Microscopic Observation of Photocatalytic Reaction Using Microelectrode: Spatial Resolution for Reaction Products Distribution

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We employed a Pd-loaded TiO_2 film as a simple model for the metal-deposited photocatalyst and carried out spatial mapping of reaction products formed by the photocatalytic reactions in a $Fe(CN)_6^{3-/4-}$ aqueous solution using a microelectrode. The experimental data were simulated with a diffusion model solved by the finite difference method. The results indicate that the spatial resolution of ca. 70 μm can be obtained with a distance of 30 μm between the sample surface and the microelectrode.

Photocatalytic reactions with metal-deposited TiO_2 particles and films have been studied extensively.[1-2] In these photocatalysts it is considered that the deposited metal acts as a reduction site, increasing the charge separation efficiency and thus expediting the transportation of photogenerated electrons in the conduction band of TiO_2 to the outer system. In all these studies, however, the reaction products were analyzed as a sum of the products at the oxidation and reduction sites. If the reactions at each site are monitored separately, significant information on the photocatalytic reactions at the metal-loaded TiO_2 surface may be obtained.

We have recently reported the separate monitoring of reaction products at the oxidation and reduction sites of ITO-TiO_2 composite film photocatalyst using a microelectrode located adjacent to the surface of each site.[3] In the present work, we employed a partially Pd-loaded TiO_2 film as a simple model for the metal-deposited photocatalyst and carried out spatial mapping of reaction products formed by a photocatalytic reaction in a $Fe(CN)_6^{3-/4-}$ aqueous solution. Furthermore, numerical simulation of concentration gradient of photogenerated species near the surface was carried out. The spatial resolution of this microelectrode method obtained by the experiments was compared to the calculated results.

Carbon microelectrodes were fabricated as follows. A 7 μm carbon fiber (Asahi Nippon Carbon Fiber) was inserted into a 1 mm o.d. pyrex glass tube. The tube was pulled on a micropipette puller (Narishige, PN-3) to yield a glass-coated carbon fiber (ca. 20 μm o.d.). The small gap between the glass and the fiber was sealed with a low-viscosity epoxy resin (Epon), then the top of the glass-coated fiber was cut off and polished using a pipette beveller (Narishige, EG-6) to produce the carbon disk.

The TiO_2 film (anatase microcrystal) was prepared on an ITO glass substrate by a spray-pyrolysis technique from 0.05 M ethanol solution of titanyl acetylacetonate (Tokyo Kasei) at 450 °C.[4] Palladium on TiO_2 (schematic illustration was shown in Figure 1(A)) was electrolytically deposited onto this film patterned with photoresist in a $PdCl_2$ aqueous solution at – 120 m V vs. SCE for 1h. Finally the photoresist was removed with the remover.

A schematic diagram of the experimental setup is shown in Figure 1(B). The TiO_2 film was placed at the bottom of the cell and the carbon-disk microelectrode was positioned in the close vicinity of the film surface using a micromanipulator. Then UV light from a 200-W Hg-Xe lamp (300 ~ 400 nm) was irradiated on the film and the change in the current response at the microelectrode was monitored. A Pt wire and a saturated calomel electrode (SCE) were used as a counter and reference electrode, respectively. All measurements were carried out in an aqueous solution containing 5 mM $K_4Fe(CN)_6$ and 0.1 M K_2SO_4.

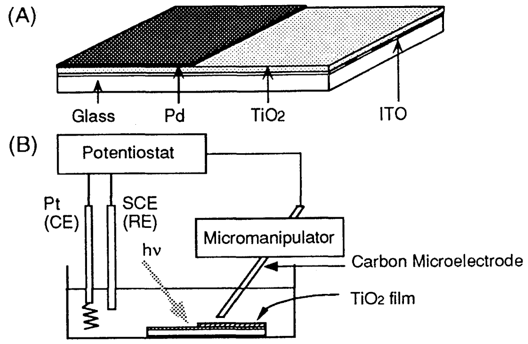

Figure 1. (A) Structure of the TiO_2-Pd composite film. (B) Schematic diagram of the experimental setup.

The nearly steady-state distribution (after more than 30 s irradiation) of reaction products adjacent to the boundary of the TiO_2 and Pd parts of the irradiated film was monitored by moving the microelectrode perpendicular to the boundary with the distance between the film and the microelectrode kept constant at 30, 50 and 100 μm. The potential of the microelectrode was kept at +500 mV vs. SCE and the distribution of $Fe(CN)_6^{4-}$ next to the surface was monitored from the oxidation current of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$. As shown in Figure 2, when the composite film was irradiated with the UV light, the anodic current at the microelectrode decreased above the TiO_2 sites and increased above the Pd sites. These current changes are due to the decrease of the $Fe(CN)_6^{4-}$ concentration near the TiO_2 surface by the oxidation reaction (2) and the increase of the $Fe(CN)_6^{4-}$ concentration near the Pd surface by the reduction reaction (3), respectively.

$$h\nu \xrightarrow{TiO_2} h^+ + e^- \quad (1)$$

$$\bullet \text{ above } TiO_2 \qquad Fe(CN)_6^{4-} + h^+ \rightarrow Fe(CN)_6^{3-} \quad (2)$$

$$\bullet \text{ above Pd} \qquad Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \quad (3)$$

Therefore, the current increase above Pd and decrease above TiO_2 correspond to the reduction and oxidation reactions, respectively. While the $Fe(CN)_6^{3-}$ concentration is very dilute at the initial stage of UV irradiation, the reduction of the dissolved oxygen mainly occurs above the Pd site instead of the reaction (3). This is the reason why the current change above Pd is smaller than that above TiO_2. The influence of the diffusion was also observed when the distance between the electrode and the film varied from 100 μm to 30 μm (see Figure 2). As the distance became larger, the difference between the $Fe(CN)_6^{4-}$ concentration above the TiO_2 site and the Pd site became smaller near the TiO_2-Pd boundary. These results showed that the photocatalytic reactions at the reduction and oxidation sites can be monitored on the metal-loaded TiO_2 photocatalyst separately. The spatial resolution in the lateral direction at the steady-state concentration was ca. 70 μm when the microelectrode was situated 30 μm above the film.[5]

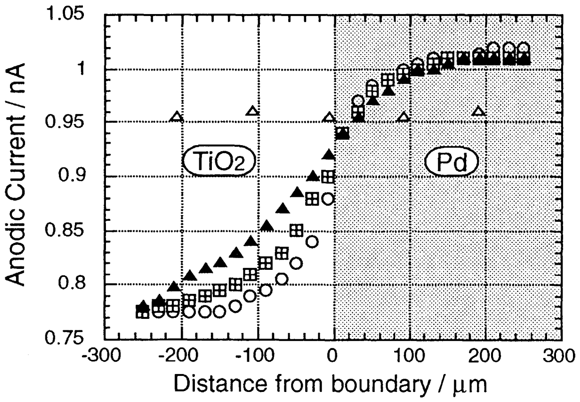

Figure 2 The steady-state distribution of reaction products. The electrode was moved perpendicularly across the TiO_2-Pd boundary with the distance between the electrode and the film kept at 30(○), 50(⊞) and 100 μm(▲). The current before the irradiation is also shown(△). Potential of the microelectrode, +500 mv vs. SCE.

The spatial resolution of this microelectrode method was simulated by a diffusion model. For the oxidation reaction $R \rightarrow O + ne^-$ at a microdisk electrode, the limiting current to the electrode is given by the eq.(4),

$$i = 4nFDCr \tag{4}$$

where F is the faradic constant, D is the diffusion coefficient of reduced species, C is the concentration of reduced species and r is a radius of the microelectrode. When the microelectrode is positioned above the TiO_2 film surface, the current response at the microelectrode represents the concentration change of the reduced species near the film surface. In order to know concentration profiles near the illuminated sample, the finite difference method (FDM) was employed. Two-dimensional diffusion eq.(5) was transformed with a dimensionless operation (eq.(6)).

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial z^2}\right) \tag{5}$$

$$D = (\Delta x)^2(\Delta t)^{-1}D' \tag{6}$$

In order to solve the eq.(5), it is assumed that all reductants at the surface of the TiO_2 site are oxidized and all oxidants at the surface of the Pd sites are reduced under UV irradiation. This is reasonable under the condition that the sample is irradiated by the light with high intensity in a dilute solution. Because the $Fe(CN)_6^{3-}$ concentration can be ignored against the $Fe(CN)_6^{4-}$ concentration before irradiation, the initial bulk concentrations C_0 of $Fe(CN)_6^{4-}$ and $Fe(CN)_4^{3-}$ are chosen to be 1 and 0, respectively. The diffusion coefficient D is assumed to be $10^{-5}cm^2/s$.

The calculated concentration profile of $Fe(CN)_6^{4-}$ near the surface of the irradiated composite film is shown in Figure 3, in which the time course change in the calculated $Fe(CN)_6^{4-}$ concentration at 30 μm away from the film is shown. The concentration gradient of $Fe(CN)_6^{4-}$ has a half width of 70 μm at the nearly steady-state condition (after 30 s irradiation). This agrees well with the resolution obtained by the experiment. Additionally, Figure 3 shows that the change in the concentration of $Fe(CN)_6^{4-}$ reaches almost the steady-state condition after 30 sec of UV irradiation. The influence of the distance from the film surface on the concentration distribution was also calculated. The resolution lowers by the influence of the diffusion when the microelectrode is apart from the film. As a result of the same calculation, the resolutions were 90 μm and 140 μm with the distance of 50 μm and 100 μm, respectively. These values agree well with the experimental results.

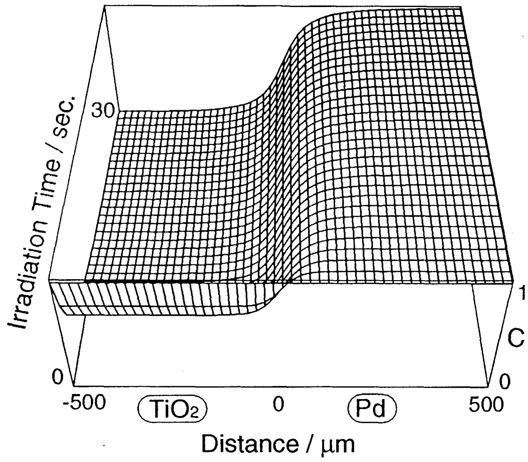

Figure 3.The time course change of the calculated $Fe(CN)_6^{4-}$ concentration at 30 μm away from the film.

In conclusion it was confirmed that separate observation of reduction and oxidation sites at the metal-loaded TiO_2 photocatalyst can be carried out using the microelectrode technique. The lateral resolution of the microelectrode method is about 70 μm when located 30 μm away from the surface. The present method has the potential for investigation of the reaction mechanism at the metal-loaded photocatalysts. Higher resolution would be possible with the scanning electrochemical microscope by which more precise positioning and scanning of the electrode can be achieved.[6]

References and Notes

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5 The spatial resolution is defined as the distance between points on the current vs. distance profile at which the deviations of the currents above TiO_2 and Pd under illumination from the values in the dark are half of their respective maximal deviations.

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