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The Direct Electrochemical Oxidation of H_2O_2 Adsorbed on TiO_2 Fine Particles Suspended in Water

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The H_2O_2 molecules deliberately adsorbed on the surfaces of TiO_2 fine particles suspended in an alkaline solution can be oxidized electrochemically on a rotating gold disk electrode.

In the usual electrochemical reactions on solid electrodes, electroactive species exist in a liquid or a gas phase. And few electrochemical reactions of species adsorbed physically or chemically on surfaces of solid powders have been known.1) We report here the first finding of the direct electrochemical oxidation of H_2O_2 adsorbed on surfaces of TiO_2 fine particles.

The TiO_2 particles adsorbing H_2O_2 ($TiO_2(H_2O_2)$ particles) were prepared by dipping Aerosil TiO_2 P-25 particles (average particle diameter 30 nm) into a 30% H_2O_2 aqueous solution. The particles were filtered off 10 min after the dipping, washed thoroughly with doubly distilled water, and then dried under air at room temperature. The $TiO_2(H_2O_2)$ particles were light yellow colored.2) Various amounts of the $TiO_2(H_2O_2)$ particles were suspended in 10 mmol dm^{-3} NaOH solutions. The suspensions were deaerated at least 1 h with highly purified N_2. Voltammetry with a rotating gold disk electrode was carried out for the suspensions.

Figure 1 shows voltammetric curves for the deaerated suspensions of $TiO_2(H_2O_2)$ and the background current without $TiO_2(H_2O_2)$ on the rotating gold disk electrode. The onset potential of -0.15 V vs. SCE of the anodic current for the $TiO_2(H_2O_2)$ suspension was almost the same potentials as that observed for H_2O_2 in an aqueous solution of the same pH.3,4) The anodic current for the $TiO_2(H_2O_2)$ particles increased as the concentration of the particles in the suspension increased. The cathodic hump appearing around ca. +0.15 V vs. SCE in the anodic plateau was due to the reduction of surface oxides of gold on the disk electrode, because the electrode potential was swept from the anodic side to avoid the accidental formation of H_2O_2 by the reduction of residual O_2. These results indicate that H_2O_2 adsorbed on the TiO_2 particles can be oxidized on the gold electrode.

After the $TiO_2(H_2O_2)$ particles were flocculated, the supernatant of the suspension gave no appreciable anodic current around the oxidation potentials for H_2O_2. This result indicates that very little H_2O_2 was dissolved into the solution. Furthermore, after the TiO_2 particles untreated with H_2O_2 were added in a dilute H_2O_2 solution, the anodic current for H_2O_2 decreased drastically compared with the current observed before addition of TiO_2. The decrease in the apparent diffusion coefficient of H_2O_2 by adsorption on TiO_2 accounts for this anodic current decrease. As we would expect, the supernatant fraction of the resulting suspension also gave no appreciable anodic current. These results indicate that the TiO_2 particles adsorb H_2O_2 strongly.2)

On the other hand, it was hard to measure the cathodic current accurately for H_2O_2 adsorbed on the TiO_2 particles, because a small amount of residual O_2 adsorbed on $TiO_2(H_2O_2)$ and in the solution was also reduced at almost the same potentials as H_2O_2 was reduced on the rotating gold disk electrode.3,4)

The photogeneration and adsorption of H_2O_2 on a surface of TiO_2 have been attracting attention with regard to the mechanism of water photolysis on the TiO_2 surface.2,5,6) We have already reported the photooxidative formation of H_2O_2 in a TiO_2 alkaline suspension by employing a novel electrochemical method with a chemically modified gold semitransparent electrode.7) In the previous report, however, it was not clear whether photogenerated H_2O_2 exists in the solution or on the surfaces of TiO_2 fine particles. The experimental findings described here support strongly that photogenerated H_2O_2 was adsorbed on the surfaces of TiO_2 fine particles.

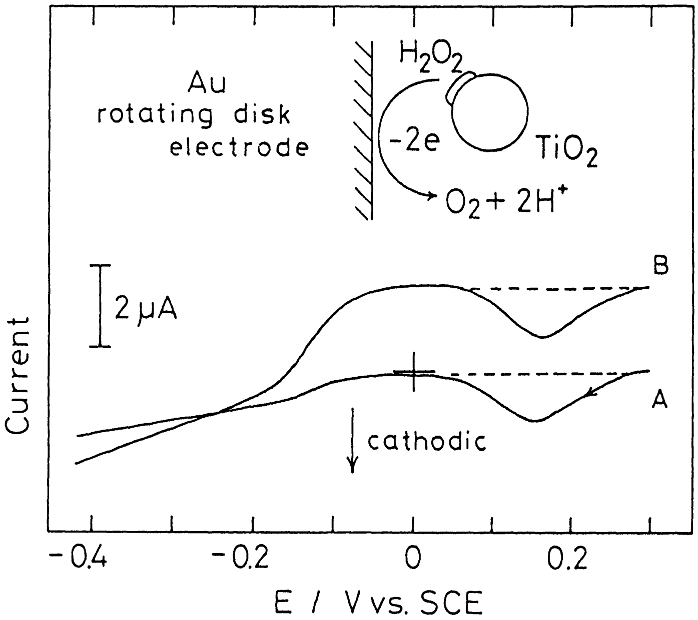

Fig. 1. Voltammetric curves of deaerated $TiO_2(H_2O_2)$ suspensions on a rotating disk gold electrode. (A) Without $TiO_2(H_2O_2)$; (B) $TiO_2(H_2O_2)$ (0.05 g dm^{-3}). NaOH (10 mmol dm^{-3}); N_2 purged; sweep rate (5 mV s^{-1}); rotation speed (3600 rpm); electrode diameter (0.62 cm); temperature (25 °C). Potential sweeps started from the anodic side at +0.3 V vs. SCE.

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