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Photoacoustic Observation of Heterogenous Photocatalytic Reactions

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The field of photoacoustics has undergone extensive developement in recent years, particularly in the area of photoacoustic spectroscopy (PAS). Photoacoustic spectroscopy offers several advantages over other conventional optical spectroscopies. As any photoacoustic signal can be produced as the result of absorption of light, light that is transmitted, reflected, or scattered by the sample is not detected by this method. Insensitivity to scattered light also permit the investigator to obtain optical absorption data on highly light-scattering materials such as powders, colloidal suspensions, gels, etc., which are very difficult to study by other techniques. Photoacoustic spectroscopy has already found many important applications in the research and characterization of materials such as solid, liquid, and gas.

Recently, in-situ observation of dye-semiconductor interface has been paid much attention particularly in the fields of photochemistry, photoelectrochemistry, and photographic science. However, few studies have been carried out by using in-situ observation of a sensitizing dye after excitation at a semiconductor surface. Photoacoustic spectroscopy is expected to give useful information on the spectral sensitization such as the correlation between energy levels of dyes and that of the conduction band of the semiconductor.

The present research discusses quite new applications of photoacoustic spectroscopy to investigations of the photochemical reaction of sensitizing dyes adsorbed on semiconductor powder.

Measurements of photoacoustic spectra of the dyes adsorbed on the surface of the semiconductor powder were carried out with a single-beam photoacoustic apparatus made in this laboratory as shown in Figure 1. This consists of a 500 W Xenon lamp, monochromator, a light chopper, a specially designed closed cell with a condenser micro-phone (Bruel and Kjaer Ltd., Model 4144), and a lock-in amplifier/preamplifier. The light beam was modulated at a frequency of 80 Hz.

ZnO powder and AgBr sheet crystal were mainly used as the semiconductor. Rhodamine B and 1,1'-diethyl-2,2'-cyanine dyes were chosen as the spectral sensitizing dye because it is well-known dye in the photographic and photoelectrochemical systems. The sensitizing dyes were adsorbed on ZnO powder and AgBr sheet crystal in aqueous solution. After centrifuging, substrates with dyes were dried by vacuum drying and kept in a desiccator.

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In order to cause the photochemical reaction before measurement of the photoacoustic spectra, the sensitizing dyes adsorbed on ZnO powder and AgBr sheet crystal were irradiated by an excitation light from the 500 W Xenon lamp. The wavelength of the excitation light was longer than 500 nm to eliminate the intrinsic absorption of the substrates. All the measurements and preparation of samples were carried out in the dark room.

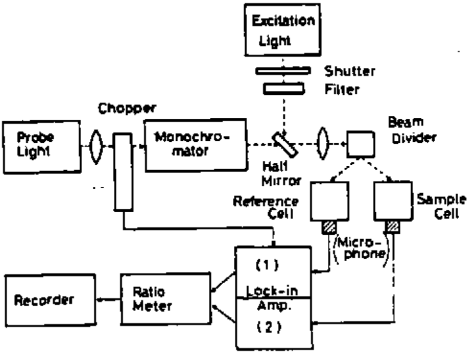

Figure 1. Block diagram of the apparatus

The photoacoustic spectra of rhodamine B adsorbed on ZnO are shown in Figure 2. Figure 3 and 4 are the spectra of rhodamine B and cyanine on AgBr, respectively. The photoacoustic spectrum of rhodamine B adsorbed on the semiconductor powder exhibited a gradual hypsochromic shift in the course of exposure, which is considered to be due to the occurence of an efficient N-deethylation of the dye (1). The photoacoustic spectrum of cyanine on AgBr decreased with exposure to the excitation light without any appreciable shift of the spectrum, which may be related with a rather drastic decomposition of the chromophores of dye. The dyes excited by the light, coinciding with the absorption of the dyes, can inject an electron into the conduction band of the semiconductor. Then, oxygen and water molecules adsorbed on the semiconductor powder could act as an acceptor of the electron. As the result, excited dyes molecules finally decompose. Similar results have also been observed when another several dyes were used as a sensitizing dye. However, there was no change of the spectra when non-semiconductor solid materials such as Al_2O_3 were employed. The correlation between energy level of the dyes and that of the conduction and valence bands of the semiconductors are illustrated in Figure 5.

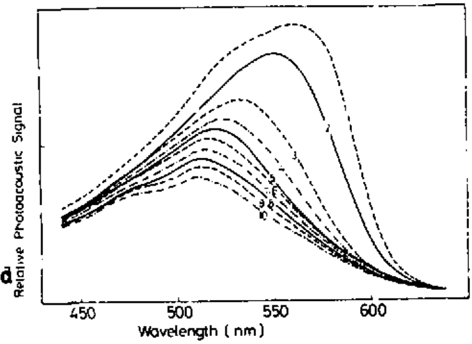

Figure 2. PA spectra of rhodamine B on ZnO. (1) before irradiation; (2) 5 sec; (3)15 s.;(4)30 s.;(5)45 s.;(6)60 s.;(7)90 s.(8)250 s.;(9) 430 s.;(10)1030 s.

In the present experiment, the thickness of the adsorbed dyes was estimated to be a few monolayers. The above-mentioned photochemical reaction occurs in the region of the semiconductor-dye interface. For better understanding of the reaction between the semiconductor and dye, direct observation of the reaction intermediate will be necessary. Eosine on ZnO powder in gelatin was used as the sample for this measurement. In addition to the decrease of the photoacoustic signal of the dye with exposure to the excitation light without any appreciable shift of the spectrum, interesting transient signals were observed in different wavelength region only during irradiation with the light. The photoacoustic signal increased when the dye adsorbed on ZnO powder was irradiated with the excitation light, and it immediately decreased when the light was blocked. There was no change in the photoacoustic signals when ZnO powder without the dye or the dye adsorbed on nonsemiconducting solid materials such as Al_2O_3 were exposed to the excitation light. Neither was any change of the signal observed when inefficient sensitizing dyes such as methylene blue was adsorbed on ZnO powder instead of eosine and exposed to the light. Therefore, the change in the photoacoustic signal must be due to the formation of transient intermediates of eosine adsorbed on ZnO powder during irradiation with the excitation light. Figure 6 shows PA spectrum

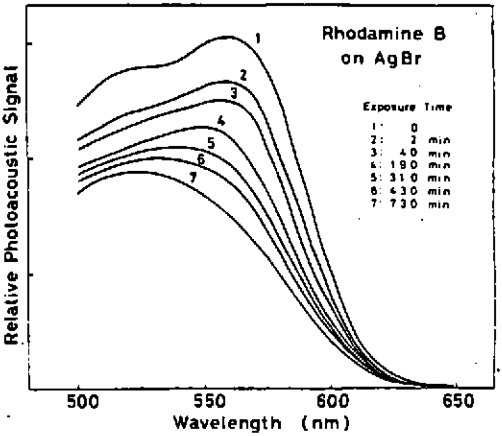

Figure 3. PA spectra of rhodamine B on AgBr.

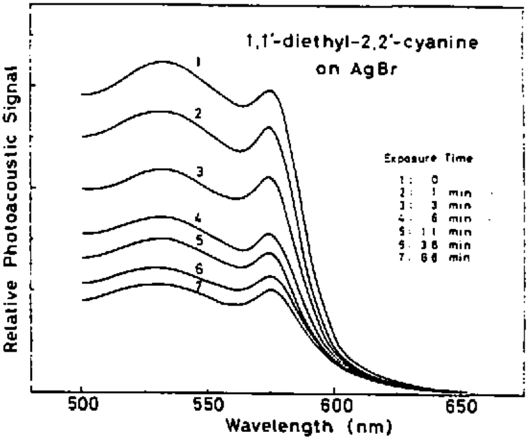

Figure 4. PA spectra of cyanine on AgBr.

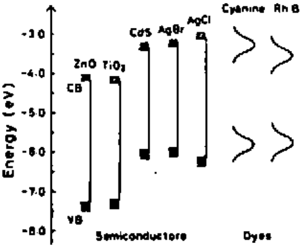

Figure 5. Correlation between energy level of the dyes and that of the conduction and valence bands of the semiconductor.

of cation radical of eosine adsorbed on ZnO powder. The existence of the cation radical would suggest strongly that the dyes in the excited state inject an electron into the conduction and of the semiconductor.

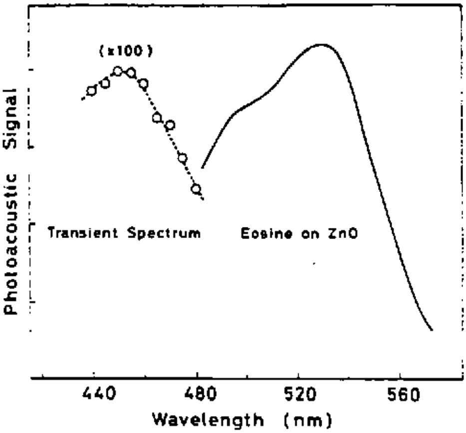

Figure 6. PA spectra of transient intermediates of eosine on ZnO.

Another confirmation of the photochemical reaction described above was done with light-induced ESR signal measurement. Though there was no signal in the dark, structureless sharp ESR signal was observed at g = 2.002 when the dye on semiconductor was exposed to the excitation light. The intensity of the observed ESR signal decreased with evacuation of the sample tube. There was no signal when the dye was adsorbed on nonsemiconducting solid material such as Al_2O_3. The ESR at g = 2.002 can be attributed to O_2^-, and it must be interpreted that the injected electron from the excited dye to the conduction band of the semiconductor in spectral sensitization processes is removed by interaction with oxygen to form O_2^-, which subsequently reacts with other electron acceptors.

Photoacoustic spectroscopy has provided useful informations on the spectral sensitization of the semiconductor-dye interface. Though the technique has offered qualitative information about surface properties at the present stage, it will be applicable to various heterogeneous photochemical and photocatalytic reactions, which had been very difficult to observe by other technique.

REFERENCES

(1) T. Watanabe, T. Takizawa, and K. Honda, J. Phys. Chem., 81, 1845(1977).