

Photocatalytic oxidation of ethanethiol on a photoelectrochemical circuit system consisting of a rod-type TiO₂ electrode and a silicon solar cell

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Abstract A unique photoelectrochemical circuit system was constructed by connecting a rod-type TiO₂ electrode with a Pt electrode through a silicon solar cell. The photoelectrochemical circuit system efficiently oxidized ethanethiol in water into CO₂, while the reaction rate strongly depended on the calcination temperature of the rod-type TiO₂ electrode. Furthermore, it was found that a negative bias applied to the rod-type TiO₂ electrode by a silicon solar cell enhances the oxidation rate of ethanethiol in water.

Keywords Photocatalysis · TiO₂ electrode · Silicon solar cell · Photoelectrochemical circuit system · Ethanethiol

Introduction

TiO₂ photocatalyst is a fascinating photo-functional material which enables various useful reactions at ambient temperature such as the complete mineralization of toxic organic compounds [1], elimination of NO_x in air [2], or hydrogen evolution from biomass [3]. These photocatalytic activities are based on the strong oxidation and reduction ability of the photo-formed holes and electrons, respectively. In addition to powdered TiO₂ photocatalysts, the photoelectrochemical properties of TiO₂ electrodes have been widely investigated. So far, it has been elucidated that photocatalytic reaction rates as well as the reaction dynamics of the photo-formed electrons and holes are significantly affected by the external electric bias applied to

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the TiO₂ electrodes. In a recent work, a unique photoelectrochemical circuit system consisting of a rod-type TiO₂ electrode and a silicon solar cell has been constructed [4]. This photoelectrochemical circuit system can effectively oxidize lactic acid in water into CO₂, while the reaction rate is enhanced by the negative bias applied on the rod-type TiO₂ electrode by the silicon solar cell [4]. These results suggest that the photoelectrochemical circuit system can be utilized for the elimination of various undesirable organic compounds having toxicity or odors. It is well known that methanethiol, which exists in the human buccal or oral cavity, is the cause of breath odor. Furthermore, it has been shown that ethanethiol is an important intermediate in the formation of methanethiol in the metabolic decomposition of sulfur-containing protein [5]. In the present work, in terms of the application of TiO₂ photocatalysts for dental care or buccal protection, especially for the prevention of bad breath, the photoelectrochemical circuit system has been applied for the oxidation of ethanethiol in water. Furthermore, the effect of the external bias as well as the calcination temperature of rod-type TiO₂ electrode on the oxidation rate of ethanethiol has also been investigated.

Experimental

Rod-type TiO₂ electrodes were prepared by the calcination of a metal Ti rod (\varnothing 3 mm \times 78 mm) at various temperatures, i.e., without calcination, 473, 673, 873, and 1,073 K, for 3 min in air and denoted as TE₂₇₃, TE₄₇₃, TE₆₇₃, TE₈₇₃, and TE_{1,073}, respectively. Photoelectrochemical circuit systems were constructed by connecting the rod-type TiO₂ electrode and the rod-type Pt electrode (denoted as PE: \varnothing 3 mm \times 78 mm) through a silicon solar cell (SSC: 2.4 V, 6 μ A at 200 lx). Two different types of photoelectrochemical circuit systems (TE–SSC–PE) were constructed, i.e., TE⁺SSC[–]–PE and TE[–]SSC⁺–PE, as shown in Fig. 1a. Here, TE is connected to the positive electrode of SSC for the former system (TE⁺SSC[–]–PE), while TE is connected to the negative electrode of SSC for the latter (TE[–]SSC⁺–PE). As shown in Fig. 2, the TE[–]SSC⁺–PE system has been practically applied for the electric circuit of a toothbrush (Soladey 3; Shiken Corp.). In addition to the TE–SSC–PE system, three kinds of circuit systems (TE–PE, TE–TE, PE–PE) were constructed by directly connecting TE and PE. The photocatalytic decomposition reaction of ethanethiol (C₂H₅SH) was performed by using a closed reaction cell (Fig. 1b) under light irradiation from various light sources such as a black light lamp (6 W) or fluorescent lamp (6 W) at 298 K. The concentration of ethanethiol aqueous solution (18 ml) was adjusted to 0.08 mol/l and K₂SO₄ was added (0.30 mol/l) as the electrolyte. The amount of evolved CO₂ in the gas phase was analyzed by gas chromatography (Shimadzu, GC-7A). The crystal structure and surface morphologies of the rod-type TiO₂ electrodes were investigated by XRD (XRD-6100; Shimadzu) and scanning electron microscopy (SEM, S-4500; Hitachi). The XPS spectra were recorded under vacuum at 298 K (ESCA3000; Shimadzu). The photoelectrochemical properties of the rod-type TiO₂ electrodes were evaluated using a potentiostat (HZ3000; Hokuto Denko) where the rod-type TiO₂ electrode, Pt electrode and saturated calomel electrode (SCE) were set as the working, counter

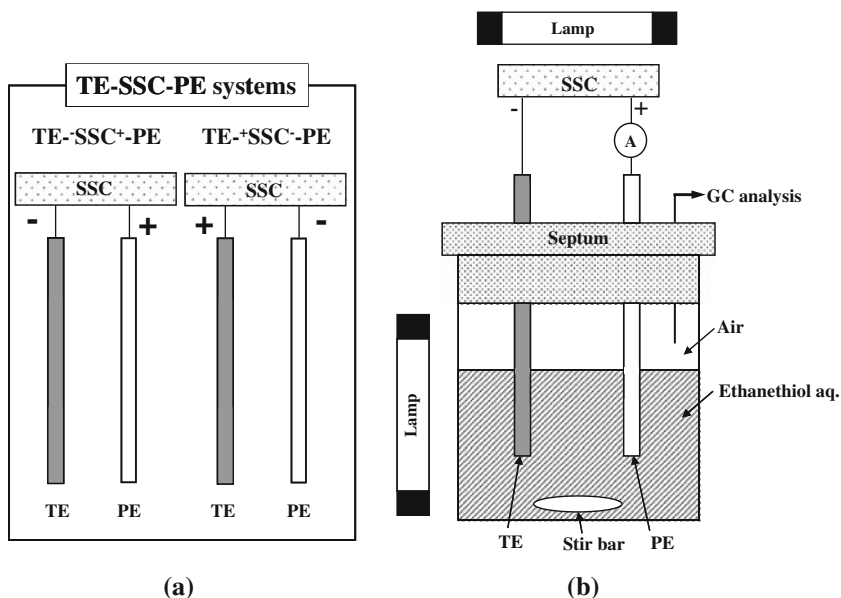


Fig. 1 Schematic diagram of: **a** TE-SSC-PE systems and **b** reaction cell for the photocatalytic oxidation of ethanethiol

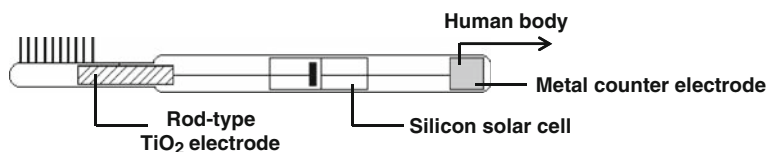


Fig. 2 Schematic diagram of the electric circuit of a commercially produced toothbrush (Soladey 3; Shiken Corp.)

and reference electrodes, respectively. For the photoelectrochemical measurements, the working electrode was immersed in 0.25 M K₂SO₄/10 vol% methanol aqueous solution and irradiated with a 500 W Xenon lamp through a water filter.

Results and discussion

Characterization of rod-type TiO₂ electrode by various spectroscopic measurements

Figure 3 shows the effect of the calcination temperature on the XRD pattern of the rod-type TiO₂ electrode (TE). Typical diffraction peaks of the Ti metal substrate ($2\theta = 38.5, 40.2$) can be mainly observed when the calcination temperature is below 673 K, while diffraction peaks due to the rutile phase of TiO₂ ($2\theta = 27.5, 54.3$) can be observed above 873 K. TE_{1,073} shows the most intense diffraction

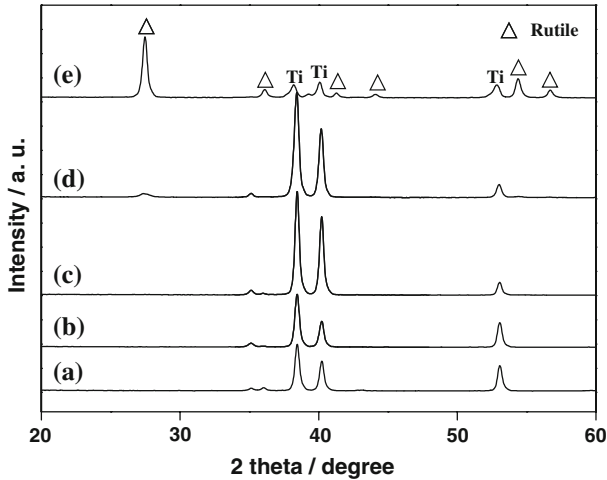


Fig. 3 Effect of the calcination temperature on the XRD pattern of the rod-type TiO_2 electrode. Calcination temperature (K): **a** before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073

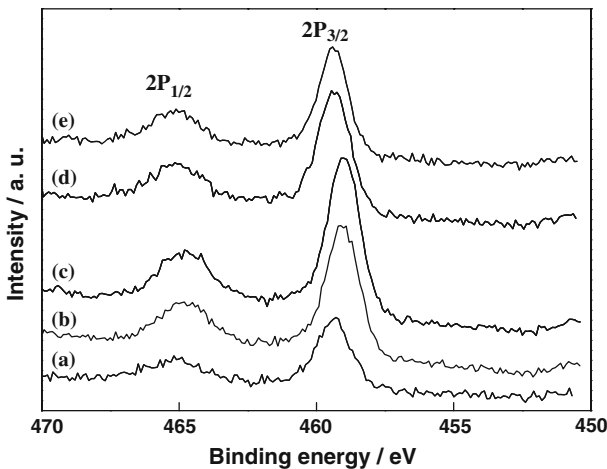


Fig. 4 Effect of the calcination temperature on the XPS spectra of the Ti $2p_{3/2}$ and $2p_{1/2}$ peaks of the rod-type TiO_2 electrode. Calcination temperature (K): **a** before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073

peaks due to the rutile phase of TiO_2 , while the intensity of the diffraction peaks due to the Ti metal substrate was remarkably decreased. These results clearly suggest that the surface of TE is covered by a rutile TiO_2 layer after calcination treatment above 873 K, while the thickness of the rutile TiO_2 layer increases with an increase in the calcination temperature. Figure 4 shows the effect of the calcination temperature on the Ti2p XPS spectrum of the rod-type TiO_2 electrode. Typical $\text{Ti}2p_{1/2}$ and $\text{Ti}2p_{3/2}$ peaks due to the Ti^{4+} species were observed at around 465.1 and 459.4 eV, respectively, regardless of the calcination temperature [6, 7]. These

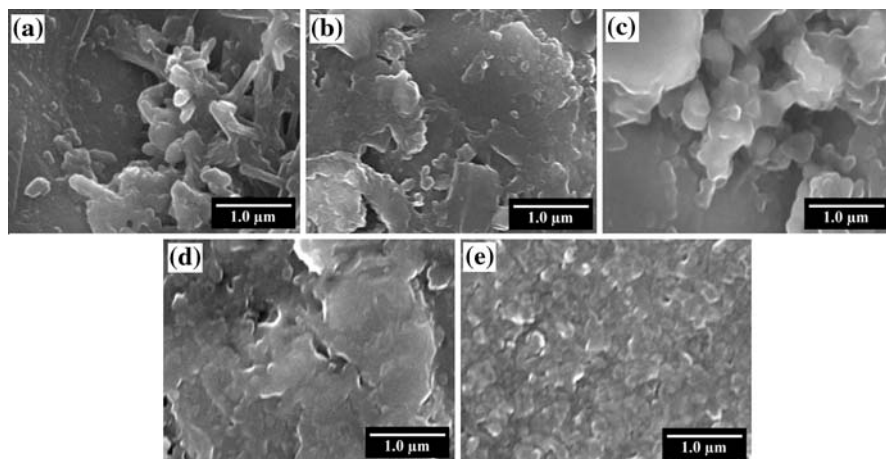


Fig. 5 Effect of the calcination temperature on SEM images of the rod-type TiO₂ electrode. Calcination temperature (K): **a** before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073

results show that the surface of the rod-type TiO₂ electrode is covered by the stoichiometric TiO₂ layer regardless of the calcination temperature. Furthermore, as shown in Fig. 5, the rod-type TiO₂ electrode prepared at calcination temperatures of less than 873 K exhibited a rough surface morphology, while TE_{1,073} showed a rather smooth and flat surface. These results indicate that calcination at 1,037 K is a suitable pretreatment to develop a dense and thick rutile TiO₂ layer on the rod-type TiO₂ electrode.

Investigations on the reactivity of rod-type TiO₂ electrode by photocurrent measurements

Photoelectrochemical measurements of rod-type TiO₂ electrodes were performed in 10 vol% methanol aqueous solution using a standard three-electrode system. Figure 6 shows the effect of the calcination temperature on the current-potential curves of rod-type TiO₂ electrodes measured in 10 vol% methanol aqueous solution under UV irradiation. For all the electrodes, the cathodic photocurrent dramatically increases under an applied negative bias of -1.0 V (SCE; pH = 6), showing that a hydrogen evolution reaction proceeds on the electrode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). On the other hand, an anodic photocurrent was observed to start under an applied potential of -0.5 V and to increase with an increase in the applied positive bias. These results suggest that the anodic oxidation of methanol by photo-formed holes occurs on these electrodes under UV irradiation of TE ($\lambda > 300$ nm). Moreover, significant increases in the anodic photocurrent were observed with an increase in the calcination temperature, especially above 873 K. These results show good agreement with XRD results showing that the dense and thick rutile TiO₂ layer can be developed on the rod-type TiO₂ electrode after calcination treatment above 873 K. Figure 7 shows the photocurrent observed for the rod-type TiO₂ electrode (TE) calcined at various temperatures as a function of the incident light. Here, the

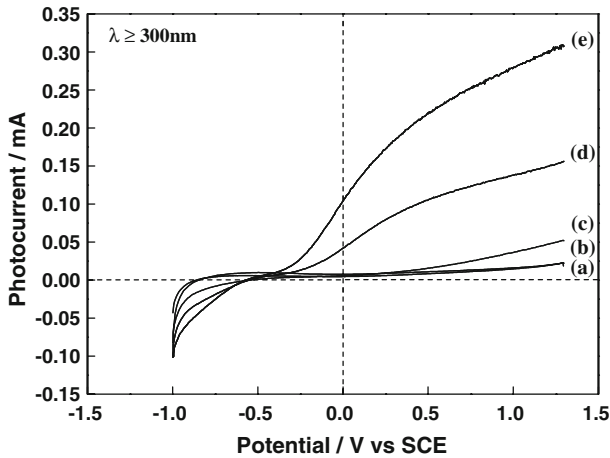


Fig. 6 Effect of the calcination temperature on the current-potential curves of the rod-type TiO_2 electrodes measured in 10 vol% methanol aqueous solution under UV irradiation ($\lambda > 300 \text{ nm}$). Calcination temperature (K): **a** before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073. Light source: 500 W Xenon lamp. Electrolyte: 0.1 M HClO_4 aq

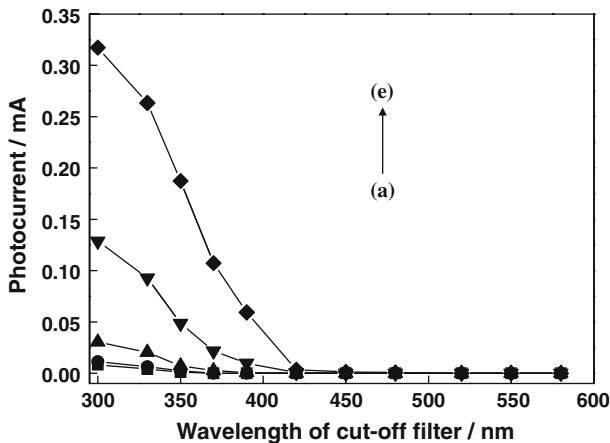


Fig. 7 The relative photocurrent as a function of the cutoff wavelength of the incident light for the rod-type TiO_2 electrodes measured in 10 vol% methanol aqueous solution (Potential: +1.0 V vs. SCE). Calcination temperature (K): **a** before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073. Light source: 500 W Xenon lamp. Electrolyte: 0.1 M HClO_4 aq

wavelengths of the incident light were controlled by various cut-off filters. The observed photocurrent increased with an increase in the calcination temperature and the highest photocurrent was observed for $\text{TE}_{1,073}$. Furthermore, the photoelectrochemical onsets locate at around 400 nm independent of the calcination temperature, suggesting that the observed photocurrent is derived from the photoexcitation of the stoichiometric TiO_2 layers.

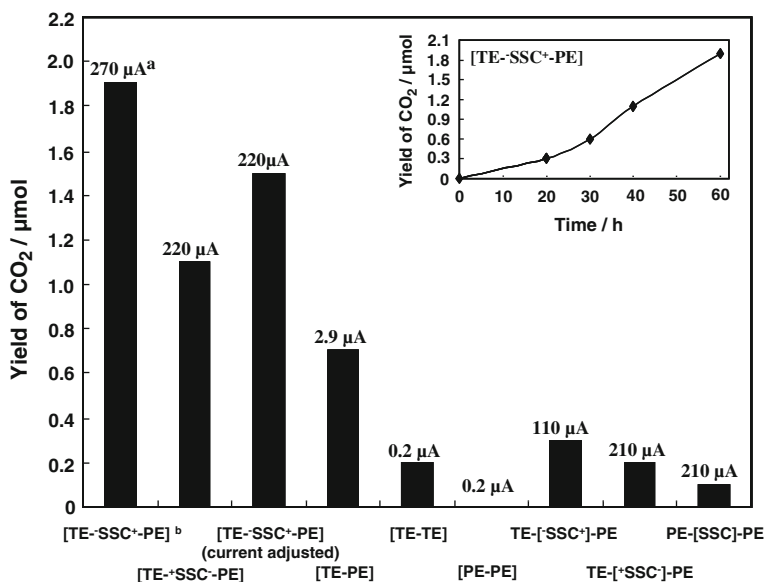


Fig. 8 Yields of CO₂ in the decomposition of ethanethiol on various photoelectrochemical circuit systems. *Inset* Time profile of the CO₂ yield on [TE-SSC⁺-PE]. ^aThe absolute values of the observed short circuit current between two electrodes are shown on each bar. ^bIrradiated parts of the photoelectrochemical circuit system are denoted in *parentheses*. Light source: black light lamp (6 W). Irradiation time: 60 h

Photocatalytic decomposition of ethanethiol on rod-type TiO₂ electrode

The decomposition reaction of ethanethiol (C₂H₅SH) was investigated under light irradiation with a black light lamp (BL: 6 W) in a closed reaction cell at 298 K, as shown in Fig. 1. Figure 8 shows the yields of CO₂ in the photocatalytic decomposition of ethanethiol on various photoelectrochemical circuit systems. Here, irradiated parts of the photoelectrochemical circuit system are denoted in *parentheses*. For example, TE-[⁺SSC⁻]-PE indicates that only the SSC was irradiated, while [TE-⁺SSC⁻]-PE indicates that all parts of TE-⁺SSC⁻-PE were irradiated. Only the negligible formation of CO₂ as well as negligible current were observed on TE-SSC-PE under dark conditions, showing that the decomposition of ethanethiol does not proceed under dark (data not shown). Moreover, CO₂ formation was not observed under light irradiation of an ethanethiol aqueous solution when the photoelectrochemical circuit system was not immersed in the solution (data not shown).

The decomposition of ethanethiol was investigated on three photoelectrochemical circuit systems (TE-[⁺SSC⁻]-PE, TE-[⁻SSC⁺]-PE, PE-[⁺SSC⁻]-PE) where only SSC was irradiated. CO₂ formations were observed for all three systems, showing that ethanethiol can be oxidized into CO₂ by electrolysis. It was also found that the circuit current observed for PE-[⁺SSC⁻]-PE (210 μA) was not affected by the presence of ethanethiol in the aqueous solution, showing that the observed

circuit current is mainly ascribed to water electrolysis under an applied voltage by SSC. A higher circuit current was observed for TE-[⁺SSC⁻]-PE than TE-[⁻SSC⁺]-PE, which can be explained by the rectification effect due to the Schottky barrier at the interface between the TiO₂ layer and metal Ti. Next, the decomposition of ethanethiol was performed on the three other kinds of photoelectrochemical circuit systems ([TE-PE], [TE-TE], [PE-PE]) where all of the electrodes were irradiated by a black light lamp. CO₂ formation was observed for [TE-TE] while only the negligible formation of CO₂ was observed for [PE-PE], showing that ethanethiol is photocatalytically decomposed into CO₂ on TE. Moreover, it was found that the yield of CO₂ increased markedly for [TE-PE] as compared to [TE-TE]. This enhancement of the photocatalytic activity can be ascribed to a decrease in the charge recombination rate due to the efficient transfer of the photo-formed electrons from TE to PE [8–11]. The decomposition of ethanethiol was performed on [TE-⁻SSC⁺-PE] and [TE-⁺SSC⁻-PE] where all parts of the photoelectrochemical circuit system was irradiated by a black light lamp. Light irradiation of both systems led to the efficient formation of CO₂, confirming that ethanethiol can be decomposed with these systems. The CO₂ yield on both systems was much higher than the sum of the CO₂ yield on TE-[⁻SSC⁺]-PE (0.3 μmol) and [TE-PE] (0.7 μmol). Moreover, [TE-⁻SSC⁺-PE] shows higher activity for the complete oxidation of ethanethiol than [TE-⁺SSC⁻-PE]. Since a higher circuit current was observed for [TE-⁻SSC⁺-PE; 270 μA] than [TE-⁺SSC⁻-PE; 220 μA], the activity of both systems was compared under the same circuit current. Here, the proper resistance was serially connected in the [TE-⁻SSC⁺-PE] circuit system, and the circuit current was adjusted at 220 μA. This reaction condition has been denoted as “[TE-⁻SSC⁺-PE] (current adjusted)”. As shown in Fig. 8, [TE-⁻SSC⁺-PE] shows higher activity than [TE-⁺SSC⁻-PE] even under the same circuit current condition (220 μA), showing that an applied negative bias on TE by SSC is more effective in enhancing ethanethiol decomposition than an applied positive bias. These results suggest that applying a negative bias on TE promoted the reduction of oxygen to form an O₂⁻ species on the surface of TE, leading to the efficient oxidation of ethanethiol into CO₂. Figure 8 shows the time dependences of the yields of CO₂ in the decomposition of ethanethiol on [TE-⁻SSC⁺-PE]. It can clearly be seen that light irradiation of the TE-⁻SSC⁺-PE system led to the formation of CO₂ with a good linearity against the light irradiation time, confirming the efficient and steady decomposition of ethanethiol on this system.

Figure 9 shows the effect of the calcination temperature of TE on the yield of CO₂ in the decomposition of ethanethiol on the [TE-⁻SSC⁺-PE] circuit system. It was clearly observed that the increase in the calcination temperature led to a marked increase in the CO₂ yields while TE_{1,073} shows the highest activity for the complete oxidation of ethanethiol. These results show good agreement with the results of the current-potential curve measurements (Fig. 6), indicating that the dense and thick TiO₂ layer formed on TE_{1,073} acted as the most efficient photocatalyst for the decomposition of ethanethiol. Finally, the decomposition reactions of ethanethiol were performed on various photoelectrochemical circuit systems under light irradiation from a fluorescent lamp (6 W) (Fig. 10). The CO₂ yield on

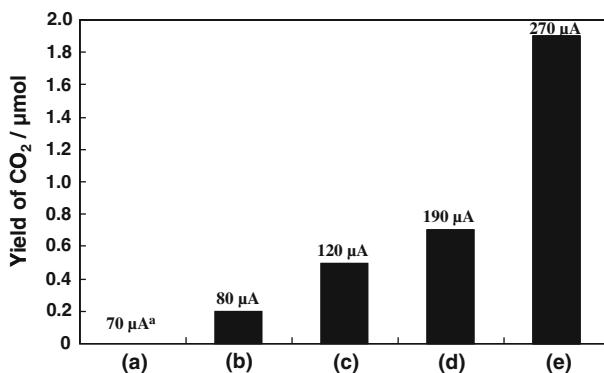


Fig. 9 Effect of the calcination temperature of TE on the yield of CO₂ in the decomposition of ethanethiol on the [TE⁻SSC⁺-PE] circuit system. ^aThe absolute values of the observed short circuit current between two electrodes are shown on each bar. Light source: black light lamp (6 W). Reaction time: 60 h. Calcination temperature (K): **a** Before calcination, **b** 473, **c** 673, **d** 873, **e** 1,073

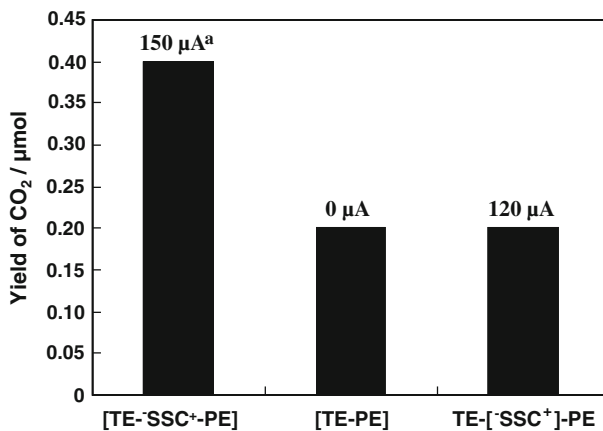


Fig. 10 Yields of CO₂ in the decomposition of ethanethiol on various photoelectrochemical circuit systems. ^aThe absolute values of the observed short circuit current between two electrodes are shown on each bar. Light source: fluorescent lamp (6 W). Reaction time: 60 h

[TE⁻SSC⁺-PE] was almost the same as the sum of the CO₂ yields on [TE-PE] and TE-[SSC⁺]-PE. Thus, a marked synergy effect when combining the TE-PE system and SSC was not observed, in contrast to the case under black light irradiation (Fig. 8). However, these results clearly show that [TE⁻SSC⁺-PE] can be practically applied for the clean and safe removal of ethanethiol in the human buccal under light irradiation from a fluorescent lamp.

Conclusions

It was found that the [TE⁻SSC⁺-PE] system can efficiently oxidize ethanethiol in water into CO₂. The activity of [TE⁻SSC⁺-PE] for the decomposition of

ethanethiol was greatly affected by the calcination temperature of TE, i.e., TE_{1,073} exhibits the highest activity for the oxidation of ethanethiol. Spectroscopic investigations have revealed that a dense and thick stoichiometric TiO₂ layer was formed on TE_{1,073} which shows the highest activity for the decomposition of ethanethiol. A negative bias applied on TE by SSC was also found to markedly enhance the reaction rate, showing a remarkable synergy effect when combining the TE-PE system and SSC for the oxidation of ethanethiol. Finally, it was shown that [TE⁻SSC⁺-PE] can be applied for the removal of ethanethiol in water even under light irradiation from a fluorescent lamp (6 W).

References

1. D.F. Ollis, H. AlEKabi, *Photocatalytic Purification and Treatment of Water and Air* (Elsevier, Amsterdam, 1993)
2. M. Anpo, in *Green Chemistry*, ed. by P. Tundo, P. Anastas (Oxford University Press, Oxford, 2000), p. 1
3. S. Fukumoto, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, *Catal. Lett.* **127**, 39 (2009)
4. M. Matsuoka, T. Kamegawa, D. Rakhmawaty, M. Kitano, K. Wada, M. Anpo, *Topics Catal.* **47**, 162 (2008)
5. K. Masatake, *Dental Magazine* **105**, 32 (2002)
6. B. Erdem, R.A. Hunsicker, G.W. Simmons, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *Langmuir* **17**, 2664 (2001)
7. M. Kitano, K. Funatsu, M. Matsuoka, M. Ueshima, M. Anpo, *J. Phys. Chem. B* **110**, 25266 (2006)
8. J. Sa, M. Fernandez-Garcia, J.A. Anderson, *Catal. Commun.* **9**, 1991 (2008)
9. M. Anpo, N. Aikawa, Y. Kubokawa, *J. Phys. Chem.* **88**, 3998 (1984)
10. M. Kitano, K. Tsujimaru, M. Anpo, *Appl. Catal. A Gen.* **314**, 179 (2006)
11. M. Kitano, K. Iyatani, K. Tsujimaru, M. Matsuoka, M. Takeuchi, M. Ueshima, J.M. Thomas, M. Anpo, *Top. Catal.* **49**, 24 (2008)