JOURNAL OF MATERIALS SCIENCE **36** (2001) 4201 – 4207

Preparation of a visible-light-active TiO_2 photocatalyst by RF plasma treatment

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In order to realize a visible (vis)-light-active TiO_2 photocatalyst, reduction treatment using low-temperature hydrogen plasma with elevated temperatures was applied on anatase TiO_2 powder of ST-01 without causing a phase transition to rutile. According to plasma-heat treatment, oxygen was evacuated from ST-01 particles and the colored ST-01, ivory to beige, was obtained. XPS results showed non-stoichiometric, expressed as TiO_{2-x} and x was increased with the increase of treating time. Plasma-heat treated ST-01 showed new ESR signal at $g = 2.003$ assigned to electrons trapped at the oxygen-defect site. This signal was strengthened when vis-light illumination was applied. Results of vis-light activity tests, evaluated by photocatalytic oxidation of benzoic acid in liquid phase and 2-propanol in gas phase using vis-light illumination (>406 nm), showed excellent activity while low ST-01 showed almost no activity on both tests. *© 2001 Kluwer Academic Publishers*

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1. Introduction

Recently, much attention has been focused on the photocatalytic properties of TiO_2, which has good stability in the outdoor environment, for the purification of environmental air and water samples, deodorization, and antibacterial and self-cleaning coatings [1–6]. However, because of its high-energy band gap (3.2 eV for the anatase form) TiO_2 can harvest only a small fraction (less than 5%) of incident solar energy. Therefore, in order for it to be used outdoors, a TiO_2 photocatalyst must respond to visible (vis) light with better efficiency, since 45% of the energy in sunlight is in the vis region. To attain efficient vis-light-active TiO_2, it is important to extend its absorption spectrum into the vis range. Several approaches have been tried such as doping various transition metals into TiO_2 [7–9]. However, the efficiency was often reduced by the formation of recombination centers [10].

It is well known that absorption spectral broadening towards the vis range appears in n-type TiO_{2-x} semiconductors prepared by reduction of single crystals of the rutile form of TiO_2 at temperatures of 1000°C or higher [11, 12]. TiO_{2-x}, represents oxygen-deficient TiO_2. The influence of the value of x in TiO_{2-x} on its photocatalytic activity when used as a photoanode is very marked [12]. It has also been reported that Ti^{3+}-VO-Ti^{3+}-centers behave as catalytically active centers in the photoassisted oxidation of water (where VO represents an oxygen vacancy generated by reduction of a rutile TiO_2 single crystal [13]). However, the relationship between vis photocatalytic activity and the oxygen defect in TiO_2 has not been elucidated. Since the probability of hole-electron recombination is lower in anatase than in rutile [14], vis-active TiO_2 is expected to be produced with oxygen-deficient anatase.

In a low-temperature plasma, high-energy species such as electrons, atoms, and radicals, are available for reactions in a nonequilibrium condition. Therefore, thermally unstable materials such as organic polymers can be substrates; only the skin layer of the substrate is modified with no deterioration of the bulk material. In order to obtain TiO_{2-x} by reduction of anatase, we have previously used a microwave H_2 plasma, in which the temperature reaches about 800°C, because rf plasma does not have enough power to cause the reduction of inorganic compounds like TiO_2. This microwave plasma is very effective in the reduction of TiO_2 [15], resulting in black-colored TiO_{2-x} easily. However, the experimental parameter settings of the microwave were so intense that a phase transition took place easily. If rf plasma is combined with an appropriately high

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temperature, control of the reduction of such a material as TiO_2 without transformation may be possible. This is thought to be the most favorable process for the preparation of vis-active anatase TiO_{2-x}.

In this work the reduction of anatase powder using an rf H_2 plasma at elevated temperatures was carried out to prepare vis-active anatase TiO_{2-x} powder. The physical and chemical properties of the plasma-treated TiO_2 powders were analyzed and correlated with the vis activity.

2. Experimental

The anatase powder used in this experiment as a raw material was commercially available (Ishihara Sangyo, ST-01, 7-nm d.). ST-01 is manufactured as a photocatalyst and gives a relatively high photoactivity when compared to other commercial products such as Degussa P-25.

The plasma apparatus, shown in Fig. 1, consists of a plasma reactor with a heater, a vacuum pump with an oil trap, a 13.56-MHz rf power supply (Adtec, AX-1000) and an automatic impedance matching unit (Adtec, AM-1000S). The cylindrical plasma reactor (1-m long and 53-mm d.), made of quartz, is wrapped spirally with a pair of strip-type electrodes, made of stainless steel, to provide a uniform plasma throughout the reactor. Except for 100 mm at each end, the reactor was covered with an electric furnace in which five heaters with five thermocouples were mounted for uniform temperature control for the entire length of the furnace. H_2 was supplied from one end of the reactor and evacuated from the other with a vacuum pump. Plasma treatment of the ST-01 powder was carried out as follows: 3 g of ST-01 powder was placed directly at the downstream side of the reactor and spread out evenly as shown in Fig. 1. H_2 was introduced into the reactor through a mass flow controller (STEC, SEC-400) after the reactor had been evacuated to below 5 Pa. At the same time, heating of the furnace was started. When the reactor was heated to a predetermined temperature, the plasma treatment was started.

As a preliminary experiment, we calcined raw ST-01 powder (anatase) in an electric furnace at different temperatures in an air atmosphere and measured the specific surface area. In this experiment, we found that the specific surface area was drastically decreased at 500°C. Therefore, we set the reaction temperature range from 200 to 400°C. As for the other experimental conditions, rf power, H_2 flow rate, and plasma irradiation time were set to 100 to 500 W, 100 to 1000 sccm and 10 to 60 minutes, respectively.

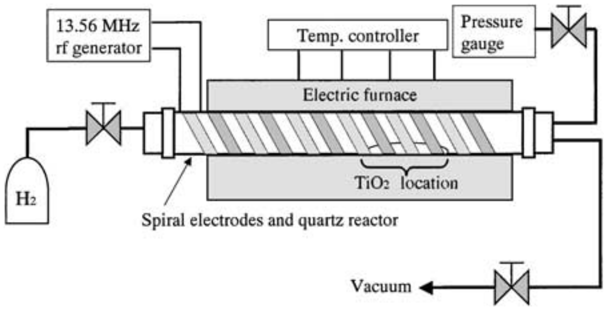

Figure 1 Schematic drawing of plasma apparatus for TiO_2 treatment.

The analyses of the treated ST-01 powder consisted of, the reflection spectrum in the visible region, the specific surface area, the X-ray diffraction (XRD) pattern, X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR). The reflection spectrum in the visible region of the treated ST-01 powder was measured with a color analyzer (Tokyo Denshoku, TC-1800). Specific surface area was measured with surface measurement apparatus (Shibata, P-850) by BET method. XRD was measured with an X-ray diffractometer (Rigaku, RINT 2000). XPS was taken with Shimadzu ESCA-750. The ESR spectra were measured at 77 K in vacuo (10^{-4} Pa) with Mn^{2+} as a marker with an ESR spectrometer (Nihon Denshi, JES-RE2X) operating in the X-band under irradiation with vis light.

Many organic compounds have been shown to be oxidized to carbon dioxide via their respective intermediates by photocatalytic oxidation with TiO_2, requiring near UV (<400 nm) irradiation [16–21]. In our experiment, the vis activity and broad-band (UV and visible) light activity of the treated and un-treated ST-01 as photocatalysts were examined in two photocatalytic oxidation processes with illumination: the first was the oxidation of benzoic acid in the liquid phase and the other was the oxidation of 2-propanol in the gas phase. In the former experiment, the extent of the decomposition of benzoic acid was determined according to the following procedure: a glass cylinder of 50-mL capacity was used as the reaction vessel. Twenty-five milligrams of treated TiO_2 and 25 mL of 0.01-M benzoic acid solution were put into the reaction vessel, which was tightly sealed with a cap. The reaction vessel was mounted at the center of the irradiation box. A 100 W halogen lamp and a 500 W xenon lamp (Ushio, SX-UI 500XQ) were used as the visible-light and the broadband light sources, respectively. In the former case, two cut filters, L-42 (Toshiba) for the UV region and IRA-25S (Toshiba) for the IR region, were mounted between the light source and the reaction vessel. In the latter case, IR cut filter, IRA-25S, was used. The reaction vessel was irradiated from one side of the irradiation box. The illumination intensities were measured with a illuminance meter (Minolta, T-10) and adjusted at the reaction vessel each run. Selected intensities were 8×10^4 lx for visible-light and 11×10^4 lx for broad-band light, respectively. Fig. 2 shows the spectral profiles of a light source ranging 300 to 525 nm with and without an L-42 filter as measured with a fiber optic spectrometer (Ocean Optics, SD 2000). It is clear from this fig. that the spectrum below 406 nm was completely cut off when the L-42 filter was mounted. The irradiation was carried out after adsorption equilibrium had been reached, a process that required two hours. Irradiation time was set to 48 h for vis and 30 min for broadband. During this process, the ST-01 suspension was stirred to maintain a uniform suspension and the reaction vessel was cooled with a small electric fan to prevent spontaneous heating. The decomposition fraction (%) of the benzoic

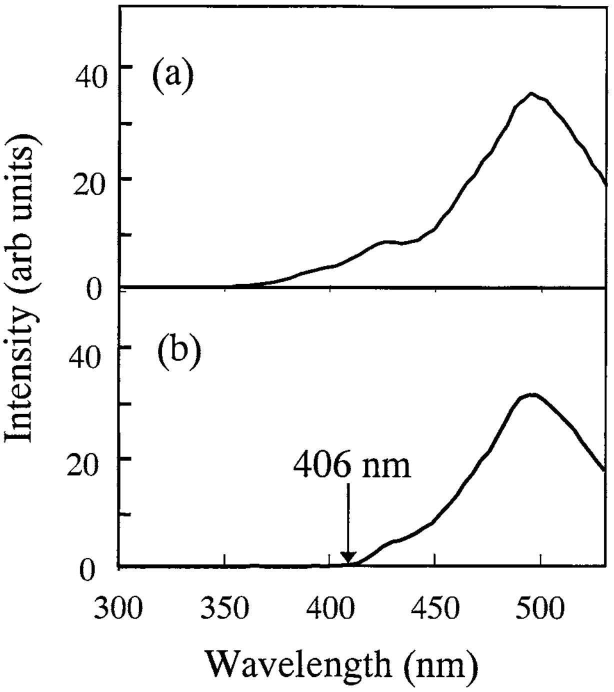

Figure 2 UV-vis spectrum profiles of the light source (halogen lamp) (a) without L-42 filter and (b) with L-42 filter.

acid was determined using the change of absorbance at 350 nm as measured with a UV/VIS spectrometer (Shimadzu, UV-1200) after filtration.

In the latter experiment, the formation of acetone by the oxidation of 2-propanol was investigated by the following procedure: A glass bell-jar reactor of 2.0-L capacity (20 cm height, 12 cm i.d.) sealed to a quartz plate with silicon-rubber was used as the reaction vessel. An irradiation plate made of quartz (50 × 50 × 2 mm) was fixed horizontally 50 mm above the bottom of the reaction vessel. The bottom side of the irradiation plate had been coated previously with 0.1 mg of ST-01 powder using several drops of water and was dried before use. We used same lamps, a 150 W halogen lamp and a 500 W xenon lamp, as the light sources and the same filters as the previous experiment. The initial concentration of 2-propanol was set to 540 ppm at atmospheric pressure with a relative humidity of 30% at 25°C in the air inside the jar. The halogen or xenon lamp illuminated the vessel from the bottom. The illumination intensity was measured and adjusted at the irradiation plate each run and set to 18×10^4 lx for halogen lamp and 11×10^4 lx for xenon lamp. After adsorption equilibrium was reached, the illumination was started and the concentrations of the decomposing 2-propanol and the acetone formed were measured every 15 minutes using gas chromatography (Shimadz, GC-14B) equipped with a 5 m PEG 1000 column and a flame ionization detector. Gas chromatography (Shimadz, GC-8A) with a 2 m SHINCARBON T column and a thermal conductivity detector was also used for the determination of carbon dioxide. All chemicals used in these experiments, such as benzoic acid, 2-propanol and etc., were analytical grade whenever possible.

The durability of the vis activity against sunlight irradiation was examined outdoors for 120 days, started from the beginning of August. Two Pyrex petri dishes (98 mm o.d.), without lids, in which the raw ST-01 and the plasma-heat treated ST-01 were placed were put into a wooden case with a quartz cover on top and side windows for ventilation. Then the wooden case was placed at the top of the laboratory building and the vis activity was checked every 30 days by gas phase reaction using 2-propanol as mentioned above.

3. Result and discussion

In the beginning, the mass spectra of the evacuated gas downstream of the plasma reactor were taken with a residual gas analyzer (Alvac, REGA RG-202P). The measurement of the three processes, the evacuation process, the H_2 feeding process, and the plasma process was done without heating. Fig. 3 shows the mass spectra of those three processes. In order to check the sensitivity and resolution of this analyzer, we mixed 5% methane into the H_2 in this experiment.

At the beginning of the evacuation process, the partial pressures of both nitrogen and oxygen decrease linearly. When the total pressure reaches a certain level, however, the oxygen partial pressure starts to increase. This increase indicates oxygen desorption from the surface of the ST-01 particles. In the gas (H_2 and CH_4) feeding process, naturally, H_2 and CH_4 increase while N_2 and O_2 decrease. When the plasma evolves, the increase of the partial pressure of oxygen is pronounced, which indicates that the plasma can be a strong evacuator of oxygen from ST-01 particles. Also, the ion strength of the $m/z = 28$ peak, which can be assigned to CO^+ formed from the added CH_4, increases.

In the removal of oxygen by the H_2 plasma heat treatment, the color of the ST-01 powder changes from ivory to beige depending on plasma conditions such as rf power, temperature, and treatment time. This color change is probably due to oxygen defects [12] caused

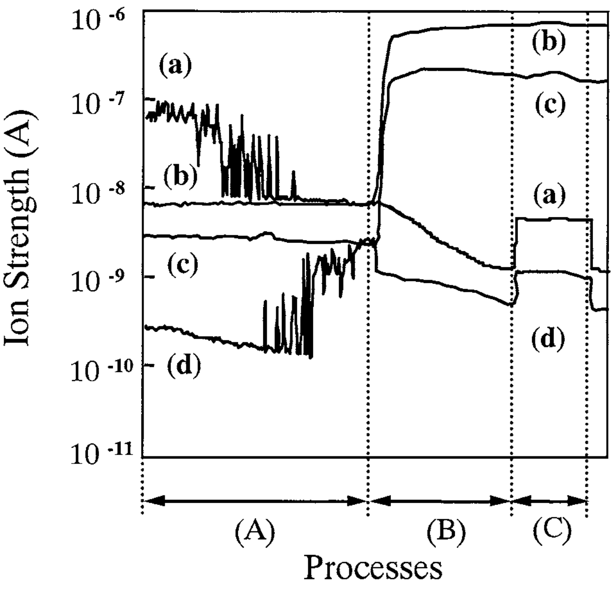

Figure 3 Results of gas analysis at (A) degassing process, (B) feeding process of mixed gas of H_2 and methane (95 : 5), and (C) plasma treating process. Detected species. (a) m/z 28 (N_2^+, CO^+); (b) m/z 2 (H_2^+); (c) m/z 16 (CH_4^+, O^+); (d) m/z 32 (O_2^+).

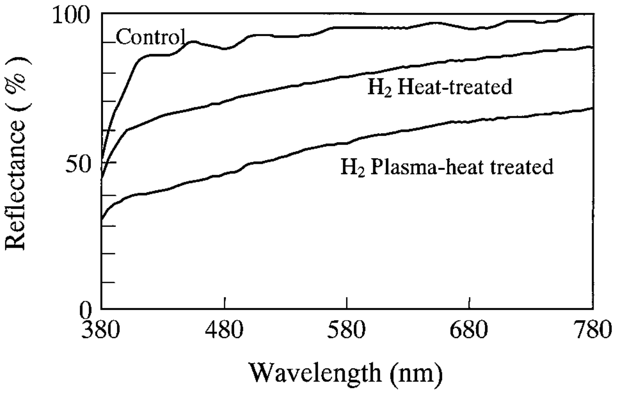

Figure 4 Reflection spectra of raw (control), heat treated and plasma-heat treated ST-01.

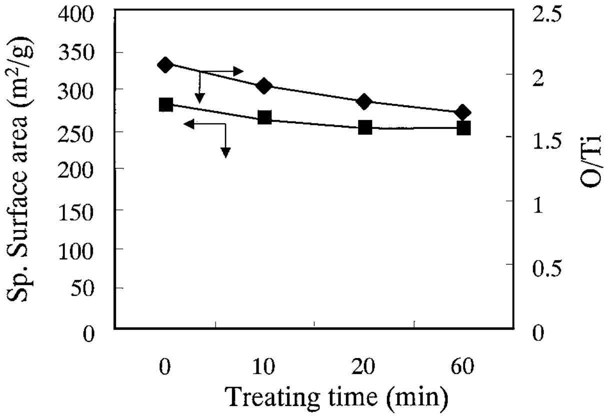

Figure 5 Specific surface area (■) and O/Ti ratio (◆) of the plasma-heat treated ST-01.

by this reduction process combined with evacuation, heating with an H_2 atmosphere, and the H_2 plasma.

Fig. 4 shows a typical reflection spectra of ST-01 treated with an H_2 plasma with heating, along with those of an H_2 heat-treated sample without plasma and raw ST-01 as a control.

As we stated earlier, TiO_2 has a strong absorption in the UV region that corresponds to the original band gap energy, and an absorption tail can be seen near the vis region less than about 400 nm.

In the case of the raw ST-01 powder, which appeared to be white by visual observation, the reflectance in Fig. 4 shows a left-sinking profile (lower reflectance at lower wavelength) in the entire visible region. For the heat-treated ST-01, the reflectance profile is similar to that for the raw ST-01 but reduced in the entire region. For the H_2 plasma heat treated ST-01, the reflectance is shifted to much lower values. The color of this treated ST-01 was ivory to beige by visible observation depending on the treatment conditions. When ST-01 was treated with H_2 plasma without heating, it turned grayish yellow in the reactor vessel if the vacuum was kept on. However, it immediately returned to white when the vessel was opened to air. On the contrary, the color of H_2 plasma heat treated ST-01 (ivory to beige) remained stable not only after contact with atmospheric air at ambient temperature and pressure but also after exposure to sunlight for a week or more. As for the durability, it is described later.

The specific surface area and O/Ti ratio of the treated ST-01 are shown in Fig. 5. The specific surface area does not seems to be effected by the plasma heat treatment at 400°C within 60 minutes of treatment. A relatively large surface area was maintained at temperatures up to 400°C, which coincides with the phase transition temperature to rutile but some significant rearrangement at the surface might have been occurred.

From XPS measurements, the O/Ti ratio of control ST-01 was found to be stoichiometric 2 : 1. When plasma heat treatment is applied, the O/Ti ratio decreased with increaseing treatment time and reached 1.68 at the treatment time of 60 minutes. The extent of this decrease depends on the treatment conditions, and the composition of TiO_2 becomes non-stoichiometric, expressed as TiO_{2-x}.

We measured the XRD in order to investigate the effect of the plasma process on the anatase structure of TiO_2. Representative XRD patterns are shown in Fig. 6. In this figure, the XRD patterns of the control ST-01 and the ST-01 which was plasma heat treated with 500 W of rf input power for 10 min at 400°C are depicted.

There is no recognizable difference between the raw ST-01 and the ST-01 which was plasma heat treated at 400°C, which indicates that the plasma does not contribute to the phase transition at all. Only the heating effect seems to be responsible for the phase transition of TiO_2.

From XPS and XRD measurements, it was found that plasma heat treated ST-01 was found to be non-stoichiometric without a phase transition at 400°C. It can be said that the low-temperature rf plasma is an efficient technique for the evacuation of oxygen under thermally non-equilibrium conditions.

The vis activity of the colored plasma heat treated ST-01 was investigated by the photocatalytic oxidation of benzoic acid in the liquid phase and 2-propanol in the gas phase. Fig. 7A–D indicates the effects of the parameters of the plasma heat treatment of ST-01, such as rf power, H_2 flow rate, treatment time, and treatment temperature, on the removal of benzoic acid. These data were correlated with the amounts of benzoic acid adsorbed on TiO_2 and the vessel walls at the adsorption isotherm in a dark experiment.

In this figure, no benzoic acid was found to be removed by the raw ST-01 as the control, while 13 to

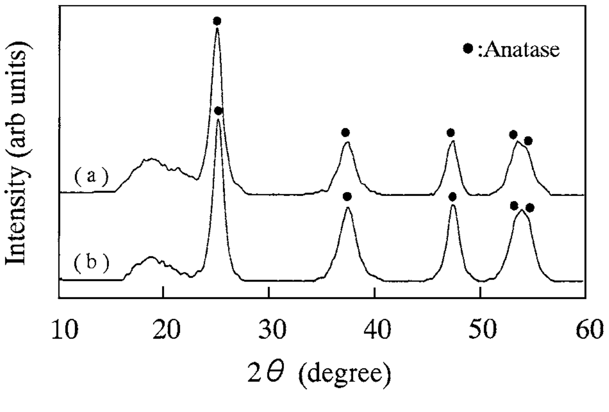

Figure 6 XRD patterns of ST-01: (a) control; (b) H_2 plasma-heat treated.

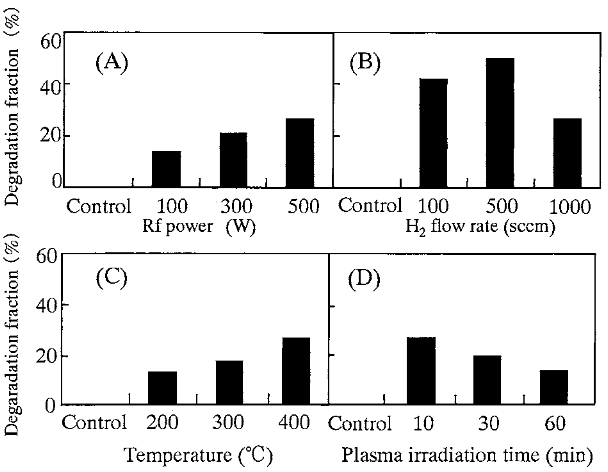

Figure 7 Effects of the parameters of plasma-heat treatment of ST-01 on the degradation of benzoic acid: (A) effect of rf power (400°C, 500 sccm, 10 min); (B) effect of H_2 flow rate (500 W, 10 min, 400°C); (C) effect of treatment time (500 W, 500 sccm, 400°C); (D) effect of treatment temperature (500 W, 500 sccm, 10 min).

50% of the benzoic acid was removed by the plasma heat treated ST-01. In the case of the heat-treated ST-01, only 1 to 2% of the benzoic acid was found to be removed. From the results above, the most effective parameter setting for the oxidation of benzoic acid seems to be the combination of the highest rf power of 500 W, medium H_2 flow rate of 500 sccm, the highest temperature of 400°C, and the shortest treatment time of 10 min.

Next, we examined the relationship between the color of the treated ST-01 and the benzoic acid removal. As an indicator of the color, we used the L-value, which indicates the brightness of the color; L-values of 100% and 0% correspond to white and black colors, respectively. The relationship between the L-value and the benzoic acid removal (%) is shown in Fig. 8. In this figure, the data for the raw ST-01 and heat treated ST-01 without plasma were also plotted. Heat treated ST-01 without plasma has an L-value of 87, indicating that the oxygen defects are formed by the heat treatment under a low-pressure H_2 atmosphere. The L-values of the plasma-heat treated ST-01 were scattered from about 80 to 90 depending on the treatment conditions, but a linear relation between them was observed: the more the L-value declined, the more the removal percentage increased.

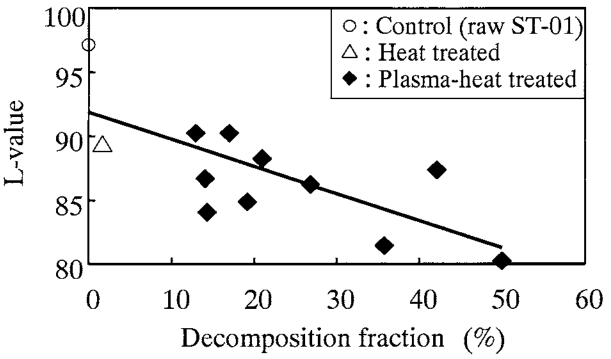

Figure 8 Relationship between L-value of ST-01 and the decomposition fraction of benzoic acid in the photocatalytic oxidation of benzoic acid in the presence of ST-01 treated by various treating conditions.

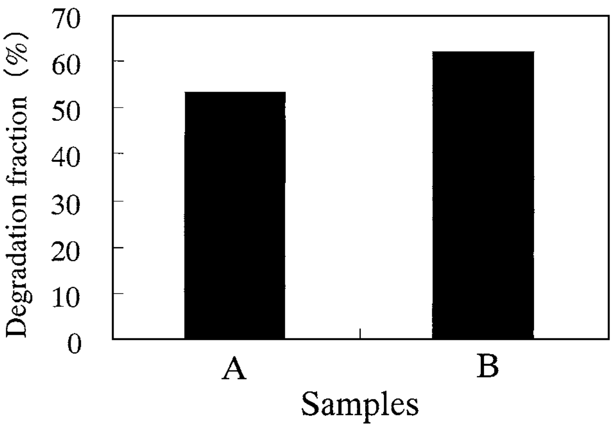

Figure 9 Comparison of the decomposition fraction of benzoic acid when the broadband (UV and visible) light was applied for 30 minutes: (A) raw ST-01; (B) plasma-heat treated ST-01 (400°C, 500 W, 500 sccm, 10 min).

Fig. 9 shows the results of the benzoic acid removal obtained by illuminating xenon lamp instead of halogen lamp. In this case, illumination time was set to 30 minutes.

As for the raw TiO_2, the removal percentage of 54% was obtained. On the other hand, for plasma treated ST-01 showed 65% indicating that the plasma-heat treated ST-01 has higher activity for broadband light illumination.

Next, the vis activity was also investigated by the photocatalytic oxidation of 2-propanol to acetone in the gas phase. It is reported that gas-phase 2-propanol is a good model system because the initial reaction pathway involves almost exclusively a partial oxidation to acetone [21]. The measurement was carried out for raw ST-01 and plasma heat treated ST-01 and the results are shown in Fig. 10.

In the case of the raw ST-01, no acetone was found under vis illumination. In contrast with the raw ST-01, the formation of acetone was observed with plasma heat treated ST-01, and the concentration increased with increasing vis illumination time. After 1000 minutes, the acetone was completely oxidized to carbon dioxide. The formation of the carbon dioxide of the quantity that it is about equivalent to the amount of one-third of the initial concentration of 2-propanol was recognized at this moment.

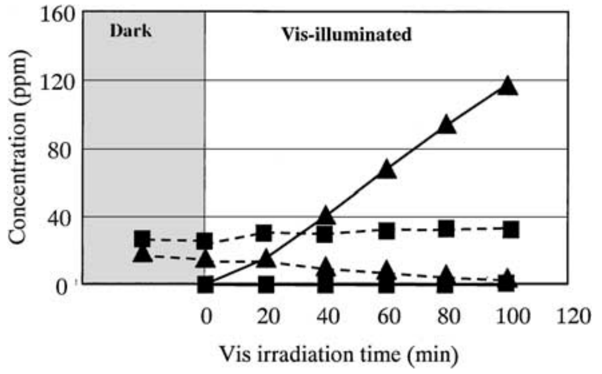

Figure 10 Concentration change of 2-propanol (dashed line) and acetone (solid line) in the photocatalitic oxidation of 2-propanol under vis irradiation with control (■) and plasma-heat treated ST-01 (▲).

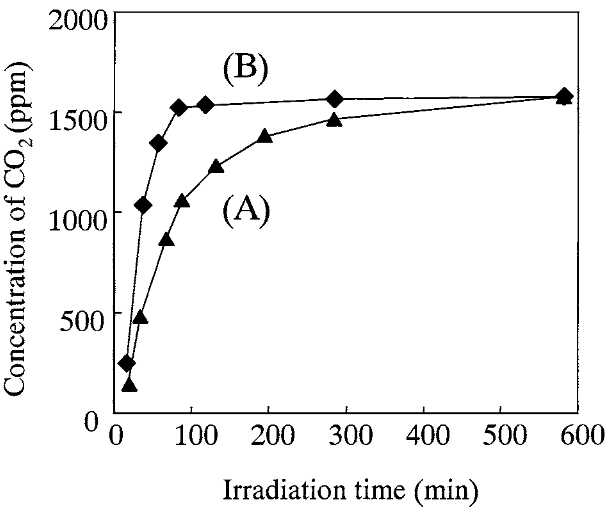

Figure 11 Concentration change of formed CO$_2$ as a final product when the broadband (UV and visible) light was applied: (A) raw ST-01; (B) plasma-heat treated ST-01 (400°C, 500 W, 500 sccm, 10 min).

The same experiment was done using xenon lamp instead of halogen lamp. In this case, the detection of the carbon dioxide of the final product was done because the oxidation reaction was too fast to detect the intermediate product, acetone. The relationship between the concentration of the carbon dioxide and the illumination time was plotted in Fig. 11.

In the case of plasma heat treated ST-01, the carbon dioxide which is nearly correspond to the volume, which 2-propanol decomposed completely, was detected after about 80 minutes from the beginning of illumination. On the other hand, with raw ST-01, the entirety decomposition of the acetone takes time for about 600 minutes, and it is understood that activity toward broadband of plasma-heat treated ST-01 is higher than ST-01.

The durability of vis activity against sunlight irradiation was examined and the vis activity after 120 days was shown in Fig. 12 together with the initial activity. Since the acetone formation linearly increased, as shown in Fig. 10, the vis activity was expressed as the acetone formation rate in this figure.

It was found that the vis activity remained almost steady in the outdoor environment after 120 days, 4% below the initial level. Exposure of the plasma-treated ST-01 to outdoor air and direct sunlight for a month resulted in a increase of the O/Ti ratio by 1.9. However the change of visible-light activity for 2-propanol oxidation was negligible. Similar tendencies were also observed in our experiments of the visible-light activity test for NO oxidation [22]. We assume that some of the defects produced by the plasma treatment are curable, while most of them (probably those in the subsurface layers) are stable against oxidation. The plasma-treated ST-01 lost most of its color and visible-light activity after heating in air at 400°C for 2 h.

ESR measurements were carried out for the control ST-01 and the plasma heat treated ST-01 at 77 K in *vacuo* and the spectra are shown in Fig. 13. There was a signal observed at $g = 2.003$ in the plasma-heat treated ST-01 in the dark. The magnitude of this signal increased when the vis illumination was applied. On the contrary, no signal was observed in the raw ST-01 regardless of the illumination by UV or vis except the signals for the Mn^+ marker. As for the assignment of the signal at $g = 2.003$, it seems to be due to the electrons trapped at the oxygen-defect site [23, 24]. This could be the reason for the Vis photocatalytic activity found using plasma heat treated ST-01.

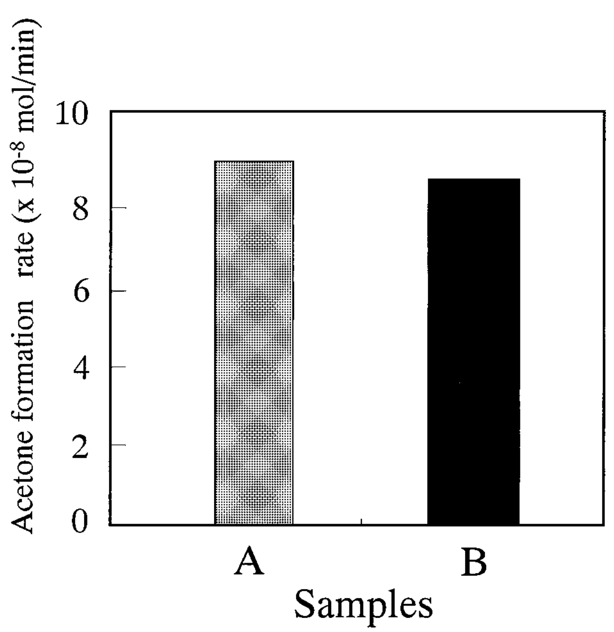

Figure 12 Durability of vis-light activity against sunlight irradiation for 120 days: (A) initial sample; (B) after 120 days exposure.

There have been a number of investigations concerning the energy level of oxygen vacancies in the TiO$_2$ single crystal [25, 26]. Based on the values reported these literatures, the oxygen vacancy state in this plasma-heat treated ST-01 thought to be about 2.02 eV above the valence band as we determined [27]. Therefore, the electron may be excited to the oxygen vacancy state from the valence band even with the energy of visible light. It is thought that the electrons excited to the oxygen vacancy state (and holes at that time) participate in the photocatalytic oxidation of benzoic acid and 2-propanol.

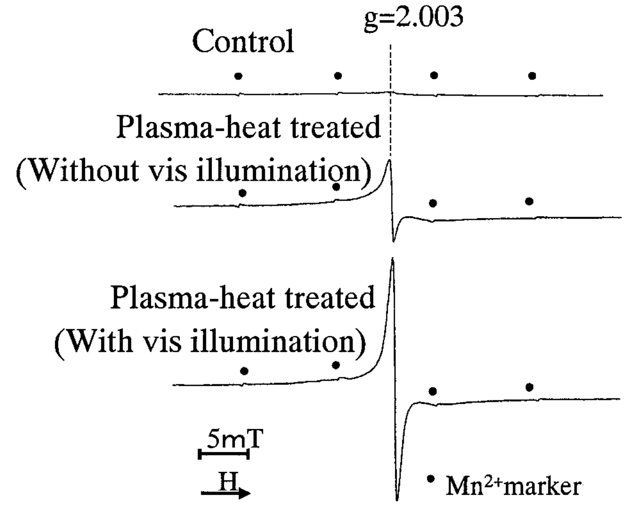

Figure 13 ESR spectra of ST-01: (a) control; (b) plasma-heat treated without vis illumination; (c) plasma-heat treated with vis-light illumination.

4. Conclusion

The hydrogen plasma-heat treated ST-01 photocatalyst showed excellent visible-light activity for the oxidation experiment with 2-propanol and benzoic acid. Neither the crystal structure nor the specific surface area was observed to change between the raw ST-01 and the plasma-heat treated ST-01. The electrons trapped on oxygen vacancies in plasma-heat treated ST-01 were detected by ESR measurement under the vis-light illumination. The appearance of the vis-light photocatalytic activity on plasma-heat treated ST-01 is due to a new photoexcitation process by the formation of the oxygen vacancy located between the valence and the conduction bands.

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Received 19 May 2000
and accepted 7 May 2001