

Electrochemical Detection of Short-lived Species Produced by Dye Sensitization Using TiO₂/Au Mosaic Electrode Array

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Short-lived species of superoxide ion (O₂⁻) produced by dye sensitization on dye (Rhodamine B: Rh-B)/TiO₂ disks under irradiation were studied using a TiO₂/Au mosaic electrode array. The oxidation current at the Au electrodes was found to increase upon irradiation of Rh-B on the TiO₂ disks in an air-saturated neutral aqueous solution, indicating the detection of reaction products. The main reaction products were identified to be O₂⁻ by adding superoxide dismutase (SOD) to the solution, which rapidly decomposed O₂⁻ in the solution.

The development of new types of functional electrode that can be applied to electrochemical or photoelectrochemical analysis is important in optimizing the efficiency of electrochemical reactions. The use of materials having ordered nanostructures for the preparation of the functional electrodes is promising because of its ability to control the mass transfer of active species in electrochemical reactions. In previous reports, we showed the preparation of several types of functional electrode based on highly ordered anodic porous alumina, which has ordered nanohole arrays.^{1,2} Among them, the mosaic electrode system composed of a central TiO₂ disk and the surrounding Au electrodes could be successfully applied to the detection of the reaction product formed by a photocatalytic reaction on a TiO₂ disk. The realization of a nanometer-scale gap between a TiO₂ disk and a Au electrode enabled the detection of short-lived species formed by a photocatalytic reaction on TiO₂ disks.² In the present report, we describe for the first time the application of a mosaic electrode to the detection of active species in dye sensitization on semiconductor electrodes.

Dye sensitization, in which photoexcited dye molecules inject an electron into semiconductor substrates, has attracted much interest because of its various possible applications, such as those to dye-sensitized solar cell fabrication, silver salt photographic process.^{3,4} There have been a considerable number of reports on research concerning the mechanism of dye sensitization.^{5,6} In the mechanism of dye sensitization, the superoxide ion (O₂⁻), hydrogen peroxide (H₂O₂), and cation radicals of dye are formed on a semiconductor surface through the transfer of electrons, which are injected into the semiconductor from a photoexcited dye under the existence of oxygen molecules. The presence of short-lived species of O₂⁻ produced by dye sensitization on TiO₂ has been examined by several methods, such as the use of a chemiluminescent probe or ESR spectroscopy.⁷⁻¹¹ However, many of these methods enable the indirect detection of O₂⁻, because the detection of active species produced by dye sensitization in an aqueous solution is difficult by conventional electrochemical techniques, such as the use of rotating ring-disk electrodes or interdigital electrodes with a gap exceeding the micrometer scale, owing to the rapid decrease in the number of active

species through disproportionation in the solution. In the present study, O₂⁻ formed by dye sensitization in dye (Rhodamine B: Rh-B)/TiO₂ disks was studied using a TiO₂/Au mosaic electrode array (Figure 1). In this electrode system, short-lived species produced by dye sensitization on TiO₂ disks can be detected directly by the surrounding Au electrodes isolated from the central TiO₂ disks by a nanometer-scale gap.

Mosaic electrode arrays were prepared by a process similar to that reported previously.² The preparation was based on the difference in the thickness of the barrier layer between imprinted and unimprinted sites in texturing.¹² The control of the etching of the barrier layer enabled the selective through-holing of the barrier layer, and made it possible to achieve the selective deposition of materials. The sizes of the TiO₂ and Au disks were 90 and 130 nm, respectively, with a gap of 60 nm. Electrochemical measurement was conducted in a quartz glass cell containing a Pt wire counter electrode and a Ag/AgCl (KCl sat.) reference electrode using an electrochemical analyzer (BAS 100 B/W). The dye sensitization on TiO₂ was examined by irradiating the dye (Rh-B) using a xenon lamp through an infrared-cut filter and under a 540-nm-cut filter in an air-saturated 0.1 M nonbuffered aqueous KF solution (pH 6.9). The irradiated area of the sample was 1 × 1 mm². The adsorption of Rh-B to the TiO₂ disk surface was carried out by dipping the electrode in 5 mM Rh-B solution.

Figure 2 shows chronoamperograms representing the dependence of oxidation current at the Au electrodes at 0.2 V vs. Ag/AgCl on the concentration of O₂ in the solution. Under air-saturated conditions, oxidation current increased with irradiation and decreased in the dark. This increase in oxidation cur-

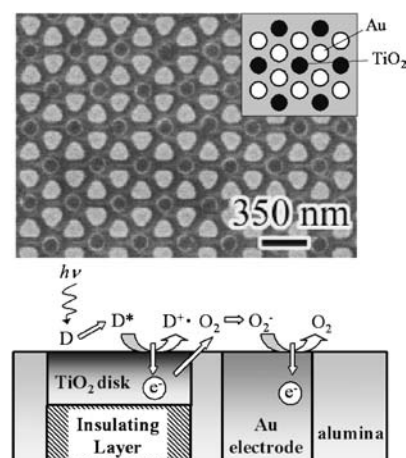


Figure 1. Surface SEM image of TiO₂/Au mosaic electrode array and schematic of electrochemical detection of active species in dye sensitization using TiO₂/Au mosaic electrode array.

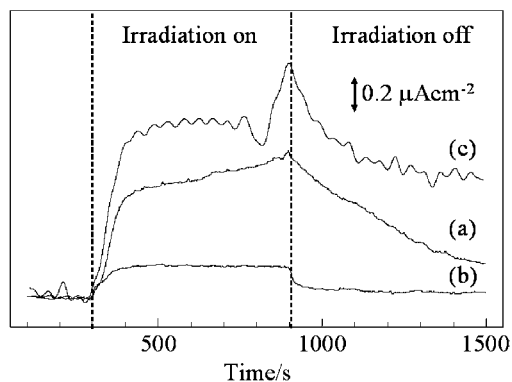


Figure 2. Current–time responses for Au disk electrodes in TiO_2/Au mosaic electrode array at 0.2 V vs. Ag/AgCl (KCl sat.) in 0.1 M KF aqueous solution with and without irradiation of Rh-B/ TiO_2 disks. Electrochemical measurement conditions: with O_2 (a), without O_2 (b), with O_2 and 300 μM hydroquinone (c).

rent was confirmed for the detection of active species produced by the irradiation of Rh-B on the TiO_2 disks, because no oxidation current was observed in the blank experiment using the irradiated Rh-B/Au disks. This result also ensured detection of the dye-sensitized reaction products formed by the irradiation of the Rh-B/ TiO_2 disk surface using the present mosaic electrode systems. In addition, the addition of hydroquinone, which acts as a supersensitizer of dyes, increased oxidation current under irradiation, indicating an increase in the number of active species produced by the dye sensitization on the TiO_2 disks. Such an increase in the number of active species was caused by the regeneration of Rh-B molecules through the transfer of electrons from hydroquinone to cation radicals. From these results, it is considered that the increase in oxidation current is caused by short-lived species produced by electrons on TiO_2 transferred from photoexcited Rh-B molecules. Furthermore, the oxidation current observed in the dark may be attributed to the accumulation of reaction products on the electrodes. The oxidation current under deaeration conditions is smaller than under air-saturated conditions. This implies that the number of active species at the Au electrodes decreases under deaeration conditions, because electrons injected from the photoexcited dye into TiO_2 disks could not react with O_2 . These results imply that the increase in oxidation current at the Au electrodes was due to the detection of short-lived species generated by the irradiation of Rh-B/ TiO_2 , where two possible candidates, O_2^- and H_2O_2 are considered as the short-lived species.

Figure 3 shows chronoamperograms representing the dependence of oxidation current at the Au electrodes at 0.2 V vs. Ag/AgCl with and without SOD in the solution. The addition of SOD, which catalyzes specifically the disproportionation of O_2^- , decreased oxidation current under irradiation. This means that O_2^- produced on the Rh-B/ TiO_2 disks under irradiation was promptly decomposed by SOD. From these results, it can be concluded that short-lived species of O_2^- produced by dye sensitization on the Rh-B/ TiO_2 surface was detected at the Au electrodes using a TiO_2/Au mosaic electrode array. Even under deaeration conditions or in the presence of SOD, small photocur-

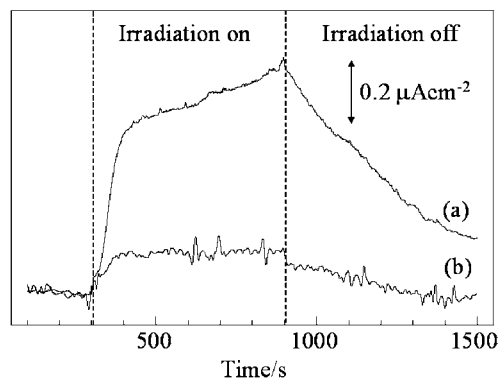


Figure 3. Current–time responses for Au disk electrodes in TiO_2/Au mosaic electrode array at 0.2 V vs. Ag/AgCl (KCl sat.) in 0.1 M KF aqueous solution with and without irradiation of Rh-B/ TiO_2 disks. Electrochemical measurement conditions: without SOD (a), with SOD (b).

rent was observed at Au electrodes. This response is thought to be attributable to the generation of cation radicals of Rh-B.

In conclusion, short-lived species of O_2^- formed by dye sensitization on Rh-B/ TiO_2 disks under irradiation were studied using a TiO_2/Au mosaic electrode array. The dependence of the observed current on O_2 concentration and effect of the addition of SOD on the current confirmed that the short-lived species of O_2^- produced by dye sensitization could be detected electrochemically.

The mosaic electrode array used in the present study will be applied to the detection of short-lived species produced by electrochemical or photoelectrochemical reactions by changing the combination of the materials of the central disks and absorbed molecules, such as proteins, enzymes, and other functional molecules.

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