

# Photocatalytic Decomposition of Lactic Acid in Water on a Photoelectrochemical Circuit System Consisting of a Rod-type TiO<sub>2</sub> Electrode and Silicon Solar Cell

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**Abstract** Lactic acid, a well-known substance causing dental caries, was dissolved in water and completely oxidized into CO<sub>2</sub> and H<sub>2</sub>O on a powdered TiO<sub>2</sub> photocatalyst under UV light irradiation. Furthermore, a unique photoelectrochemical circuit system consisting of a rod-type TiO<sub>2</sub> electrode and counter electrode connected through a silicon solar cell was constructed and its photocatalytic activity for the decomposition of lactic acid was investigated. The photoelectrochemical circuit system was found to effectively mineralize the lactic acid in water into CO<sub>2</sub> while the negative bias applied on the rod-type TiO<sub>2</sub> electrode enhanced the photocatalytic decomposition rate of the lactic acid.

**Keywords** Photocatalysis · Silicon solar cell · Lactic acid

## 1 Introduction

Photocatalysis has attracted a great deal of attention as an environmentally harmonious catalytic process that can reduce toxic agents diluted in air and water under UV or solar light irradiation. In fact, semiconducting TiO<sub>2</sub> photocatalysts have been practically applied for various

reactions such as the decomposition of NO<sub>x</sub> in air [1, 2] and the degradation of toxic organic impurities diluted in water [3–10]. Studies on the dynamics and mechanisms behind such photocatalytic reactions have shown that the electrons and holes produced by UV irradiation of semiconducting TiO<sub>2</sub> play a significant role in the formation of an active intermediate species such as O<sub>2</sub><sup>-</sup>, OH<sup>-</sup>, H<sup>+</sup>, etc., depending on the reaction conditions [9, 10]. Photoelectrochemical investigations have also elucidated that the photocatalytic reaction rates on TiO<sub>2</sub> electrodes as well as the reaction dynamics of the photo-formed electrons and holes are significantly affected by the external electric bias applied on the TiO<sub>2</sub> electrodes. In the present work, the photocatalytic decomposition of lactic acid in water on powdered TiO<sub>2</sub> photocatalysts have been investigated for practical applications of TiO<sub>2</sub> photocatalysts in dental care. Lactic acid, which exists abundantly in the human buccal or oral cavity, is the cause of dental caries so that the effective and efficient elimination of lactic acid is essential in cavity protection [11, 12]. In the present work, a unique photoelectrochemical circuit system was constructed by connecting a rod-type TiO<sub>2</sub> electrode with a counter electrode through an silicon solar cell (SSC) and its photocatalytic activity for the decomposition of lactic acid in water was investigated. The effect of the applied external bias on the photocatalytic decomposition rate of lactic acid for the photoelectrochemical circuit system was also investigated.

## 2 Experimental

Powdered TiO<sub>2</sub> was supplied by the Catalysis Society of Japan as a standard reference catalyst (JRC-TiO-4: P-25, surface area: 50 m<sup>2</sup>/g). The rod-type TiO<sub>2</sub> electrode was prepared by the calcination of a metal Ti rod

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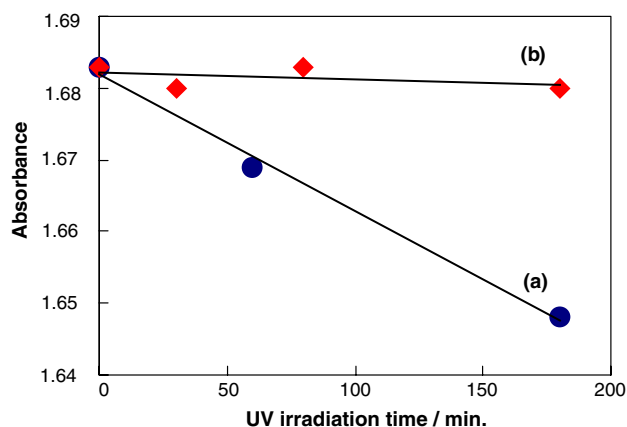
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( $\phi$  3 mm  $\times$  78 mm) at 1,073 K for 3 min in air. The photoelectrochemical circuit system was constructed by connecting the rod-type TiO<sub>2</sub> electrode with a counter electrode through an SSC (2.4 V, 6  $\mu$ A; 200 lx). Photocatalytic reactions were carried out by suspending the powdered TiO<sub>2</sub> (10 mg) or immersing the photoelectrochemical circuit system in an aqueous solution of lactic acid (20 mL) under light irradiation from various light sources such as a high-pressure mercury lamp (500 W) or a fluorescent lamp (20 W) at 298 K. The photoelectrochemical current between the rod-type TiO<sub>2</sub> electrode and counter electrode was adjusted at 70  $\mu$ A by a variable resistor only for the pH measurement experiment. The reaction products were analyzed by gas chromatography (Shimadzu, GC-9A). The XPS spectra were recorded under vacuum at 298 K using an ESCA3200 (Shimadzu). The surface morphologies of the rod-type TiO<sub>2</sub> electrode were investigated by scanning electron microscopy (SEM, Hitachi, S-4500).

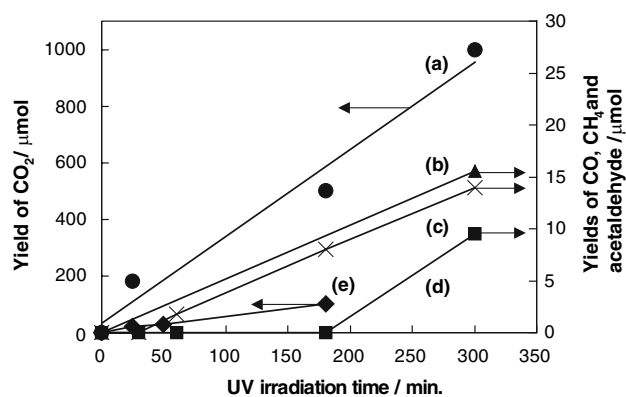
### 3 Results and Discussion

#### 3.1 Photocatalytic Decomposition of Lactic Acid in Water on Powdered TiO<sub>2</sub> Photocatalysts

An aqueous solution of lactic acid exhibited a UV absorption band at around 350 nm due to the lactic acid. As shown in Fig. 1, UV irradiation of the lactic acid aqueous solution suspended with powdered TiO<sub>2</sub> led to an efficient decrease in the intensity of the UV absorption band at around 350 nm due to the lactic acid, suggesting that it is photocatalytically mineralized. In fact, as shown in Fig. 2, UV irradiation of the aqueous solution of lactic acid



**Fig. 1** Time dependences of the intensity of the absorption band ( $\lambda = 350$  nm) of lactic acid in water in the (a) presence and (b) absence of powdered TiO<sub>2</sub> (P-25) under UV irradiation (full arc). Light source: 500 W high-pressure mercury lamp. Concentration of lactic acid: 0.01 M

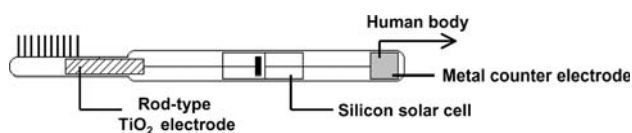


**Fig. 2** Time dependences of the yields of: (a, e) CO<sub>2</sub>, (b) CO, (c) CH<sub>4</sub>, and (d) acetaldehyde from an aqueous solution of lactic acid in: (a–d) the presence and (e) the absence of powdered TiO<sub>2</sub> (P-25) under UV irradiation (full arc). Light source: 500 W high-pressure mercury lamp. Concentration of lactic acid: 1.0 M

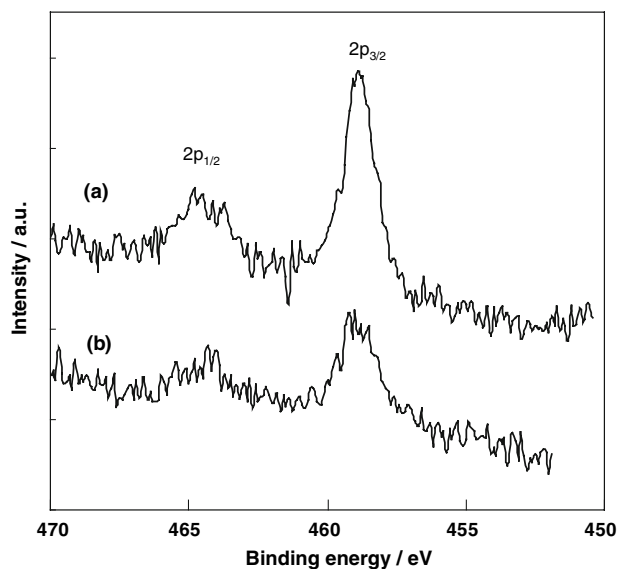
suspended with powdered TiO<sub>2</sub> led to the formation of CO<sub>2</sub> with a good linearity against the UV irradiation time. The formation rate of CO<sub>2</sub> was around five times higher than that observed for the reaction conducted without TiO<sub>2</sub>, showing that the complete oxidation of lactic acid proceeded photocatalytically. The formation of CO (16  $\mu$ mol), CH<sub>4</sub> (14  $\mu$ mol), and acetaldehyde (9  $\mu$ mol) as by-products were observed after UV irradiation of 5 h (Fig. 2), however, their yields were negligible as compared to CO<sub>2</sub>. The complete oxidation of lactic acid in water was, thus, found to proceed efficiently on powdered TiO<sub>2</sub> under UV light irradiation, showing that photocatalysis can be effectively applied for the safe removal of lactic acid in the human buccal cavity.

#### 3.2 Characterization of the Rod-type TiO<sub>2</sub> Electrode and the Photocatalytic Activity of the Photoelectrochemical Circuit System for the Decomposition of Lactic Acid in Water

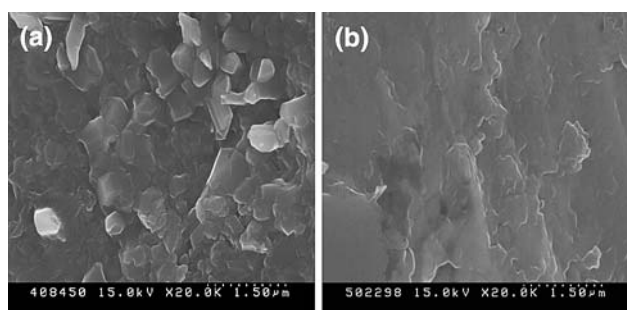
In order to apply a TiO<sub>2</sub> photocatalyst for the complete mineralization of lactic acid in the human buccal cavity, TiO<sub>2</sub> was first fixed onto a substrate. In the present work, the rod-type TiO<sub>2</sub> electrode was prepared by calcination of a metal Ti rod ( $\phi$  3 mm  $\times$  78 mm) at 1,073 K for 3 min in air. This rod-type TiO<sub>2</sub> electrode had already been applied for toothbrushes (Soladey 3; Shiken Corp.) equipped with an SSC (2.4 V, 6  $\mu$ A) and counter electrode. Scheme 1 shows a schematic diagram of the electric circuit of Soladey 3 which consists of a rod-type TiO<sub>2</sub> electrode and metal counter electrode connected through an SSC where a negative bias is applied on the rod-type TiO<sub>2</sub> electrode by the SSC. The rod-type TiO<sub>2</sub> electrode was characterized by SEM and XPS investigations. Figure 3 shows the Ti 2p XPS spectra of the rod-type TiO<sub>2</sub> electrode and metal Ti



**Scheme 1** Schematic diagram of the electric circuit of a commercially produced toothbrush (Soladey 3; Shiken Corp.)



**Fig. 3** XPS spectra of the Ti  $2p_{3/2}$  and  $2p_{1/2}$  peaks of: (a) a rod-type  $\text{TiO}_2$  electrode and (b) a metal Ti rod

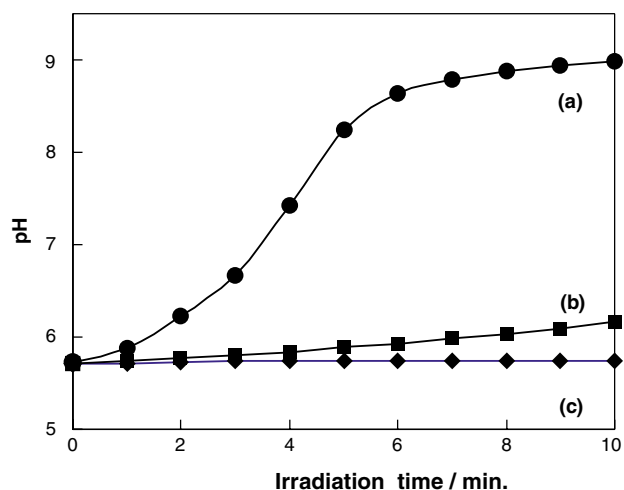


**Fig. 4** SEM images of: (a) a rod-type  $\text{TiO}_2$  electrode and (b) a metal Ti rod

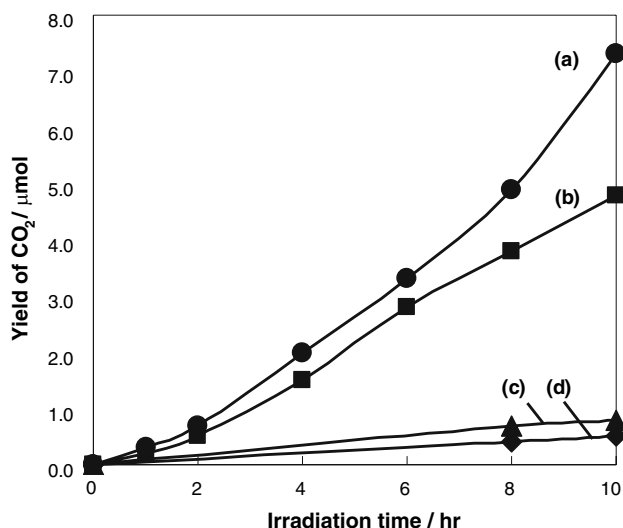
rod before calcination. Both samples show typical XPS peaks due to the  $\text{TiO}_2$  (Ti  $2p_{3/2}$ : 458.5 eV, Ti  $2p_{1/2}$ : 464.2 eV), suggesting that the surfaces of the rod-type  $\text{TiO}_2$  electrode and metal Ti rod are covered with a stoichiometric  $\text{TiO}_2$  layer [13, 14]. Figure 4 shows the SEM images of the rod-type  $\text{TiO}_2$  electrode and metal Ti rod. The metal Ti rod exhibits a rather flat surface while the rod-type  $\text{TiO}_2$  electrode exhibits a rough surface structure covered with  $\text{TiO}_2$  crystallites with particle sizes of 300–700 nm, a desirable catalytic surface morphology enabling facile diffusions of the photo-formed electrons

and holes from the deep inside bulk to the  $\text{TiO}_2$  electrode surface where the photocatalytic reactions proceed.

The photocatalytic activity of the rod-type  $\text{TiO}_2$  electrode (TE) has been investigated and, here, it was connected with a rod-type stainless steel electrode (SSE:  $\phi$  3 mm  $\times$  78 mm) through an SSC in the same sequence as depicted in Scheme 1. The constructed photoelectrochemical circuit system (denoted TE-SSC-SSE) was immersed in an aqueous solution containing lactic acid and  $\text{K}_2\text{SO}_4$ . Both the TE and SSC were then irradiated by a fluorescent lamp (20 W). Figure 5 shows the time dependence of the pH of the lactic acid aqueous solution with the TE-SSC-SSE system. Light irradiation of the TE-SSC-SSE system led to an increase in the pH of the solution, indicating that the lactic acid is efficiently decomposed by this system under light irradiation. The same experiment was conducted with a SSE-SSC-SSE system composed of two SSEs connected through SSC. As shown in Fig. 5, an increase in the pH of the aqueous solution was observed for the SSE-SSC-SSE system, while a much more significant pH increase was observed for the TE-SSC-SSE system. These results suggest that lactic acid can be electrochemically decomposed on a SSE-SSC-SSE system while the decomposition rate is significantly enhanced when using TE as the photoelectrochemically active electrode instead of SSE. It should be noted that only a negligible change in the pH can be observed under light irradiation when no photoelectrochemical circuit system was immersed in an aqueous solution of lactic acid. Figure 6 shows the time dependences of the yields of  $\text{CO}_2$  from aqueous solutions of lactic acid (0.1 M) with various photoelectrochemical



**Fig. 5** Time dependences of the pH of aqueous solutions of lactic acid with: (a) TE-SSC-SSE, (b) SSE-SSC-SSE, and (c) without any photoelectrochemical circuit system under light irradiation. Initial pH value was adjusted at 5.7 by adding a NaOH aqueous solution. Composition of aqueous solution: lactic acid (0.001 M),  $\text{K}_2\text{SO}_4$  (0.3 M). Light source: 20 W fluorescent lamp



**Fig. 6** Time dependences of the yields of  $\text{CO}_2$  from aqueous solutions of lactic acid (0.1 M) with: (a) TE-SSC-SSE, (b) SSE-SSC-SSE, (c) TE-SSE, and (d) without any photoelectrochemical circuit system under light irradiation. Composition of aqueous solution: lactic acid (0.1 M),  $\text{K}_2\text{SO}_4$  (0.3 M). Light source: 20 W fluorescent lamp

systems under light irradiation with a fluorescence lamp. Light irradiation of the TE-SSC-SSE system led to the efficient formation of  $\text{CO}_2$ , confirming that the lactic acid can be decomposed with this system. The  $\text{CO}_2$  evolution rate on the TE-SSC-SSE system was found to be higher than that on the SSE-SSC-SSE system, suggesting that the decomposition rate of lactic acid can be significantly increased by using TE as a photochemically active electrode instead of SSE. Moreover, the negligible formation of  $\text{CO}_2$  was observed on the TE-SSE system where TE is directly connected to SSE, showing that an external negative potential applied on TE by SSC plays an important role in increasing the photocatalytic activity of the TE-SSC-SSE system. Only a negligible formation of  $\text{CO}_2$  was observed under light irradiation when no photoelectrochemical circuit system was immersed in the aqueous solution of lactic acid. From these findings, it could be concluded that the TE-SSC-SSE system can be practically applied for the clean and safe removal of lactic acid in the human buccal cavity. Further investigations on the detailed mechanisms behind the decomposition of lactic acid on photoelectrochemical circuit systems are now underway.

## 4 Conclusions

It was found that the complete oxidation of lactic acid in water into  $\text{CO}_2$  proceeds efficiently on powdered  $\text{TiO}_2$  photocatalyst under UV light irradiation. Negligible formations of by-products such as  $\text{CO}$ , methane and acetaldehyde were also observed. A unique photoelectrochemical system, i.e., TE-SSC-SSE, was constructed with a rod-type  $\text{TiO}_2$  covered with stoichiometric crystallites of  $\text{TiO}_2$  having particle sizes of 300–700 nm. Light irradiation of this TE-SSC-SSE system led to the efficient mineralization of the lactic acid in water into  $\text{CO}_2$ , suggesting that the TE-SSC-SSE system can be practically applied for the safe removal of lactic acid in the human buccal cavity. Furthermore, it was shown that a negative bias applied on the rod-type  $\text{TiO}_2$  electrode by an SSC enhances the decomposition rate of the lactic acid in water.

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