

TiO₂-Photocatalyzed Epoxidation of 1-Decene by H₂O₂ under Visible Light

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1-Decene was converted to 1,2-epoxydecane on UV-irradiated TiO₂ powder using molecular oxygen as the oxygen source. Other main products were nonanal and 2-decanone. For anatase-form TiO₂ powders, the reaction rate was hardly affected by addition of hydrogen peroxide to the solution. In contrast, for rutile-form TiO₂ powders, the rate of epoxide generation was significantly increased by addition of hydrogen peroxide. In this case, the reaction occurred under visible light as well as UV light. The selectivity of the production of 1,2-epoxydecane was higher under visible light than under UV light. The conversion efficiency of an incident photon to 1,2-epoxydecane was about 2% when irradiated with visible light in a range 440 - 480 nm. UV-Vis diffuse reflection spectroscopy, FT-IR spectroscopy, and X-ray photoelectron spectroscopy suggested the generation of a Ti-η²-peroxide on rutile TiO₂ surface after treatment with hydrogen peroxide. The initial step of the reaction under visible light was attributed to a photochemical reaction of this peroxide with 1,2-epoxydecane.

Key Words: titanium dioxide; epoxide; hydrogen peroxide; visible light

INTRODUCTION

Semiconductor photocatalysts have attracted attention because of their possible applications in treatment of wastes and pollutants. As a result of these photocatalytic reactions, organic compounds are usually mineralized.¹⁻⁴ Under some conditions, it is also possible to partially oxidize organic compounds using semiconductor photocatalysts, such as TiO_2 ⁵⁻¹¹, ZnS ,¹² and CdS .¹³ The partial oxidation is important from the viewpoint of organic synthesis. We have reported that olefins, such as 1-decene and 2-hexene, are converted to the corresponding epoxides on UV-irradiated TiO_2 particles.^{6,7} Kanno *et al.*¹⁴ and Fox *et al.*^{15,16} have also reported generation of epoxides from olefins, especially from aromatic olefins using TiO_2 particles. However, in most of their results, the main products were not epoxides, but carbonyl compounds.¹⁴⁻¹⁶

We succeeded in increasing the efficiency for the epoxidation of linear olefins by selecting appropriate TiO_2 powders and optimizing experimental conditions.^{6,7} However, the efficiency is still not high enough for practical applications. In addition,

the effective light for the reactions is limited to the UV region as long as TiO_2 is used as the photocatalyst. Further increase of the reaction efficiency and expansion of the effective wavelength region are the keys to the practical application of photocatalytic reactions.

In order to enhance the photocatalytic reactions for mineralization of organic compounds, it has been reported that addition of hydrogen peroxide is effective.^{17,18} In this paper, we report that the epoxidation of 1-decene is also enhanced by addition of hydrogen peroxide. Furthermore, we found that the reaction occurs even under irradiation with visible light, if rutile TiO_2 particles are used as the photocatalyst in the presence of hydrogen peroxide.

EXPERIMENTAL

Materials.

Various kinds of titanium dioxide (TiO_2) powders having anatase and rutile

crystal structures were obtained from Catalysis Society of Japan (JRC-TIO-3 and -5), Ishihara Sangyo Co. (ST-01, PT-101), and Toho Titanium Co. (NS-51). The content of the rutile phase and the relative surface area of these powders are as follows: JRC-TIO-3, 99.0%, 42.5 m²/g; JRC-TIO-5, 90.7%, 2.2 m²/g; ST-01, 0.1%, 192.5 m²/g; PT-101, 99.9%, 25.0 m²/g; NS-51, 98.6%, 6.5 m²/g. 1-Decene, 2-decanone, nonanal, butyronitrile, and acetonitrile were purchased from Wako Pure Chemical Industries Co. 1,2-Epoxyhexadecane and titanium tetrachloride were purchased from Tokyo Kasei Co. They were all guaranteed-grade reagents and used without further purification.

Peroxotitanic acid was prepared according to the procedures described in literature.¹⁹ Titanium peroxide was obtained as fine yellow powder by completely evaporating the peroxotitanic acid solution under reduced pressure at 90°C.

Photocatalytic reaction of 1-decene on TiO₂ powder.

Photocatalytic reactions were carried out in Pyrex glass tubes (ϕ 10 mm), which contained TiO₂ powder (200 mg), water (0.2 g), acetonitrile (1.8 g), butyronitrile (1.5 g), and 1-decene (0.5 g). In order to study the effect of hydrogen peroxide, 30%

hydrogen peroxide (0.2 g) was added to the glass tubes instead of water. The TiO_2 powder was suspended in the solution using a magnetic stirrer. The suspension was photoirradiated using a 500 W Xe lamp (Wacom R&D, XDS-501I), which emits both UV and Vis light over a wide wavelength. To limit the irradiation wavelength, the light beam was passed through a UV-34, L-42, or Y-44 filter (Kenko Co.) to cut-off wavelengths shorter than 340, 420, or 440 nm, respectively. Products were analyzed by a Shimadzu GC-8A gas-liquid chromatography. The products were identified by coinjecting authentic samples. Details of the analysis have been described previously.^{6,7} For determination of the conversion efficiency of an incident photon to the reaction products, the suspensions were irradiated using band pass filters (Kenko Co.) which select the irradiation wavelength in a region from 440 to 480 nm. The power of incident light was determined using a thermopile (Eppley Laboratory), and the number of incident photons was estimated by assuming that the average wavelength of incident light was 460 nm.

Deposition of TiO_2 films by RF sputtering.

TiO₂ films were deposited on p-type Si(100) wafers in a planar RF sputtering apparatus using a titanium disk (99.5%, 80 mm in diameter) as the target. The target-substrate spacing was 25 mm, and the applied RF power was 140-170 W. We used pure O₂ or a mixture of Ar and O₂ as the sputtering gas. The thickness of the TiO₂ film was about 550 nm. Pure rutile films were obtained by heating the deposited TiO₂ films at 800°C for 2 h.

XRD, FT-IR, and XPS measurements

The contents of anatase and rutile phases in the powders and films were determined by X-ray diffraction (XRD) using a Philips X'Pert-MRD X-ray diffraction meter with a CuK α source. The absorption and diffuse reflection spectra were measured using a Shimadzu UV-2500PC spectrophotometer. Fourier-transform infrared (FT-IR) spectra of TiO₂ thin films deposited on Si wafers were obtained using a Nicolet Nexus 370S FT-IR spectrometer with a Harrick-type ATR unit. The FT-IR spectra were measured by internally multi-reflecting the IR beams in 20 mm-long Si substrates. X-ray photoelectron spectra (XPS) of single-crystalline TiO₂ (001) samples

were measured using a Shimadzu ESCA1000 photoelectron spectrometer with an Al K α source (1486.6 eV). The TiO₂ (001) single crystals were obtained from Earth Chemical Co. The shift of binding energy due to surface charging was corrected using the C 1s level at 285 eV as the internal standard. The XPS peaks were assumed to have Gaussian line shapes, and were resolved into components by a non-linear least squares procedure after proper subtraction of the baseline. For the measurements of XPS spectra of H₂O₂-treated TiO₂ surfaces, the single crystalline TiO₂ samples were immersed in 30% H₂O₂ for 24 h. The samples were introduced into the XPS chamber after blow-drying.

RESULTS AND DISCUSSION

Photocatalytic epoxidation of 1-decene on photoirradiated TiO₂ powder.

1,2-Epoxydecane, 2-decanone, and nonanal were the main products obtained as a result of photocatalytic reaction of 1-decene on irradiated TiO₂ particles in solution

containing molecular oxygen as the electron acceptor. Figure 1 (a) shows the products obtained after irradiation for 4 h using 4 kinds of TiO_2 powders, which were suspended in solutions bubbled with pure oxygen. In these reactions, light with wavelengths shorter than 340 nm was removed to prevent photochemical reactions in solution. No reaction occurred in the dark or under irradiation with visible light for any kinds of TiO_2 powders. When the reaction was carried out under UV irradiation in neat 1-decene, the reaction rate was significantly increased, and the anatase powder (ST-01) showed the highest activity.⁷ In this study, we did the measurements in mixed solutions containing TiO_2 powder (200 mg), water (0.2g), acetonitrile (1.8 g), butyronitrile (1.5 g), and 1-decene (0.5 g). In this solution, the difference in the activity among the TiO_2 powders is smaller than that observed in neat 1-decene. An exception is the rutile powder (TIO-3) which exhibited a very low activity, as shown in Fig. 1 (a).

When H_2O_2 is added to the solution, the activity increases significantly for rutile TiO_2 powders, as shown in Fig. 1 (b). No reaction occurred in the dark. The rutile TIO-3 powder, which exhibited very poor photocatalytic activity, shows drastic increase of its activity by addition of H_2O_2 . The other rutile powders also show an

increase of their activity by addition of H_2O_2 . In contrast, for the anatase ST-01 powder, practically no enhancement of the activity is observed. Other anatase TiO_2 powders did not show either an increase in the activity by addition of H_2O_2 either (not shown in Fig. 1). The enhancement of the activity of rutile TiO_2 powders by addition of H_2O_2 has been observed for photocatalytic oxidation of naphthalene.⁹ In this reaction, the enhancement is attributed to the increase of the rate of electron transfer from rutile TiO_2 to the electron acceptor (H_2O_2) in solution because H_2O_2 is a stronger electron acceptor than molecular oxygen.

Interestingly, we found that the reaction of 1-decene on rutile TiO_2 particles occurs under visible light irradiation when H_2O_2 is added to the solution. The wavelength dependence of the photocatalytic reaction was measured using different cut-off glass filters and a Xenon lamp. Typical results are shown in Fig. 2, for TIO-3 as a photocatalyst. The photocatalytic reaction proceeds even by photoirradiation at wavelengths longer than 440 nm. The content of 1,2-epoxydecane in the products increases when the UV component is removed from irradiation. More precisely, the yield of 1,2-epoxydecane (based on consumed 1-decene) reaches 52% for irradiation

longer than 440 nm, while it is only 42% for irradiation lowered than 340 nm. In contrast, production of nonanal is lowered when UV light is removed from the light. The main path for the production of nonanal is probably oxidation of the olefin by photogenerated holes, as reported by Fox *et al.* for the reaction of aromatic olefins.^{15,16} Under visible light, the production of nonanal is lowered because visible light does not generate electrons and holes in TiO₂.

Other rutile TiO₂ powders also show photocatalytic activity under visible light in the solution containing H₂O₂, as depicted in Fig. 3. Contrarily, practically no reaction occurred under visible light when anatase particles were used as the photocatalysts. Among rutile TiO₂ powders, the TIO-3 showed the highest activity under visible light irradiation, although this powder showed very low activity under UV irradiation, as shown in Fig. 1. This powder has the largest surface area among the rutile powders we used. Hence, the reaction under visible light is considered to be due to species generated on the surface of rutile particles.

Using the TiO-3 powder, the conversion efficiency of an incident photon to 1,2-epoxydecane was estimated to be about 2% by irradiation in a wavelength region

from 440 to 480 nm. The real quantum efficiency is higher than this value because in this estimation we assumed that all the incident photons were absorbed by the suspension.

Diffuse reflectance spectra of TiO₂ powders.

In order to identify the surface species, which are effective for the reaction under visible light, we measured diffuse reflectance spectra of TiO₂ powders before and after treatment with 30% H₂O₂ for 8 h. As shown in Fig. 4, all TiO₂ powders after the H₂O₂ treatment show absorption up to about 550 nm. The absorption becomes stronger with the increase of surface area of TiO₂ powders. This result suggests that peroxides are generated on the surface of TiO₂ particles by the treatment with H₂O₂.²⁰

The photocatalytic activity of the H₂O₂-treated TiO₂ powders under visible light must be related to this absorption in the visible region. However, we have to recall that the anatase powder (ST-01) shows very poor photocatalytic activity under visible light, although its absorption in the visible region after the treatment with H₂O₂ is very strong. Hence, further information about the species generated on the

H₂O₂-treated TiO₂ surface is necessary.

XPS analysis.

The O1s XPS spectrum of a rutile TiO₂(001) single crystal before the treatment with H₂O₂ is shown in Fig. 5 (a). The band at 529.8 eV is assigned to the lattice oxygen (Ti⁴⁺-O).²² The one at 531.8 eV is attributed to Ti³⁺ (Ti³⁺-O)²¹⁻²³ and Ti⁴⁺-OH.²⁴ The spectrum did not changed by immersing the sample in pure water for 24 h. On the other hand, after the H₂O₂ treatment, a new band appears at 533 eV, as shown in Fig. 5 (b). This band is considered to be due to the peroxide generated on the surface. This assumption is confirmed by comparing the peak to that of a Ti-peroxide powder, which shows a strong peak at 532.8 eV, as shown in Fig. 5 (c). The synthesis of the Ti-peroxide powder was described in the experimental section, and the sample contained both Ti-peroxide and TiO₂; the corresponding O1s peaks are seen in Fig. 5 (c).

We also measured the XPS spectra of TiO₂ powders before and after the H₂O₂ treatment. For these powder samples, however, we were unable to isolate the band at

533 eV because the band at 531 eV was too intense. Although we did not observe the O1s band due to the Ti-peroxide on the surface of TiO₂ powders, it is reasonable to assume the generation of the Ti-peroxide on the surface, which was confirmed on the surface of TiO₂ (001) single crystals.

IR spectra of TiO₂ thin films.

In order to obtain information about the Ti-peroxide generated on the surface of TiO₂, we measured the ATR FT-IR spectra of TiO₂ films which were deposited on the Si(100) substrates. The spectra of the TiO₂ films were measured just after the treatment with 30% H₂O₂, and later after 20 minutes from the treatment. Figures 6 (a) and (b) display the **difference spectra of the H₂O₂-treated samples and water-treated samples (used as backgrounds)** for anatase (80%) and rutile (100%) films, respectively.

Bands in the range 950 – 700 cm⁻¹ are ascribed to different Ti-peroxo species.²⁵⁻²⁸

These absorption bands disappear after 20 min from the H₂O₂ treatment, suggesting that they are very reactive. Ti-η²-peroxide is reported to have absorption bands in the range 932 - 800 cm⁻¹.^{25,28} On the other hand, Ti-μ-peroxide is reported to have

absorption bands in the range $770 - 700\text{ cm}^{-1}$, which are often observed for solid-state peroxides.^{27,28} On the basis of these assignments, the absorption bands in the ranges $940 - 820\text{ cm}^{-1}$ and $800 - 740\text{ cm}^{-1}$, seen in Fig. 6, are attributed to the stretching vibrations of the -O-O- bonds of $\text{Ti-}\eta^2\text{-peroxide}$ and $\text{Ti-}\mu\text{-peroxide}$, respectively.

From the spectra of Fig. 6 (a) and (b), the content of $\text{Ti-}\eta^2\text{-peroxide}$ in the rutile TiO_2 film is much higher than that in the anatase (80%) TiO_2 film. The small absorption in the region $940 - 820\text{ cm}^{-1}$ for the anatase (80%) film may be due to the rutile component (20%) included in the film. On the other hand, the absorption band ($800 - 740\text{ cm}^{-1}$) due to $\text{Ti-}\mu\text{-peroxide}$ is larger for the anatase film than for the rutile film. These results strongly suggest that the active species formed on rutile TiO_2 powders for the epoxidation of 1-decene under visible light is $\text{Ti-}\eta^2\text{-peroxide}$.

Proposed mechanism of the epoxidation under visible light.

On the basis of the results, we propose a mechanism, shown in Scheme 1, for the production of 1,2-epoxydecane on the surface of TiO_2 under visible light. The $\text{Ti-}\eta^2\text{-peroxide}$ generated on the surface of rutile TiO_2 is considered to be the active

species. Under visible light, one of the oxygen atoms in the peroxo group is assumed to be transferred to the olefin via a transition state, shown in Scheme 1. Similar transition state was proposed for the catalytic epoxidation of olefins by molybdenum peroxo compounds.^{29,30} After the detachment of the epoxide, the Ti- η^2 -peroxide complex is regenerated by H₂O₂.

The generation of the epoxide on rutile TiO₂ was also enhanced under UV light by H₂O₂. This result suggests that the intermediate is efficiently generated by UV light. Under UV irradiation, the production of nonanal and 2-decanone was also enhanced by the addition of H₂O₂. These compounds are probably produced by the photogenerated holes in the TiO₂ particles. The effective transfer of electrons to H₂O₂ helps the separation of electrons and holes in TiO₂, leading to improved reaction efficiency.

The important point of the reactions under visible light is that no electron – hole pairs are generated in the bulk of TiO₂. Instead of electrons and holes, the reaction occurs via the surface species, which absorb visible light. To realize high efficiency of such reactions, the surface area of TiO₂ particles is very important. Since

it is possible to prepare rutile TiO_2 particles with a very large surface area by a sol-gel processing,³¹ we expect that the reaction efficiency under visible light can be further increased. This method can probably be applied to the epoxidation of many kinds of olefins.

CONCLUSION

We found that epoxidation of 1-decene on photoirradiated TiO_2 powder is enhanced by addition of H_2O_2 , when rutile TiO_2 is used as the photocatalysts. Furthermore, rutile TiO_2 powders show activity for the reaction under visible light, when H_2O_2 is added to the solution. This finding opens the door to the utilization of visible light in the photocatalytic reactions on TiO_2 photocatalysts, and to the effective utilization of solar light.

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FIGURE CAPTIONS

FIG. 1. Photocatalytic activities of TiO₂ powders for the photocatalytic reaction of 1-decene in solutions without (a) and with (b) H₂O₂. In the reaction, the TiO₂ particles suspended in the solution were irradiated for 4 h with light at wavelengths longer than 340 nm using a Xe lamp. The content of the rutile phase in the TiO₂ powders is listed beneath the figure.

FIG. 2. Effect of irradiated wavelengths on the TiO₂-photocatalyzed reaction of 1-decene in the solution containing H₂O₂. A rutile TiO₂ powder (TIO-3) was used as the photocatalyst, and the suspension was irradiated for 4 h. A Xe lamp was used as the light source, and irradiation wavelength was controlled using cut-off glass filters.

FIG. 3. Photocatalytic activities of 4 kinds of rutile TiO₂ powders for the reaction of 1-decene under visible light ($\lambda > 440$ nm) in the solution containing H₂O₂. A Xe lamp was used as the light source, and irradiation wavelength was controlled using a cut-off

glass filter (Y-44). The suspension was photoirradiated for 4 h. The surface area of the TiO_2 powders is listed beneath the figure.

FIG. 4. Diffuse reflection spectra of TiO_2 powders before and after the treatment with H_2O_2 ; ST-01 (a), TIO-3 (b), and TIO-5 (c). The content of the rutile phase and the surface area of the TiO_2 powders are shown in the figure.

FIG. 5. X-ray photoelectron spectra of the O1s band of a TiO_2 (001) single crystal before (a) and after (b) the treatment with H_2O_2 , and that of a Ti-peroxide powder (c).

FIG. 6. FT-IR spectra of TiO_2 thin films with the anatase form (80%) (a) and with the rutile form (100%) (b). The spectra were measured just after H_2O_2 treatment, and later after 20 minutes after the treatment. The TiO_2 films were about 550 nm thick, and the light beam was internally reflected 20 times.

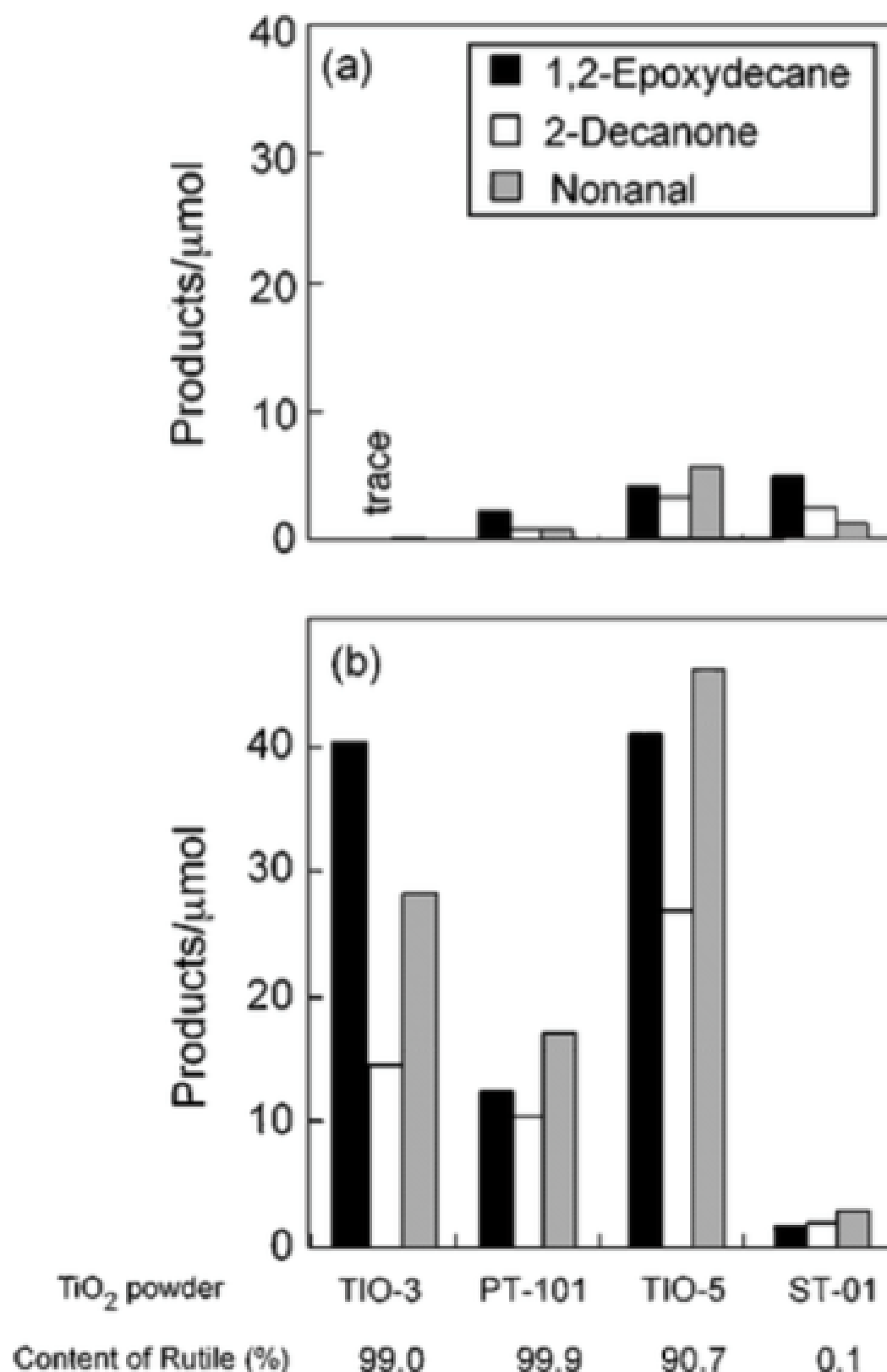


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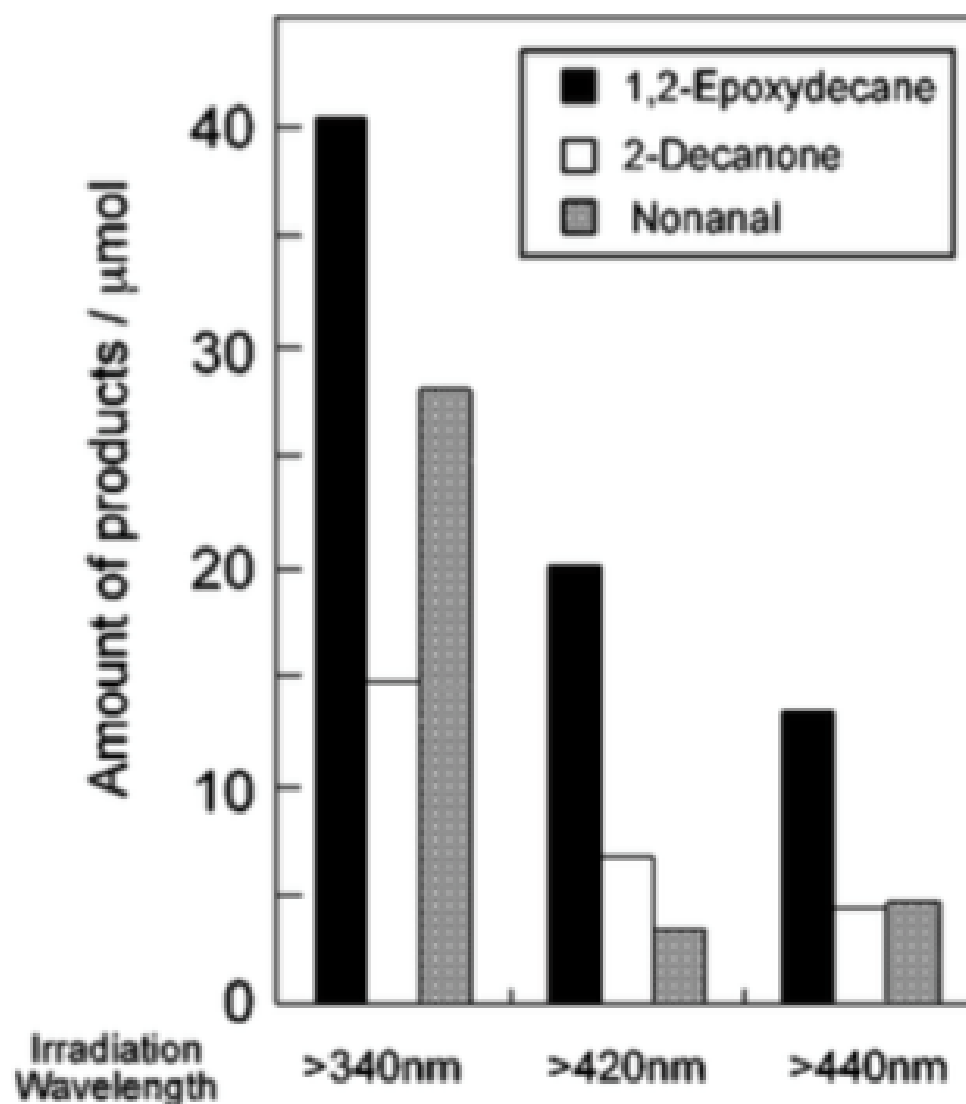


FIG. 2. Effect of irradiated wavelengths on the TiO_2 -photocatalyzed reaction of 1-decene in the solution containing H_2O_2 . A rutile TiO_2 powder (TIO-3) was used as the photocatalyst, and the suspension was irradiated for 4 h. A Xe lamp was used as the light source, and irradiation wavelength was controlled using cutoff glass filters.

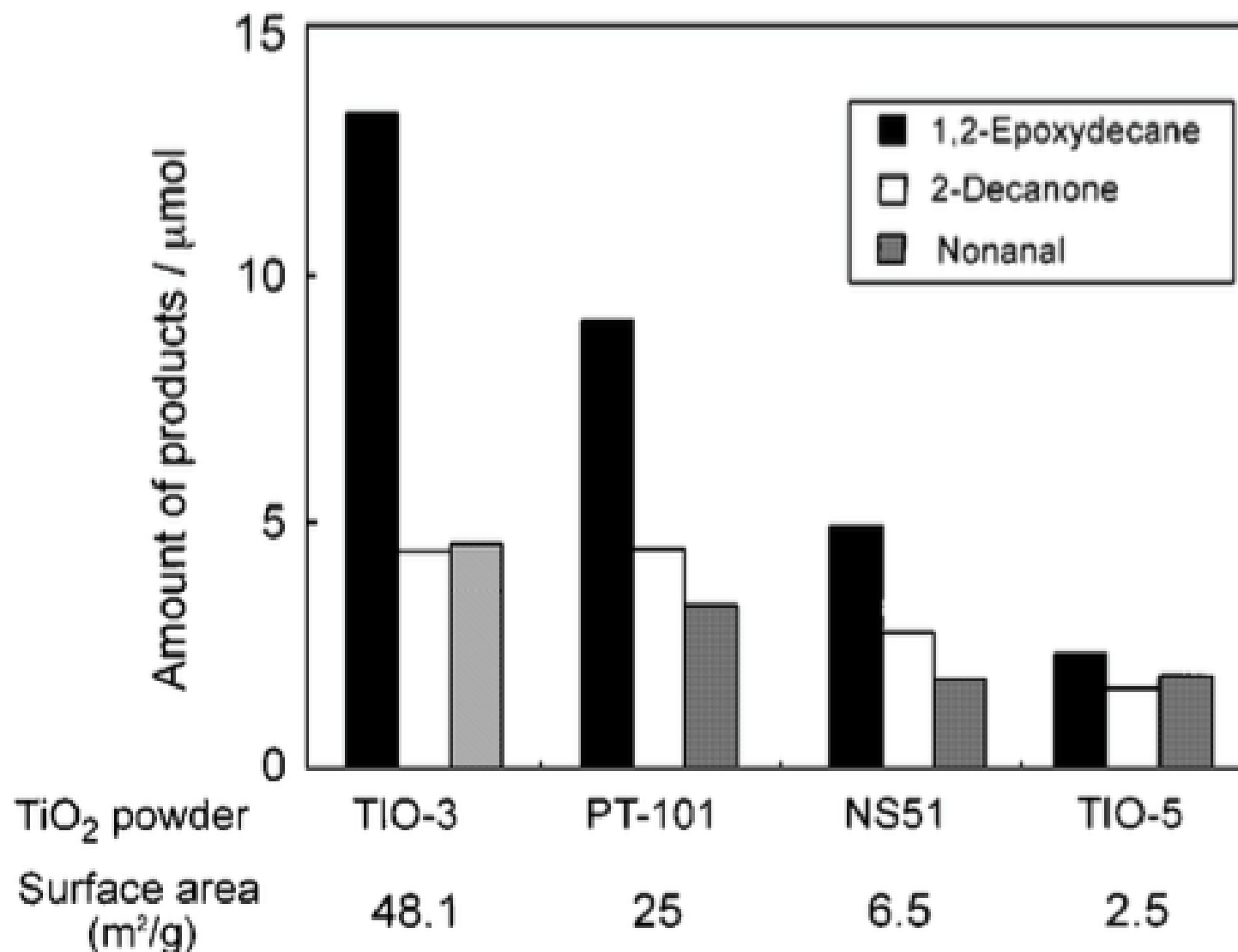


FIG. 3. Photocatalytic activities of four kinds of rutile TiO_2 powders for the reaction of 1-decene under visible light ($\lambda > 440 \text{ nm}$) in the solution containing H_2O_2 . A Xe lamp was used as the light source, and irradiation wavelength was controlled using a cutoff glass filter (Y-44). The suspension was photoirradiated for 4 h. The surface area of the TiO_2 powders is listed beneath the figure.

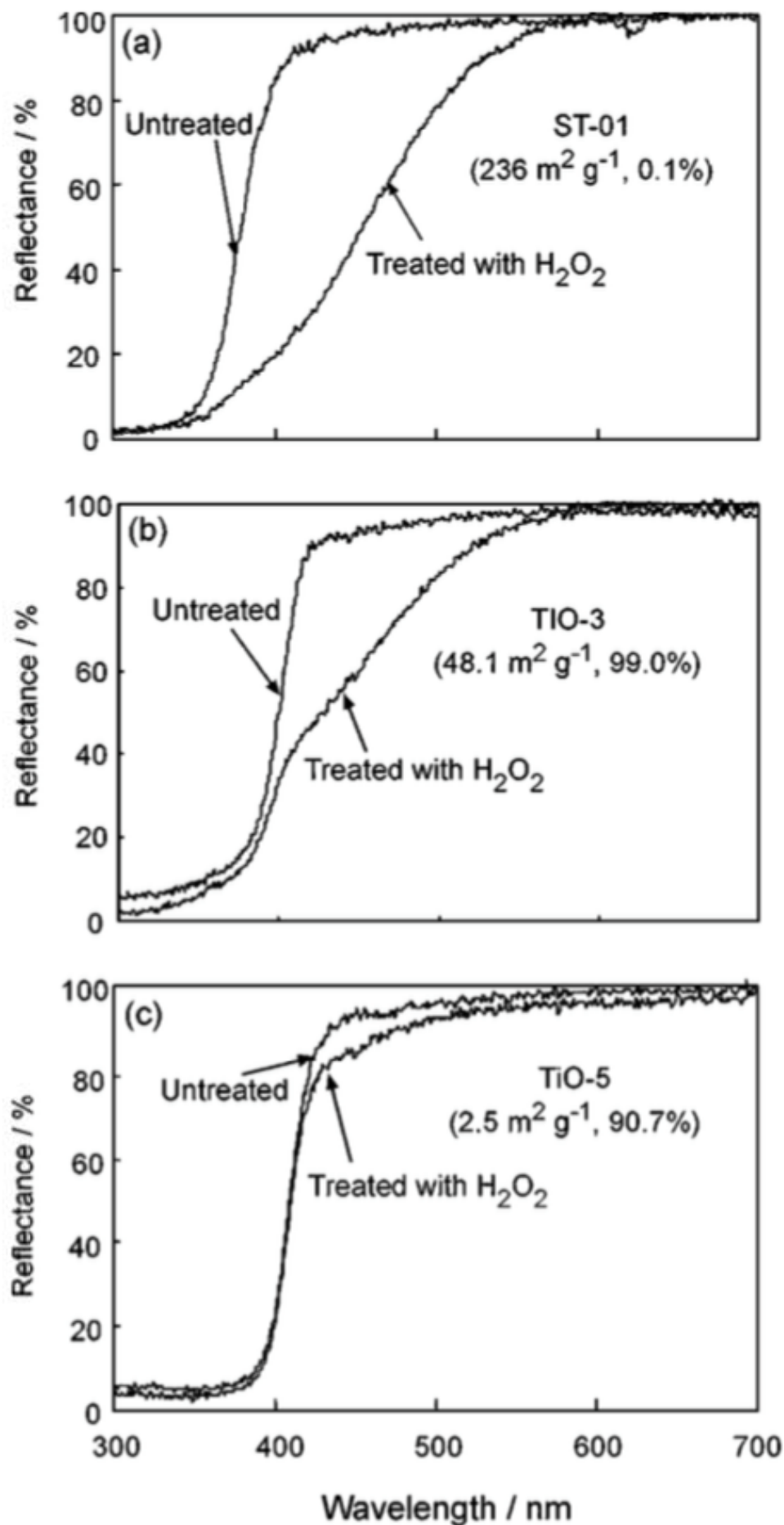


FIG. 4. Diffuse reflection spectra of TiO_2 powders before and after the treatment with H_2O_2 : ST-01 (a), TIO-3 (b), and TIO-5 (c). The content of the rutile phase and the surface area of the TiO_2 powders are shown in the figure.

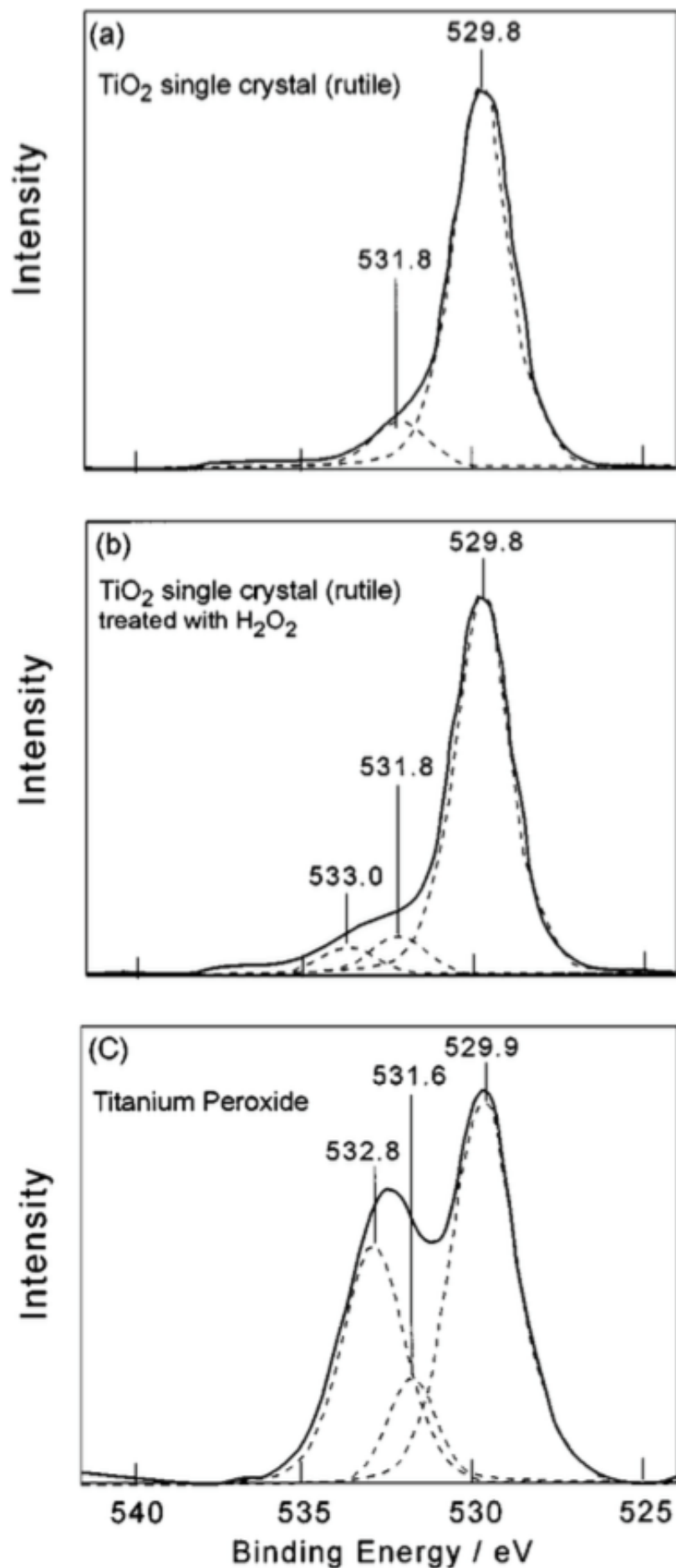


FIG. 5. X-ray photoelectron spectra of the O 1s band of a TiO₂(001) single crystal before (a) and after (b) the treatment with H₂O₂, and that of a Ti-peroxide powder (c).

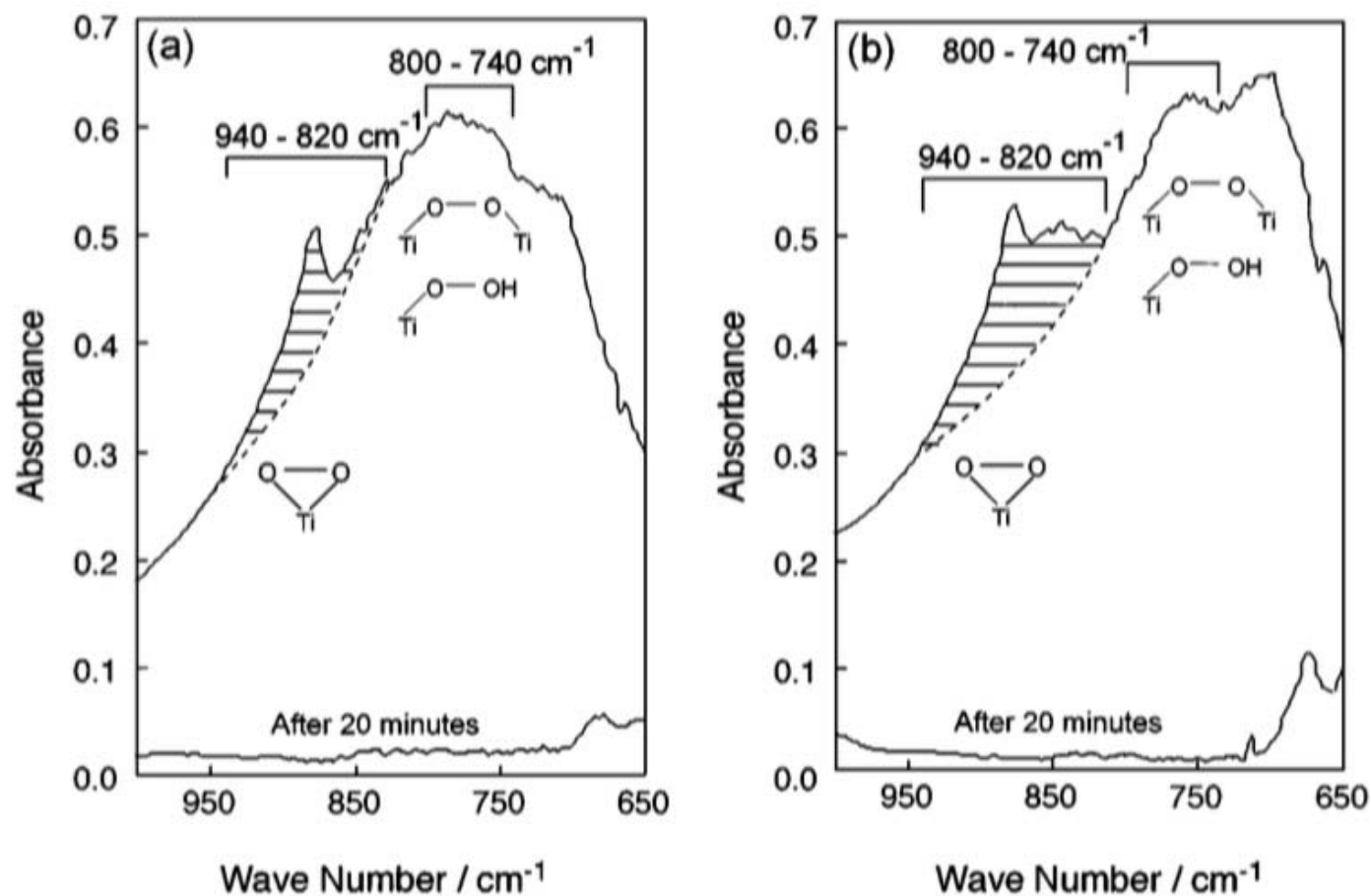
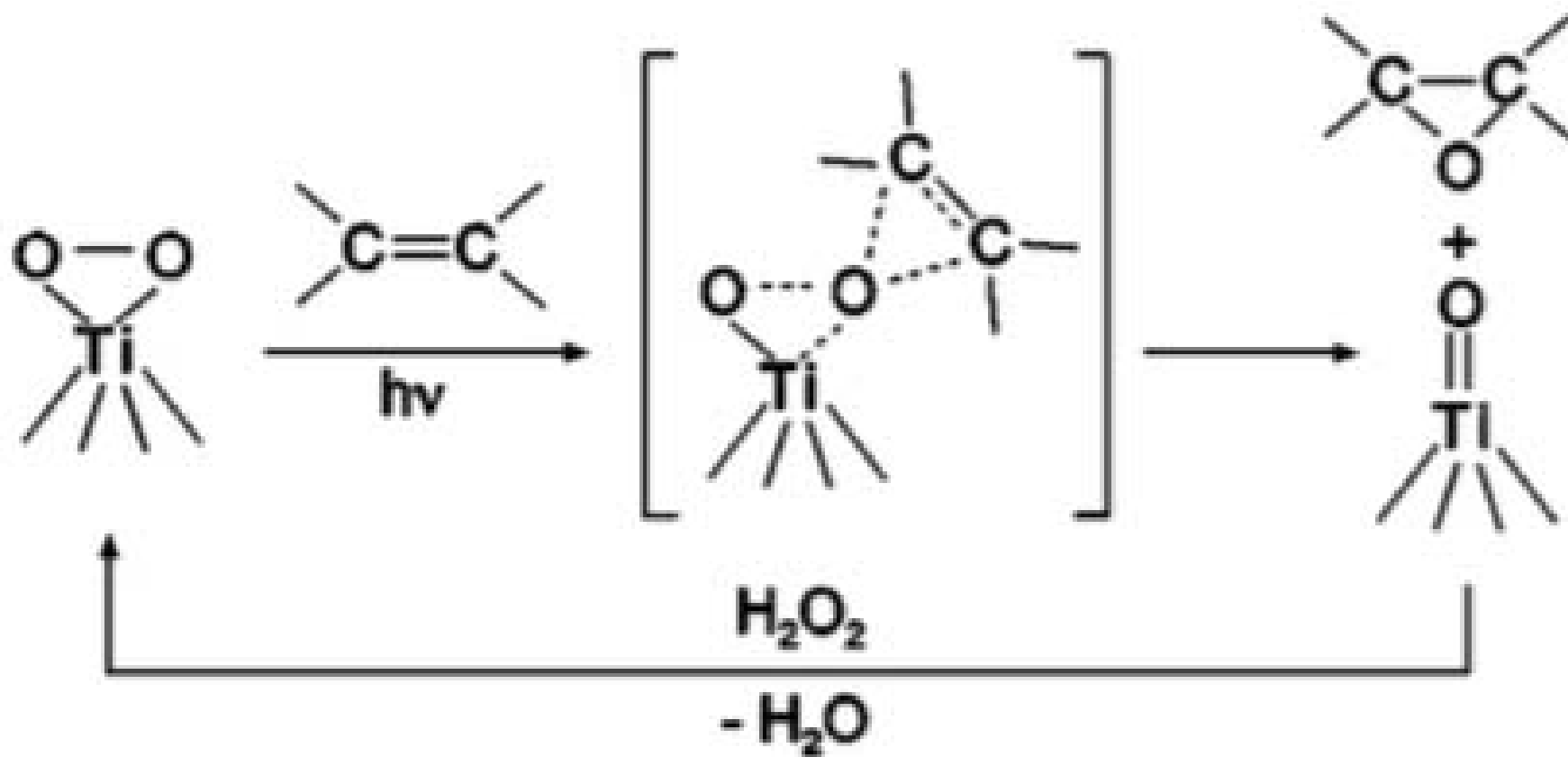


FIG. 6. FT-IR spectra of TiO₂ thin films with the anatase form (80%) (a) and with the rutile form (100%) (b). The spectra were measured just after H₂O₂ treatment, and 20 min after the treatment. The TiO₂ films were about 550 nm thick, and the light beam was internally reflected 20 times.



SCHEME 1