

Chapter One

Spatial separation of reaction sites on rutile TiO₂ nanorod by exposing crystal faces and development of visible light responsive rutile TiO₂ nanorod *

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1.1 INTRODUCTION

TiO₂ has been intensively investigated for environmental remediation and energy conversion in the past several decades as a select platform on which an exceptionally wide range of appealing solid-state physical-chemical properties coexist with the potential for low cost and environmental remediation and energy technologies [1-3].

TiO₂ exists in three crystal structures: rutile, anatase and brookite. Each crystalline structure exhibits specific physical properties, band gap, surface states, etc. Rutile TiO₂ has some advantages over anatase such as higher chemical stability and higher refractive index. It is of fundamental significance to explore mild synthetic techniques by which particle shapes, nano- and micro-meter-scale morphologies, and crystallinity are well defined and controlled[3-5]. Moreover, surface chemistry of single crystalline rutile particles has been the subject of intensive studies because their chemical activity depends greatly on surface structures[6].

It has been reported that well-crystallized faceted particles showed enhanced photocatalytic activity compared to particles with poorly crystalline surfaces and that the photocatalytic activity increased with increase in crystallite size, the surface itself being an intrinsic defect[7].

Morphology, exposed crystal face-controlled synthesis of TiO₂ nanoparticles has long been paid attention in order to develop a high active TiO₂ photocatalyst. Among several kinds of synthetic methods for TiO₂ nanoparticles, a hydrothermal treatment has been drawing much attention for one of main synthetic techniques of TiO₂ nanocrystals because it directly produces well-crystallized nanocrystallinities of a wide range of compositions of crystal phases under mild conditions. In addition, controlling exposed crystal faces of rutile nanorod TiO₂ by using surface morphology controlled reagents or chemical-etching reagents was also important strategy for further improvement their photocatalytic activities.

So many intensive efforts to improve the visible-light responsibility of TiO₂ photocatalyst involving impurity doping have been made in the last few decades [8-13].

However, impurity doping sometimes increase defects in TiO₂, which also work as recombination center and result in decrease of photocatalytic activity[14,15]. Recently, some visible-light responsive TiO₂ photocatalyst were developed by modification of metal surface complex which works as a sensitizer for a visible light[16-20]. This method has large advantages in simple preparation method and no introduction of defects in TiO₂. However, back electron transfer between

* Title footnote.

injected electrons in TiO₂ bulk and oxidized metal ions on the surface of TiO₂ may easily proceed resulting in significant decrease in a photocatalytic activity. Therefore, it is necessary for further improvement of photocatalytic activity under visible-light irradiation to modify metal ion site-selectively in the specific site on TiO₂ particles.

Our previous studies suggest that redox reaction proceed preferentially on specific exposed crystal faces of TiO₂[21-23]. This kind of preferential reaction was assigned by site-selective deposition of metal or metal oxide on the specific exposed crystal faces under photoexcitation[21-25].

As mentioned above, metal ion modification on TiO₂ for exhibiting visible light activity can be also applied to shape-controlled rutile TiO₂ nanorod for remarkable improvement of photocatalytic activity under visible light. In this case, crystal face-selective metal ion modification on shape-controlled particles with specific exposed crystal faces should be achieved, which results in remarkable suppression of back electron transfer in order to develop an ideal visible light responsive TiO₂ photocatalyst[26].

In this manuscript, a preparation of the morphology controlled rutile TiO₂ nanorod with exposed crystal faces by hydrothermal technique is summarized. The obtained rutile fine particles showed high levels of activity for degradation of organic compounds compared to the activity levels of anatase fine particles (ST-01) developed for environmental clean up by the company. In addition, exposition of a new high active crystal face of rutile TiO₂ nanorod is also demonstrated by using morphology controlled reagent or chemical etching reagents. After the treatments, remarkable photocatalytic activity improvement of the second step morphology controlled TiO₂ nanorod is observed compared to the original TiO₂ nanorod. Finally, the technology of visible light responsive treatment for morphology controlled rutile TiO₂ nanorod with exposed crystal faces by crystal face selective modification of metal ions on rutile TiO₂ nanorod is discussed. The metal ion modified rutile TiO₂ nanorod shows much higher activity than conventional visible light responsive N-doped TiO₂, which is commercially available in Japan.

1.2 MORPHOLOGY CONTROLLED RUTILE

TiO₂ NANOROD WITH EXPOSED CRYSTAL FACES

We carried out hydrothermal growth of rutile TiO₂ nanorod by using titanium trichloride (TiCl₃) with NaCl. Under our experimental conditions, rutile uniform TiO₂ nanorods were obtained, and developed crystal faces were observed. The obtained rutile TiO₂ nanorod showed high levels of activity for degradation of 2-propanol and acetaldehyde under UV irradiation compared to that of anatase fine particles (ST-01) developed for environmental clean up by the company in Japan. The surface chemistry of the rutile TiO₂ nanorod was also investigated. From photodeposition of Pt and PbO₂, we suggest that the (110) face provides reductive sites and that the (111) face provides oxidative sites. The results suggested that the crystal faces facilitate the separation of electrons and holes, resulting in improvement of photocatalytic activity.

1.2.1 Experimental details for preparation and activity evaluation of rutile TiO₂ nanorod with exposed crystal faces

In a typical synthesis procedure, a chemical solution was put in a sealed Teflon-lined autoclave reactor containing aqueous solution of titanium trichloride (TiCl₃) and sodium chloride (NaCl). The solutions were then put into a 200 °C oven. The substrate was centrifuged and rinsed with deionized water and then dried in a vacuum oven. Throughout this paper, samples are referred to as SH1 (NaCl 1 M), SH3 (NaCl 3 M) and SH5 (NaCl 5 M).

Photodeposition technique of Pt and PbO₂ was used for assignment of reduction and oxidation sites on exposed crystal faces of rutile TiO₂ nanorod, respectively.

For assignment of reduction site, rutile TiO₂ nanorod aqueous suspension (SH3) containing 2-propanol and hexachloroplatinic acid (H₂PtCl₆·6H₂O) was irradiated with a mercury UV lamp. N₂ gas was purged through the suspension prior to UV irradiation in order to remove oxygen. After irradiation, the color of the powder changed from white to silver, and the suspension was centrifuged and washed with distilled water and then collected as powder (Pt loaded rutile TiO₂

nanorod) after drying at 70 °C under reduced pressure.

Photodeposition of PbO₂ as a result of oxidation of Pb²⁺ ions performed in order to assignment of oxidation site on exposed crystal face of Pt loaded rutile TiO₂ nanorod. This reaction was carried out in an aqueous Pt loaded rutile TiO₂ nanorod suspension containing Pb(NO₃)₂ under aerated conditions. The pH of the solution for this reaction was adjusted at 1.0 by the addition of nitric acid according to the literature[21–26]. After photoreaction using a 500 W Hg lamp, the color of the powder changed from silver to brown, indicating that PbO₂ had been deposited on the surface. Pt and PbO₂ particles deposited on rutile TiO₂ nanorod were observed in SEM, EDX and TEM images.

The photocatalytic activity of TiO₂ nanoparticles was evaluated by measuring the change in concentration of acetaldehyde and evolved CO₂ as a function of irradiation time. A Tedlar bag was used as the photoreactor vessel. TiO₂ powder was spread on the bottom of a glass dish, and this was placed in the reaction vessel. Five hundred ppmv of acetaldehyde was prepared in the vessel. The irradiation was conducted at room temperature after equilibrium between the gas and adsorbed acetaldehyde had been reached. The light source was a 500 W Xe-lamp. The light beam was passed through a UV-35 filter to cut off wavelength shorter than 350 nm. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity (10 or 30 mW cm⁻²). After starting the irradiation, the decrease in acetaldehyde concentration and evolved carbon dioxide concentration was measured using a gas chromatograph. ST-01 having an anatase phase fine TiO₂ produced by Ishihara Sangyo CO. Ltd. was usually used as a reference catalyst.

1.2.2 Results and discussion for rutile TiO₂ nanorod with exposed crystal faces

XRD patterns of all the obtained particles were assigned to pure rutile phase and no other phases were detected. The intensity of diffraction peaks of the rutile TiO₂ nanorod becomes stronger with increase in NaCl concentration, indicating improvement in crystallinity of the rutile TiO₂ rod. The mean grain size was determined from Scherrer's equation. By applying Scherrer's formula to the rutile (110) diffraction peaks, the average

crystallite sizes of the samples were found to be 66.0, 72.7 and 97.2 nm for samples SH1, SH3 and SH5, respectively.

Figure 1 shows TEM images and selected area electron diffraction (SAED) patterns taken from nanorods shown in TEM images. TEM images showed the rod-like shape with a triangular end and tetragonal rutile structure. TEM images (Figure 3a, 3c and 3e) showed that the shape of end of the rod changed from symmetric triangular tip to asymmetric triangular tip when the concentration of NaCl was increased. The SAED patterns of the exposed surface of the end of the rod and side surface of the rod are assigned to (111) and (110), respectively. The growth direction of the TiO₂ rod is the (001) direction. In addition, (001) crystal faces are exposed gradually with increase in NaCl concentration. A spot pattern indicates a single-crystalline nature of the rutile TiO₂ nanorods. From Figure 3, surface morphology of rutile TiO₂ is controlled with changing the concentration of NaCl.

Figure 2 shows photocatalytic evolution of CO₂ by

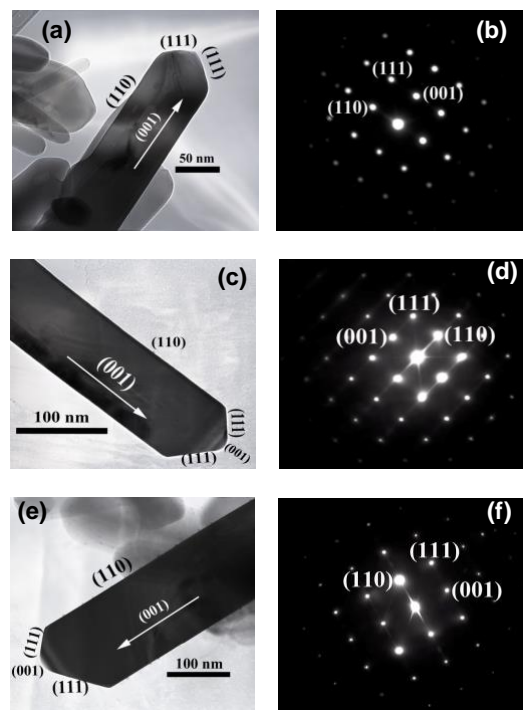


Figure 1. TEM images (a, c, e) and SAED patterns (b,

decomposition of acetaldehyde on reference TiO₂ and SH1, SH3 and SH5 at the light intensity of 10 mW cm⁻². Photocatalytic activity levels of rutile TiO₂ nanorods are higher than those of MT-600B and

ST-01. Among the rutile TiO₂ nanorods, SH5 showed the highest photocatalytic activity. The order of photocatalytic activities was SH5 > SH3 > ST-01 > SH1 > MT-600B as shown in Figure 2.

In order to clarify the origin of the remarkable photocatalytic activity improvement of rutile TiO₂

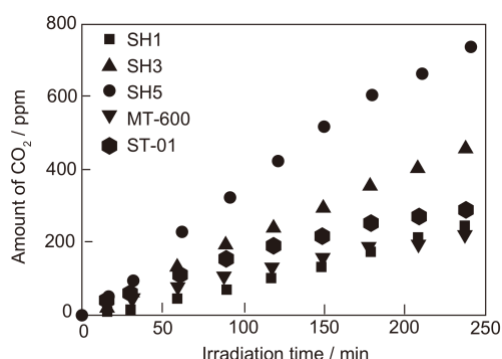


Figure 2. Time profiles of CO₂ evolution as a result of decomposition of acetaldehyde on TiO₂ at different concentrations of NaCl at light intensity 10 mW cm⁻². The experimental conditions were: [acetaldehyde]_i = 500 ppm, [TiO₂] = 10.4 mg/cm², UV light ($\lambda > 350$ nm) irradiated

nanorods, it is important to identify the actual reactive sites on the surface of rutile TiO₂ nanorods.

It has been reported that oxidation and reduction sites on rutile micro particles were exposed on the (011) and (110) faces, respectively[21]. Therefore,

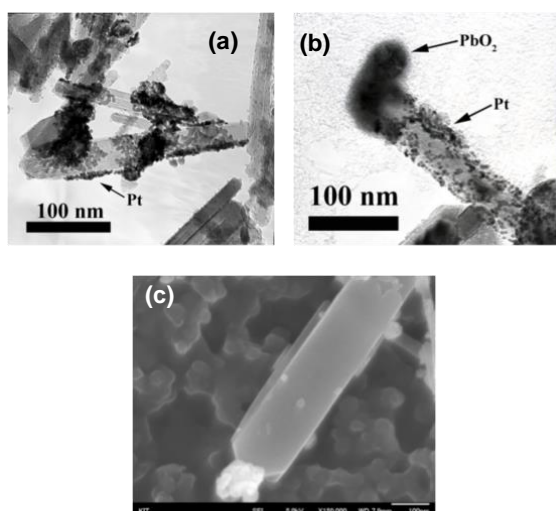


Figure 3. TEM image (a) of rutile TiO₂ nanorod (SH3) on which Pt particles were deposited. TEM image (b) and SEM image (c) of rutile TiO₂ nanorod (SH3) on which Pt and PbO₂ particles were deposited.

the exposing of well-developed faces on TiO₂

particles is advantageous for providing both oxidation and reduction sites which lead to remarkable suppression of back reactions on the surface of TiO₂ nanorod. Moreover, it is expected that the efficiency of electron-hole separation should be enhanced because of the difference in the electronic band structure between different crystals surfaces. Figure 3 shows TEM and SEM images of rutile TiO₂ nanorods showing rutile TiO₂ nanorods loaded with Pt (a) and PbO₂ (c), which were loaded on the Pt loaded rutile TiO₂ nanorod under UV irradiation. The deposited metals were analyzed by EDX (which is now shown here). Figure 3c shows SEM images of rutile TiO₂ particles showing PbO₂ deposits. Pt particles were deposited only on the (110) face as shown in Figure 3a. This result indicates that the reduction mainly proceeded on the (110) face of rutile TiO₂ nanorods. Figure 3b and 3c show that the PbO₂ particles were deposited on the (111) faces. This means that the (111) face provides the oxidation site for rutile TiO₂ nanorods. Our results suggest that the (110) face of rutile TiO₂ nanorods provides an effective reduction site and that the (111) face works as the oxidation site. Because of the spatial separation of reaction sites on TiO₂ nanorods such as reduction and oxidation sites are considered to be very efficient for some kinds of photocatalytic reactions.

Different surface energy levels of the conduction and valence bands are expected for different crystal faces of TiO₂ because of the atomic arrangements characteristic of these faces. The difference in the energy levels drives the electrons and holes to different crystal faces, leading to separation of electrons and holes[21]. The effective separation of oxidation and reduction sites of rutile particles, as shown in Figure 3, suggests that the electronic energy levels of the (110) face are lower than those of the (111) face[27]. Ohno et al. suggested that the isolation of oxidation or reduction site on the surface of TiO₂ particles is large enough to drive the photocatalytic oxidation of water on rutile particles when suitable electron acceptors are added to the solution[21]. The effective separation of oxidation and reduction sites on the surface of rutile TiO₂ particles should be important factor to obtain the high efficiency of some photocatalytic reactions.

As shown in Figure 2, an increase in particle size resulting from crystal growth did not cause a

decrease in photocatalytic activity, indicating that the photodegradation process is not surface-limited. However, control of rutile TiO₂ nanorods with exposed crystal surfaces is also one of important factor for improving photocatalytic activity of TiO₂. The large specific surface areas and small crystal sizes as well as high crystallinity of TiO₂ might usually play important roles in the enhancement of photocatalytic activities. However, spatial separation of reaction sites on the photocatalyst nanoparticle by controlling exposed crystal surface of the rutile TiO₂ nanorod is a more important factor for improvement of photocatalytic activity because a rutile TiO₂ nanorod having a small surface area (10-30 m²g⁻¹) showed a higher level of photocatalytic activity than that of ST-01 with a large surface area (300 m²g⁻¹).

1.3 NEWLY EXPOSDE CRYSTAL FACE OF RUTILE TiO₂ NANOROD BY USING CHEMICAL ETCHING TECHNIQUE

Rutile TiO₂ nanorods synthesized by hydrothermal treatment were etched by using of H₂O₂-NH₃ or H₂SO₄ solution as chemical etching reagents. New crystal faces were exposed on rutile TiO₂ nanorods by means of chemical etching treatment. In the case of H₂O₂-NH₃ solution treatment, the shape of the rutile TiO₂ nanorod changed to a sepal-like structure with reaction time. The dissolution of rutile TiO₂ nanorod mainly proceeded along [001]. When treated with sulfuric acid, the end [(111) face] of the rutile TiO₂ nanorod was gradually etched. The rutile TiO₂ nanorod finally exposed (001) and (021) faces during prolonged treatment time. In both cases, rutile TiO₂ nanorods were differently etched. The etched rutile TiO₂ nanorod showed higher photocatalytic activity for degradation of toluene in gas phase than the original particles.

1.3.1 Experimental details for preparation and activity evaluation of chemically etched rutile TiO₂ nanorod

The starting material for rutile TiO₂ nanorods was synthesized by using aqueous titanium trichloride with sodium chloride by means of hydrothermal treatment[22].

A synthesized rutile TiO₂ nanorod was added to the H₂O₂-NH₃ mixed solution and stirred for several hours at room temperature. After the treatment, the etched TiO₂ particles were separated by filtration, washed with water several times, and dried under aerated condition. For etching with sulfuric acid, prepared rutile TiO₂ nanorod was added to a flask containing concentrated sulfuric acid at room temperature and stirred for 6 h to 1 week. After the treatment, the etched TiO₂ particles were filtered and washed with 1% aqueous ammonia solution and then with deionized water.

Photocatalytic activity of rutile TiO₂ nanorods before and after etching treatment was evaluated by decrease in toluene in gas phase and evolved CO₂ as a result of photocatalytic mineralization of toluene. The evaluation procedure is as follows. TiO₂ powder was spread on a glass dish and the dish was placed in a reaction vessel with a volume of 125 cm³ in the presence of 100 ppmv of toluene. A 500 W Xe-lamp was used as a light source. The light beam was passed through a UV-35 filter to cut off wavelengths shorter than 350 nm. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity (30 mW cm⁻²). Irradiation was started at room temperature after a reaching equilibrium condition. After starting the irradiation, the evolved carbon dioxide and toluene were measured using a gas chromatograph equipped with a methanizer.

1.3.2 Results and discussion for chemically etched rutile TiO₂ nanorod

Rutile TiO₂ can be easily dissolved in H₂O₂-NH₃ mixed solution. Ohtani et al. reported that isolation of anatase TiO₂ was achieved by selective dissolution of rutile from P25 having a mixture of anatase and rutile phases[28]. Therefore, a small amount of NH₃ solution was used to prevent complete dissolution of rutile TiO₂ nanorods.

TiO₂ powder was suspended in H₂O₂-NH₃ mixed solution and stirred for several hours at room temperature, leading to dissolution of the solid to give a light-yellow sol which is a Ti⁴⁺-H₂O₂ complex[28]. Figure 4 shows TEM and SEM images of a rutile TiO₂ nanorod with exposed crystal faces prepared according reference[22]. The assignment of crystal faces was reported previously[22].

SEM and TEM images of the rutile TiO₂ nanorod after treatment with H₂O₂-NH₃ mixed solution are shown in Figure 5. The rutile TiO₂ nanorod became

thinner with increase in etching time. As previously reported[22], (a) SAED patterns of the

exposed surface of the rod end and side surfaces of the rutile TiO₂ rod were

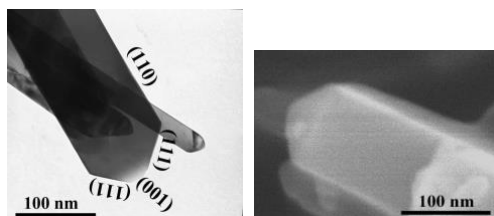


Figure 4. (a) TEM image and (b) SEM image of rutile particles present in the TiO₂ powder used in this study.

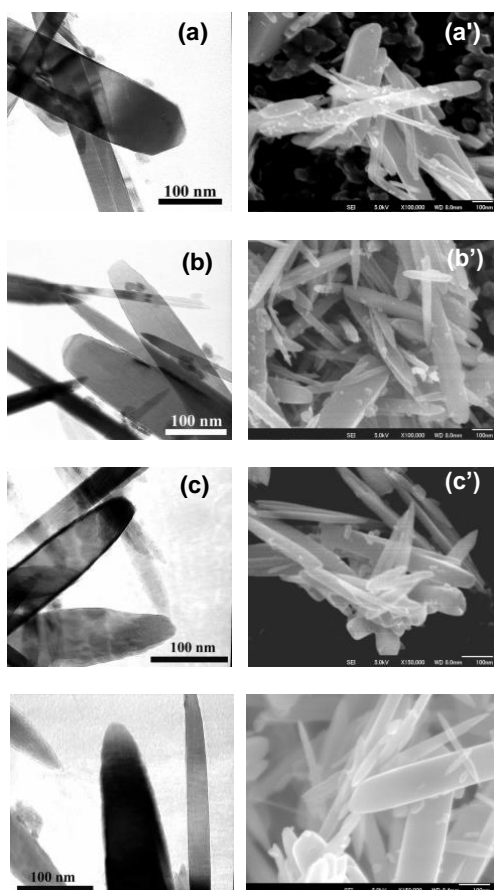


Figure 5. TEM images and SEM images of rutile particles after treatment with aqueous H₂O₂-NH₃ solution. The etching periods were about (a), (a'), 0

assigned to (111) and to (001) and (110), respectively (data not shown). The area of exposed (111) and (001) crystal faces gradually decreased with increase in reaction time. At the same time, a cone-shaped rod end was newly exposed and a crystal face assigned to the (110) face gradually decreased as shown in Figure 5. To assignment of the oxidation site, photodeposition of PbO₂ was carried out. PbO₂ was deposited on the oxidation site of (a) TiO₂ by oxidation of Pb²⁺ ions dissolved in aqueous media[22, 29].

Figure 6 shows TEM and SEM images of chemically etched rutile TiO₂ nanorods

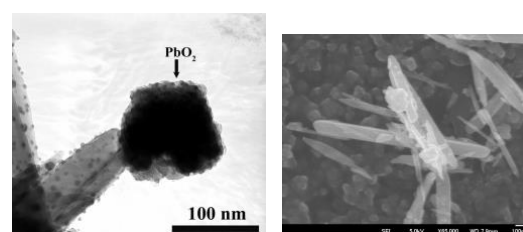


Figure 6. (a) TEM image and (b) SEM image of a rutile TiO₂ nanorod (H₂O₂-NH₃-1h) on which PbO₂

deposited with PbO₂ that were obtained after 1 h etching treatment. The deposited PbO₂ was analyzed by EDX (figure not shown). Figure 6 shows that the PbO₂ particles were deposited on the (111) and (001) faces on the rutile nanorod. The results indicate that the oxidation site on the rutile particles is on the exposed new cone-shaped rod end which agree with our previous studies[22, 29]. Therefore, the results suggest that effective isolation of oxidation sites of rutile TiO₂ nanorods is one of important factor for high reactivity.

Taguchi et al. reported that H₂SO₄ treatment at 200 °C generated new faces of rutile particles[30]. We tried this treatment for TiO₂ powder containing rutile TiO₂ nanorod. However, the color of rutile TiO₂ particles changed from white to pale gray and the shape of the particles became to deform at high temperatures (100 °C and 200 °C). The conditions for etching of rutile TiO₂ nanorods by sulfuric acid should be too severe to expose new crystal faces because particle size of our rutile TiO₂ nanorod is smaller than that reported in previous paper.[29] Therefore, sulfuric acid treatment of the rutile TiO₂ nanorod had been carried out at room temperature. Figure 7 shows TEM and SEM images of rutile TiO₂ nanorod after sulfuric acid treatment for different time periods. TEM and SEM images before etching (Fig. 1) revealed that the shape of rod end of rutile TiO₂ was triangular-like tip. After sulfuric acid treatment, (001) face was exposed as a result of dissolution of (111) face as shown in Fig. 5. Generation of another new face was observed after treatment for one week. As seen in Figure 7e and 7e', this new face is assigned

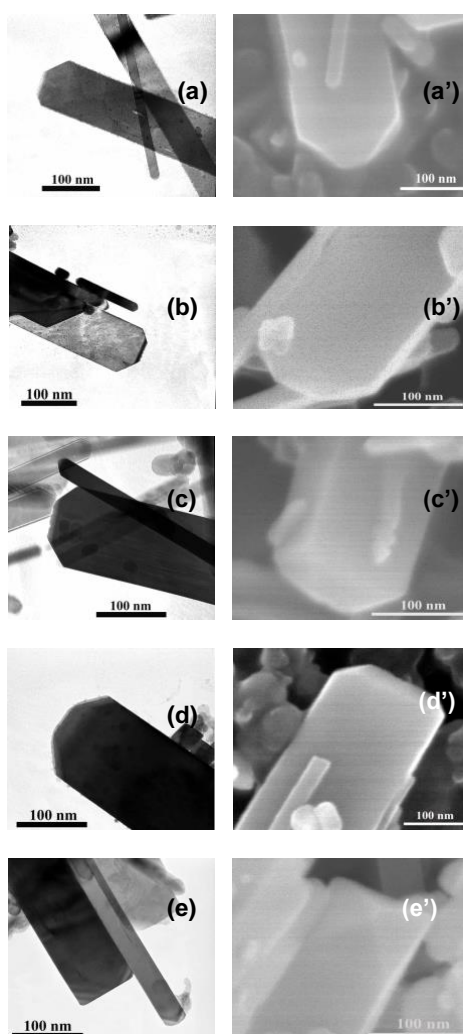


Figure 7. TEM images and SEM images of rutile particles after treatment with sulfuric acid. The etching periods were about (a), (a'): 6 h, (b), (b'): 15

to the (021) face which had been already assigned from previous paper[30]. As a result, (001) and (021) faces are generated at the tip of TiO₂ and, at the same time, the (111) face disappears from the rutile TiO₂ nanorod. However, no change in the (110) face of the rutile TiO₂ nanorod was detected after treatment.

Figure 8 shows

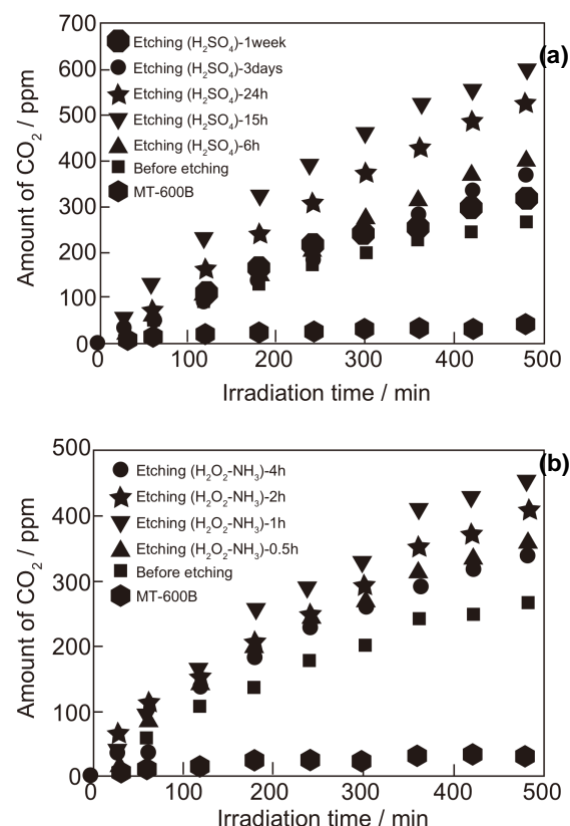


Figure 8. Time profiles of CO₂ evolution of toluene decomposition over TiO₂ particles prepared by treatment with (a) H₂O₂-NH₃ and (b) sulfuric acid at light intensity 30 mW cm⁻². The experimental conditions were: toluene 100 ppm, TiO₂ 10 mg

photocatalytic activity of chemically etched rutile TiO₂ nanorod for evolution of CO₂ as a result of degradation of toluene at light intensity of 30 mW cm⁻².

Figure 8a shows the time course of CO₂ evolution over the rutile TiO₂ nanorods before and after treatment with H₂O₂-NH₃ solution. The photocatalytic activities of the etched rutile TiO₂ nanorod for toluene degradation were higher than those before etching, suggesting that etching is effective for improving the reaction. Rutile TiO₂ nanorod etched for 1 h with H₂O₂-NH₃ solution showed the highest photocatalytic activity among the treatments of rutile TiO₂ nanorods samples despite similar surface areas. These results suggest that the balance between oxidation and reduction

sites or newly exposed crystal faces is an important for high photocatalytic activity in the H₂O₂-NH₃ etching method. The rate-determining step of the reaction is thought to be not reduction of oxygen by photoexcited electrons but oxidation of toluene by holes generated photocatalytically because toluene is difficult to oxidize. Therefore, it is thought that photocatalytic activity of a rutile TiO₂ nanorod increases with increase in the oxidation sites on the rutile TiO₂ nanorod.

Figure 8b shows CO₂ evolution in degradation of toluene over rutile TiO₂ nanorods before and after treatment with an H₂SO₄ solution as a function of irradiation time. Commercially available MT-600B TiO₂ having rutile phase was also used as a reference for comparison. The etched rutile TiO₂ nanorods with a higher percentage of (001) faces showed higher photocatalytic performance. Therefore, the new exposed crystal face, (001), was thought to play an important role in improvement of photocatalytic activity of rutile TiO₂ nanorods. We previously reported that the exposed crystal face, (001), showed stronger oxidation power than that of the (111) crystal face[29].

1.4 VISIBLE LIGHT RESPONSIBLE RUTILE TiO₂ NANOROD WITHOUT ETCHING TREATMENT MODIFIED SELECTIVELY WITH IRON(III) ION MODIFICATION OF EXPOSED CRYSTAL FACE

Trivalent iron(III) (Fe³⁺) ions were site-selectively modified on {111} exposed crystal faces of rutile TiO₂ nanorod without etching treatment by utilizing adsorption property of iron(III)/iron(II) (Fe³⁺/Fe²⁺) ion on TiO₂ surface. The rutile TiO₂ nanorods with site-selective modification of Fe³⁺ ion showed a remarkable high photocatalytic activity under visible-light irradiation because separation of redox sites, i.e., oxidation and reduction proceed over Fe³⁺ ion modified on {111} faces and bare TiO₂ surface on {110} faces, respectively. Double-beam photoacoustic spectroscopic analyses suggest that the high activity of the TiO₂ with site-selective modification of Fe³⁺ ion is attributed to not only an efficient electron injection from Fe³⁺ ion but also an efficient reduction by injected electron on {110} faces.

1.4.1 Experimental details for preparation and activity evaluation of Fe(III) modified rutile TiO₂ nanorod

Non-site-selective modification of Fe³⁺ ion on the entire surface of rutile TiO₂ nanorod is as follows. An aqueous suspension composed of rutile TiO₂ nanorod and an aqueous solution of Fe(NO₃)₃ was stirred under an aerated condition. After filtration, the residue was washed with deionized water several times until the ionic conductivity of the supernatant was <10 μS cm⁻² in order to achieve complete removal of NO₃⁻ ion, and then the particles were dried under reduced pressure.

Preparation procedure of site-selective modification of Fe³⁺ ions on specific exposed faces is as follows. An aqueous suspension composed of rutile TiO₂ nanorod and an aqueous solution of Fe(NO₃)₃ with and without ethanol was stirred under an aerated condition. The stirring was carried out under UV irradiation with a 500-W super-high-pressure mercury lamp, the light intensity of which was 1.0 mW cm⁻². The supernatant and residue was separated by filtration immediately after the stirring. The residue was washed with deionized water several times until the ionic conductivity of the supernatant was <10 μS cm⁻¹, and then the particles were dried under reduced pressure.

Photocatalytic activities of samples were evaluated by photocatalytic decomposition over acetaldehyde. The glass dish contained 100 mg samples was placed in a 125 cm³ Tedlar bag. Five hundred ppm of gaseous acetaldehyde was injected into the Tedlar bag, and photoirradiation was performed at room temperature after the acetaldehyde had reached adsorption equilibrium. The gaseous composition in the Tedlar bag was 79% of N₂, 21% of O₂, < 0.1 ppm of CO₂ and 500 ppm of acetaldehyde, and relative humidity was ca. 30%. A LED emitted light at a wavelength of ca. 455 nm (±15 nm) with an intensity of 1.0 mW cm⁻², was used for visible light irradiation. The concentrations of CH₃CHO and CO₂ were estimated by gas chromatography.

A gas-exchangeable photoacoustic (PA) cell equipped with two valves for gas flow was used, and a TiO₂ sample was placed in the cell. The atmosphere was controlled by a flow of nitrogen containing ethanol vapor (N₂ + EtOH) or artificial air containing ethanol vapor (air + EtOH), and the

measurements were conducted after shutting off the valves, i.e., in a closed system at room temperature. A LED emitting light at ca. 625 nm was used as a probe light, and the output intensity was modulated by a digital function generator at 80 Hz. In addition to the modulated light, a blue-LED (emitting light at ca. 470 nm, 8.1 mW cm⁻²) was also used as simultaneous continuous irradiation for photoexcitation. The PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier. Detailed setups of double-beam photoacoustic (DB-PA) spectroscopic measurements have been reported previously[31].

1.4.2 Results and discussion for visible light responsive rutile TiO₂ nanorod modified with Fe(III) ions

The rutile TiO₂ nanorod without etching treatment have been prepared according to our previous paper[22,29]. The rutile TiO₂ nanorods used in this paper have exposed crystal faces with {110} and {111}. The specific surface area of the bare rutile rod was 34 m² g⁻¹.

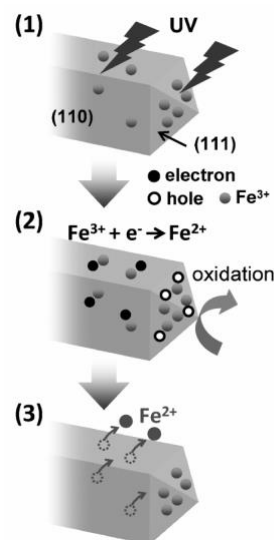
Table 1 shows summary of Fe³⁺-modified samples prepared by three kinds of Fe³⁺-modification method. Valence state of iron ion on TiO₂ particles

Table 1. Fe³⁺-modified TiO₂ prepared by different kinds of method and samples.

Name	Sample	Fe ³⁺ (init) / wt%	Fe ²⁺ (net) / wt%	preparation condition
D-004	rutile rod	0.04	0.04	dark
P-004	rutile rod	0.04	0.04	photo
D-01	rutile rod	0.10	0.10	dark
P-01	rutile rod	0.10	0.09	photo
PE-01	rutile rod	0.10	0.04	photo + EtOH
D-032	rutile rod	0.32	0.32	dark
P-032	rutile rod	0.32	0.22	photo
DMT	MT-600B	0.05	0.05	dark
PEMT	MT-600B	0.10	0.05	photo + EtOH

was confirmed to be trivalent state by XPS analyses. UV irradiation during Fe³⁺ modification decreased net amount of Fe³⁺ ion modified on the TiO₂ surface while almost of Fe³⁺ ion was adsorbed on the TiO₂ surface in dark. It is reported that Fe²⁺ ion hardly adsorb on TiO₂ surface compared to Fe³⁺ ion[32]. Therefore, Fe²⁺ ion produced as a result of reduction of Fe³⁺ ion by photoexcited electron in TiO₂ desorbed from TiO₂ surface into aqueous media. Addition of ethanol decreased net amount of modified Fe³⁺ ion because reduction of Fe³⁺ ion was accelerated due to an electron accumulation in TiO₂, which was induced by

efficient hole consumption. Our previous study suggested that reduction and oxidation on the rutile TiO₂ nanorod proceed predominantly on {110} and {111} exposed crystal faces, respectively[22]. Therefore, Fe³⁺ ions mainly are expected to adsorb on {111} faces under UV irradiation because Fe³⁺ ion on {110} faces desorbs due to reduction of Fe³⁺ to Fe²⁺ (Scheme 1).



Scheme 1. Site selective modification on the shape controlled rutile rod with {110} and {111} exposed crystal faces

Modification of Fe³⁺ ion induced color change from white to pale yellow as reported in previous study[19].

Figure 9 show UV-vis spectra of bare and Fe³⁺-modified TiO₂. In the wavelength region between 400-500 nm of DR spectra, a red shift of photoabsorption edge was observed. Photoabsorption was increased with an increase in the net amount of Fe³⁺ ion adsorbed on the rutile TiO₂ nanorod.

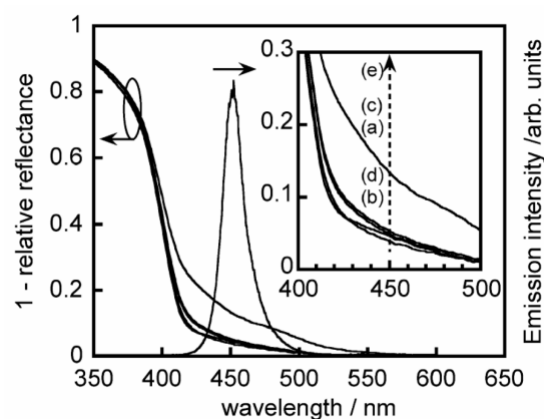


Figure 9. UV-vis spectra of (a) D-01, (b) P-01, (c) PE-01, (d) bare, and (e) D-032 and emission spectrum of LED used for photocatalytic evaluation.

Photocatalytic activity of Fe³⁺-modified TiO₂ for decomposition of acetaldehyde was evaluated under visible light irradiation. Figure 10 shows CO₂ evolution as a result of acetaldehyde degradation as a function of photoirradiation time under visible-light irradiation. Photocatalytic activity of Fe³⁺-modified TiO₂ was higher than bare TiO₂. This result indicates that Fe³⁺ ion modified on TiO₂ induce photocatalytic reaction under visible-light irradiation as follows[19];

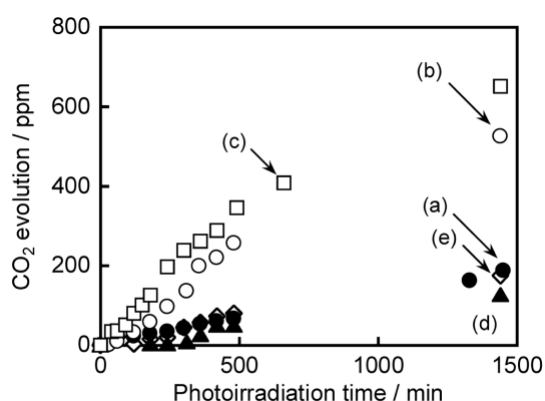


Figure 10. Time courses of CO₂ evolution for acetaldehyde decomposition over (a) D-01, (b) P-01, (c) PE-01, (d) bare TiO₂, and (e) N-TiO₂ under visible-light irradiation.

(1) photoexcited Fe³⁺ ions injected electrons into TiO₂ and became an oxidized state of Fe³⁺ (Fe⁴⁺), (2) injected electrons, which was trapped by Ti⁴⁺ in the bulk resulting in generation of Ti³⁺, migrated to the surface of TiO₂ and reduced oxygen species on TiO₂ surface and (3) the oxidized state of Fe³⁺ ions (Fe⁴⁺) oxidized acetaldehyde and go back to the initial state of metal ions (Fe³⁺). PE-01 and P-01 showed higher photocatalytic activity than nitrogen-doped TiO₂ (N-TiO₂; Sumitomo Chemical Co.), which is well-known as a conventional visible-light responsive TiO₂. Moreover, photocatalytic activity of Fe³⁺-modified TiO₂ showed dependence on its preparation method (PE-01 > P-01 > D-01). The plausible reason for difference of photocatalytic activity should be site selectivity of Fe³⁺ modification. In order to make clear it, following experiments were carried out.

Same modification method was applied to commercial rutile TiO₂, which has spherical shape without specific exposed crystal faces. Therefore, UV irradiation during Fe³⁺ modification is thought to induce no site-selective modification on the particle because redox reaction proceeds in the

neighboring sites without being separated. Figure 11 shows CO₂ evolution for decomposition of

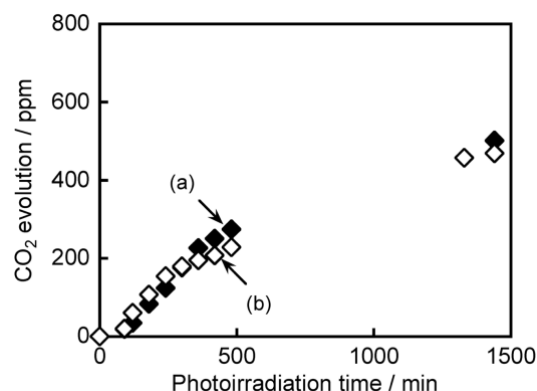


Figure 11. Time courses of CO₂ evolution for acetaldehyde decomposition over (a) DMT and (b) PEMT under visible-light irradiation.

acetaldehyde over Fe³⁺-modified commercial rutile TiO₂ under visible-light irradiation as a function of irradiation time. These two samples were prepared by different kind of modification method, but same net amount of Fe³⁺ ion was modified between these samples by adjusting initial amount of Fe³⁺. No difference of photocatalytic reaction was observed, regardless of the presence or absence of UV irradiation during Fe³⁺ modification. This indicates that the UV irradiation induced formation of same Fe³⁺ species for photocatalytic reaction as that prepared in dark. Therefore, the reason for high activity of P- and PE-samples is that UV irradiation during Fe³⁺ modification induces site-selective modification of Fe³⁺ ion. An excess amount of Fe³⁺ modification decreased photocatalytic activity even for P-samples because saturation limit of Fe³⁺ modification on {111} faces deteriorate site-selectively of Fe³⁺ modification, resulting in modification of Fe³⁺ ion on {110} faces. This indicates that modification on {110} faces decrease photocatalytic activity because an efficient reduction on {110} faces was retarded due to coverage of Fe³⁺ ion.

Behavior of injected electron in TiO₂ was observed by DB-PAS[31]. Figure 12 shows PA intensity for D-01, P-01, PE-01 and bare TiO₂ as a function of irradiation time under visible-light irradiation in the presence of N₂ + EtOH. PA intensity increased with visible-light irradiation because Ti⁴⁺ was reduced to Ti³⁺ by injected electrons from photoexcited Fe³⁺ ion. The saturation limit of PA intensity showed no

dependence on Fe^{3+} -modification method. This is reasonable result because photoabsorption of these samples was not so different from each other. This indicates that the plausible factor may

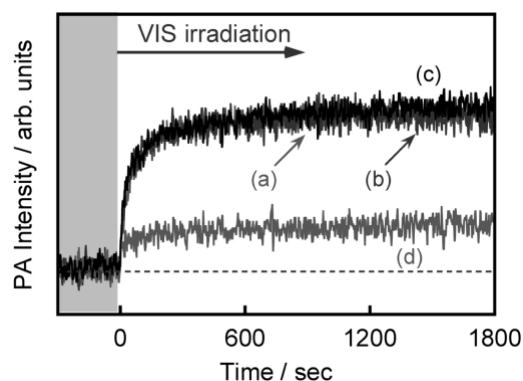


Figure 11. Time-course curves of PA signals of (a) D-01, (b) P-01, (c) PE-01, and (d) bare TiO_2 under visible-light irradiation in the presence of $\text{N}_2 +$

be efficiency of reduction on rutile TiO_2 nanorod modified with Fe^{3+} by injected electron.

DB-PA measurements in the presence of oxygen were also carried out in order to estimate efficiency of reduction by injected electron. Figure 12 shows time-course curve of PA intensity for D-01, P-01, PE-01 and bare TiO_2 under visible-light irradiation in the presence of air + EtOH. PA intensity attributed to Ti^{3+} formation was largely decreased because an electron accumulation was suppressed due to electron consumption by oxygen species on TiO_2 surface. Steady-state value of PA intensity showed dependence on modification method (D-01 > P-01 > PE-01). This suggests that reduction efficiently proceed on surface of P-01 and PE-01

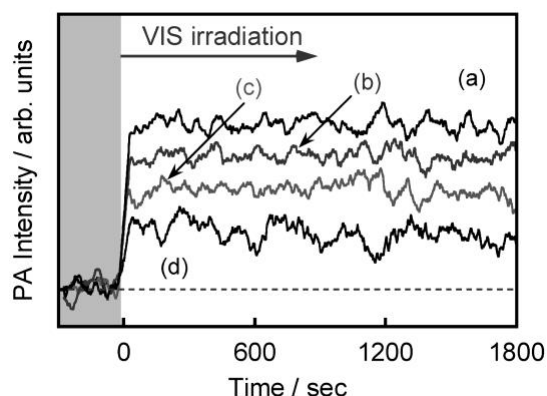


Figure 12. Time-course curves of PA signals with 50 points smoothing of (a) D-01, (b) P-01, (c) PE-01, and (d) bare TiO_2 under visible-light irradiation in

than that of D-01 because an efficient reduction of oxygen on {110} faces proceeded without retardation by site-selective coverage of Fe^{3+} ion on {111} face. The injected electron in the rutile TiO_2 nanorod site-selective modification of Fe^{3+} ions is thought to be prevented from being trapped by oxidized Fe^{3+} (Fe^{4+}) because the injected electrons should be efficiently consumed on {110} faces.

1.5 CONCLUSION

We have demonstrated that the morphology of rutile TiO_2 particles can be controlled by means of hydrothermal process and chemical etching treatment. The each exposed crystal surfaces of rutile nanorod shows the different activity such as oxidation and reduction, respectively resulting in improvement of charge separation. The photocatalytic activity of rutile TiO_2 nanorod shows higher activity than that of commercially available anatase TiO_2 fine particles in Japan.

The etched rutile TiO_2 nanorods showed higher photocatalytic activities than that of rutile TiO_2 nanorod without the etching treatment due to new exposed crystal faces. It was found that the photocatalytic activity depends on not surface area but surface structure of the TiO_2 nanorods, suggesting that electron-hole pair recombination plays an important role during the photodegradation of organic compounds.

UV irradiation during Fe^{3+} -modification on shape-controlled rutile TiO_2 nanorod showed high photocatalytic activity under visible-light irradiation because Fe^{3+} ion was site-selectively modified on {111} exposed crystal faces and redox reactions were spatially separated. DB-PA analyses indicate that photocatalytic activity was determined by not efficiency of electron injection but efficiency of reduction by injected electron. The efficiency of reduction was influenced by site-selectivity of Fe^{3+} -modification on {111} faces because Fe^{3+} ion on {110} faces retard an efficient reduction on bare TiO_2 surface.

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