Pulsed photoacoustic spectroscopy for powder suspension using a flash lamp

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Pulsed Photoacoustic Spectroscopy for Powder Suspension Using a Flash Lamp

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A pulsed photoacoustic spectrometer for powder suspensions was constructed by using a flash lamp, interference filters, a cylindrical piezoelectric transducer, a digital memory, and a microcomputer. Photoacoustic response signals were characterized by both the interval of the first peak and the vibrational frequency of the transducer. The light-absorption signals were different from the false signals caused by scattered light. Photoacoustic absorption spectra were measured for CdS powder suspensions and for methylviologen cation radical formed on UV-irradiated Pt/TiO$_2$ powder in solution.

Photoacoustic spectroscopy (PAS) is useful for measuring the absorption spectra of light scattered materials (*1*). The advantage of PAS is based on its spectra detection method in which the absorbed light is measured as heat energy. The instrumental principle of the conventional PAS method is to detect the heating and cooling of the sample being irradiated by a chopped light beam. Several reports (*2–4*) investigated powder suspension samples. However, a microphone was used as a detector in these experiments such that acoustic transmission from the condensed sample to the gaseous medium which connects the microphone may be the source of some error. In order to attach the transducer directly to the condensed phase, piezoelectric ceramics, PZT, have been used recently (*5–7*). The PAS technique using a lock-in amplifier, however, seems not to be suitable for measuring samples of powder suspension, since the light scattering may induced false signals. To decrease the effect of scattered light, Morishita, Fujishima, and Honda (*8*) used a T-shaped cell of which the irradiated part and PZT transducer were separated by an adequate distance to eliminate the scattered light effect. Although this device may be effective, the sensitivity is low. This drawback is inappropriate for the suspension samples having weak absorption in the presence of intense scattered light, which will be encountered in the case of the semiconductor photocatalytic system.

As an alternative technique, a pulsed light beam and a gated detector or time-responsive amplifier were used to replace the chopped light beam and a lock-in amplifier, respectively (*9*). The pulsed photoacoustic spectroscopy was extensively studied by Patel and Tam (*10*). Using a pulsed dye laser, they measured the absorption spectra with a very high sensitivity. In their technique, the observed signal was acoustic pulse which was generated by the sample when excited by pulsed light. The acoustic pulse transmits through the medium at the velocity of sound, while a part of the scattered light is absorbed directly on the surface of the PZT transducer. The transmission of the acoustic pulse may cause a time difference between the two signals. When the duration of pulsed light and response time of the transducer are significantly shorter than the time difference, the two signals can be detected separately. Therefore, the pulsed photoacoustic technique seems suitable for measuring samples of powder suspension.

In pulsed photoacoustic spectroscopy, a pulsed laser has been used exclusively. Although the pulsed laser provides the fine, intense, and well-monochromatized light beam, it is difficult to vary wavelength over a wide spectral range. On the other hand, a xenon flash lamp emits pulsed light in the wavelength range from the UV to visible region. However it must be focused and monochromatized by some devices. As far as we know, no attempt to employ a flash lamp as a light source of the pulsed photoacoustic spectroscopy has been reported. In this paper, we will show that such a flash lamp can be used as a pulsed light source for PAS of powder suspension samples.

EXPERIMENTAL SECTION

Figure 1 shows a schematic diagram of the photoacoustic spectrometer used in this study. As a light source for acoustic signals, a FX-279 flash tube (EG&G Electro-Optics) was employed with a homemade power source of 1.6 J/pulse (1.8 kV, 1 μF). The repetition frequency was 5 Hz. The duration of the light pulse was about 1 μs at the half magnitude. The light from the flash lamp having the arc discharge length of 1.5 mm was gathered by a convex lens into a parallel beam, and passed through a cold filter and an interference band-pass filter of 30 mm diameter. The interference filter was arranged so as to be changed by a slide projector mechanism. The wavelengths of the filters ranged from 400 nm to 700 nm at intervals of 10 nm. The bandwidth was about 10 nm at half value of maximum transmittance. The monochromatized light was focused onto an aperture of 6 mm diameter by a convex lens and into a sample cell. Since the irradiation energy of the flash lamp was insufficient to induce a photoacoustic signal, a monochromator was not used. The energy of the incident light was estimated to be the order of microjoules per pulse from the measurement with a power meter (Coherent Radiation, Model 210) for unfiltered light. As shown in Figure 2, the sample cell is composed of a cylindrical piezoelectric ceramic PZT (Tohoku Kinzoku, type N-21), a quartz window, and a Pyrex glass vessel. A cylindrical PZT cell is known to be sensitive to photoacoustic signals generated along its center axis (*6*). The sample cell was mounted in a double shielding box in order to eliminate the noise from the discharge of the flash lamp. For in situ measurements during the photocatalytic reactions, a 250-W high-pressure mercury lamp was used to irradiate the suspension with a UV-pass filter (Toshiba, UV-D33S) and a partially reflecting glass plate.

The electric signal of the PZT transducer was fed to a LI-75A low-noise preamplifier (NF Circuit Block Inc., ×100), and amplified 100-times with a homemade circuit. The amplified signal was fed into a transient digital memory (Riken Denshi, Inc., TCH-1000) and accumulated with a microcomputer (OKI Electric, if-800). Since the signal intensity obtained by one flash was similar to that of the thermal noise of the amplifier, the accumulation was carried out 1280 times in most measurements. The accumulation and averaging of the photoacoustic response signals also reduced the effect of the fluctuation in the flash lamp intensity. An interface circuit was made for the microcomputer to exchange the interference filters, operate the transient digital memory, and control the discharge of the flash lamp.

RESULTS AND DISCUSSION

Figure 3A represents the time response of photoacoustic signal for a dilute solution of Rotring black ink. The first peak of the time profile was observed at 8 μs after the flash discharge. For the suspended solution of titanium dioxide (TiO$_2$) powder, the first peak was 6 μs after the flash as shown in Figure 3B. The TiO$_2$ powders of about 1 μm diameter did not absorb, but scatter the light beam of 490 nm. The first
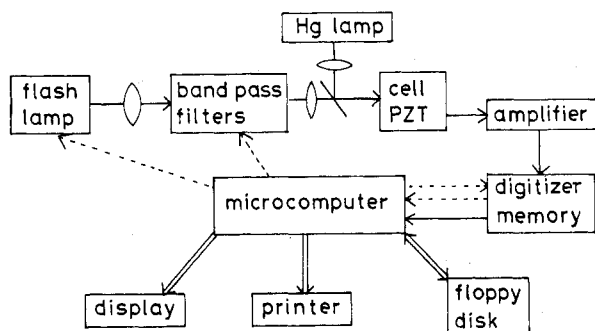
Figure 1. Schematic diagram of the pulsed photoacoustic spectrometer and flash lamp.
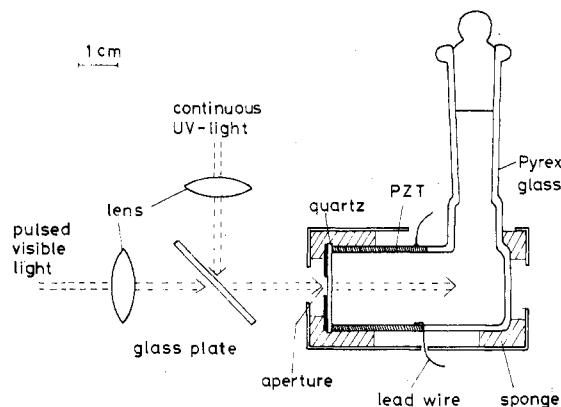

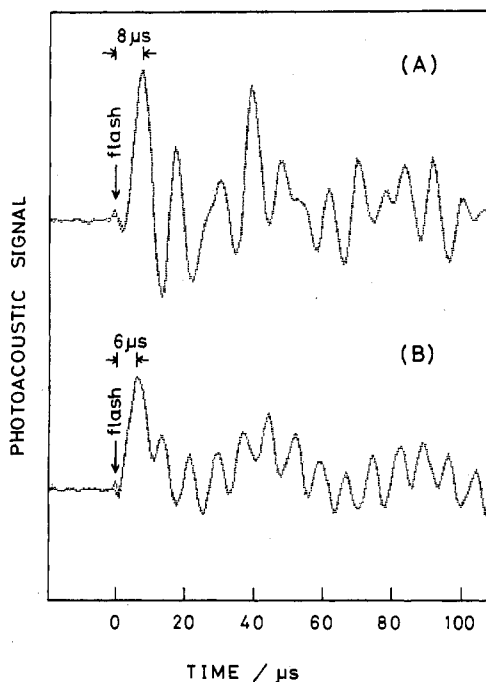**Figure 2.** Sample cell for powder suspension.

Figure 3. Photoacoustic response signal generated by the flash light of 490 nm. Averaged after 1280 times accumulation and subtracted from the response curve for pure water: (A) diluted black ink solution of absorbance 0.04 cm⁻¹; (B) TiO₂ powder suspension of apparent absorbance 0.05 cm⁻¹.

response peak of the scattered sample was observed 2 μs sooner than that for the black ink. Since the velocity of sound in water is 1.5 km/s, the acoustic pulse propagates by 3 mm in 2 μs. By considering the expansion of the light beam which is focused on the aperture at the front of the cell, we can attribute the 2-μs delay of the first peak to the time for the propagation of the acoustic pulse in the medium. The first peak caused by the scattered light occurs 6 μs after the flash.

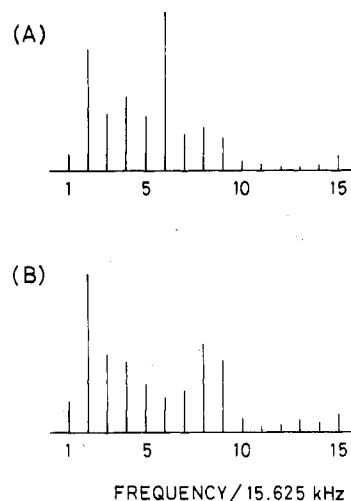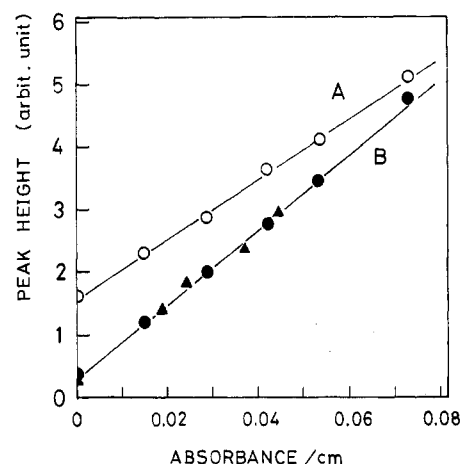**Figure 4.** Discrete Fourier analysis for Figure 3A,B, respectively.

Figure 5. Peak heights vs. absorbance of aqueous solution of black ink (O, ●) and Co(NO₃)₂ aqueous solution with TiO₂ suspension (▲): (A) peak height of the photoacoustic signal 8 μs after the flash; (B) peak height at 94-kHz component (sixth peak) of the Fourier spectrum analysis of the photoacoustic signal.

Since the absorption of light at the inner surface of the PZT cylinder is instantaneous, this delay of 6 μs may be attributed to the time to induce strain in the transducer. Direct irradiation on the PZT surface also showed the delay of the first peak in the response signal. Recently, the report for a numerical model calculation has shown that the response of strain for cylindrical PZT delays, while that for disk PZT is rather instantaneous (11).

It is noteworthy that the oscillating feature which appeared after the first peak in the response signal of Figure 3A is dissimilar to that in Figure 3B. In order to clarify the difference, the time profiles were analyzed by the method of discrete fast Fourier transformation with the microcomputer. Figure 4A and Figure 4B show the resulting response spectra for Figure 3A and Figure 3B, respectively. The representative frequency for the medium-propagated photoacoustic signal (Figure 4A) was 94 kHz, while that for the scattered light was about 130 kHz. The difference in the vibrational frequencies may be attributed to that of the resonance mode of the sample cell. Although the reason for the difference is not clear, it may be used for eliminating the effect of light scattering.

The peak height for 94-kHz component of the Fourier spectrum is plotted in Figure 5 (line B) as a function of the absorbance of dilute black ink solution. The peak height of the first response peak, 8 μs after the flash, is also plotted (line A). Both methods of signal analysis show the linearity against the absorbance up to about 0.08 cm⁻¹. It is notable that the intersection of line B is near to the origin, which indicates that
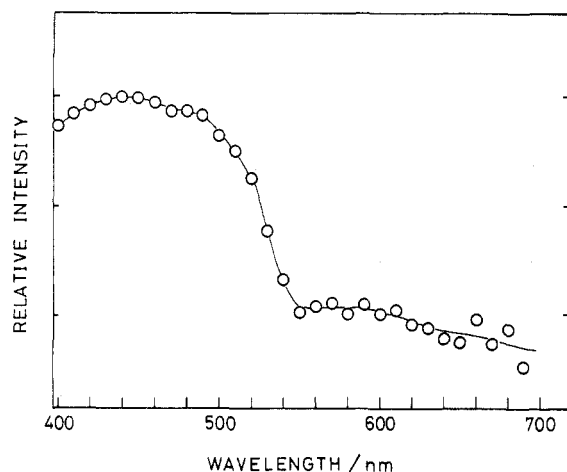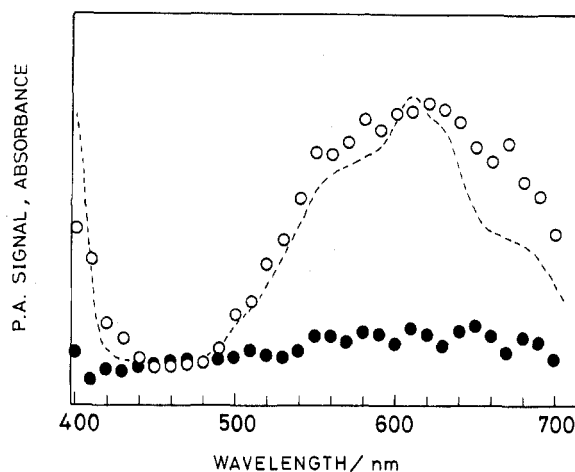
Figure 6. Photoacoustic spectrum of CdS powder suspension. Apparent absorbance was about 0.06 cm^{-1} at 450 nm. The signal intensity at 8 μs is calibrated with that of the black ink solution for each wavelength.

Figure 7. Photoacoustic spectrum of methylviologen cation radical formed by the UV-irradiated Pt/TiO$_2$ photocatalyst with (O) and without (●) irradiation of about 100 mW/cm^2 in the solution containing 0.15 mM methylviologen, 0.2 mM EDTA, and 1 mg/20 mL Pt/TiO$_2$ powder. Broken line shows the absorption spectrum of the radical formed by Na$_2$S$_2$O$_4$ reduction in solution.

the Fourier transformation is applicable to decrease the effect of light scattering. In order to confirm this merit, in the presence of TiO$_2$ powders intensities of photoacoustic signal were measured for Co(NO$_3$)$_2$ solution. To prevent the effect of adsorption on the powder, a solution of inorganic salt was employed instead of black ink. As shown in Figure 5, the peak height for the 94-kHz component was linearly correlated to the calculated absorbance of Co(NO$_3$)$_2$, where the amount of TiO$_2$ had been constant. This shows that the signals from the PZT transducer are approximately given by the superposition of two kinds of vibrating signals. However, for the following spectral measurements, the peak height 8 μs after the flash was employed because of the limitation in the memory capacity of the microcomputer used.

In order to check the utility of this spectrometer a CdS suspension was employed. Figure 6 shows the absorption spectrum of CdS powder suspension. In this case the signal intensity at each wavelength is calibrated to that of dilute black ink which had an even absorbance in all spectral ranges measured. The photoacoustic spectrum shows the distinct change in the absorbance at about 520 nm which corresponds to the band gap energy of CdS semiconductor. With a conventional spectrophotometer, the distinct change in absorbance could not be observed for either the present sample or colloidal CdS solution (12). The present spectrum in aqueous suspension is similar to that of CdS powder measured by a conventional photoacoustic spectrometer in gaseous medium (13).

The ultimate purpose for the present study was to investigate the photocatalytic reaction at the surface of the semiconductor photocatalyst, which involves reduction and oxidation caused by photoinduced electron-hole pairs. As mentioned earlier, photoacoustic spectroscopy has the advantage of being insensitive to scattered light, especially, when continuous irradiation which hardly affects the signal intensity is used. Then it is expected to be able to measure the in situ absorption spectrum of the reaction species during photocatalytic reaction. As an example, the reduction of methylviologen on TiO$_2$ semiconductor surface was measured under UV irradiation. The amount of methylviologen in sample solution was the order of a monolayer if deposited on the powder surface. Without UV excitation of TiO$_2$, no absorption band was observed, as shown in Figure 7. With UV irradiation, however, absorption bands were observed at shorter

than 410 nm and at 620 nm. These correspond to those of the chemicaly reduced methylviologen as illustrated in Figure 7. Decreasing the intensity of UV irradiation decreased the magnitude of photoacoustic signal. This indicates that the reduced species was formed stationary by the photocatalytic reaction. Broadening of the absorption band at 620 nm may be due to the adsorption of the methylviologen on the solid surface.

In conclusion, a monochromatized flash light was successfully used as a light source of the pulsed photoacoustic spectrometer in which pulsed dye lasers had been used exclusively. In order to increase further the efficiency of the new apparatus, the following points must be considered: (1) increasing peak power of the flash lamp, (2) increasing resolution of the digitizer, (3) expansion of the computer memories, (4) selection of size and shape of the sample cell with PZT transducer.

ACKNOWLEDGMENT

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