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The pH dependence of OH radical formation in photo-electrochemical water oxidation with rutile TiO_2 single crystals

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It has been believed that photocatalytic oxidation in water proceeds with the reaction of OH radicals generated on the photocatalysts. To explore the actual contribution of OH radicals to the photocatalytic oxidation, OH radicals were detected by fluorescence probe method in photoelectrolysis with rutile TiO_2 of (100) and (110) faces. The effect of hydrogen peroxide on the OH radical formation at pH 6.7 was investigated to confirm the relevant intermediate which was suggested in our previous report for water oxidation. In alkaline solutions at pH 9.6 and 12.5, the current efficiencies of OH radical formation were 0.01-0.05%, which are far smaller than those at pH 6.7 (0.2-0.6%) due to the deprotonation of reaction intermediate as confirmed by FT-IR measurements. These experimental results support a plausible reaction mechanism that the surface Ti-O-O-Ti structure is an intermediate of water oxidation process, by which mechanism the O_2 production becomes favorable in alkaline solution.

1.Introduction

To date, photocatalytic water splitting is gathering much attention[1-12] because it is a promising technology for solar energy to produce hydrogen fuel. Besides the water reduction to produce hydrogen, the water oxidation to produce oxygen (O_2) is also one of the intriguing objectives for developing efficient water-splitting photocatalysts. However, the detailed mechanism of water oxidation has not been completely clarified yet.[13] During water oxidation, photo-excited holes (h^+) are quenched by the processes such as electron-hole recombination, light emission, and photo-corrosion along with the formation of the oxidation products.[14-19] Therefore, the investigation of detailed oxidation mechanism would be prerequisite to improve the efficiency of O_2 production.

Since the first report on the photo-induced water splitting by Fujishima and Honda[1] appeared more than four decades ago, enormous efforts have been devoted to clarify the mechanism of water oxidation to utilize titanium dioxide (TiO_2) photocatalysts.[14-20] At the present time, two types of water photo-oxidation mechanism have been proposed, in which the formation process for oxygen-oxygen (O-O) bond is different each other.

For a long time, it has been suggested that the water photo-oxidation accompanies with OH radical (・OH) formation by photo-oxidation of a terminal hydroxyl group (Ti-OH) on TiO_2,[20] followed by the formation of O-O bond by dimerizing OH radicals to produce hydrogen peroxide (H_2O_2). However, photo-oxidation of Ti-OH has already been suspected, because the electronic energy of the O 2p orbital for Ti-OH is 1.8 eV lower than that for valance band top of TiO_2 as revealed by UPS measurements.[21] On the other hand, the formation of OH radicals has been confirmed by ESR (electron spin resonance spectroscopy) measurements[22-26] and by fluorescence probe method.[27] Based of these reports, OH radical has been believed to contribute considerably to the oxidation reaction of photocatalysts.[28-31] Additionally, the photocatalytic activity of the metal oxide surface is known to be changed in alkaline solution.**[32]**

Recently, another water photo-oxidation mechanism has been proposed. The O-O bond is formed by photo-oxidation of a surface bridged structure (Ti-O-Ti) into a peroxo structure (Ti-O-O-Ti) which is observed by FT-IR measurements,[33] and equivalent to H_2O_2 adsorbed on TiO_2.[16,17] In this mechanism, OH radical must not be produced, however the formation of OH radical was experimentally confirmed as sated above. The actual contribution of OH radical to O_2 production is the indispensable information to determine which types of water photo-oxidation mechanisms is major. If the mechanism is clarified, the strategy for developing efficient water-splitting photocatalysts could be narrowed down.

For investigating the mechanism of photocatalytic reactions, OH radicals produced in aqueous solution could be detected by fluorescence probe method.[26,34-41] Different from photocatalytic system of powders, photo-electrochemical systems enable us to investigate oxidation reaction alone by applying potential, and furthermore the reaction rate can be calculated with the measured electric current. In our previous study,[34] the formation of OH radical in the water photo-oxidation at pH 6.7 was quantitatively investigated for rutile TiO_2 electrode of different crystalline surfaces. In the report, we proposed a mechanism of OH radical production related to the formation of Ti-O-O-Ti surface structure in neutral solution.[34]

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In alkaline solutions, the following advantages for photo-electrochemical water splitting are reported;

(1) More negative flat band potentials under light irradiation[42,43] to decrease the potential barrier.
(2) Accelerating the charge transfer at the interface between TiO_2 electrodes and electrolyte solutions.[42]
(3) Suppressing photo-corrosion process for TiO_2 electrodes.[17]

In the present study, therefore, effect of alkaline solution on the OH radical formation was investigated. Firstly, to confirm the previously proposed mechanism of OH radical formation, the effect of H_2O_2 on the OH radical formation was investigated at pH 6.7. Then, the current efficiency of OH radical formation was measured at pH 9.6 and 12.5. Thus, considering proton transfer process, more detailed mechanism for O_2 evolution was proposed.

2.Experimental

2.1 Chemical reagents

Sodium sulphate (Na_2SO_4, Nacalai Tesque, Inc.), sodium hydroxide (NaOH, Nacalai Tesque, Inc), hydrogen peroxide (H_2O_2, 30% solution, Santoku Chemical Industries, Co., Ltd), terephthalic acid (TA, Nacalai Tesque, Inc.), 2-hydroxytelephthalic acid (TAOH, Wako Pure Chemical Industries, Ltd) were used without further purification. All the solutions were prepared with water purified by a Milli-Q system.

2.2. TiO_2 Single Crystal Electrodes

Rutile TiO_2 single crystals of (100) and (110) orientations (supplied from Nakazumi Crystal Laboratory Co.) were heat-treated in a tubular furnace (AT-E58, Isuzu Seisakusho Co., Ltd.) filled with 0.5% hydrogen diluted with argon gas (Sumitomo Seika Chemical Co., Ltd.) at 700 ºC for 6 hrs to increase the carrier density.[14] After cutting the TiO_2 crystal (10 mm × 10 mm × 1 mm) into four pieces, the back side of the piece was connected to a lead wire by soldering and then covered with an epoxy adhesive. Figure 1 shows single crystal TiO_2 electrode used in the present study. The surface of the electrode was cleaned by cyclic-voltammetric scans from -0.9 to 1.8 V (vs Ag/AgCl) at the scan rate of 50 mV s^{-1} in 0.1M Na_2SO_4 solution until the voltammograph became reproducible. The surface flatness of the single crystals was confirmed previously by using an AFM.[34] The orientation of the single crystals was confirmed by the measurements of electron back scattering diffraction (EBSD) by using FE-SEM (SU-8230, Hitachi).

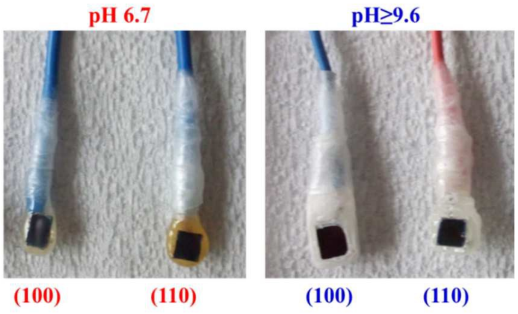


Fig. 1 Single crystal TiO_2 electrodes used in the present study.

2.3. Water photo-oxidation conditions

Water oxidation was carried out in a home-made electrochemical cell equipped with a platinum coil counter electrode and an Ag/AgCl (Type RE-1C, BAS, Inc.) reference electrode as illustrated in Fig.2. The electrochemical cell was filled with 0.1M Na_2SO_4 electrolyte solution of pH 9.6 or 12.5. The volume of the cell solution was 40 ml, while that for the experiments at pH 6.7 was 115 ml as the same experimental condition to the previous report.[34] The TiO_2 working electrode and the platinum counter electrode were separated by an ion exchange membrane (Nafion®117, Aldrich Science). During water oxidation, the solution was stirred vigorously with a magnetic stirrer.

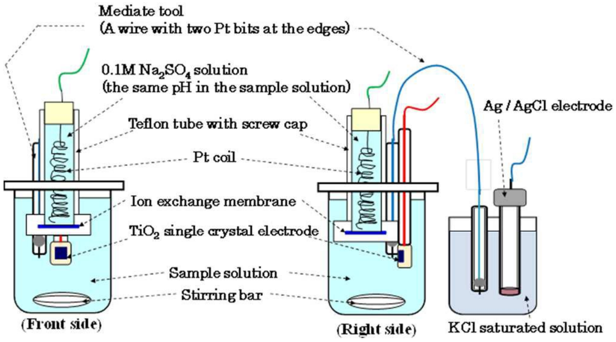
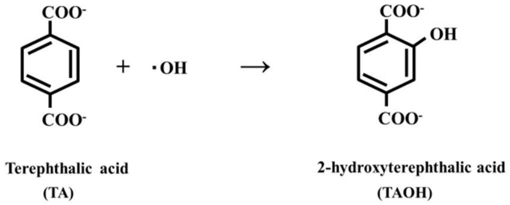


Fig. 2 Illustration for the three electrode cell used in the present study.

The electrochemical cell was operated with a potentiostat (HSV-100, Hokuto Denko, Inc.) connected with a voltage logger (Type GL200, Graphtec Co.). The TiO_2 electrode was irradiated from the front side with a UV-LED (365 nm, Model L10561, Hamamatsu Photonics). The incident light power was ca. 7.0 mW cm^{-2} measured with a power meter (TQ8210 with Q82017A sensor, Advantest Co.). Before the water photo-oxidation, N_2 gas was purged in the electrolyte solution for 1h.

2.4. Quantitative analysis of OH radical formation



Scheme 1 Formation of 2-hydroxyterephthalic acid (TAOH) by the reaction of terephthalic acid (TA) with OH radical in alkaline solution.

The fluorescence probe method with terephthalic acid (TA)[26,35,36] was employed to measure amount of OH radical in alkaline solution. Though coumarin was employed in our previous study at pH 6.7,[34] in alkaline solution it slowly transforms to o-hydroxycinnamic acid,[39] which is useless for OH radical detection. However, we used coumarin to detect OH radicals at pH 6.7 in the present study, because TA could be adsorbed on TiO_2 by the -COOH groups[38] to influence the photo-oxidation reaction. On the other hand, coumarin was not adsorbed on TiO_2 at pH 6.7.[38]

By the reaction with OH radical, TA becomes 2-hydroxyterephthalic acid (TAOH) as shown in Scheme 1. Figure 3(a) shows the fluorescence spectra of TA and TAOH solutions measured with a fluorescence spectrophotometer (Model 850, Hitachi. Ltd.). The sample solutions were 0.1 M Na_2SO_4 at pH 12.5 containing 0.1 mM TA and various concentrations of TAOH. On the excitation at 312 nm, TA and TAOH show the fluorescence peaked at 356 nm and 426 nm, respectively.[26,36]

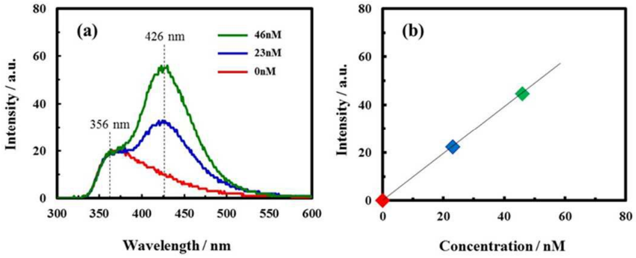


Fig. 3 (a) Fluorescence spectra for a mixture of 0.1 mM TA and TAOH. (b) A correlation chart of the concentration of TAOH and increment of the fluorescence intensity at 426 nm.

The increment of the fluorescence intensity at 426 nm was measured to calculate the concentration of TAOH. As shown in Figure 3(b), a linear relationship between the fluorescence intensity at 426 nm and the TAOH concentration was obtained. From this plot, we can calculate the TAOH concentration in the sample solutions. In the experimental procedure, all the cell solutions at pH 9.6 and 12.5 were diluted by Na_2SO_4 and NaOH solutions to prepare the sample containing 0.1 mM TA at pH 12.5 for fluorescence measurements. The real concentration of TAOH in the electrolysis cell was calculated by considering the dilution.

To calculate the yield of OH radicals from the TAOH concentration, we considered the radiation chemical yields, *i.e.,* G values. The G value is defined by the number of the molecules produced in aqueous solution with the radiation chemical reaction under the radiation of 100 eV. It is reported that the G values of OH radical in pure water[33] and TAOH in 0.1 mM TA solution[45] are 2.2 and 0.99, respectively. Since OH radical is the only reactant for the TAOH formation, it is calculated that (0.99/2.2)×100=45% of OH radical was detected as TAOH. Therefore, the concentration of OH radicals can be calculated by dividing the concentration of TAOH by 0.45.

For the solutions of pH 6.7, the experimental procedure to detect OH radicals with coumarin florescence probe was the same as the previous study.[34]

3. Results

3.1 Effect of H_2O_2 on the OH radical formation

For rutile TiO_2 powder suspensions, we reported that OH radical formation is increased in the presence of H_2O_2.[35,36,38] However, in photocatalysis we cannot discriminate the OH radicals produced by oxidation from those by reduction, because the oxidation by photoinduced holes and the reduction by photoinduced electrons should equally occur. Therefore, we must investigate the effect of H_2O_2 on OH radical produced in the oxidation process on rutile TiO_2 electrodes at pH 6.7.

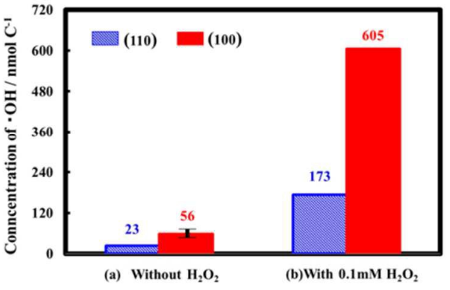


Fig. 4 Effect of H_2O_2 on the OH radical formation for TiO_2 electrodes of (110) (striped column) and (100) (filled column) faces; (a) in the absence of H_2O_2 [34] and (b) in the presence of 0.1 mM H_2O_2 in 0.1 M Na_2SO_4 solution containing 2 mM coumarin at pH 6.7.

Figure 4 shows the produced amounts of OH radicals at pH 6.7, which were normalized by the electric charges of the photo-currents to compensate the difference in the surface areas of the electrodes. In the presence of H_2O_2, the amounts of OH radicals were increased for both (100) and (110) faces, indicating that the photo-oxidation reaction for OH radical formation was accelerated. When H_2O_2 is oxidized, it becomes either O_2[19] or superoxide radical ($\cdot O_2^-$),[35, 36] and then the water oxidation to form OH radicals is supposed to be decreased. Therefore, the observed acceleration of OH radical formation would be attributed to a catalytic function of adsorbed H_2O_2 as proposed previously.[34] The adsorbed H_2O_2 is equivalent to the surface Ti-O-O-Ti structure, and the catalytic action to produce OH radical for (100) face was more active than that for (110) face as discussed previously.[34]

3.2 Effect of pH on the OH radical formation

To clarify the mechanism of OH radical production in the process of O_2 evolution, we also investigated OH radical formation in alkaline solutions at pH 9.6 and 12.5. Figure 5 shows the current-voltage (I-V) curves for the TiO_2 electrodes of (100) and (110) faces. Under the UV light irradiation, photo-currents appeared at around -0.5 V and increased moderately with the increase of anodic potential. The transitional current was observed at -0.4 V only for (110) face at pH 9.6 (left bottom side in Fig.5) is attributable to the deprotonation of adsorbed water ($Ti\text{-}OH_2^+$) to form Ti-OH as observed at pH≤10.7.[46] We selected the potentials of 1.3V (pH 9.6) and 0.8V (pH 12.5) for efficient water photo-oxidation.

The photocurrents during UV irradiation at the constant applied potential were shown in Fig.6. Based on the surface area of the electrode of about 0.25 cm^2, the photo current of ca. 0.3 mA observed in Fig. 4 corresponds to the photocurrent density of around 1.2 mA cm^{-2}. Since the photon energy of 365 nm light is 3.4 eV, the light intensity of 7.0 mW cm^{-2} corresponds to 7.0/3.4=2.06 mA cm^{-2}. Therefore, apparent photocurrent efficiency is calculated to be (1.2/2.06)×100 ≈ 60%. Since the refractive index of rutile TiO_2 at 365 nm is about 3.0, the reflections of light at the electrode surface and the cell surface is at least 25%. Accounting the scattering at the cell surface, this rough estimation suggests that the loss of ca. 40% of the light energy is mainly attributable to the loss of the light absorption. Therefore, the fraction of the electron - hole recombination is probably very small.

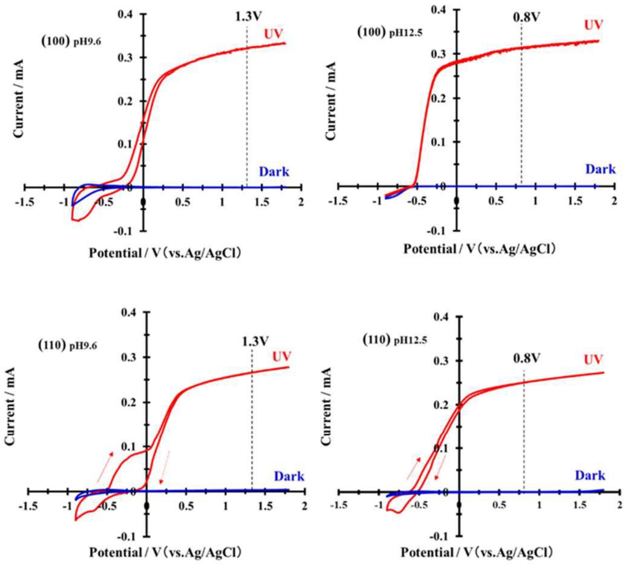


Fig. 5 Current-voltage curves of the TiO_2 electrodes of (100) and (110) faces in 0.1M Na_2SO_4 solutions at pH 9.6 and pH 12.5 under UV light irradiation (red) and dark condition (blue) at scanning rate of 50 mV s^{-1}.

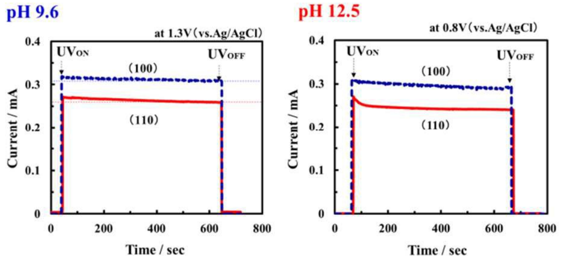


Fig. 6 Photo-anodic current for the TiO_2 electrodes of (100) and (110) faces in alkaline 0.1M Na_2SO_4 solutions at pH 9.6 and 12.5. The applied potentials are shown in the figure.

Figure 7 shows representative fluorescence spectra of the electrolyte solution before and after photo-electrochemical water oxidation. From the increase of the fluorescence intensity at 426 nm, the concentration of TAOH was calculated based on the calibration chart in Figure 1(b).

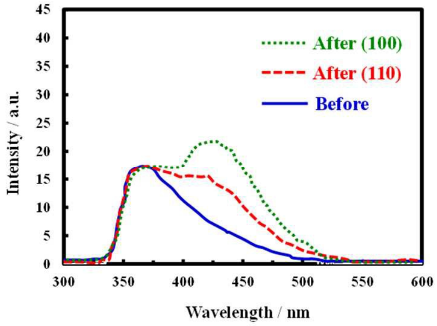


Fig. 7 Fluorescence spectra of the sample solutions prepared from the cell solutions at pH 12.5 containing 0.4 mM TA and 0.1 M Na_2SO_4 before and after water photo-oxidation with the TiO_2 electrodes of (110) and (100) faces.

Table 1. Current efficiency of OH radical formation η for TiO_2 electrodes of (100) and (110) faces at different solution pH.

pH	TiO_2	Area / cm^2	Time / hour	Q / mC	[TAOH] / nM	η (·OH)×10^2/ %	η (O_2) / %
6.7*	(100)	0.218	0.5	289±16	10.2±0.8	56 ±5	93 ±7
	(110)	0.177		433±19	6.30±0.52	23 ±2	105 ±5
9.6	(100)	0.266	1.0	1235±78	75.2±2.9	5.2±0.2	N/A.
	(110)	0.248		873±21	56.3±2.7	5.5 ± 0.3	N/A
12.5	(100)	0.266	3.0	3138±69	60.6±5.5	1.66±0.15	N/A
	(110)	0.248		2905±75	34.4±3.8	1.02 ± 0.11	N/A

*Taken from our previous report.[34] N/A: not available with the present method.

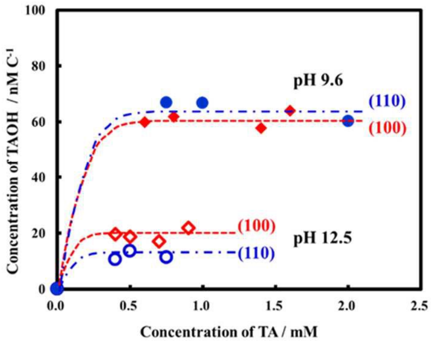


Fig. 8 The concentrations of TAOH are plotted against TA in 0.1 M Na_2SO_4 solutions at pH 9.6 and pH 12.5 for the TiO_2 electrodes of (100) and (110) faces.

In Table 1 listed are the experimental data; surface area of the electrodes, photo irradiation time, total charge (Q) of photocurrent, the concentration of TAOH in the cell solution, and current efficiency (η) of OH radical formation. Figure 8 shows the concentration of TAOH detected with various concentration of TA. To compensate the differences in the surface areas of the electrodes and the irradiation time, the concentration of TAOH was normalized with the electric charges Q of the photocurrent. When the TA concentration was changed, the values of Q were hardly dispersed and the concentrations of TAOH remain constant as shown in Figure 6. Although the rate constant for the dimerization of OH radicals is 5.5×10^9 $M^{-1}s^{-1}$,[47] the rate constant for the reaction of OH radical with TA is as large as 3.9×10^9 $M^{-1}s^{-1}$.[48] Therefore the observed constant TAOH concentration as the higher TA concentration indicates that the produced OH radicals completely react with TA. The invariance in the TAOH concentration suggests that TA was not photo-electrochemically oxidized and did not influence the water photo-oxidation.

As shown in Table 1, the current efficiency for OH radical formation, $\eta(\cdot OH)$, at pH $\geq$ 9.6 was calculated from the concentration of TAOH by multiplying Faraday constant and solution volume, and then being divided by Q and the yield of 0.45. The current efficiencies at pH 9.6 (0.01-0.05%) were much smaller than those at pH 6.7 (0.2-0.6%) for both (100) and (110) faces. Additionally, the difference in the current efficiencies between (100) and (110) faces observed at pH 6.7 became small in alkaline solution. As the current efficiencies for O_2 evolution in 0.1 M Na_2SO_4 solution were found to be ca. 100% for both (100) and (110) faces,[34] the photocurrents were mainly attributed to water oxidation to produce O_2. Since the current efficiency for OH radical formation was at most 0.6%, the OH radicals hardly contributed to O_2 production in the range from pH 6.7 to pH 12.5.

4. Discussion

As shown in Fig. 6, the addition of H_2O_2 increased the OH radical yields, suggesting that surface Ti-O-O-Ti structure functions as a catalyst to produce OH radicals. According to the water photo-oxidation mechanism on rutile TiO_2 proposed by Nakato and co-workers,[16,17] The surface Ti-O-O-Ti is formed by opening Ti-O-Ti with the attack of photoinduced holes, h^+, accompanying with nucleophilic attack of water, as shown in eqn (1) and (2).

$$\text{Ti-O-Ti} + H_2O + h^+ \rightarrow [\text{Ti-O}\cdot\ \text{HO-Ti}] + H^+ \quad (1)$$

$$[\text{Ti-O}\cdot\ \text{HO-Ti}] + h^+ \rightarrow \text{Ti-O-O-Ti} + H^+ \quad (2)$$

Actually, the formation of Ti-O-O-Ti on rutile TiO_2 under UV light irradiation was indicated by FT-IR[49].

In the following step as shown in Fig.9, the attack of h^+ to Ti-O-O-Ti (1) is able to form two different intermediates (2a) and (2b) by dissociating either Ti-O bond or O-O bond. In the process (a), Ti-O bond is dissociated to [Ti-O-O· HO-Ti] structure by the attack of h^+ accompanying with the nucleophilic attack of water to the Ti atom (2a), as proposed previously.[17] The structure releases O_2 by oxidation of Ti-O-O· (3a), and then Ti-O-Ti is regenerated by following dehydration process (4a). In contrast, in the process (b), O-O bond is dissociated to [Ti-O-OH ·O-Ti] structure by the attack of h^+ accompanying with the nucleophilic attack of water to the O atom (2b).[34] The structure releases an OH radical by dissociation of O-O bond, and then Ti-O-O-Ti is regenerated (3b).

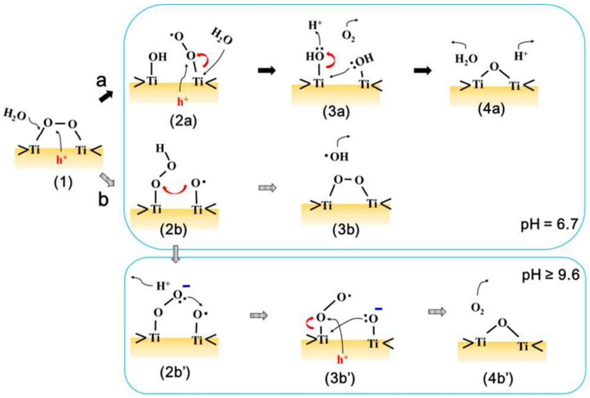


Fig.9 Plausible reaction steps starting from Ti-O-O-Ti to form (a) O_2 and (b) OH radicals at the TiO_2 surface. The process (b) is altered by process (b') in alkaline solution.

The [Ti-O-OH ·O-Ti] structure would be changed by the increase of pH in the solution as studied by Nakato and the co-workers.[33] They measured FT-IR spectra for rutile TiO_2 in acid (pH 2.4) and alkaline (pH 11.5) solutions under UV light irradiation. In the acid solution, the peaks of the structures for both the structures of Ti-O-O-Ti and Ti-O-O-H were observed. On the other hand, in the alkaline solution, only the peak of the Ti-O-O-Ti structure was observed. We also measured the FT-IR absorption of Ti-O-O-Ti increased with UV irradiation in neutral solution.[49] In alkaline solution at pH 11.5, the signal of Ti-O-O-Ti at 940 cm^{-1} was increased with the UV irradiation similarly to the case of pH 6.7 as shown in Fig.10. However, a broad signal in the wavenumber range of 700-850 cm^{-1} (attributable to Ti-O stretching) appeared and in the range of 1100-1150 cm^{-1} no absorption was observed on UV irradiation. This suggests the formation of TiO・ or TiOO$^-$ species at the surface by UV irradiation in alkaline solution. Therefore, when the pH of the solutions was increased, the [Ti-O-O$^-$ ・O- Ti] structure (2b') may be more dominant than [Ti-O-OH ・O-Ti] structure (2b) by prompt proton transfer. By the further oxidation, the [Ti-O-O- ・O-Ti] structure may release O_2 and then transforms into original Ti-O-Ti structure (4b'). Thus, at a higher pH, OH radical production is suppressed by the deprotonation of the [Ti-O- OH ・O-Ti] structure.

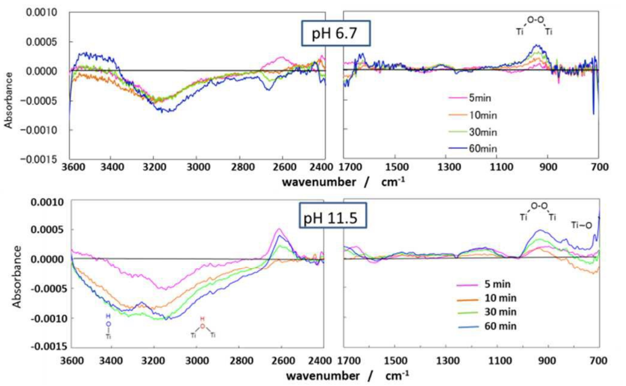


Fig.10 Change in the ATR FT-IR spectra with UV irradiation time (5, 10, 30, and 60 min) for rutile TiO_2 surface in neutral (pH 6.7) solution[49] and in alkaline (pH 11.5) solution. Experimental details were shown in Ref.49. Adapted from Ref 49 with permission from the PCCP owner Society.

The Ti atoms in Ti-O-O-Ti have formal charge of +(1/3) and -(1/3) on (100) and (110) faces, respectively, because the Ti atoms were coordinated by 5 and 6 of O atoms on (100) and (110) faces, respectively.[34] The dissociation by positive holes for (a) Ti-O bond and (b) O-O bond were competed each other. The one dissociation reaction will become favourable, when the other is suppressed. In the case that the Ti atom in Ti-O-O-Ti has positive charge, the dissociation by positive holes for O-O bond (b) become more favourable than Ti-O bond (a), because (a) is slightly suppressed by the charge repulsion. Therefore, the OH radical formation on (100) surface exceeded that on (110) at pH 6.7.[34] With the increase of pH, hydroxyl anion (OH^-) is adsorbed on the positively (+1/3) charged Ti atom in Ti-O-O-Ti on the (100) surface, resulting in that the Ti atoms have negative charges of -(2/3). As the Ti atoms on both (100) and (110) faces have negative charge, the strength of Ti-O bond for the dissociation become nearly equal to be favourable for O_2 formation. Therefore, the OH radical yield for (100) surface was supressed similarly to that for the (110) surface with the increase of pH as shown in Table 1.

5. Conclusions

In the present study, the OH radical formation in water photo-oxidation was investigated in the pH range of 6.7–12.5 by using TiO_2 electrodes of rutile (100) and (110) faces. It was found that in the presence of H_2O_2, OH radical formation at pH 6.7 was accelerated. The adsorbed H_2O_2 which is equivalent to Ti-O-O-Ti is suggested to function as a catalyst for OH radical formation.

In alkaline solution, the current efficiencies of OH radical formation (0.01 - 0.05%) were much smaller than those at pH6.7 (0.2-0.6%) for both (100) and (110) faces. As the current efficiencies for O_2 production for (100) and (110) faces are estimated to be ca. 100%, it is concluded that OH radicals hardly contribute to the O_2 production even at the alkaline pH. Since the surface [Ti-O-O$^-$ ・O-Ti] structure would be dominant in alkaline solutions by the deprotonation of [Ti-O-OH ・O-Ti] structure, OH radical formation would be suppressed. This suggests that the O_2 generation in alkaline solution is more favourable.

Additionally, the current efficiency for the (100) surface decreased similarly to that for the (110) surface. Since the formal charge of the Ti atoms in Ti-O-O-Ti for (100) becomes negative by the adsorption of OH^- in alkaline solution, the resistivity to the Ti-O dissociation became same for two crystal phases, which caused the similar efficiency to the OH radical formation.

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Abstract

It has been believed that photocatalytic oxidation in water proceeds with the reaction of OH radicals generated on the photocatalysts. To explore the actual contribution of OH radicals to the photocatalytic oxidation, OH radicals were detected by fluorescence probe method in photoelectrolysis with rutile TiO_2 of (100) and (110) faces. The effect of hydrogen peroxide on the OH radical formation at pH 6.7 was investigated to confirm the relevant intermediate which was suggested in our previous report for water oxidation. In alkaline solutions at pH 9.6 and 12.5, the current efficiencies of OH radical formation were 0.01-0.05%, which are far smaller than those at pH 6.7 (0.2-0.6%) due to the deprotonation of reaction intermediate as confirmed by FT-IR measurements. These experimental results support a plausible reaction mechanism that the surface Ti-O-O-Ti structure is an intermediate of water oxidation process, by which mechanism the O_2 production becomes favorable in alkaline solution.