ESR Spin-Trapping Study of Active Oxygen Radicals from Photoexcited Semiconductors in Aqueous H_2O_2 Solutions

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Experiments were carried out concerning the relation between the production of active oxygen radicals from three semiconductors [TiO_2 (anatase and rutile) and WO_3] and the concentration of H_2O_2 by the ESR spin-trapping technique using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin trap. Two natures of hydroxyl radicals were produced from photoexcited semiconductors in aqueous H_2O_2 solutions. These originated in the reduction of H_2O_2 and the oxidation of water, which were confirmed using ^{17}O-labeled water. The mechanism for the generation of active oxygen radicals is discussed regarding the energy band structures of the semiconductors, the redox potentials of the oxygen radicals, and the surface acidity and basicity of semiconductors.

A photoexcited semiconductor has strong oxidation and reduction abilities. These abilities have been used for the photodecomposition of water (or organic compounds)[1—5] as well as the photosynthesis of organic compounds.[6—10] Active-oxygen radicals (such as the superoxide ion, hydroxyl radical) play an important role as the reaction intermediate in these systems.[11] However, these radicals have very short lifetimes and can not be observed at room temperature. For the past twenty five years, the spin-trapping technique has been developed for the detection of short-lived radicals.[12] This technique has been widely used for photocatalytic systems.[11,13—16] For example, Harbour and Hair[13] have applied photoexcited CdS in aqueous media and detected a superoxide ion. Jaeger and Bard[14] have applied photoexcited TiO_2 in aqueous media to detect hydroxyl and hydroperoxyl radicals. We[11] have also applied photoexcited semiconductors (TiO_2, CdS, WO_3, and Fe_2O_3) in water and aqueous H_2O_2 solutions to detect the superoxide ion as well as hydroxyl and hydroperoxyl radicals. The mechanism for the generation of active oxygen radicals from powdery semiconductors has been rationalized in terms of the energy-band structures of semiconductors and the redox potentials of active oxygen radicals.

However, the H_2O_2 concentration dependence of various semiconductors has not been reported. In this study, experiments were carried out concerning the relation between the production of active oxygen radicals from three semiconductors [TiO_2 (anatase and rutile) and WO_3] and the concentration of H_2O_2 by the ESR spin-trapping technique.

Experimental

Materials. Powdery semiconductors [TiO_2 (99.9%, rutile and anatase), WO_3 (99.5%)] were obtained from Wako Pure Chemical Industries, Ltd. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO), as a spin trap, was purchased from Dojindo Laboratory. ^{17}O labeled water (20.7% ^{17}O) was purchased from Isotec Inc. (USA). Hydrogen peroxide (H_2O_2, 30%) was obtained from Wako Pure Chemical Industries, Ltd.

Apparatus. A flat, quartz ESR cell was used in all of the experiments. 2.5 mg of powdery semiconductors were dispersed in 1 ml of water. 50 μl of semiconductor powder suspensions were mixed with 21.8 μl of 9.2 mol dm^{-3} DMPO and 28.2 μl of aqueous H_2O_2 solutions. The suspension was fed into the ESR cell, which was inserted into the cavity of an ESR spectrometer (JEOL JES-RE3X). The sample was irradiated with a 500-W xenon lamp for 60 s using a 370-nm interference filter. ESR measurements were conducted under the following conditions: magnetic field, 336±5 mT; field modulation, 0.1 mT; microwave power, 8 mW.

Results

The ESR spectra of the DMPO spin adducts observed when anatase TiO_2 suspensions were irradiated with an energy greater than the band-gap energy (380 nm) in water and aqueous H_2O_2 solutions are shown in Fig. 1. These spectra comprise signals from the hydroxyl and hydroperoxyl (or superoxide ion) radicals spin adducts, and can be assigned according to the respective hyperfine splitting constants (hfsc) values of $a_N = a_H{}^\beta = 1.49$ mT[17] and $a_N = 1.41$ mT, $a_H{}^\beta = 1.13$ mT, and $a_H{}^\gamma = 0.13$ mT.[13] The intensities of the hydroxyl radical spin adducts observed in H_2O_2 solutions were larger than those in distilled water, and the increase in the concentration of H_2O_2 led to an increase in the hydroperoxyl radical spin adducts.

The relation between the intensities of the hydroxyl and hydroperoxyl radical spin adducts and the concentration of H_2O_2 are shown in Figs. 2 and 3. The intensities of the hydroxyl and hydroperoxyl radicals spin adducts were defined with respective values of 2a and 2b as shown in Fig. 1. In anatase suspensions, an increase in the concentration of H_2O_2 up to 1 mmol dm^{-3} led to an increase in the hydroxyl radical spin adducts; an increase in the concentration of H_2O_2 over 1 mmol dm^{-3} led to a slight decrease in the hydroxyl spin adducts. Further, the increase in the concentration of H_2O_2 led to an increase in the hydroperoxyl spin adducts. The slope of line changed at 1 mmol dm^{-3}. In rutile suspensions, the increase in the concentration of H_2O_2 up

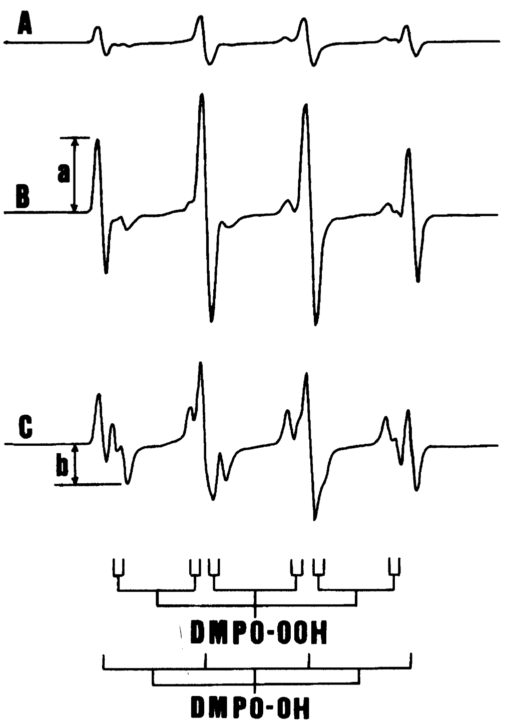

Fig. 1. ESR spectra of the DMPO spin adducts obtained by 60-s irradiation of anatase TiO_2 suspensions. A: in water, B: in 1 mmol dm^{-3} H_2O_2, C: in 100 mmol dm^{-3} H_2O_2, receiver gain: ×20.

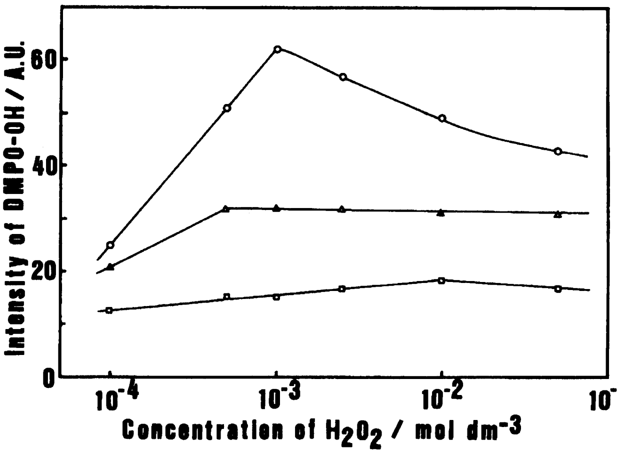

Fig. 2. H_2O_2 concentration dependence of the DMPO-OH spin adducts. open circle: anatase, open triangle: rutile, open tetragon: WO_3.

to 0.5 mmol dm^{-3} led to an increase in the hydroxyl spin adducts, and an increase in the concentration of H_2O_2 over 0.5 mmol dm^{-3} led to a constant value. Further, the increase in the concentration of H_2O_2 led to an increase in the hydroperoxyl radical spin adducts. In WO_3 suspensions, the increase in the concentration of H_2O_2 up to 10 mmol dm^{-3} led to an increase in the hydroxyl radical spin adducts, and the increase in the concentration of H_2O_2 over 10 mmol dm^{-3} led to slight decrease in the hydroxyl radical spin adducts. Further, the increase in the concentration of H_2O_2 led to an increase in the hydroperoxyl radical spin adducts. The slope of line changed at 10 mmol dm^{-3}.

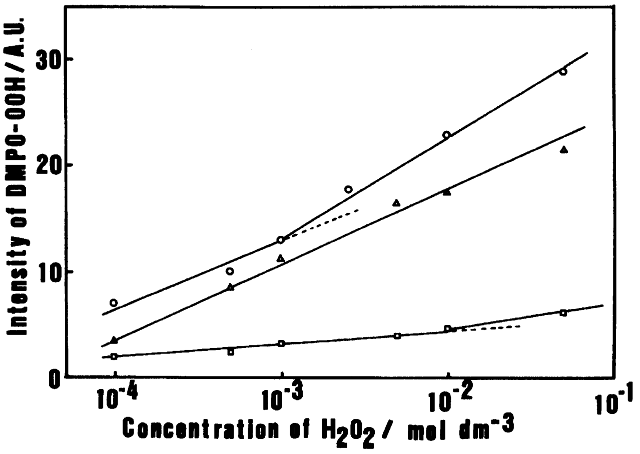

Fig. 3. H_2O_2 concentration dependence of the DMPO-OOH spin adducts. open circle: anatase, open triangle: rutile, open tetragon: WO_3.

From these results the existence of two natures of hydroxyl radicals can be seen. One is from the oxidation of water, and other is from the reduction of H_2O_2. Experiments were attempted to confirm the existence of two natures of hydroxyl radicals using ^{17}O [has the nuclear spin (I)=5/2 and appear the hyperfine splitting] labeled water. The ESR spectra of the DMPO spin adducts from anatase in water and aqueous H_2O_2 solutions using ^{17}O-labeled water (17% of $H_2{}^{17}O$, 37% of $H_2{}^{18}O$) are shown in Fig. 4. In water, the DMPO spin adducts of the hydroxyl radical [^{16}OH (from 46% of $H_2{}^{16}O$), ^{17}OH (from 17% of $H_2{}^{17}O$), ^{18}OH (from 37% of $H_2{}^{18}O$), and the signal pattern of the ^{18}OH adducts was the same as that of the ^{16}OH adducts] were observed, and the ^{17}OH spin adducts can thus be assigned with hfsc values of a_N=1.43 mT, $a_H{}^\beta$=1.43 mT, $a_O{}^\beta$=0.45 mT.[18] The signal intensity for the first signal of the ^{17}OH spin adducts showed 0.025 [nearly value of 0.17($H_2{}^{17}O$)×1/6(hyperfine splitting of ^{17}O)=0.028] times that of the ^{16}OH spin adducts. Therefore, the observed spin adducts of the hydroxyl radical are believed to originate from the oxidation of water. In 1 mmol dm^{-3} H_2O_2 solutions (contained 17% of $H_2{}^{17}O$), the same intensities of the ^{17}OH spin adducts and the large intensities of the ^{16}OH(+^{18}OH) spin adducts were observed in comparison with those in distilled water. This means that the production of the two natures of the hydroxyl radicals originated in the oxidation of water ($H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$) and the reduction of $H_2{}^{16}O_2$ by photogenerated electron-hole pairs. In 0.1 mol dm^{-3} H_2O_2 solutions (contained 17% of $H_2{}^{17}O$), no ESR spectrum of ^{17}OH spin adducts was observed. Therefore, the observed hydroxyl radical spin adducts are believed to have originated in the reduction of $H_2{}^{16}O_2$. In another two semiconductors, the occur-

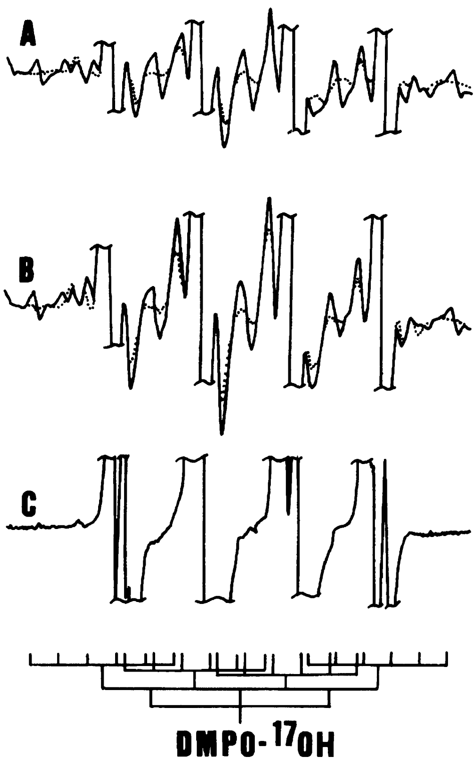

Fig. 4. ESR spectra of the DMPO spin adducts obtained by 60-s irradiation of anatase TiO_2 suspensions containing ^{17}O labeled water. A: in water, B: in 1 mmol dm^{-3} H_2O_2, C: in 100 mmol dm^{-3} H_2O_2, receiver gain: ×2000, dotted lines: background.

rence of similar reactions was also confirmed using ^{17}O-labeled water.

Discussion

The energy-band structures of semiconductors[19] and the redox potentials of active oxygen radicals[13,14] are shown in Fig. 5. The potentials for the reduction of oxygen and that of H_2O_2 to the superoxide ion and to the hydroxyl radical lie below the conduction-band edge of the semiconductors, and the potentials for the oxidation of water and that of H_2O_2 to the hydroxyl radical and to the hydroperoxyl radical lie above the valence-band edge of the semiconductors. Therefore, these four reactions are sufficiently energetic to occur due to a photogenerated electron-hole pair.[11] Moreover, the reduction and oxidation of H_2O_2 are more easily energetic to occur than the reduction of oxygen and the oxidation of water. These reactions seem to be related to the concentration of the redox species as well as the reactivity of the semiconductor surface. The following, however, can be generally concluded. In low-concentration of H_2O_2 solutions, the hydroxyl radical is produced from the reduction of H_2O_2 and the oxidation of water by photogenerated electron-hole pairs. In high concentrations of H_2O_2 solutions, however, the hydroxyl radical is mainly produced from the reduction of H_2O_2 by photogenerated electrons, and the hydroperoxyl radical is produced from the oxidation of H_2O_2 by photogenerated holes. These results were confirmed by irradiated anatase TiO_2 suspensions using the ^{17}O-labeled water, as shown in Fig. 4.

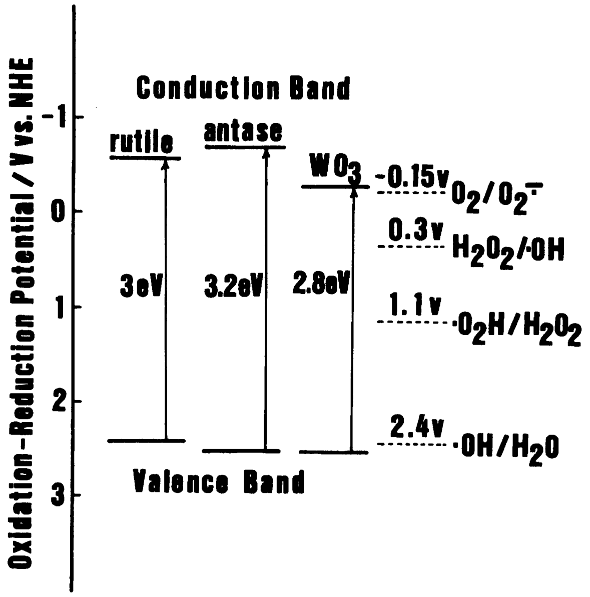

Fig. 5. Energy-band structures of semiconductors and redox potentials of active oxygen radicals (pH 7).

As shown in Figs. 2 and 3, the different concentration dependence of the hydroxyl and hydroperoxyl radicals spin adducts were observed on anatase, rutile, and WO_3 suspensions, respectively. The reactions for the production of the hydroxyl radical from the reduction of H_2O_2 are shown as follows:

$$H_2O_2 + H^+ + e \rightarrow \cdot OH + H_2O \quad \text{(acidic)} \qquad (1)$$

and

$$H_2O_2 + e \rightarrow \cdot OH + OH^- \quad \text{(basic)}. \qquad (2)$$

The production of the hydroxyl radical from the reduction of H_2O_2 could be promoted in the presence of a proton, as shown in reaction (1). The surface acidity examined by the adsorption of the sodium ion showed a trend for WO_3>anatase>rutile. These results are in line with the results of the PZC (point of zero charge, this value obey the surface acidity and basicity) measurements.[20] Therefore, the production of the hydroxyl radical from the reduction of H_2O_2 depends on the surface acidity of semiconductors, which is has the same meaning as the presence of a proton. A change in the slope of the lines was observed in the production of the hydroxyl radical spin adducts in anatase and WO_3 suspensions. These results can be explained by the occurrence of reaction (3), due to a decrease in the hydroxyl radical, as well as an increase in the hydroperoxyl radical spin adducts under a high concentration of H_2O_2:

$$H_2O_2 + \cdot OH \rightarrow \cdot O_2H + H_2O. \qquad (3)$$

No change in the slope of the line was observed during the production of the hydroxyl radical spin adducts in rutile suspensions. The reason for this difference is not clear, but may also be related to the surface acidity.

It is well known that H_2O_2 is produced when ZnO aqueous suspensions are irradiated with light with a wavelength shorter than 380 nm.[15] The mechanism for the production of H_2O_2 is known to involve the reduction of dissolved oxygen. In ZnO suspensions in the presence of H_2O_2, no spectral change was observed compared with that in distilled water. These results suggest that the reduction of H_2O_2 does not occur. Therefore, H_2O_2, which is produced from the reduction of oxygen, is accumulated in aqueous ZnO suspensions. These facts can be explained in terms of the restraint of reaction (2) in the presence of the hydroxyl ion, since ZnO is basic oxide and hydroxyl ions are contained in ZnO suspensions. All of the semiconductors used in this study were acidic oxide. Therefore, the reduction of H_2O_2 is promoted in the presence of proton and do not accumulate in aqueous acidic semiconductor suspensions. The results of this study are in line with those concerning the degradation of halogenated organic compound in H_2O_2 added photocatalytic system.[21]

Conclusions

It has been demonstrated that the two natures of hydroxyl radicals are produced from photoexcited semiconductors (anatase, rutile, and WO_3) in aqueous H_2O_2 solutions. One is due to the oxidation of water, and other is due to the reduction of H_2O_2. This evidence was confirmed using ^{17}O-labeled water. The mechanism for the generation of active-oxygen radicals can be rationalized in terms of the energy-band structures of the semiconductors, the redox potentials of the oxygen radicals, and the surface acidity and basicity of the semiconductors.

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