

Development of a visible-light-responsive rutile rod by site-selective modification of iron(III) ion on {1 1 1} exposed crystal faces

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Abstract

Trivalent iron(III) ( $\text{Fe}^{3+}$ ) ions were site-selectively modified on {111} exposed crystal faces of shape-controlled rutile titanium(IV) oxide ( $\text{TiO}_2$ ) by utilizing adsorption property of iron(III)/iron(II) ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) ion. The rutile  $\text{TiO}_2$  with site-selective modification of  $\text{Fe}^{3+}$  ion showed high photocatalytic activity under visible-light irradiation as a result of separation of redox sites, i.e., oxidation and reduction proceed over  $\text{Fe}^{3+}$  ion modified on {111} faces and bare  $\text{TiO}_2$  surface on {110} faces, respectively. Double-beam photoacoustic spectroscopic analyses suggest that the high activity of the  $\text{TiO}_2$  with site-selective modification of  $\text{Fe}^{3+}$  ion is attributed to not an efficient electron injection from  $\text{Fe}^{3+}$  ion but an efficient reduction by injected electron on {110} faces.

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## 1. Introduction

Environmental purification with a utilization of self-cleaning effect on a semiconductor photocatalyst has attracted much attention [1,2]. Among various kinds of semiconductor photocatalyst, titanium(IV) oxide ( $\text{TiO}_2$ ) is most suitable photocatalyst for an application of environmental purification in the view point of chemical stability, availability and no toxic properties. However, only fault of  $\text{TiO}_2$  photocatalyst is inactive under visible-light irradiation because of its wide bandgap energy (3.0 eV for rutile and 3.2eV for anatase), i.e., ultraviolet (UV) light, the amount of which corresponds to only few percentage of total solar energy, is essential for photocatalytic reaction over  $\text{TiO}_2$  photocatalyst.

So many intensive efforts to improve the visible-light responsibility of  $\text{TiO}_2$  photocatalyst involving impurity doping have been made in the last few decades [3-8]. However, impurity doping sometimes increase defects in  $\text{TiO}_2$ , which also work as recombination center and result in decrease of photocatalytic activity [9,10]. Recently, some visible-light responsive  $\text{TiO}_2$  photocatalyst were developed by modification of metal surface complex which works as a sensitizer for a visible light [11-15]. This method has large advantages in simple preparation method and no introduction of defects in  $\text{TiO}_2$ . In our previous study, the method was applied to titania nanotube, and metal ion was site-selectively modified outside/inside surface of titania nanotube for separation of photocatalytic redox sites [16]. Although its tubular structure enabled site-selective modification of metal ion, diffusion-controlled reaction was inevitable on the inside surface of TNT. 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  $\text{TiO}_2$  particles.

A utilization of shape-controlled particles with specific exposed crystal faces may be another plausible method for site-selective modification in specific site. It is well known that physical and chemical properties of semiconductor particles strongly depend on exposed crystal faces [17-19]. For example, certain chemical compounds work as shape-control reagent during nucleation process by preferential adsorption on specific crystal faces [20]. Therefore, site-selective modification of metal ion on shape-controlled nanocrystal may be possible by preferential adsorption properties

depending on crystal surface. Our studies suggest that redox reaction proceed preferentially on specific exposed crystal faces of TiO<sub>2</sub>, i.e., reduction on {110} and oxidation on {111} for rutile, reduction on {011} and oxidation on {001} for anatase [21-23]. This kind of preferential reaction induces site-selective deposition of metal or metal oxide on the specific exposed crystal faces under photoexcitation [21-25].

In the present study, we modified iron(III) (Fe<sup>3+</sup>) ion on shape-controlled rutile TiO<sub>2</sub> with specific exposed crystal faces. In our previous report, modification of Fe<sup>3+</sup> ion on rutile TiO<sub>2</sub> largely improved photocatalytic reaction under visible-light irradiation by working as a sensitizer for visible light. Moreover, characteristic adsorption properties of Fe<sup>3+</sup>/Fe<sup>2+</sup> ion on TiO<sub>2</sub>, which is strongly depended on valence states of iron ion, induced site-selective adsorption on the specific exposed crystal faces on the rutile TiO<sub>2</sub> particle.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. Preparation of rutile rod

50 dm<sup>3</sup> of aqueous titanium(III) chloride solution (0.15 mol dm<sup>-3</sup>) containing sodium chloride (5 mol dm<sup>-3</sup>) in a Teflon bottle was stirred for 1 h, and then the bottle sealed with a stainless jacket was heated at 200 °C for 6 h in an oven. After the hydrothermal treatment, the residue in the Teflon bottle was washed with Milli-Q water several times until ionic conductivity was <10 μS cm<sup>-1</sup>. The particles were dried under reduced pressure. In the present study, commercial rutile TiO<sub>2</sub> (TAYCA, MT-600B) with 27 m<sup>2</sup> g<sup>-1</sup> of specific surface area was used as a reference sample.

#### 2.1.2. Non-site-selective modification of Fe<sup>3+</sup> ion on the entire surface

An aqueous suspension composed of samples and an aqueous solution of iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>) was stirred for 6 h under an aerated condition. After stirring, the supernatant and residue was separated by filtration, and the residue was washed with deionized water several times until the ionic conductivity of the supernatant was <10 μS cm<sup>-2</sup> in order to remove NO<sub>3</sub><sup>-</sup> ion, and

then the particles were dried under reduced pressure.

### 2.1.3. Site-selective modification of Fe<sup>3+</sup> ions on specific exposed faces

An aqueous suspension composed of samples and an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> with and without ethanol was stirred for 6 h under an aerated condition. The stirring was carried out under UV irradiation with a 500-W super-high-pressure mercury lamp (Ushio, SX-UI501UO), the light intensity of which was 1.0 mW cm<sup>-2</sup>. The supernatant and residue was separated by filtration immediately after 6 h of the stirring. The residue was washed with deionized water several times until the ionic conductivity of the supernatant was <10 μS cm<sup>-1</sup>, and then the particles were dried under reduced pressure.

## 2.2. Characterization

The crystal structures of the powders were confirmed by using an X-ray diffractometer (Rigaku, MiniFlex II) with Cu Kα radiation ( $\lambda = 1.5405 \text{ \AA}$ ). The diffuse reflectance (DR) spectra were measured using a UV-VIS spectrophotometer (Shimadzu, UV-2500PC) equipped with an integrating sphere unit (Shimadzu, ISR-240A). The specific surface areas of the particles were determined with a surface area analyzer (Quantachrome, Nova 4200e) by using the Brunauer-Emmett-Teller equation. The morphology of prepared TiO<sub>2</sub> particles was observed by using transmission electron microscopy (TEM; Hitachi, H-9000NAR) and scanning electron microscopy (SEM; JEOL, JSM-6701FONO). The net amount of Fe<sup>3+</sup> ions on the TiO<sub>2</sub> surface was estimated by analysis of filtrate with inductively coupled plasma optical emission spectroscopy (ICP-OES; Shimadzu, ICPS-8000). X-ray photoelectron spectra (XPS) of the TiO<sub>2</sub> particles were measured using a photoelectron spectrometer (JEOL, JPS90SX) with an Mg Kα source (1253.6 eV). The shift of binding energy was corrected using the C 1s level at 284.6 eV as an internal standard.

### 2.3. Photocatalytic decomposition of acetaldehyde

Photocatalytic activities of samples were evaluated by photocatalytic decomposition over

acetaldehyde. One hundred milligrams of powder, which has a complete extinction of the incident radiation, was spread on a glass dish, and the glass dish was placed in a 125 cm<sup>3</sup> Tedlar bag (AS ONE Co. Ltd.). Five hundred parts per million 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 N<sub>2</sub>, 21% of O<sub>2</sub>, < 0.1 ppm of CO<sub>2</sub> and 500 ppm of acetaldehyde, and relative humidity was ca. 30%. A light emitting diode (LED; Lumileds, Luxeon LXHL-NRR8), which emitted light at a wavelength of ca. 455 nm with an intensity of 1.0 mW cm<sup>-2</sup>, was used for visible light irradiation. The emission spectrum of the LED is shown in figure 1. The concentrations of acetaldehyde and carbon dioxide (CO<sub>2</sub>) were estimated by gas chromatography (Shimadzu, GC-8A, FID detector) with a PEG-20 M 20% Celite 545 packed glass column and gas chromatography (Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and a methanizer (GL Sciences, MT-221), respectively.

#### 2.4. Double-beam photoacoustic spectroscopic measurement

A gas-exchangeable photoacoustic (PA) cell equipped with two valves for gas flow was used, and a TiO<sub>2</sub> sample was placed in the cell. The atmosphere was controlled by a flow of nitrogen containing ethanol vapor (N<sub>2</sub> + 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 (Lumileds, Luxeon LXHL-ND98) was used as a probe light, and the output intensity was modulated by a digital function generator (NF, DF1905) at 80 Hz. In addition to the modulated light, a blue-LED (Lumileds, Luxeon LXHL-NB98, emitting light at ca. 470 nm, 8.1 mW cm<sup>-2</sup>) 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 (NF, LI5640). Detailed setups of double-beam photoacoustic (DB-PA) spectroscopic measurements have been reported previously [26].

### 3. Results and discussion

#### 3.1. Physical and chemical properties of bare and Fe<sup>3+</sup>-modified TiO<sub>2</sub> samples

The crystal structure of sample prepared by hydrothermal treatment of titanium(III) chloride solution in the presence of sodium chloride was attributed to rutile TiO<sub>2</sub> without other crystal phases from XRD pattern. Moreover, SEM, TEM and electron diffraction analyses indicate that prepared TiO<sub>2</sub> has rod shape with {110} and {111} exposed crystal faces. The specific surface area of the bare rutile rod was 34 m<sup>2</sup> g<sup>-1</sup>. These results coincident with the reported studies [23,27,28].

Table 1 shows summary of Fe<sup>3+</sup>-modified samples prepared by three kinds of Fe<sup>3+</sup>-modification method. Valence state of iron ion on TiO<sub>2</sub> particles was confirmed to be trivalent state by XPS analyses. UV irradiation during Fe<sup>3+</sup> modification decreased net amount of Fe<sup>3+</sup> ion modified on the TiO<sub>2</sub> surface while almost of Fe<sup>3+</sup> ion was modified on the TiO<sub>2</sub> surface in dark. It is reported that Fe<sup>2+</sup> ion hardly adsorb on TiO<sub>2</sub> surface compared to Fe<sup>3+</sup> ion [29]. Therefore, it is thought that Fe<sup>2+</sup> ion was produced as a result of reduction of Fe<sup>3+</sup> ion by photoexcited electron in TiO<sub>2</sub> and then produced Fe<sup>2+</sup> ion desorbed from TiO<sub>2</sub> surface. Addition of ethanol decreased net amount of modified Fe<sup>3+</sup> ion because reduction of Fe<sup>3+</sup> ion was accelerated due to an electron accumulation in TiO<sub>2</sub>, which was induced by efficient hole consumption.

Our previous study suggested that reduction and oxidation on the rutile rod proceed predominantly on {110} and {111} exposed crystal faces, respectively [23]. Therefore, Fe<sup>3+</sup> ions mainly are expected to adsorb on {111} faces under UV irradiation because Fe<sup>3+</sup> ion on {110} faces desorbs due to reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> (Scheme 1). Produced Fe<sup>2+</sup> ion is thought to be recovered to Fe<sup>3+</sup> ion as a result of reoxidation by oxygen and/or positive holes on {111} faces [30]. Actually, further decrease of net amount of modified Fe<sup>3+</sup> ion was observed in same modification method under deaerated condition.

Modification of Fe<sup>3+</sup> ion induced color change from white to pale yellow as reported in previous study [15]. Figure 1 show UV-vis spectra of bare and Fe<sup>3+</sup>-modified TiO<sub>2</sub>. In the wavelength region between 400-500 nm of DR spectra, an upward shift of photoabsorption was observed.

Photoabsorption was increased with an increase of net amount of  $\text{Fe}^{3+}$  ion in the  $\text{TiO}_2$  prepared by same modification method. However, increase of photoabsorption disagreed with net amount of modified  $\text{Fe}^{3+}$  ion among D-01, P-01 and PE-01. This indicate that not only amount of  $\text{Fe}^{3+}$  ion but also modification method have an influence in photoabsorption of  $\text{Fe}^{3+}$ .

### 3.2. Photocatalytic activity for decomposition of acetaldehyde under visible light irradiation

Figure 2 shows time course of  $\text{CO}_2$  evolution for decomposition of acetaldehyde under visible-light irradiation. Photocatalytic activity of  $\text{Fe}^{3+}$ -modified  $\text{TiO}_2$  was higher than bare  $\text{TiO}_2$ . This indicate that  $\text{Fe}^{3+}$  ion modified on  $\text{TiO}_2$  induce photocatalytic reaction under visible-light irradiation as follows [15]; (1) photoexcited  $\text{Fe}^{3+}$  ions injected electrons into  $\text{TiO}_2$  and became an oxidized state of  $\text{Fe}^{3+}$  ( $\text{Fe}^{4+}$ ), (2) injected electrons migrated in the bulk and reduced oxygen species on  $\text{TiO}_2$  surface and (3) the oxidized state of  $\text{Fe}^{3+}$  ions ( $\text{Fe}^{4+}$ ) oxidized acetaldehyde and go back to the initial state of metal ions ( $\text{Fe}^{3+}$ ). PE-01 and P-01 showed higher photocatalytic activity than nitrogen-doped  $\text{TiO}_2$  (N- $\text{TiO}_2$ ; Sumitomo Chemical Co.), which is well-known as a conventional visible-light responsive  $\text{TiO}_2$ . Moreover, photocatalytic activity of  $\text{Fe}^{3+}$ -modified  $\text{TiO}_2$  showed dependence on its preparation method (PE-01 > P-01 > D-01). There are three plausible reasons for difference of photocatalytic activity; (1) net amount of  $\text{Fe}^{3+}$  modified on  $\text{TiO}_2$ , (2) structure of  $\text{Fe}^{3+}$  species depending on modification condition and (3) site selectivity of  $\text{Fe}^{3+}$  modification. In order to make clear it, following experiments were carried out.

Figure 3 shows dependence of net amount of  $\text{Fe}^{3+}$  ion modified on photocatalytic activity ( $\text{CO}_2$  evolution at 240 min of photoirradiation). Photocatalytic activity was increased by small amount of  $\text{Fe}^{3+}$  modification because of increase of visible-light photoabsorption. On the other hand, an excess amount of  $\text{Fe}^{3+}$  modification decreased photocatalytic activity presumably due to decrease of reduction sites by coverage of  $\text{TiO}_2$  surface and/or formation of inactive aggregated  $\text{Fe}^{3+}$  species. Therefore, increase of photocatalytic activity of  $\text{Fe}^{3+}$ -modified rutile nanorod prepared by UV irradiation might be attributable to the removal of an excess amount of  $\text{Fe}^{3+}$  because UV irradiation decreased net amount of  $\text{Fe}^{3+}$  ion as indicated in table 1. However, the hypothesis is denied by a

different dependence of photocatalytic activity on net amount of  $\text{Fe}^{3+}$  ion of non-site-selective  $\text{Fe}^{3+}$  modified rutile nanorod as indicated in figure 3. Thus, high photocatalytic activity of  $\text{Fe}^{3+}$ -modified rutile nanorod prepared by UV-irradiation was not attributed to removal of excess amount of  $\text{Fe}^{3+}$  ion.

Same modification method was applied to commercial rutile  $\text{TiO}_2$ , which has spherical shape without specific exposed crystal faces. Therefore, UV irradiation during  $\text{Fe}^{3+}$  modification is thought to induce no site-selective modification on the particle because redox reaction proceeds in the neighboring sites without being separated. Figure 4 shows time course of  $\text{CO}_2$  evolution for decomposition of acetaldehyde over  $\text{Fe}^{3+}$ -modified commercial rutile under visible-light irradiation. These two samples were prepared by different kind of modification method, but same net amount of  $\text{Fe}^{3+}$  ion was modified between these samples by adjusting initial amount of  $\text{Fe}^{3+}$ . A large difference of photocatalytic reaction was not observed, regardless of the presence or absence of UV irradiation during  $\text{Fe}^{3+}$  modification. This indicate that the UV irradiation induced formation of same  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  modification induces site-selective modification of  $\text{Fe}^{3+}$  ion.

An excess amount of  $\text{Fe}^{3+}$  modification decreased photocatalytic activity even for P-samples because saturation limit of  $\text{Fe}^{3+}$  modification on  $\{111\}$  faces deteriorate site-selectively of  $\text{Fe}^{3+}$  modification, resulting in modification of  $\text{Fe}^{3+}$  ion on  $\{110\}$  faces. Moreover, D-samples show lower photocatalytic activity than DMT (Fig. 2 and Fig. 4). This indicate that modification on  $\{110\}$  faces decrease photocatalytic activity because an efficient reduction on  $\{110\}$  faces was retarded due to coverage of  $\text{Fe}^{3+}$  ion.

### 3.3. PA spectroscopic detection of electron behavior under visible-light irradiation

Behavior of injected electron in  $\text{TiO}_2$  was observed by DB-PAS [26]. Figure 5 shows time-course curve of PA intensity for D-01, P-01, PE-01 and bare  $\text{TiO}_2$  under visible-light irradiation in the presence of  $\text{N}_2 + \text{EtOH}$ . PA intensity increased with visible-light irradiation



because  $\text{Ti}^{4+}$  was reduced to  $\text{Ti}^{3+}$  by injected electrons from photoexcited  $\text{Fe}^{3+}$  ion. Thus, increase of PA intensity is attributed to amount of injected electrons. The saturation limit of PA intensity showed no dependence on  $\text{Fe}^{3+}$ -modification method. This is reasonable results because photoabsorption of these samples was not so different from each other. This indicate that the main factor of high photocatalytic activity was not oxidation on oxidized  $\text{Fe}^{3+}$  ( $\text{Fe}^{4+}$ ) generated by electron injection from  $\text{Fe}^{3+}$  ion into  $\text{TiO}_2$ . Another plausible factor may be efficiency of reduction on rutile  $\text{TiO}_2$  nanorod modified with  $\text{Fe}^{3+}$  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 6 shows time-course curve of PA intensity for D-01, P-01, PE-01 and bare  $\text{TiO}_2$  under visible-light irradiation in the presence of air + EtOH. PA intensity attributed to  $\text{Ti}^{3+}$  formation was largely decreased because an electron accumulation was retarded due to electron consumption by oxygen species on  $\text{TiO}_2$  surface. Steady-state value of PA intensity showed dependence on modification method ( $\text{D-01} > \text{P-01} > \text{PE-01}$ ), and site selectivity of  $\text{Fe}^{3+}$  modification induced smaller PA intensity. This suggests that reduction efficiently proceed on surface of P-01 and PE-01 than that of D-01 because an efficient reduction of oxygen on  $\{110\}$  faces proceeded without retardation by coverage of  $\text{Fe}^{3+}$  ion. The injected electron in the rutile nanorod is thought to be prevented from being trapped by oxidized  $\text{Fe}^{3+}$  ( $\text{Fe}^{4+}$ ) because the injected electrons should be efficiently consumed on  $\{111\}$  faces.

#### 4. Conclusion

UV irradiation during  $\text{Fe}^{3+}$ -modification on shape-controlled rutile  $\text{TiO}_2$  induced high photocatalytic activity under visible-light irradiation because  $\text{Fe}^{3+}$  ion was site-selectively modified on  $\{111\}$  exposed crystal faces and redox reactions were spatially separated. On the other hand, photocatalytic activity of non-site-selectively modified  $\text{TiO}_2$  showed low activity. 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  $\text{Fe}^{3+}$ -modification on  $\{111\}$  faces because  $\text{Fe}^{3+}$  ion on  $\{110\}$  faces retard an

efficient reduction on bare TiO<sub>2</sub> surface.

### Acknowledgements

This work was supported by a grant of Knowledge Cluster Initiative implemented by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the New Energy and Industrial Technology Development Organization (NEDO).

Table 1. Fe<sup>3+</sup>-modified TiO<sub>2</sub> prepared by different kinds of method and samples.

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

Figure 1. 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.

Figure 2. Time courses of CO<sub>2</sub> evolution of acetaldehyde decomposition over (a) D-01, (b) P-01, (c) PE-01, (d) bare, and (e) N-TiO<sub>2</sub> under visible-light irradiation.

Figure 3. CO<sub>2</sub> evolution at 240 min of photoirradiation for photocatalytic decomposition over (a) D-samples, (b) P-samples, and (c) PE-01 as a function of net amount of Fe<sup>3+</sup> ion.

Figure 4. Time courses of CO<sub>2</sub> evolution of acetaldehyde decomposition over (a) DMT and (b) PEMT under visible-light irradiation.

Figure 5. Time-course curves of PA signals of (a) D-01, (b) P-01, (c) PE-01, and (d) bare under visible light irradiation in the presence of N<sub>2</sub> + EtOH.

Figure 6. Time-course curves of PA signals of (a) D-01, (b) P-01, (c) PE-01, and (d) bare under visible light irradiation in the presence of air + EtOH.

Figure 6. Time-course curves of PA signals with 50 points smoothing of (a) D-01, (b) P-01, (c) PE-01, and (d) bare under visible light irradiation in the presence of air + EtOH.

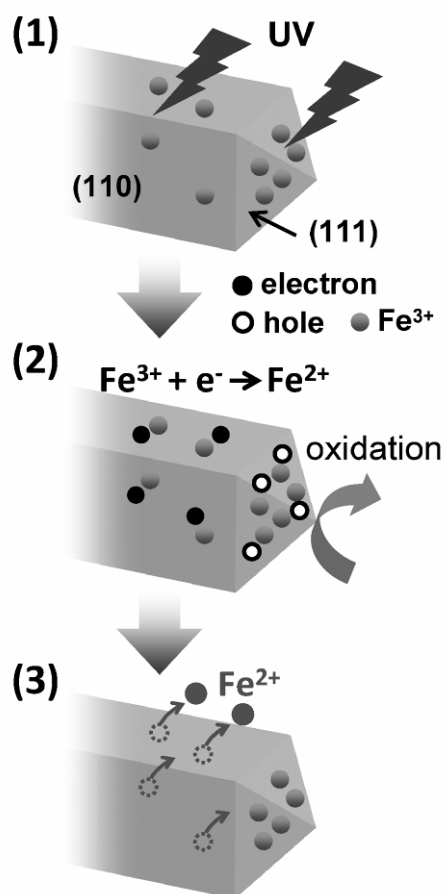
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Table 1. Fe<sup>3+</sup>-modified TiO<sub>2</sub> prepared by different kinds of method and samples.

Name	Sample	Fe <sup>3+</sup> (init) / wt%	Fe <sup>3+</sup> (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



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

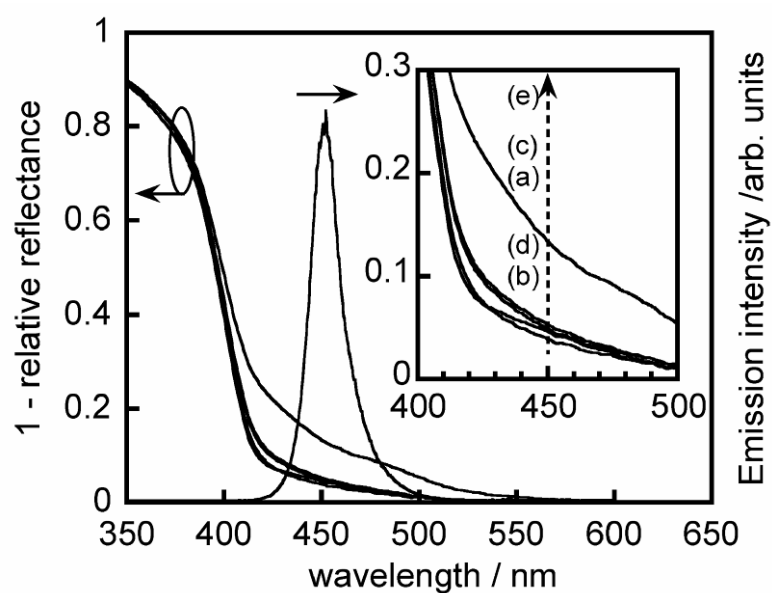


Figure 1. UV-vis spectra of (a) D-01, (b) P-01, (c) PE-01, (d) bare, and (e) D-032 and emission spectrum of LED used for photocatalytic evaluation.

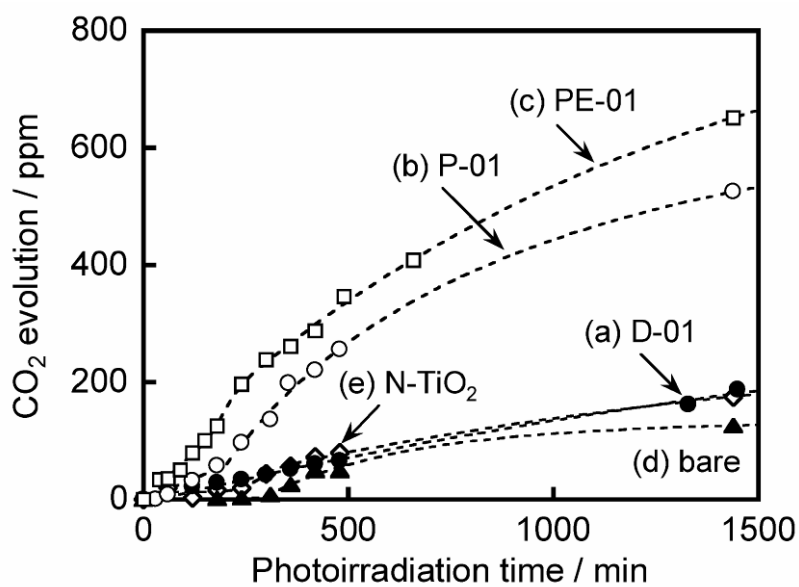


Figure 2. Time courses of CO<sub>2</sub> evolution of acetaldehyde decomposition over (a) D-01, (b) P-01, (c) PE-01, (d) bare, and (e) N-TiO<sub>2</sub> under visible-light irradiation.

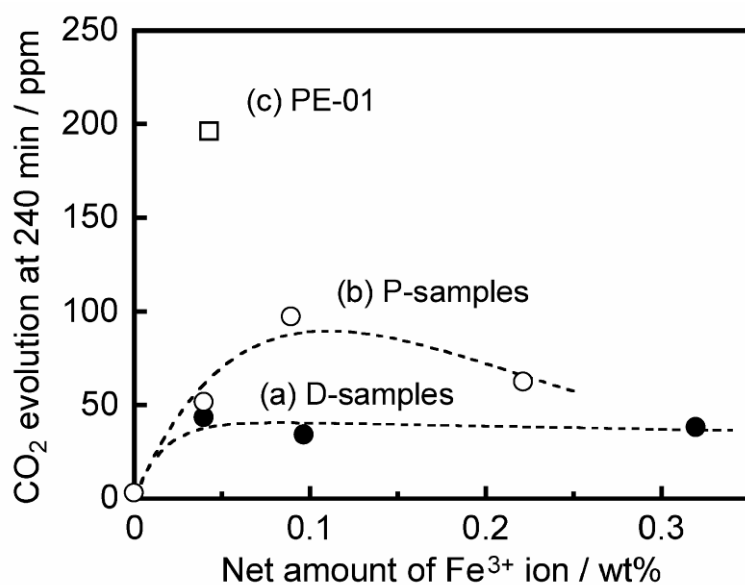


Figure 3. CO<sub>2</sub> evolution at 240 min of photoirradiation for photocatalytic decomposition over (a) D-samples, (b) P-samples, (c) PE-01 as a function of net amount of Fe<sup>3+</sup> ion.

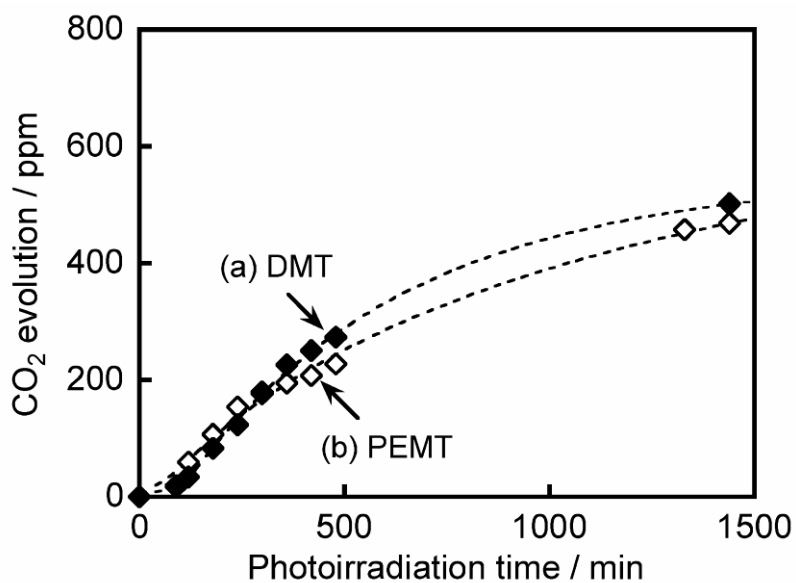


Figure 4. Time courses of CO<sub>2</sub> evolution of acetaldehyde decomposition over (a) DMT and (b) PEMT under visible-light irradiation.

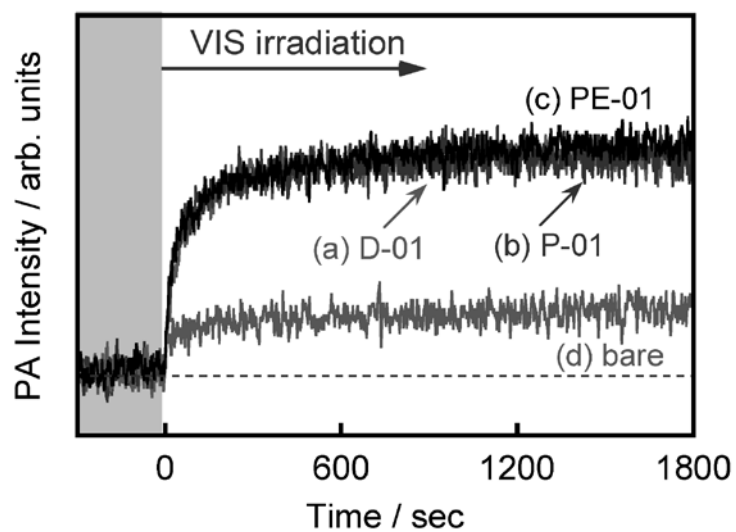


Figure 5. Time-course curves of PA signals of (a) D-01, (b) P-01, (c) PE-01, (d) bare under visible light irradiation in the presence of  $N_2 + EtOH$ .

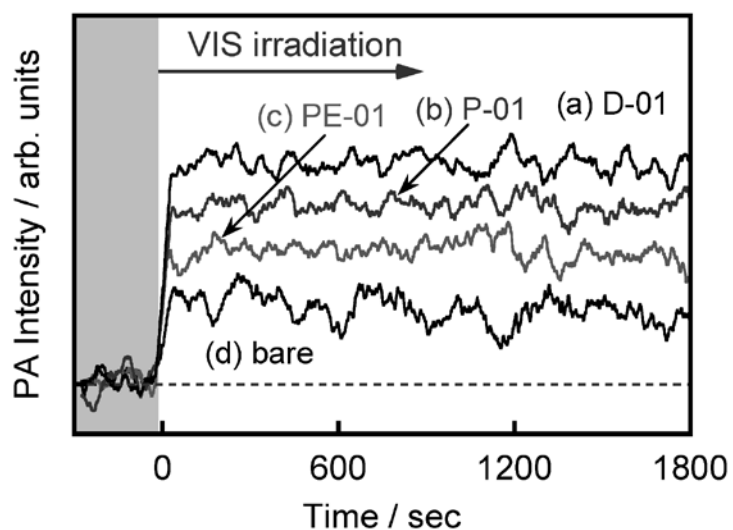


Figure 6. Time-course curves of PA signals with 50 points smoothing of (a) D-01, (b) P-01, (c) PE-01, (d) bare under visible light irradiation in the presence of  $air + EtOH$ .