

# Microscopic Observation of TiO<sub>2</sub> Photocatalysis Using Scanning Electrochemical Microscopy

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Photocatalytic reactions were monitored on a macroscopic model system, containing millimeter scale regions for oxidation and reduction, for a microscopic photocatalytic particle containing both oxidizing and reducing sites, with the use of the scanning electrochemical microscopy (SECM) technique. We employed a TiO<sub>2</sub>–ITO (indium–tin oxide) composite film: half of a macroscopic ITO glass substrate was coated with a TiO<sub>2</sub> film, leaving the ITO exposed on the other half of the sample, in an aqueous solution containing 5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.1 M K<sub>2</sub>SO<sub>4</sub>. When the microelectrode was placed at a relatively large distance above the TiO<sub>2</sub> portion of the illuminated surface, there was a small effect: ferrocyanide was photooxidized, thereby decreasing the amount that could be oxidized at the microelectrode. In contrast, when the microelectrode was placed very close to the TiO<sub>2</sub> portion of the surface, the oxidation current at the microelectrode increased significantly after turning on the UV light, and the oxidation current increase observed after turning on the UV light became even larger when the exposed ITO portion was covered by epoxy resin. This current increase is due to positive feedback; i.e., ferricyanide produced electrochemically at the microelectrode is rereduced at the illuminated TiO<sub>2</sub> surface by photogenerated electrons. We propose that both oxidation and reduction reactions can occur simultaneously on the illuminated unbiased TiO<sub>2</sub> photocatalyst film. These results indicate the utility of the SECM method for clarifying the mechanisms of photocatalytic reactions on TiO<sub>2</sub> surfaces.

## Introduction

Photocatalytic and photosynthetic reactions occurring at TiO<sub>2</sub> semiconductor electrodes, particles, and thin films have been the subject of numerous studies because of the strong oxidative power of TiO<sub>2</sub>.<sup>1–8</sup> It is well-known that the modification of the TiO<sub>2</sub> surface by the deposition of a catalytic metal is effective in increasing the quantum efficiency of photocatalytic reactions.<sup>9–13</sup> For instance, the photoassisted water splitting reaction is significantly accelerated on a Pt-loaded TiO<sub>2</sub> surface compared with the unmodified surface, because Pt acts as a good catalyst for H<sub>2</sub> production.<sup>11</sup> Wang et al. reported that modification of the TiO<sub>2</sub> surface with palladium increases the efficiency of photoassisted oxidation on photocatalyst slurries.<sup>12</sup> For these catalysts, it is considered that the TiO<sub>2</sub> surface acts mainly as an oxidation site, and the deposited metal acts as a reduction site, increasing the charge separation efficiency and thus expediting the transport of photogenerated electrons in the conduction band of TiO<sub>2</sub> to an external chemical system.

In fact, we have reported the separate monitoring of both oxidation and reduction reactions above TiO<sub>2</sub> sites and metal sites, respectively, using a microelectrode technique.<sup>14–17</sup> However, both oxidation and reduction reactions can occur simultaneously at TiO<sub>2</sub> sites when the consumption of photoexcited

electrons is slow on the reduction sites. In addition, the use of nonmetallized TiO<sub>2</sub> photocatalysts is well-known, in which case the reduction and oxidation processes must take place on essentially the same surface at the same rate. Our long-range objective is to understand the factors controlling the oxidation and reduction processes at the microscopic level on TiO<sub>2</sub> surfaces.

In the present work, we have employed a TiO<sub>2</sub>–ITO (indium–tin oxide) composite film formed by coating polycrystalline TiO<sub>2</sub> onto half of a macroscopic ITO glass substrate, leaving the ITO exposed on half of the sample, upon which the bulk of the reduction process occurs, as a simple macroscopic model for the metal-deposited photocatalyst. We then monitored the electrochemically assisted and/or photoassisted reactions on the TiO<sub>2</sub> surfaces using scanning electrochemical microscopy (SECM).

In recent years, progress in SECM has been rapid, and numerous applications in electrochemical measurement, imaging, and microfabrication have been reported.<sup>18,19</sup> For instance, SECM has been used to monitor electroassisted or photoassisted reactions on semiconductor surfaces.<sup>20–24</sup> By use of the SECM technique, we will show clear evidence that, in addition to oxidation reactions, reduction reactions are also simultaneously occurring on the photoirradiated TiO<sub>2</sub> portion of the TiO<sub>2</sub>–ITO composite film.

## Experimental Section

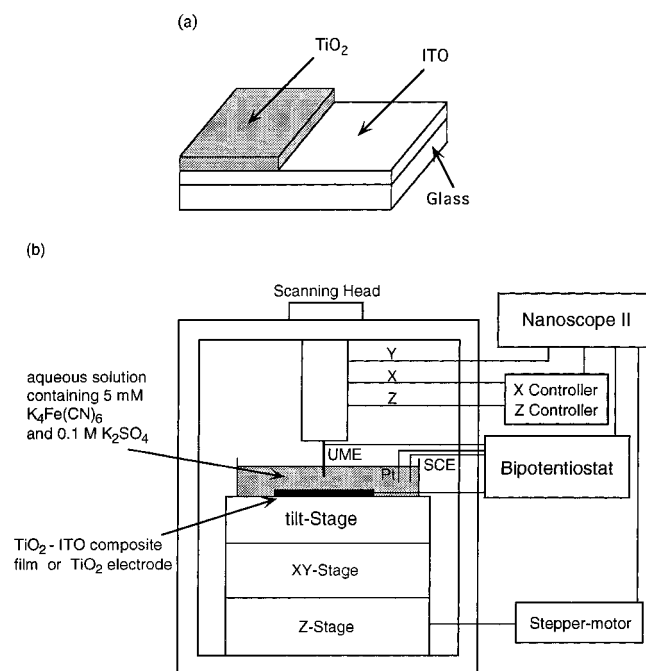
**Preparation of TiO<sub>2</sub>–ITO Composite Film and TiO<sub>2</sub> Electrode.** TiO<sub>2</sub> film (microcrystalline anatase) was prepared

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**Figure 1.** (a) Structure of the TiO<sub>2</sub>-ITO composite film. (b) Schematic diagram of the experimental setup (UME = ultramicroelectrode).

on an ITO glass substrate by a spray-pyrolysis technique from a 0.1 M ethanol solution of titanyl acetylacetonate (Tokyo Kasei) at 400 °C.<sup>25</sup> A TiO<sub>2</sub>-ITO composite film was prepared by forming TiO<sub>2</sub> film on half (2 cm × 2 cm) of the total area of the ITO glass, leaving a 2 cm × 2 cm area of ITO exposed, as illustrated in Figure 1a.

**Preparation of Pt-Ir Microelectrodes.** Pt-Ir microelectrodes were fabricated as follows.<sup>26</sup> A 2–3 cm long Pt-Ir wire (250 μm diameter) was sharpened by electrochemical etching in a solution containing saturated CaCl<sub>2</sub> (20% v/v), H<sub>2</sub>O (80% v/v) at 2 V AC(rms, 50 Hz). A carbon rod served as the counter electrode in the two-electrode etching cell. A 1 mm o.d. Pyrex glass tube was pulled on a micropipet puller (Narishige, PN-3). Low-viscosity epoxy resin (Polysciences) was injected into the glass tube, and then the sharpened wire was transferred inside the glass tube. The top of the glass-coated wire was cut off and polished using a pipet beveller (Narishige, EG-6) until the top of the sharpened Pt-Ir wire was exposed. The diameter of the exposed Pt-Ir disk could be controlled from ~0.8 to 30 μm by controlling the extent of this final polishing. In the present work, both ~30 μm and 3 μm diameter microelectrodes were used.

**Photoelectrochemical Measurements.** A schematic diagram of the home-built SECM system used in this work is shown in Figure 1b. This SECM system was made by modification of a commercial STM system (Nanoscope II, Digital Instruments). An electrochemical cell was set on an XYZ stage and a tilt stage. The TiO<sub>2</sub>-ITO composite film or TiO<sub>2</sub> electrode was placed at the bottom of the cell and positioned under the Pt-Ir microelectrode using the XYZ stage and tilt stage, and then the microelectrode was moved adjacent to the TiO<sub>2</sub> surface using a stepper-motor controlled by the Nanoscope II. Potentials of the microelectrode and the TiO<sub>2</sub> electrode were controlled independently using a bipotentiostat (Hokuto Denko, HA150P). UV light from a 200 W Hg-Xe lamp (300–400 nm) was directed at the TiO<sub>2</sub> film, after passing through a 365 nm band-pass filter, and changes in the current response at the microelectrode were monitored. The light intensity, 8.5 mW/cm<sup>2</sup>, was not high enough that the transformation of absorbed photons

into heat at the irradiated surface influenced the delivery of electroactive species to the microelectrode. We checked for the possible influence of thermal gradients due to the UV illumination as follows: when the TiO<sub>2</sub> thin film sample was immersed in an aqueous solution, the change in the temperature of the TiO<sub>2</sub> surface and solution on the TiO<sub>2</sub> surface was monitored using a thermometer (~1 mm diameter). No change (<0.1 °C) was observed during three minutes of UV illumination. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively, and all of the photoelectrochemical and electrochemical measurements were carried out in an aqueous solution containing 5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.1 M K<sub>2</sub>SO<sub>4</sub>.

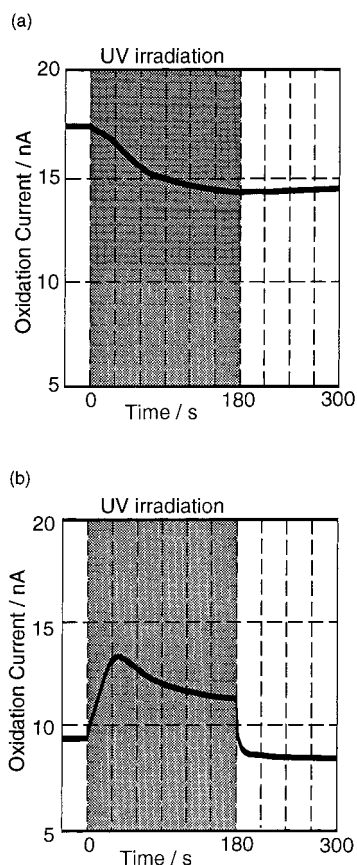
## Results and Discussion

To study the reaction processes occurring on the TiO<sub>2</sub> surface, we paid attention to so-called positive and negative feedback effects. As reported by Arca et al.,<sup>27</sup> the basic principle of the feedback effect is as follows. When a microelectrode is used as a working electrode in an electrochemical cell containing oxidizable species (Red) and a sufficiently positive potential is applied to the microelectrode, a steady-state oxidation current,  $i_{T,\infty}$ , flows in the microelectrode. However, by positioning the microelectrode closer to an inert insulating surface, the current becomes smaller (negative feedback), because the surface blocks the diffusive flux of Red to the microelectrode. In contrast, when the microelectrode is positioned closer to a conductive surface, the current becomes larger (positive feedback). This is because there is a flux of Red to the microelectrode from the surface in addition to that from the bulk solution.

**Negative Feedback Effect above the TiO<sub>2</sub> Surface in the Dark.** First, the oxidation current at a microelectrode above the TiO<sub>2</sub> portion was observed in the dark. The potential of the microelectrode was maintained at +700 mV vs SCE, such that the oxidation of Fe(CN)<sub>6</sub><sup>4-</sup> to Fe(CN)<sub>6</sub><sup>3-</sup> occurs at a diffusion-controlled rate, corresponding to the diffusion of Fe(CN)<sub>6</sub><sup>4-</sup> to the microelectrode. When the microelectrode was located far from the TiO<sub>2</sub> surface, the oxidation current showed a steady-state current,  $i_{T,\infty}$ . The closer the microelectrode was positioned to the TiO<sub>2</sub> surface, the smaller the current became. This change in the current vs the relative distance  $L = d/a$ , where  $d$  is the microelectrode-to-surface spacing and  $a$  is the radius of the microelectrode, is consistent with negative feedback behavior. Therefore, this result shows that the TiO<sub>2</sub> surface acts as an insulating substrate in the dark.

**Positive Feedback Effect above the Irradiated TiO<sub>2</sub> Surface.** The oxidation current response of a microelectrode maintained at +700 mV vs SCE was measured as a function of time when the TiO<sub>2</sub> surface was irradiated with UV light. First, a 30 μm diameter microelectrode was located relatively far from the TiO<sub>2</sub> surface, at a position  $L = 7$  (i.e.,  $d = 105 \mu\text{m}$ ). As shown in Figure 2a, the current for Fe(CN)<sub>6</sub><sup>4-</sup> oxidation decreased after turning on the UV light and increased again slowly after turning it off. In contrast, no current change was observed above the ITO surface with UV irradiation. These results show that the current change is due to photochemical reactions occurring on the TiO<sub>2</sub> surface, i.e., the oxidation of Fe(CN)<sub>6</sub><sup>4-</sup> to Fe(CN)<sub>6</sub><sup>3-</sup> by photogenerated holes (h<sup>+</sup>).

When the microelectrode was located above the TiO<sub>2</sub> surface at a position  $L = 1$  (i.e.,  $d = 15 \mu\text{m}$ ), however, the current increased when the UV light was turned on (Figure 2b). There are two possible mechanisms to explain this phenomenon. One is that the photochemical oxidation of Fe(CN)<sub>6</sub><sup>4-</sup> is suppressed at the initial stage because, for example, the TiO<sub>2</sub> surface was

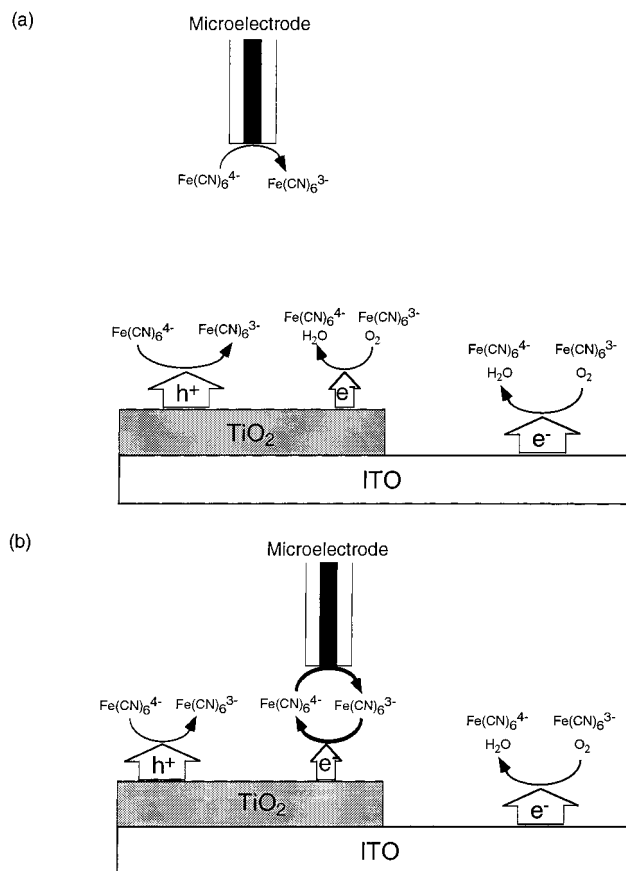


**Figure 2.** Oxidation current vs time curves at a microelectrode ( $a = 15 \mu\text{m}$ ) located at a position (a)  $L = 7$  (i.e.,  $d = 105 \mu\text{m}$ ) and (b)  $L = 1$  ( $d = 15 \mu\text{m}$ ) above the irradiated TiO<sub>2</sub> surface of a TiO<sub>2</sub>-ITO composite film in an aqueous solution containing 5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.1 M K<sub>2</sub>SO<sub>4</sub>. Hatched areas represent the time duration of the photoirradiation (light intensity, 8.5 mW/cm<sup>2</sup>; microelectrode potential, +700 mV vs SCE).

shaded by the microelectrode, as reported by Yoneyama et al.<sup>28</sup> The other is that Fe(CN)<sub>6</sub><sup>3-</sup> produced at the microelectrode is reduced to Fe(CN)<sub>6</sub><sup>4-</sup> at the irradiated TiO<sub>2</sub> surface. In other words, a positive feedback effect is proceeding on the irradiated surface.

Experiments were carried out using a microelectrode with a radius of 1.5  $\mu\text{m}$ , and similar results were obtained; i.e., the current decreased at a position  $L = 7$  (i.e.,  $d = 10.5 \mu\text{m}$ ) after turning on the UV light and increased at a position  $L = 1$  (i.e.,  $d = 1.5 \mu\text{m}$ ) after turning on the UV light. All of the experiments show that the current response depends not on  $d$  but on  $L$ , suggesting that the current increase behavior is due to positive feedback occurring between the microelectrode and the irradiated TiO<sub>2</sub> surface.

The current response behavior can be explained reasonably assuming that, on the irradiated surface, the oxidation reaction predominates, but a reduction reaction also occurs simultaneously to a slight degree, while the bulk of the reduction reaction, initially O<sub>2</sub> reduction, as discussed later, occurs on the conductive ITO portion of the sample, which acts as a macroscopic model for the microscopic reduction sites. When the oxidation reaction is predominant on the irradiated surface, the concentration of Fe(CN)<sub>6</sub><sup>4-</sup> decreases gradually under UV irradiation. Also, the thickness of the diffusion layer for Fe(CN)<sub>6</sub><sup>4-</sup> increases gradually with time and influences the oxidation current at the microelectrode far above the TiO<sub>2</sub> surface (Figure 3a). Therefore, when the microelectrode was located at a position where the positive feedback effect is



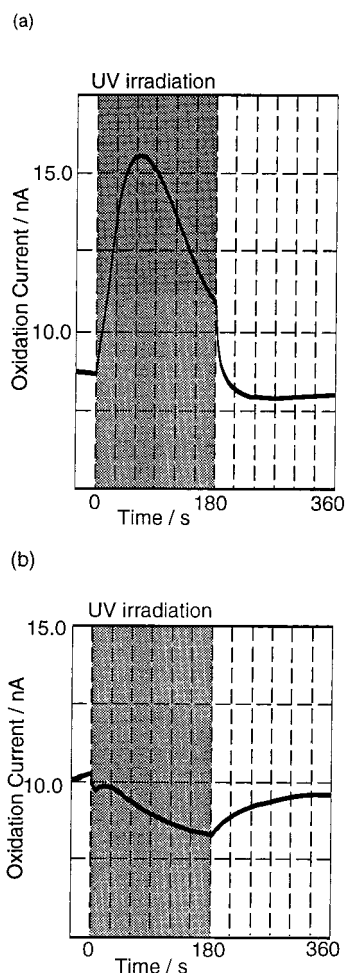
**Figure 3.** Mechanisms proposed for the photochemical reactions between the microelectrode and the irradiated TiO<sub>2</sub> surface when the microelectrode is located at a position (a) where the positive feedback effect is negligible ( $L = 7$ ) and (b) where the positive feedback effect is nonnegligible ( $L = 1$ ).

negligible ( $L = 7$ ), the current decreased under UV irradiation, because the Fe(CN)<sub>6</sub><sup>4-</sup> concentration decreased due to the photooxidation reaction on TiO<sub>2</sub>. However, when the microelectrode was located close to the irradiated surface, where the positive feedback effect is nonnegligible ( $L = 1$ ), the current increased after turning on the UV light. This is because a reduction reaction also occurs to a small extent, and positive feedback proceeds between the microelectrode and the TiO<sub>2</sub> surface (Figure 3b). When the microelectrode was located very close to the surface, the decrease of the Fe(CN)<sub>6</sub><sup>4-</sup> concentration as a result of the photooxidation reaction on the TiO<sub>2</sub> is so effective that the Fe(CN)<sub>6</sub><sup>4-</sup> concentration near the surface becomes very low, and the positive feedback gradually becomes less effective during UV irradiation.

To model a photocatalytic system in which there are no metallic reduction sites, we covered the exposed conductive ITO portion of the sample with epoxy resin and measured the oxidation current response at the microelectrode after turning on the UV light when the microelectrode was located at a position  $L = 1$  from the TiO<sub>2</sub> surface. The observed current increase was even larger, compared to the case in which the ITO portion was exposed to the aqueous solution. This is because the photogenerated electrons cannot be consumed on the ITO portion, and thus electrons tend to accumulate in the TiO<sub>2</sub> portion, thereby increasing the rate of the reduction reactions on the TiO<sub>2</sub> (discussed later in detail).

**Control of the Positive Feedback Effect.** For the composite film TiO<sub>2</sub>-ITO, i.e., with both areas exposed, it is certain that the bulk of the cathodic current flows from the conductive ITO,



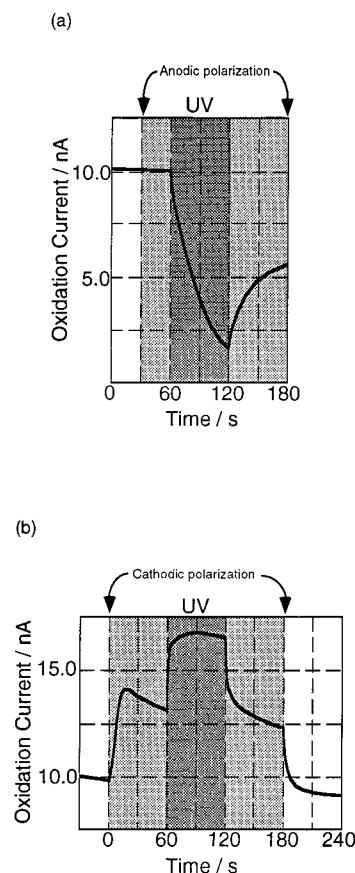


**Figure 4.** Influence of the dissolved oxygen concentration on the oxidation current response at the microelectrode after (a)  $\text{N}_2$  saturation and (b)  $\text{O}_2$  saturation. All other conditions are as in Figure 2 except that  $L = 1$ .

just as in the case of our previous work with  $\text{TiO}_2$ -Pd composite films.<sup>17</sup> At the initial stage of UV irradiation, the reduction of dissolved oxygen ( $\sim 0.3$  mM) occurs on ITO. By continuing the irradiation, the concentration of  $\text{Fe}(\text{CN})_6^{3-}$  in the bulk of the solution increases gradually, as a result of the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  on the  $\text{TiO}_2$  portion, and its rereduction begins to occur on ITO, competing with  $\text{O}_2$  reduction.

We have just shown that the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  also proceeds on the irradiated  $\text{TiO}_2$  surface. Therefore, the concentration of dissolved oxygen may influence the reduction reaction on the irradiated  $\text{TiO}_2$  surface. The time dependence of the current response was observed in the presence and absence of dissolved oxygen at a position  $L = 1$  on the  $\text{TiO}_2$  surface. In Figure 4, a and b, are shown the time dependences of the current for  $\text{N}_2$ -saturated and  $\text{O}_2$ -saturated solutions, respectively. It can clearly be seen that the presence of  $\text{O}_2$  inhibits the positive feedback effect.

This can be explained as follows. In the absence of  $\text{O}_2$ , there is initially no electroactive species that can be reduced at the ITO portion of the sample, and photogenerated electrons thus accumulate in the  $\text{TiO}_2$  portion, just as in the case of the epoxy-covered ITO described above. This negative charge on the  $\text{TiO}_2$  results in  $\text{Fe}(\text{CN})_6^{3-}$  produced at the microelectrode being effectively rereduced at the  $\text{TiO}_2$  surface (Figure 4a). On the other hand, in the presence of  $\text{O}_2$ , because most of the photogenerated electrons are consumed by the reduction of dissolved oxygen on the ITO portion, there is little accumulation



**Figure 5.** Oxidation current vs time curves at the microelectrode ( $a = 15$   $\mu\text{m}$ ) positioned at  $L = 1$  on the surface of the  $\text{TiO}_2$  electrode when the  $\text{TiO}_2$  electrode potential is poised at (a)  $+500$  mV vs SCE and (b)  $-700$  mV vs SCE.

of electrons in the  $\text{TiO}_2$  portion, and the oxidation reaction by photogenerated holes predominates. Thus there is little positive feedback effect (Figure 4b).

Since the magnitude of the positive feedback effect, i.e., the reduction reaction on the irradiated  $\text{TiO}_2$  surface, can be controlled by changing the concentration of the electron acceptor (dissolved oxygen), it is expected that a similar current response would be observed when a potential is applied to the  $\text{TiO}_2$  electrode (biased conditions). The  $30$   $\mu\text{m}$  diameter microelectrode, with the potential hold at  $+700$  mV vs SCE, was located at a position  $L = 1$  on the surface of the  $\text{TiO}_2$  electrode in an aqueous solution containing  $5$  mM  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $0.1$  M  $\text{K}_2\text{SO}_4$ . No change was observed in the oxidation current at the microelectrode when a positive potential ( $+500$  mV vs SCE) was applied to the  $\text{TiO}_2$  electrode in the dark. By turning on and off the UV light at this potential, the current at the microelectrode decreased and increased, respectively (Figure 5a). This current response can clearly be attributed to the photogenerated electrons being removed to the external circuit and thence to the counter electrode and the photogenerated holes being consumed at the  $\text{TiO}_2$  surface, so that only the photo-oxidation reaction occurred on the surface of the  $\text{TiO}_2$  electrode during UV irradiation. The oxidation current at the microelectrode thus decreases due to the depletion of ferrocyanide near the  $\text{TiO}_2$  surface.

However, when a negative potential ( $-700$  mV vs SCE) was applied to the  $\text{TiO}_2$  electrode, the oxidation current at the microelectrode increased, even in the dark. This is because  $\text{Fe}(\text{CN})_6^{3-}$  produced at the microelectrode was rereduced to  $\text{Fe}(\text{CN})_6^{4-}$  on the surface of the  $\text{TiO}_2$  electrode (positive

feedback). Moreover, the current increased further under UV irradiation at this potential, because photogenerated electrons can also come to the surface of the TiO<sub>2</sub> electrode and reduce Fe(CN)<sub>6</sub><sup>3-</sup> to Fe(CN)<sub>6</sub><sup>4-</sup> leading to more effective positive feedback (Figure 5b). These results show that only in cases in which a reduction reaction occurs on the TiO<sub>2</sub> surface in addition to the oxidation reaction does the oxidation current at a microelectrode positioned at  $L = 1$  increase with UV irradiation by means of the positive feedback effect.

## Conclusions

We have shown that positive feedback occurs for a microelectrode positioned close ( $L = 1$ ) to an irradiated TiO<sub>2</sub> surface, indicating that both oxidation and reduction reactions occur simultaneously on the illuminated unbiased TiO<sub>2</sub> photocatalyst film in the TiO<sub>2</sub>-ITO composite, even though most of the reduction process occurs on the ITO portion.

If a Schottky-type barrier exists at the interface between the TiO<sub>2</sub> thin film and the solution, it could be expected that only photogenerated holes would move to the interface due to band bending, and photogenerated electrons would not. However, the present results suggest that the barrier height at the interface under open-circuit conditions is small enough under irradiation that there is a significant contribution from the cathodic reaction.<sup>29</sup> As an extreme case, when no ITO is exposed to the solution, that is, only the TiO<sub>2</sub> portion of the thin film sample is exposed to the solution, the photogenerated electrons are easier to discharge from the TiO<sub>2</sub> thin film. With both TiO<sub>2</sub> and ITO exposed, when a positive bias potential was applied, it became possible to effectively turn off the cathodic reaction. On the other hand, with a negative bias potential, the cathodic reaction was induced, even in the dark.

In the present work, we have made further refinements in our previously reported microelectrode technique that help to obtain a more detailed understanding of the photoelectrochemical reactions.<sup>14-17</sup> In future work, with submicrometer-scale microelectrodes, it may be possible to obtain specific information of heterogeneous photoelectrochemical reactions in even greater detail. We are now investigating the relationship between photocatalytic reactions and the surface properties of TiO<sub>2</sub> thin films using the SECM technique.<sup>30</sup>

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