Proceedings of the 6th International Symposium
on
Advanced Nuclear Energy Research
—INNOVATIVE LASER TECHNOLOGIES IN NUCLEAR ENERGY—

Photoacoustic and Photothermal spectroscopies

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Photoacoustic and photothermal spectroscopy methods can be effectively applied to the analysis of microparticles in condensed matter. A more violent photothermal conversion phenomenon of a particle, laser breakdown and accompanying plasma and acoustic emission, was applied to individual detection and analysis of ultrafine particles in ultrapure water. Laser-like nonlinear emission from the plasma was observed.

Key words : Photoacoustic spectroscopy, Photothermal spectroscopy, Trace analysis, Nonlinear emission

1. Introduction

Nowadays, the principle idea of the photoacoustic effect has been enlarged to that of a "photothermal" effect in which the basic physical phenomenon providing spectroscopical information is an energy conversion from photo-energy to thermal energy. Some methods to detect and analyze the photothermal effect have been proposed, such as thermal lens, optical beam deflection and laser induced grating methods. In addition to the methodological studies in this early period including theory and instrumentation, various applications of photothermal spectroscopy have been developed over a wide range of science and technology, including physics, chemistry, biology, medicine, agriculture, electronics, semiconductor engineering, nuclear engineering and others. Many original articles and reviews have been published for the respective fields, since it has now become too popularized to prepare an overall review. Hence, this paper focuses on recent progress in spectroanalytical application of photothermal spectroscopy to mainly condensed matter.

2. Photothermal effect in the condensed phases

Phenomenological representations of typical photothermal phenomena in solid and liquid samples are illustrated in Fig. 1. Other, new photothermal phenomena are described in later sections. As shown in Fig. 1, intermittent optical excitation and relaxation of a sample generates a periodical variation of the temperature field, resulting in changes of pressure, stress, mass density, refractive index, and other mechanical, thermal and optical parameters. Photoacoustic spectroscopy utilizes the acoustic, elastic and thermal waves, and detects them with a microphone and piezoelectric transducers as shown in the drawing. In photothermal deflection spectroscopy, a probe laser beam, which passes horizontally through the neighborhood of the excitation beam irradiated surface, is deflected due to diffraction or refraction by a refractive index wave, and the signal is measured from its deflection angle. Any surface deformation also deflects the reflected probe beam on the irradiated spot.

Hereafter, these photothermal effects are briefly summarized with a general description to clarify the spectroanalytical, spectrochemical and physical meanings of the signals. Signal generation is phenomenologically classified into two processes as show in Fig. 2. The first process is a photothermal energy conversion and migration from optical energy to thermal energy. This energy conversion is achieved mainly through optical excitation and nonradiative relaxation. Other energy conversion processes, such as a photochemical reaction, photosynthesis, and phase transition are also able to provide thermal energy as a source term of the signal. The generated thermal energy macroscopically migrates in the medium by thermal diffusion, leading to formation of a heat distribution. This process, in which the optical energy is converted into thermal energy and the heat distribution is formed, is referred to as the photothermal process herein.

When the excitation beam irradiation is intermittent, the heat distribution fluctuates periodically. This, in turn, causes a fluctuation of the temperature field in the medium which then causes various mechanical and optical parameters to fluctuate. The second process is referred to as the thermodynamic process. These fluctuations of mechanical and optical parameters are detected by the individual photothermal spectroscopical method as mentioned in Fig. 1.

3. Ultrafine Particle Analysis by Laser Breakdown Effect

For an example of a more violent photothermal conversion process, laser breakdown and accompanying acoustic emission have been applied to individual detection and counting of ultrafine particles in liquids.[1,2,3] An ultrafine particle smaller than 0.1μm cannot be detected by the conventional laser scattering method, which is one of the most sensitive methods, because of the background due to medium Rayleigh scattering. In place of the laser scattering method, a laser breakdown acoustic method was proposed, in which plasma formation from the ultrafine particle in liquids is induced by irradiation with a focused pulsed laser beam and the ultrafine particles are counted individually by detecting an acoustic pulse.

Figure 3 shows a particle in a focused excitation beam. When the power density of the optical radiation exceeds the threshold of particle breakdown, the particle becomes a plasma and a strong acoustic emission due to explosive expansion and strong absorption of the plasma is induced. This plasma formation and acoustic emission process can be considered as one of the most violent photothermal energy conversion processes, because the plasma temperature is estimated to be at least 10^4K (several eV).[3] The particle breakdown threshold is lower than those of liquid media and air bubbles, so only the particle can be broken down, and miscounting due to air bubbles and liquid breakdown can be avoided.[1] Using this method, it was demonstrated that 38 nm polystyrene ultrafine particles, which are one of the smallest standard particles on the market, were counted individually at the number density level of ultrapure water, 10^2 particles per 1 ml as shown in Fig. 4. The minimum detectable particle size, expected to be smaller than 10 nm, was at least one to two orders smaller than for the conventional laser scattering method. The acoustic pulse height showed a tendency to be proportional to the particle size,[2] and atomic and ionic emission lines of particle component elements could be observed in the plasma emission.[3] Therefore, laser breakdown acoustic spectrometry is expected to be a novel analytical method for ultrafine particles in liquids.

Furthermore, we have found a non-linear optical phenomenon in the plasma emission. A line-like atomic emission line for hydrogen at 656.3 nm, which was measured in the forward direction plasma emission induced from a 0.3 μm polystyrene particle, is shown in Fig. 5. The mechanism of this laser-like emission is not clear at the present time; however, it is considered to be a secondary laser emission from the underwater plasma due to non-equilibrium population kinetics of atomic levels in the plasma. This effect is expected to be a basis for another novel spectrometric method for microparticles.[4]

4. References

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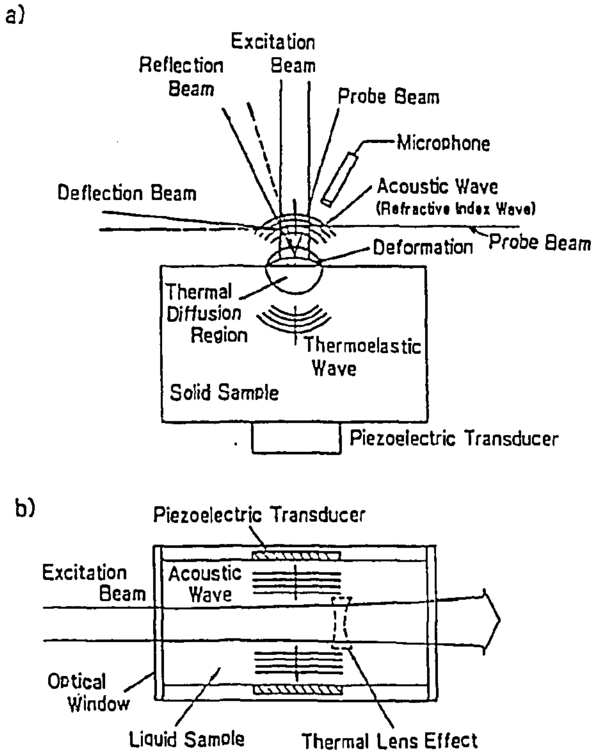

Fig. 1. Photothermal effects on and in condensed phase samples. (a) Solid sample, and (b) liquid sample [1].

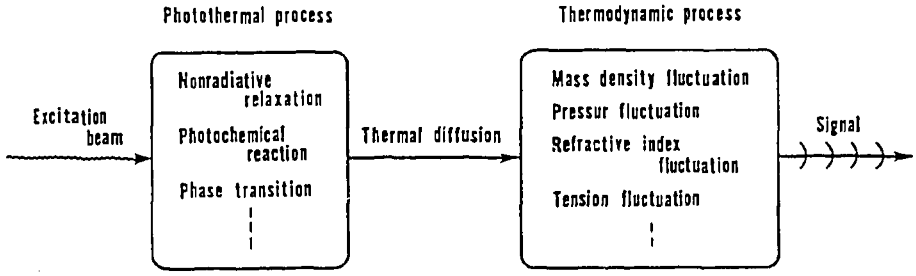

Fig. 2. Phenomenological representation of the photothermal signal generation process.

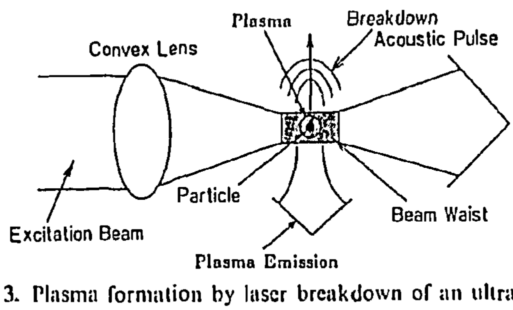

Fig. 3. Plasma formation by laser breakdown of an ultrafine particle.

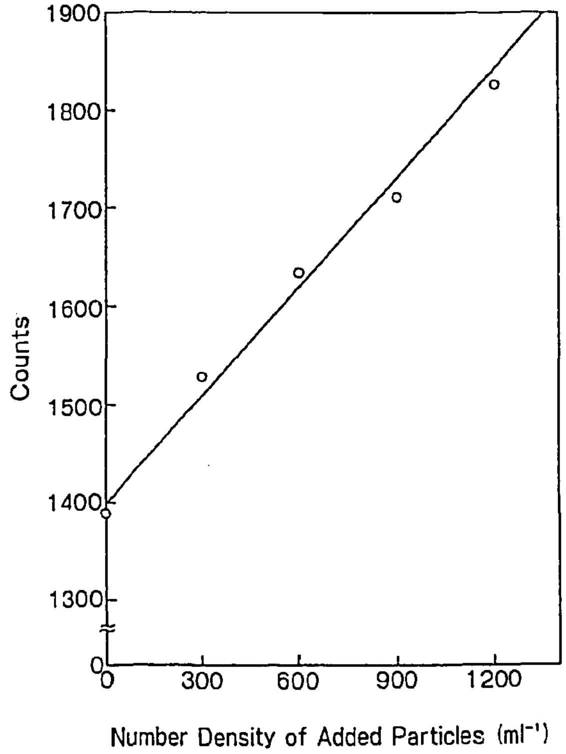

Fig. 4. Dependence of the breakdown acoustic pulse counts on the number density of the added 0.038 μm polystyrene ultrafine particles.

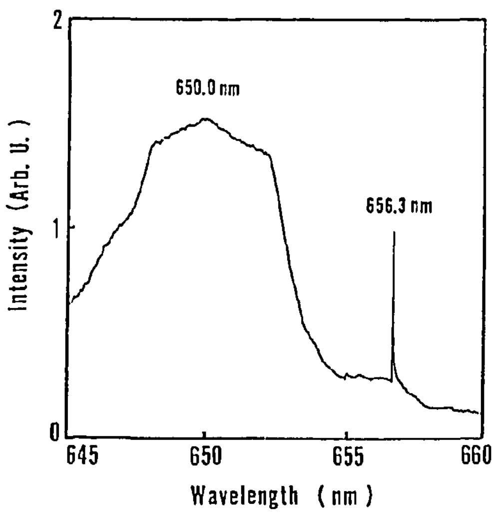

Fig. 5. Forward direction plasma emission spectrum of an underwater plasma generated from a 0·3 μm polystyrene microsphere.