Photodegradation of Veratryl Alcohol on a Titanium Dioxide Photoelectrode in Aqueous Solution Containing Chloride Ions

Daiyu KODAMA, Eriko UCHIYAMA, Yoshiumi KOHNO, Yasumasa TOMITA, Kenkichiro KOBAYASHI and Yasuhisa MAEDA

A titanium dioxide film with nanopores was prepared by the anodic oxidation of titanium in nitric acid solution. The photoactivity of the titanium dioxide film depended on the heat treatment temperature under air. The titanium dioxide electrode treated at 500 °C showed a high photoanodic response to veratryl alcohol (VA) in aqueous solution. The photodegradation of VA was rapid in aqueous NaCl solution compared with NaClO₃, Na₂SO₄, and NaNO₃ solutions. The oxidants Cl₂ or HClO were photogenerated on the titanium dioxide photoanode in NaCl solution. The photoanodic oxidation of VA on the titanium dioxide in NaCl solution was caused by the attack of photogenerated holes and oxidants. High-performance liquid chromatography revealed the formation of vanillyl alcohol, veratraldehyde, vanillin, and benzyltriol as the main intermediates, and the formation of ketomalonic acid, suggesting aromatic ring cleavage on the titanium dioxide electrode during the photoanodic oxidation of VA in aqueous NaCl solution.

Keywords: Photoanodic Behavior, Titanium Dioxide Photoelectrode, Veratryl Alcohol, Chloride Ion

1. Introduction

Titanium dioxide, an n-type semiconductor, has been studied as a photofunctional material. Irradiating titanium dioxide with UV light with a higher energy than its band gap energy generates electron-hole pairs. Titanium dioxide effectively photooxidizes organic materials in aqueous solution under UV irradiation because the photogenerated holes in the valence band are strong oxidizing agents. There are many studies of photodegrading organic materials in aqueous solution by titanium dioxide photocatalysis.

We have studied the photoanodic response of titanium dioxide to organic materials in aqueous solution for water purification. Anodic oxidation of titanium may be suitable for the simple, reproducible preparation of titanium dioxide. We examined the characteristics of titanium dioxide prepared from anodic oxidation of titanium in different aqueous solutions of nitric acid, phosphoric acid, acetic acid, and oxalic acid and confirmed that titanium dioxide treated in nitric acid solution showed high photoelectrochemical activity.

The photocatalytic and photoelectrochemical degradation of organic materials by titanium dioxide is affected by the supporting electrolytes in aqueous solution. The purification of seawater with titanium dioxide has also been reported. In this paper, we chose veratryl alcohol (VA) (Fig. 1), which is a structural unit of lignin, as a model organic compound, and fabricated the photoelectrode from titanium dioxide treated in nitric acid solution. We investigated the photooxidation of VA on the titanium dioxide electrode in aqueous solution containing chloride ions to simulate seawater and analyzed the dependence of VA photooxidation on anions in solution.

2. Experimental

2.1 Preparation of titanium dioxide

A titanium plate (size: 50 × 50 × 0.2 mm, Nilaco) was polished with alumina powder and chemically etched in 5.8 M hydrochloric acid. The plate was oxidized electrochemically with a constant current of 300 mA for 1 h in 0.1 M nitric acid by using a DC power supply (R6145, Advantest). In this process, the voltage between the titanium working electrode and the carbon counter electrode was 21.5 V, and the electrode potential of titanium was 19.0 V vs. Ag/AgCl.

The oxidized plate was rinsed repeatedly with ion-exchanged water and dried at room temperature. The plate was heated at temperatures of 400–800 °C under air in an electric furnace (FUW 210PA, Advantec). This titanium dioxide/titanium plate was characterized by X-ray diffraction (XRD; RINT 2500, Rigaku) and field emission scanning electron microscopy (FE-SEM; JSM-7001M, JEOL).

2.2 Cell assembly for photoanodic oxidation of VA

The titanium dioxide/titanium plate connected to a lead wire was used as a titanium dioxide working electrode. The counter electrode was a platinum plate (size: 50 × 50 × 0.1 mm, Nilaco). The working and counter electrodes were separated in the acrylic resin cell by a cation-exchange membrane (Selemion CMV, AGC

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* E-mail: tyamaeda@ipc.shizuoka.ac.jp
or ammonium fluoride solution has been reported. Nitric acid also formed nanopores in the oxidized film, although the film did not have a nanotube structure. Nanopores were observed on the surface of the sample heat-treated at 400 and 650 °C, although the nanopores disappeared in the sample heat-treated at 800 °C.

Because it was difficult to distinguish between the titanium dioxide film and the titanium substrate in the cross-sectional SEM image, we measured the change in the Ti:O ratio in the depth direction of the samples by energy-dispersive X-ray spectroscopy. Figs. 3 a and b show the relationship between the atomic ratio and depth for the samples heat-treated at 500 °C for 60 min and at 800 °C for 10 min, respectively. The Ti:O ratio increased with depth and reached a constant value. The threshold depth showing the constant ratio, that is 1.5 and 1.9 μm for the samples heat-treated at 500 and 800 °C, respectively, which corresponded to the thickness of the oxidized film. The film thicknesses were 1.5, 1.5, and 1.8 μm for the samples without heat treatment, heat-treated at 400 °C, and heat-treated at 650 °C, respectively. The sample heat-treated at 500 °C had an oxidized film with a Ti:O ratio of 33:67, corresponding to a titanium dioxide film 0.2 μm thick (Fig. 3a).

Figs. 4 a-e show the XRD patterns of the sample without heat treatment and samples heat-treated at 400, 500, and 650 °C for 60 min, and 800 °C for 10 min, respectively. Only titanium peaks were observed for the sample without heat treatment. This indicates amorphous structure of the film before heat treatment. For the samples heat-treated at 400 and 500 °C, anatase diffraction peaks were observed. In addition to the anatase peaks, rutile peaks were also observed for the sample heat-treated at 650 °C. For the sample heat-treated at 800 °C, the intensity of the rutile peaks increased instead of the much weaker anatase peaks. For the titanium heat-treated in air, the anatase peaks were not observed. Anodic oxidation may be necessary to prepare anatase titanium dioxide from titanium. We confirmed that titanium dioxide films with different intensity ratios of anatase and rutile peaks were obtained by controlling the time and temperature of the heat treatment after anodic oxidation in nitric acid.

3. Results and discussion

3.1 Characterization of the titanium dioxide film

The surface morphology of the samples prepared by the anodic oxidation and heat treatment was examined by FE-SEM. Addition of electrical conductivity to the sample was done by silver paste and conductive carbon tape without sputtering treatment. Figs. 2 a and b show the FE-SEM images of the samples heat-treated at 500 °C for 60 min and at 800 °C for 10 min, respectively, after the anodic oxidation. Pores with an approximate diameter of 50 nm were observed on the surface of the sample heat-treated at 500 °C, similar to the sample without heat treatment. The nanoporous structure of the titanium dioxide film achieved by the anodic oxidation of titanium in hydrogen fluoride solution: or ammonium fluoride solution has been reported. Nitric acid also formed nanopores in the oxidized film, although the film did not have a nanotube structure. Nanopores were observed on the surface of the sample heat-treated at 400 and 650 °C, although the nanopores disappeared in the sample heat-treated at 800 °C.

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3.2 Photoanodic response of the titanium dioxide electrodes

Fig. 5 shows the relationship between the relative VA concentration and irradiation time on the titanium dioxide electrode
heat-treated under different conditions. The relative VA concentration, C/C0, was evaluated, where C0 and C were the VA concentration before and after irradiation, respectively, obtained by HPLC. The five titanium dioxide electrodes were as follows: not heat-treated, and heat-treated at 400, 500, and 650 °C for 60 min, and at 800 °C for 10 min. The electrolytic solution was aqueous 0.54 M NaCl containing an initial concentration of 50 μM VA and the potential of the titanium dioxide electrode was held at 2.0 V vs. Ag/AgCl. Fig. 5 shows that the photoactivity of the titanium dioxide electrode strongly depended on the heat treatment. Low photoactivity was observed for the electrode without heat treatment. The electrode heat-treated at 500 °C showed the highest activity for the photoanodic oxidation of VA.

Fig. 6 shows the relationship between the photocurrent and irradiation time for the titanium dioxide electrode heat-treated under different conditions in aqueous 0.54 M NaCl containing an initial concentration of 50 μM VA at a potential of 2.0 V vs. Ag/AgCl.

There was a large difference in the magnitude of the photocurrent between the five titanium dioxide electrodes. The electrodes heat-treated at 500 and 650 °C showed similar high photocurrents. The photocurrent quantum efficiency was calculated from \( n/N \times 100 \), where \( n \) is the number of electrons for the photocurrent charge and \( N \) is the number of incident photons, as 5.0%, 7.1%, 7.1%, 3.1%, and 0.6% for the titanium dioxide electrodes treated at 400, 500, and 650 °C for 60 min, at 800 °C for 10 min, and not heat-treated, respectively. We used the titanium dioxide electrode heat-treated at 500 °C to investigate further the photoanodic oxidation of VA in aqueous solution because this electrode had high activity for the photodegradation of VA and a high photocurrent response compared with other electrodes.

3. 3 Photodegradation of VA on the titanium dioxide in different electrolytes

Fig. 7 shows the relationship between relative VA concentration and irradiation time for the titanium dioxide electrode in aqueous solutions containing an initial VA concentration of 50 μM and supporting electrolytes of NaCl, NaSO4, NaNO3, or NaClO4 at a concentration of 0.54 M. The artificial seawater consisted of NaCl (0.41 M), NaSO4 (0.028 M), NaHCO3 (0.002 M), MgCl2 (0.053 M), CaCl2 (0.010 M), and KCl (0.010 M). The electrode potential was held at 2.0 V vs. Ag/AgCl. Fig. 7 shows that the VA photodegradation rate depended on the type of anion in the solution. The photodegradation of VA was remarkable in NaCl solution. The rate of photodegradation of VA in the artificial seawater was different from that in NaCl solution. We also examined the relationship between relative VA concentration and irradiation time on the titanium dioxide electrode in two similar artificial seawaters without Na2SO4 or NaHCO3. The relationship between C/C0 and \( r \) in the NaCl (0.41 M), NaHCO3 (0.002 M), MgCl2 (0.053 M), CaCl2 (0.010 M), and KCl (0.010 M) solution was similar to that in the artificial seawater. The relationship between C/C0 and \( r \) in the NaCl (0.41 M), NaSO4 (0.028 M), MgCl2 (0.053 M), CaCl2 (0.010 M), and KCl (0.010 M) solution was close to that in 0.54 M NaCl solution. This indicates that the lower VA photodegradation rate in the artificial seawater compared with
NaCl solution might be due to the presence of NaHCO₃.

3.4 Photoanodic oxidation of VA on the titanium dioxide electrode in the presence of chloride ions

We detected oxidants that could oxidize VA photogenerated on the titanium dioxide photoanode in electrolytic solutions by using the KI method, measuring the absorbance of the solution at a wavelength of 350 nm. In 0.54 M NaCl, the concentration of the photogenerated oxidant increased markedly with irradiation time on the titanium dioxide electrode, whereas the photogenerated oxidant was not observed in other aqueous solutions with supporting electrolytes (0.54 M) of Na₂SO₄, NaNO₃, and NaClO₄. On the UV-irradiated titanium dioxide electrode in the solution containing chloride ions, the photoanodic oxidation of chloride ions may proceed as in equation (1).

\[ 2Cl^- + 2h^+ \rightarrow Cl_2 \]  

Here, \( h^+ \) is the photogenerated hole in the valence band of the titanium dioxide. The chlorine may react with water as in equation (2).

\[ Cl_2 + H_2O \rightarrow HClO + HCl \]

The oxidant detected in NaCl solution may correspond to Cl₂ or HClO. Zanoni et al. investigated the photoelectrochemical production of chlorine on a titanium dioxide electrode in aqueous NaCl under UV irradiation. Thus, the marked degradation of VA in NaCl solution could be caused by the additional effect of these oxidants.

We examined the degradation behavior of VA on the platinum electrode to understand the oxidation mechanism of VA without UV irradiation. Fig. 8 shows the relationship between relative VA concentration and oxidation time on the platinum anode and the titanium dioxide photoanode in aqueous 0.54 M NaCl solution with an initial VA concentration of 50 \( \mu \)M. The relationship between the relative VA concentration and time on the titanium dioxide electrode without UV irradiation is also shown in Fig. 8. The degradation of VA on the titanium dioxide electrode was caused by UV irradiation. The platinum anode was supplied with a constant current of 1.56 mA for 6 h, which corresponded to the photocurrent charge on the titanium dioxide photoanode. The potential of the platinum anode was 1.25 V vs. Ag/AgCl(1.47 V vs. normal hydrogen electrode (NHE)). This potential was more positive than the equilibrium potential of the Cl₂(aq)/Cl·(aq) couple of 1.41 V vs. NHE, which could be derived from the standard equilibrium potential and chloride ion concentration. The degradation rate of VA on the platinum anode resembled that on the titanium dioxide photoanode.

Fig. 9 shows the chromatograms of aqueous 10 mM NaCl solution containing an initial VA concentration of 50 \( \mu \)M before and after UV irradiation on the titanium dioxide electrode. The potential of the titanium dioxide electrode was held at 2.0 V vs. Ag/AgCl. Before irradiation, only the VA peak was observed at a retention time of 6.9 min. After UV irradiation for 6 h, the intensity of the VA peak decreased and new vanillinalcohol, veratraldehyde, vanillin, benzencetriol, protocatechuic acid, protocatechualdehyde, and vanillic acid peaks appeared at retention times of 17.5, 3.6, 8.7, 2.3, 3.2, 4.4, and 5.7 min, respectively. The structures of these intermediates are shown in Fig. 10.

Figs. 11 a and b show the relationship between the concentration of intermediates and time, and between relative VA concentration and time on the titanium dioxide photoanode and the platinum anode, respectively, in aqueous 10 mM NaCl solution containing an initial VA concentration of 50 \( \mu \)M. The potential of the titanium dioxide photoelectrode was held at 2.0 V vs. Ag/AgCl. The anodic oxidation on the platinum electrode was performed at a constant current of 1.56 mA for 6 h, corresponding to the charge for the photoanodic process on the titanium dioxide electrode. The potential of the platinum anode was 1.71 V vs. NHE, which was more positive than the equilibrium potential of...
Cl\textsubscript{2} (aq)/Cl\textsuperscript{−} (aq) couple, 1.51 V vs. NHE. Vanillyl alcohol, veratraldehyde, vanillin, and benzenetriol were detected as the main intermediates in the oxidation of VA on the titanium dioxide photoanode. Veratraldehyde, vanillyl alcohol, and protocatechualdehyde were the main intermediates in the oxidation of VA on the platinum anode. The formation of a large amount of veratraldehyde was distinctive, and benzenetriol, the highly oxidized intermediate, did not appear on the platinum electrode.

HPLC analysis for organic acids showed the formation of ketomalonic acid, suggesting aromatic ring cleavage on the titanium dioxide photoanode. Because the formation of benzenetriol and ketomalonic acid were not observed on the platinum anode in NaCl solution, Cl\textsubscript{2} or HClO may be weaker oxidants compared with photogenerated holes in titanium dioxide. On the UV-irradiated titanium dioxide electrode in NaCl solution, VA was oxidized by the attack of the holes and Cl\textsubscript{2} or HClO oxidants. Ketomalonic acid was also formed on the titanium dioxide photoanode in aqueous NaClO solution containing VA. This implies that photogenerated holes could form ketomalonic acid because they are a strong oxidant.

4. Conclusion

A titanium dioxide film with a nanoporous structure was prepared from the anodic oxidation of titanium in nitric acid. We investigated the photoanodic oxidation of VA in aqueous solution containing chloride ions on the titanium dioxide electrode treated at 500 °C. The oxidation of VA was accelerated by the oxidants Cl\textsubscript{2} or HClO that were photogenerated simultaneously on the UV-irradiated titanium dioxide electrode. Although the oxidation rate of VA on the platinum anode appeared the same as that on the titanium dioxide photoanode in aqueous NaCl solution, there was a large difference in the degree of oxidation of VA between these electrodes. On the titanium dioxide photoanode, VA was oxidized to benzenetriol through several intermediates and the aromatic ring was cleaved to form ketomalonic acid. Based on our results, the titanium dioxide photoelectrode is expected to oxidize organic materials in aqueous solutions containing chloride ions such as seawater.

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References

1) A. Fujishima, T. N. Rao, D. A. Tryk ; J. Photochem. Photobiol. C: Photochem. Rev., 1, 1 (2000).
2) Y. Shiraishi, T. Hirai ; J. Photochem. Photobiol. C: Photochem. Rev., 9, 157 (2008).
3) K. Rajeshwar, M. E. Osugi, W. Chanmanee, C. R. Chenthamarakan, M. V. B. Zanoni, P. Kajitvichyanukul, R. Krishnan-Ayer ; J. Photochem. Photobiol. C: Photochem. Rev., 9, 171 (2008).
4) H. Selekuk, W. Zaltner, J. J. Sene, M. Bekbolet, M. A. Anderson ; J. Appl. Electrochem., 34, 653 (2004).
5) E. Valatka, Z. Kulěšius ; J. Appl. Electrochem., 37, 415 (2007).
6) S. Zhou, A. K. Ray ; Ind. Eng. Chem. Res., 42, 6020 (2003).
7) T. Hathway, W. S. Jenks ; Photochem. Photobiol. A: Chem., 200, 216 (2008).
8) T. T. Guarraldo, S. H. Pulcinelli, M. V. B. Zanoni ; J. Photochem. Photobiol. A: Chem., 217, 259 (2011).
9) R. Gaghir, P. Drogu, I. Ka, M. A. E. Khakani, D. Robert ; J. Appl. Electrochem., 43, 467 (2013).
10) K. Esquivel, M. G. Garcia, F. J. Rodriguez, L. A. Ortiz-Frade, L. A. Godinez ; J. Appl. Electrochem., 43, 433 (2013).
11) Y. Maeda, H. Tsukakoshi ; Japan Patent No. 5093801 (2012).
12) Z. Zainal, C. Y. Lee, M. Z. Hussein, A. Kassim, N. A. Yusof ; J. Photochem. Photobiol. A: Chem., 172, 316 (2005).
13) K. Naeem, O. Feng ; J. Environ. Sci., 21, 527 (2009).
14) M. V. B. Zanoni, J. J. Sene, M. A. Anderson ; J. Photochem. Photobiol. A: Chem., 157, 55 (2003).
15) M. Kim, K. Choo, H. Park ; J. Photochem. Photobiol. A: Chem., 216, 215 (2010).
16) M. Makita, A. Harata ; Chem. Eng. Proces., 47, 859 (2008).
17) J. M. Macák, H. Tsuchiya, P. Schmuki ; Angew. Chem. Int. Ed., 44, 2100 (2005).
18) H. Liang, X. Li ; J. Hazard. Mater., 162, 1415 (2009).
19) D. V. Portan, G. C. Papanicolau, G. Jiga, M. Caposi ; J. Appl. Electrochem., 42, 1013 (2012).
20) M. V. B. Zanoni, J. J. Sene, H. Selekuk, M. A. Anderson ; Environ. Sci. Technol., 38, 3203 (2004).