Electron Spin Echo Investigation for Radicals Produced on ZnS Semiconductor Photocatalysts

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Pulsed electron spin resonance technique was applied to the investigation into radicals formed on photo-irradiated ZnS semiconductor powder. From the decay profile of the signal intensity of electron spin echo, the spin relaxation times for surface holes and S_n radicals were measured to be 1.2 and 6 μs, respectively.

Semiconductor photocatalysis is taken a special interest for the purposes of solar energy conversion and environmental purification.[1] In order to understand the mechanism of photocatalytic reaction, it seems important to know the nature of the photoinduced carriers trapped on the semiconductor surface. Electron spin resonance (ESR) investigations of various radicals formed on photocatalysts have been widely studied. We have also been studying the properties of photoinduced radicals over semiconductor powders, such as CdS,[2] ZnS,[3] and TiO_2, by using conventional cw (continuous wave) ESR method. Since the observed signals exhibited broad and structureless patterns and then sometimes overlapped, they were distinguished by their saturation properties.[3] Recently the pulse technique in ESR spectroscopy came into wide use,[4] by which transient radicals induced with laser pulse could be detected. The irradiation of pulsed laser light, however, causes a large disturbance of the microwave detector in the ESR cavity, because of the generation of photoinduced carriers in the semiconductor particles. Although this phenomenon was used to study the kinetics of the carriers,[5] it interferes essentially the sensitive detection of radicals by ESR method. Another advantage of the pulsed ESR spectroscopy is the availability of measuring the electron-spin relaxation time, which correlates with the saturation properties of the signal. Since there are very few reports on the relaxation properties of the electron spins in semiconductor photocatalysts, in the present study we investigated the photo-irradiated semiconductor powders with a pulsed ESR spectrometer. We tried to measure electron spin echo signals for photoirradiated powders of CdS, ZnS, and TiO_2. Only ZnS powders gave precise signals because of the limitation of the sensitivity of the apparatus used.

Powder of ZnS (Nacalai Tesque, GR) was placed in a quartz sample tube and then it was sealed under vacuum. Pulsed ESR measurements were performed with a JEOL RSV-1000 X-band ESR spectrometer equipped with a PX-1050 pulse unit. The pulse sequence was $\pi/2$–τ–π–τ and 20 data were accumulated. The duration of the microwave π pulse of the pulse unit was 75 ns. The sample was cooled at 77 K and irradiated continuously with the light of an ultra-high-pressure mercury lamp through glass filters.

Figure 1 shows spectra of photo-irradiated ZnS powder at 77 K. Figure 1c is an electron spin echo (ESE) spectrum which is obtained as the signal intensity of electron spin echo for τ = 380 ns. This τ was the shortest time for obtaining a distinct echo signal. For comparison, a conventional ESR spectrum was measured with the same apparatus and showed in Figure 1a. This

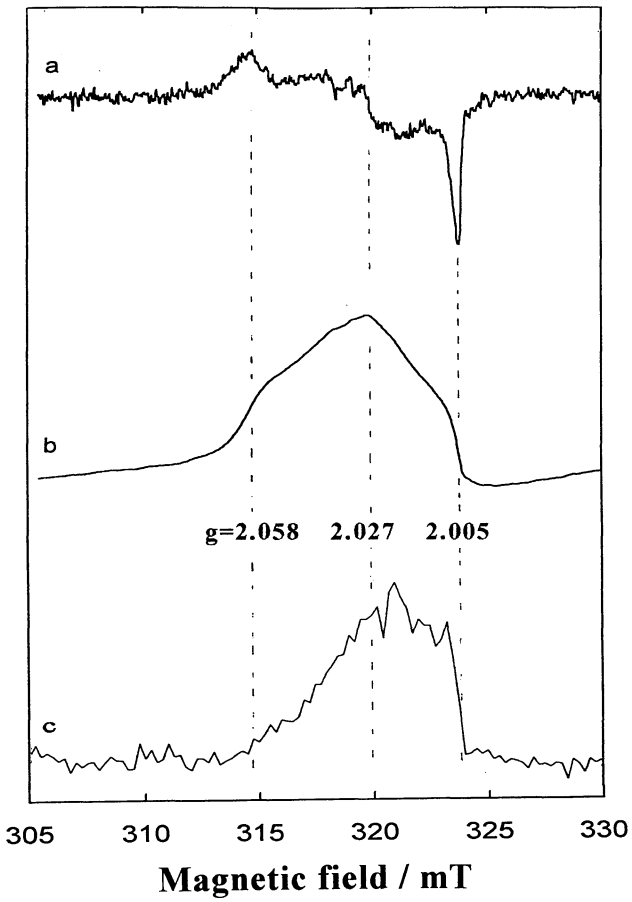

Figure 1. a), Electron spin resonance (ESR) spectrum of ZnS powder under photoirradiation at 77 K; b), numerical integration of spectrum a; c), electron spin echo (ESE) spectrum observed at 2τ = 760 ns in the same condition above.

is essentially the same spectrum as in the previous report.[3] Since the cw ESR spectrum is recorded in the first-derivative mode, the spectrum was numerically integrated as shown in Figure 1b to compare with the ESE spectrum. In the previous study, it is revealed that the cw ESR spectrum consists of mainly four kinds of radicals.[3] The photoinduced holes trapped on the surface sulfur atoms appear as a signal of $g_{//}$ = 2.005 and $g_{\perp}$ = 2.040. The signal of $g_{//}$ = 2.005 and $g_{\perp}$ = 2.058 was assigned to the holes trapped on sulfur atoms inside the particle. The signal at g = 2.023 is attributable to S_n radicals at the surface. The small signal having g = 2.0035, 2.027, and 2.051 was observed without irradiation and left as an unknown paramagnetic species.

In the present study, the saturation properties of the unknown radicals was measured. By combining it with the data

in the previous study,[3] the spin relaxation time is suggested to become long in the following order; the unknown paramagnetic species, the inner holes, the surface holes, and S_n radicals. Comparison between spectrum c and spectrum b in Figure 1 shows the effect of the spin relaxation. Since the spectrum c was measured at 380 ns after the spin polarization, the signal of inner holes at g = 2.058 and the peak of the unknown species at g = 2.027 have disappeared because of the fast relaxation. The observed peak in spectrum c at the magnetic field of 321 mT is attributable to S_n radicals at g = 2.023, whose signal has the longest relaxation time at this magnetic field. Since the clear signal of S_n radicals appeared only at g = 2.023[3], the remaining broad signal in spectrum c is attributable to the surface holes which gave a hill in middle region of spectrum b. The lack of the peak at $g_\perp$ = 2.040 for the surface holes may be caused by a broad distribution of chemical structures and then the electronic energies at different radical sites.

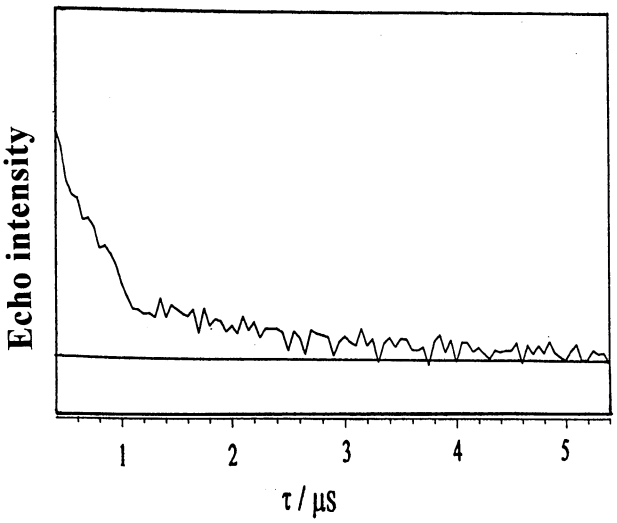

Figure 2. Decay profile of the intensity of electron spin echo at the magnetic filed of 321 mT.

Figure 2 shows the spin echo intensity as a function of τ at the peak of the electron spin echo spectrum. Two components in the decay curve were observed, whose relaxation times are 1.2 and 6 μs. Since the echo signal at τ = 380 ns consists of the surface holes and S_n radicals as discussed above, the fast large decay is attributable to the spins of the surface holes and the slower one to S_n radicals. It seems reasonable that the spin relaxation times of the surface holes and S_n radicals are 1.2×10^{-6} and 6×10^{-6} s, respectively, because the spin-lattice relaxation time (T_1) of Mn^{2+} is reported to be 1.3×10^{-7} s at 77 K.[6]

The measurement of relaxation times by means of pulsed ESR spectroscopy provides the assignment of the broad overlapped signals of irradiated semiconductor powders. Furthermore, improving the experimental conditions and measurement at different temperatures may provide an essential knowledge of electron spin relaxation. It gives the information of lifetime of radicals or the structural flexibility around the electron orbitals of photoinduced radicals. These information must be useful to understand the primary steps of photocatalytic reactions.

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