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Original Research Paper

Size-dependent effect of gold nanospheres on the acoustic pressure pulses from laser-irradiated suspensions

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ABSTRACT

We carried out the experimental measurements of photoacoustic responses, where the suspensions of spherical gold nanoparticles (NPs) of different diameters (20, 40, and 50 nm) in water at different concentrations and different temperatures (4 and 20 °C) were irradiated by 0.8-ns laser pulses. In the case of 20 °C, the values of photoacoustic signals normalized by the light absorbance of the NP suspension decreased with increasing the NP size. The photoacoustic signals at 4 °C were significantly reduced compared with those at 20 °C. These experimental results are in fair agreement with the estimations from our phenomenological model, where the acoustic pressure pulse is represented by a sum of two contributions from the NPs and the surrounding liquid medium.

1. Introduction

In recent years, bioimaging techniques for clinical diagnostics have received great attention and various techniques have been developed to improve detection sensitivity and treatment outcome in patients. One example is photoacoustic imaging (PAI), which is a nonionizing and noninvasive imaging modality based on the photoacoustic effect: the irradiated light is absorbed by a target to be converted into a thermoacoustic wave that is detected by an acoustic transducer [1,2]. The contrast in PAI counts on the optical-to-acoustic conversion (optoacoustic) efficiency, and can be exogenously improved by use of nanoparticles (NPs) as contrast agents [2–4]. With recent growing advancement in nanotechnology, a large variety of NPs have been developed for the PAI contrast agents [5,6].

Henceforth, for the sake of clarity, let us consider a simple system, that is, a weakly light-absorbing liquid dispersed with strongly absorbing NPs, where the amplitude of the photoacoustic signal should depend largely on the transfer of heat between two materials of the NPs and host liquid. At low laser fluence, the acoustic signal results from the thermoacoustic response of the heated host liquid as well as that of the heated NPs. If the laser fluence reaches a threshold, the temperature of the NPs can exceed the boiling temperature of the host liquid. Subsequently, a vapor layer appears on the surface of every NP to undergo rapid expansion, thus giving rise to an effective photoacoustic signal. This cavitation-induced enhancement of the photoacoustic signal at high laser fluence has been investigated in several experimental and theoretical studies [7–17], the principal focus of which was placed on direct observations and theoretical descriptions of bubble formation around heated particles and the resultant enhanced amplitude of the acoustic signal. On the other hand, very few studies have reported experimental results and physical modeling in the case of low-level laser irradiation that help us to better understand the fundamentals of the acoustic signal resulting from the thermoacoustic response of the heated NPs and heated host liquid in the absence of cavitation, except for the following studies.

In a recent study, Chen et al. [18] have demonstrated that the acoustic signal generated from laser-irradiated suspensions of spherical 26-nm gold NPs is influenced by the temperature- and material-dependent properties of the host liquids (i.e., water, toluene, and silicone oil), and that the photoacoustic signal is dominated by the surrounding liquid rather than the NPs although the light absorbance of the former is still weaker than that of the latter. Only a few studies [18–22] have reported physical modeling of the acoustic signal produced from such a heated inhomogeneous solution including NPs (other than the particles of the larger sizes ranging from micrometers to millimeters) in the case of low-level laser irradiation. Nevertheless, the effects of NPs on the photoacoustic

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phenomena are not understood well and remain to be explored experimentally and theoretically from a fundamental point of view.

Main focus of the present study is placed on how the thermoacoustic responses from a laser-irradiated suspension of NPs are influenced by the size of the NPs. We report the experimental measurements of the photoacoustic signals, where the suspensions of spherical gold NPs of different diameters in water at different concentrations and temperatures are irradiated by nanosecond laser pulses at low laser fluence. The results from the experiments are compared with those from our phenomenological model that is developed from our previous study [19].

2. Experimental methods

2.1. Gold nanospheres

The aqueous suspensions of spherical gold NPs of different diameters (d_p = 20, 40, and 50 nm at the number concentrations of 7.0×10^{11}, 9.0×10^{10}, and 4.5×10^{10} particles/mL, respectively) were purchased from British BioCell International (Cardiff, UK). The concentrated suspensions were prepared in clean test tubes by solvent evaporation at 60 °C [19]. Before and after this concentration process, no significant change was found in the profile of the absorption spectra of the gold NP suspensions, indicating that the concentration process hardly affected the morphology and the monodispersity of the gold NPs.

2.2. Setup for photoacoustic signal detection

Fig. 1 depicts our experimental setup for photoacoustic signal detection, which is the same as employed in our previous study [19]. A sample cuvette was immersed in a temperature-controlled water bath and illuminated by a pulsed beam from a dye laser pumped by a nitrogen laser (OB-401/OB-4300; Optical Building Blocks, Birmingham, NJ, USA), where the pulse width and repetition rate were 0.8 ns (=t_L) and 5 Hz, respectively. The wavelength of this laser was set at 522 nm, where the energy was $I_0 \equiv 107$ μJ/pulse. The cross section of the specific region irradiated by the laser pulse was $s_L \equiv 0.524$ mm^2 and the laser fluence was $F_0 \equiv I_0/s_L = 204$ J/(m^2 pulse). The acoustic signal from the laser-irradiated gold suspension was detected by a membrane-type hydrophone (H9C-036; Toray Engineering, Japan) with a measurable frequency range of 0.5–10 MHz. The distance between the hydrophone and the center of the sample cuvette was ≈ 38 mm. The output signal from the hydrophone was recorded by an oscilloscope (TDS-2012; Tektronix, Beaverton, OR, USA) through an amplifier (Model 5682; Olympus NDT, Waltham, MA, USA). The split laser beam was detected by a photo-diode (DET10A; Thorlabs, Newton, NJ, USA) and fed to the oscilloscope as the trigger signal. The measurements were performed at the suspension temperatures of 4 and 20 °C, using the cuvettes of light pass length of L = 0.92 mm.

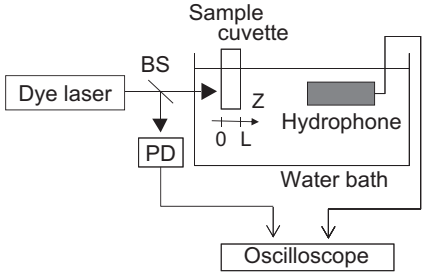

Fig. 1. Illustration of the experimental setup. BS: beam splitter, PD: photo-diode.

The results were obtained after averaging over 128 signals from every sample at each temperature. After that, the absorption spectra of these laser irradiated suspensions were measured. Before and after the laser irradiation, no significant change was observed in the profile of the absorption spectra of the suspensions, implying that the laser irradiation hardly caused the fragmentation/aggregation of the gold NPs.

3. Theoretical descriptions

3.1. Thermodynamic relation for a heated monodispersed suspension containing particles

Let us consider a heated monodispersed suspension containing particles at the number density of n_p. Supposed that every particle has the thermal energy therein (e_p) and the surrounding medium has the energy resulting from the heat conduction from the particle thereto (e_m) immediately after the laser irradiation with a nanosecond pulse, where e_{tot} ($\equiv e_p + e_m$) represents the total energy per particle. The physical properties of the particle and medium are defined as follows: c_i, the specific heat capacity; ρ_i, the mass density; κ_i, the isothermal compressibility; β_i, the thermal coefficient of volume expansion, where the subscript i denotes the particle (p) or the medium (m). Hereafter, we assume that the physical properties of the particle and medium (i.e., c_i, ρ_i, κ_i, and β_i) are constant at the initial temperature.

Starting from the thermodynamic relation ($\Delta V/V = -\kappa\Delta P + \beta\Delta T$, where ΔV, ΔP, and ΔT denote the volume, pressure, and temperature changes of a system of interest, respectively), we have derived the local pressure rise p_{tot} of an inhomogeneous liquid containing particles upon short-pulsed laser irradiation and two contributions from the particles (p_p) and the medium (p_m), as elaborated in Ref. [19]:

$$p_{tot} = n_p e_{tot} \cdot [(\kappa_p \Gamma_p/\kappa_m) \cdot x + \Gamma_m \cdot (1 - x)] = p_p + p_m \tag{1a}$$

$$p_p \equiv (\kappa_p \Gamma_p/\kappa_m) \cdot (n_p e_{tot}) x \tag{1b}$$

$$p_m \equiv \Gamma_m \cdot (n_p e_{tot})(1 - x) \tag{1c}$$

with

$$\Gamma_i \equiv \beta_i/\kappa_i c_i \rho_i \tag{2}$$

$$x \equiv e_p/e_{tot}, \quad 1 - x \equiv e_m/e_{tot} \tag{3}$$

where Γ_i denotes the Grüneisen parameter for the particle (i = p) or medium (i = m) and n_p e_{tot} represents the volumetric optical absorption by the particle suspension. As will be expected from Fig. 5, the limiting of x ($\equiv e_p/e_{tot}$) → 0 is equivalent to that of (particle size) → 0, where the particles are considered to be dissolved as solute molecules in the medium at a certain concentration. In this case, Eq. (1a) reduces to $p_{tot} = (n_p e_{tot})\Gamma_m$, which is a popular form of the acoustic pressure [1,23]. It is worth noting that Eq. (1) is consistent with the idea given in Ref. [18]: If the pressure is measured in the medium far from the particle, the contributions from the solid particle and the liquid environment can be separated by setting the liquid and the solid volume expansion coefficients, respectively, to zero. Consequently, we can estimate the pressure rise p_{tot} and two contributions, p_p and p_m, from (1), if the thermal energies per particle, e_{tot}, e_p, and e_m, are obtained.

3.2. Heat production by a laser-irradiated metal nanosphere and the heat transfer into its surrounding liquid

Let us consider a single spherical particle of diameter d_p (=$2r_p$) suspended in an infinite liquid medium irradiated by a laser pulse,