement, the following equation is used to calculate the divergence angle

$$\theta = 2\tan^{-1}\left(\frac{D - D_0}{2L}\right) \cong \frac{D - D_0}{L} \tag{5}$$

where D_0 and D are the measured Gaussian width of laser beam through water and GNP colloid, respectively. Here L is the inside width of the cuvette; $L = 1$ cm. The unit of divergence angle is in milliradian (mrad). We expected that the divergence angle of the laser beam through GNP colloid should be strongly related to the plasmonic light scattering of GNPs, depending on the concentration of GNPs.

3. Results and discussion

A GNR colloid was synthesized for experiment. The TEM is shown in Fig. 3(a). The absorbance spectrum was measured to identify the longitudinal SPR of GNR (706 nm), as shown in Fig. 3(b). We measured the concentration of GNR colloid using ICP-OES in advance, and then prepared several solutions of different concentrations for experiment. Using the measurement system of Fig. 1, the PA and PD signals of a PLIMB in water irradiated by pulse energy of 3.56 mJ at 700 nm, close to the longitudinal SPR of GNR, are detected, as shown in Fig. 4(a). Fig. 4(a) indicates that

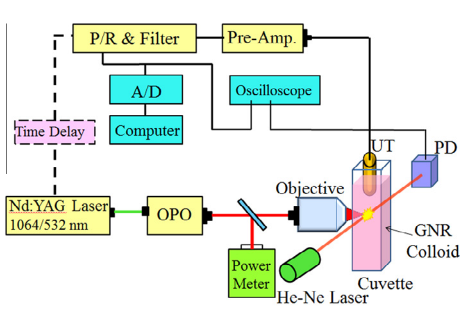

Fig. 1. Experimental setup for the measurement of PLIMB in GNR colloid. UT: ultrasonic transducer. PD: photodetector.

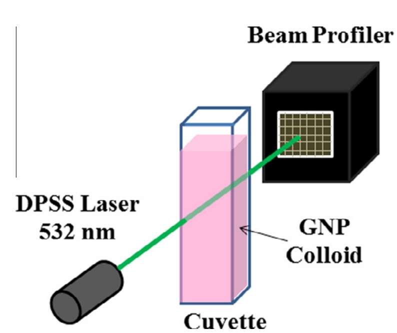

Fig. 2. Schematic of divergence angle measurement of laser beam through GNP colloid.