

Voltammetric Determination of Superoxide Ion Generated by Photo-Irradiation of TiO₂ in Aqueous Solution

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Introduction

Quantitative analysis of active oxygen species is required for the studies in biochemical and photocatalytic fields. It is difficult to determine precisely active oxygen species except hydrogen peroxide because of the very short life even in neutral solution and the low concentration in natural occurrence systems. In addition interconversion of them makes the simultaneous and separate determination difficult. Although the ESR technique has been generally used for the separate detection of hydroxyl radical and superoxide ion using a spin trap reagent, it is not straightforward and lacks quantitiveness. In this paper we describe the precise and accurate voltammetric determination of superoxide ion in aqueous solution in the presence of dissolved oxygen and hydrogen peroxide. We also apply this method to the trace analysis of superoxide ion generated by photocatalytic reaction on TiO₂.

Experimental

A three electrode-system consisting of a glassy carbon microdisk working electrode with a diameter of 33 μm, a platinum wire counter electrode and an Ag|AgCl reference electrode was employed. Calibration curves of superoxide ion were obtained by chronoamperometric determination of KO₂ in phosphate buffer solution of pH 7.7. A high-pressure Hg-lamp was used for the generation of superoxide ion in TiO₂ aqueous suspension in the presence of 2-propanol.

Results and discussion

Superoxide ion is electroactive and decomposes to produce hydrogen peroxide and oxygen which are also electroactive. It is very important to select the applied potential where the current response for the oxidation of superoxide ion is observed and no current of hydrogen peroxide flows. Hydrogen peroxide gives the oxidation or reduction current at the whole potential range at a gold electrode. The glassy carbon electrode (GCE), however, exhibits higher overpotential for both oxidation and reduction of hydrogen peroxide, giving the potential range of no current flow of -0.1 ~ 0.1 V as shown in Fig. 1. Figure 2 shows the oxidation current-time responses at 0 V on the addition of KO₂ in phosphate buffer solution. No current response in the presence of superoxide dismutase (SOD) confirms that the observed current is due to the one-electron oxidation of superoxide ions to oxygen. The current decay obeys the second-order decomposition corresponding disproportionation of superoxide ion. The addition of hydrogen peroxide gives no current at this potential. These results indicate that the concentration of superoxide ion is selectively and successfully determined without interference from hydrogen peroxide. We applied the voltammetric method to the quantitative analysis of superoxide ion generated by photocatalytic reaction of TiO₂. Figure 3 shows the current responses on photo-irradiation in TiO₂ suspensions in the presence of 2-propanol as a hole scavenger. The steady current during exposure deduces satisfactorily the concentration of superoxide ion of 4.4 μM in the solution.

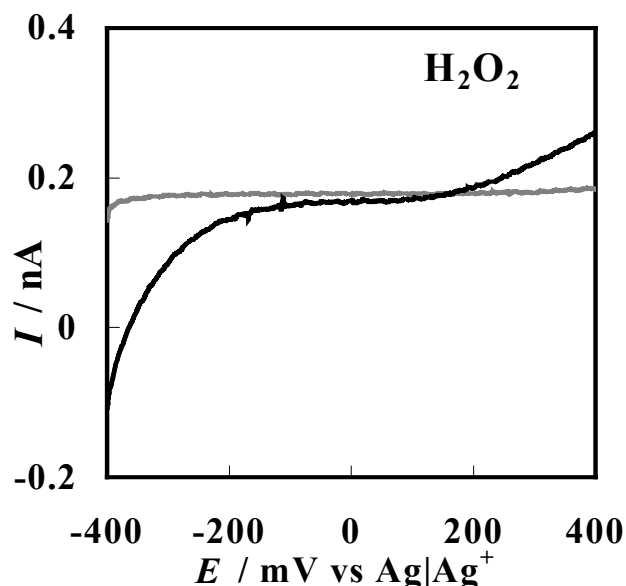


Fig. 1. Voltammogram of H₂O₂ at GCE in phosphate buffer solution (pH 7.7) with a scan rate of 5 mV/s.

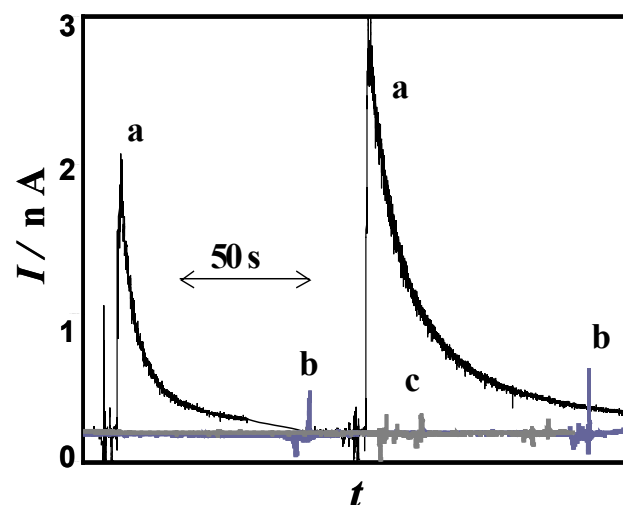


Fig. 2. Current-time responses at GCE in phosphate buffer solution. (pH = 7.7) $E_{app} = 0$ V vs Ag|AgCl. Addition of a) KO₂ (0.39, 1.03 mM), b) KO₂ (2 mM) in the presence of SOD, c) H₂O₂ (5 mM).

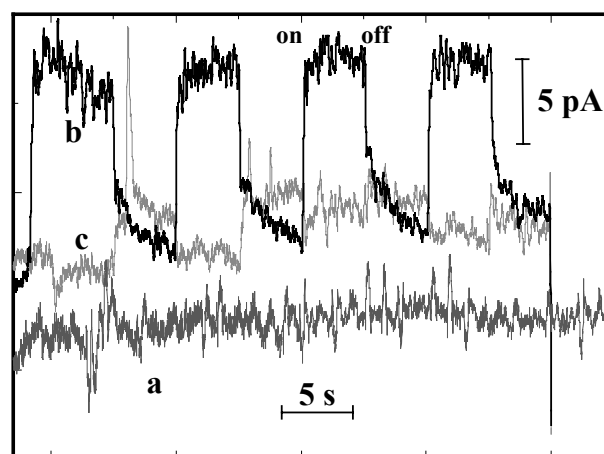


Fig. 3. Current-time responses for O₂⁻ generated by photo-irradiation in a) TiO₂ suspension (0.25 mg/mL), b) TiO₂ suspension containing 2-propanol, c) TiO₂ suspension containing 2-propanol and SOD. pH = 7.7, $E_{app} = -0.1$ V vs Ag|AgCl.