Photocatalytic effects of plasma-heated TiO$_{2-x}$ particles under visible light irradiation

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Abstract−The photocatalytic characteristics of partially reduced TiO$_2$ (TiO$_{2-x}$) by plasma treatment and plasma-heated treatment were investigated in the visible-light region. For the visible-light photocatalytic activity of TiO$_{2-x}$, plasma-heated treatment shows stronger than plasma treatment significantly. The TiO$_{2-x}$ by plasma-heated treatment shows broader red-shifted absorption bands than one by plasma treatment in the visible-light region. The surface color of TiO$_{2-x}$ by plasma treatment and plasma-heated treatment changed from white to sky blue, and to navy, respectively. After exposure to air, the surface color of TiO$_{2-x}$ changed from sky blue to white for plasma treatment and from navy to beige for plasma-heated treatment.

Key words: TiO$_{2-x}$, Photocatalytic Oxidation of 2-Propanol, Plasma-heated Treatment, Photocatalyst, Visible-light Irradiation

INTRODUCTION

Titanium dioxide has been intensively studied because of its excellent optical transmittance, high refractive index and chemical stability. It has been applied widely to optical and protective coatings, optical fibers and photocatalysts, self-cleaning paints and window panes [1-3]. The bandgap energy of TiO$_2$ is 3.0-3.2 eV, which can be excited by UV light of wavelengths shorter than 385 nm. An input of ultra-band gap energy to the semiconductor particle causes a valence band electron to be promoted to the conduction band, causing charge separation. The conduction band electron and valence band hole can then migrate to the surface of the TiO$_2$ semiconductor and participate in the oxidation-reduction reactions, respectively. The O$_2$ molecule scavenges the e$^-$ from the conduction band of the TiO$_2$ semiconductor, forming superoxide radical (O$_2^-$) because the conduction band of TiO$_2$ is nearly isoenergetic with the reduction potential of oxygen [4-6]. However, a disadvantage of the TiO$_2$ photocatalyst is that it reacts only to radiation in the ultraviolet (UV)-light region owing to its large band gap of 3.2 eV (for anatase TiO$_2$). Therefore, a TiO$_2$ photocatalyst that has visible-light photocatalytic activity would be more useful and more convenient, as 45% of solar spectrum is in the visible region. To attain efficient visible-light-active TiO$_2$, it is important to extend the absorption spectrum of this compound into the visible range. A partially reduced TiO$_2$ was expressed as TiO$_{2-x}$ (oxygen-deficient TiO$_2$). The oxygen-defect states of anatase TiO$_2$ were determined to be located within a small band gap energy (<3.2 eV) between the valence band and the conduction band. This band gap energy corresponds to a wavelength in the visible-light region (>420 nm), which is needed to produce the electron for the oxygen defects in the TiO$_2$ partially reduced by hydrogen (H$_2$) plasma treatment. The oxygen defects were created by treating

anatase TiO$_2$ with the H$_2$ plasma, which resulted in oxygen-defect states between the valence and the conduction bands being newly formed in the TiO$_2$ band structure. It is assumed that the oxygen-defect states participate in a new photoexcitation process. That is, the electron may be excited to the oxygen-defect states from the valence band, even with the energy of visible light. In recent years, several groups have attempted to realize the photocatalysis of partially reduced TiO$_2$ by plasma treatment or heat treatment, to obtain a photo-response in the visible-light region and to improve the photocatalytic activity [7,8]. Miao et al. reported that N-doping TiO$_2$ thin film by N$_2$-H$_2$ plasma treatment causes the narrowing of bandgap that resulted in the observed significant red shift of the absorption edge to the visible-light region [9]. And, Chiba et al. reported that TiO$_2$ thin film by plasma surface treatment generated the oxygen defect by the reduction of hydrogen and the absorption edge shifted to the visible light region side [10]. The photocatalytic reaction of TiO$_2$ that is partially reduced by H$_2$ plasma treatment shows a good photo-response in the visible-light region.

Our purpose was to perform the partial reduction of TiO$_2$ by plasma treatment and plasma-heated treatment and to investigate the effect of partial reduction by plasma-heated treatment. And, to investigate the photocatalytic characteristics and the surface color change of anatase TiO$_{2-x}$ by plasma treatment and plasma-heated treatment in the visible-light region.

EXPERIMENTAL

1. Preparation for Partial Reduction of TiO$_2$

Fig. 1 shows a schematic of the experimental set-up for assessing the visible-light photocatalytic activity of anatase TiO$_2$ by plasma treatment and plasma-heat treatment. The reactor, which consists of a 26-mm outer diameter quartz tube, is set in an electric furnace. Anatase-type TiO$_2$ particles (0.5 g, ST-01, 7-nm, Ishihara Sangyo Co., Japan) set in a quartz boat (150×24×5 mm) were placed inside

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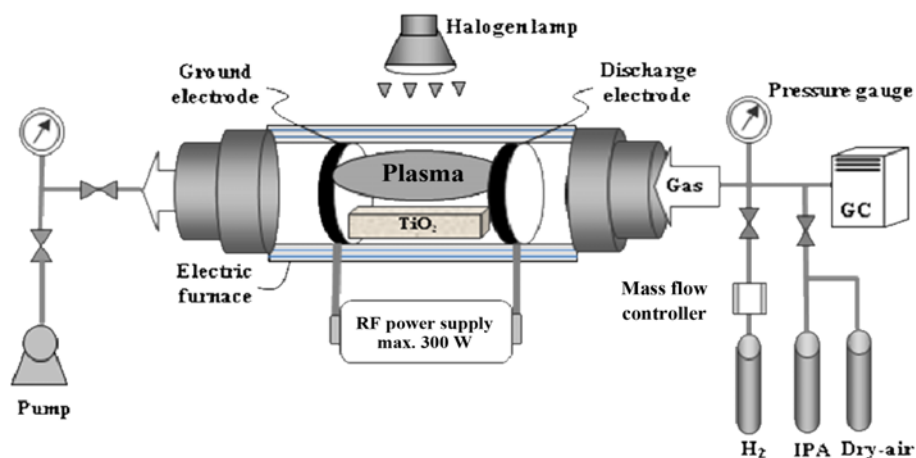E-mail: chaeguy@yonsei.ac.kr

Fig. 1. Experimental set-up for assessing the visible-light photocatalytic activity of anatase TiO$_2$ by plasma-heated treatment.

the plasma reactor. ST-01 gives a relatively high photoactivity when compared to other commercial products such as Degussa P-25 (Japan Aerosil), AMT-100, AMT-600, MT-500B, MT-600B (Tayca Ltd.) [7]. In the experiment, an RF power supply (13.56 MHz) was used to generate glow plasma discharged between copper electrodes attached to the outer surface of the quartz tube. The distance between the electrodes was defined as the electrode gap (150 mm). The sample temperature, which changed depending on the plasma discharge power, was kept constant by additional heating via the electric furnace, and the temperature of the reactor was measured with thermocouples attached to the reactor. After the reactor was evacuated with a rotary pump, H$_2$ gas was introduced into the reactor from the direction of the upstream electrode (discharge electrode) towards the downstream electrode (ground electrode). The flow rate of H$_2$ was controlled with a mass flow controller (model 3200SR, KOFLOC) and it was fixed at 100 sccm. The pressure in the reactor was measured at the upstream and downstream points of the reactor by using pressure gauges, and the average value was defined as the reaction pressure, which was 300 Pa.

2. Plasma Treatment of TiO$_2$

The anatase TiO$_2$ was treated by hydrogen plasma with discharge input power of 10, 30, 60, and 90 W for 10 min.

3. Plasma-heated Treatment of TiO$_2$

In case of plasma-heated treatment, the heating temperature was fixed at 400 °C, and once the reactor was heated to a fixed temperature, the power source for the plasma was switched on with various discharge input powers of 10, 30, 60, and 90 W. The experiments were performed with changes of the RF power delivered to the plasma.

4. Characteristics of Partially Reduced TiO$_2$

The photocatalytic oxidation of 2-propanol was examined to in-

Table 1. Experimental condition for the degradation of 2-propanol using visible-light active TiO$_{2-x}$

2-Propanol (ppm)	10000
Dry-air gas (atm)	0.1
Intensity of Halogen lamp (lx)	1.8×10^4
Irradiation time (min)	80
Distance of lamp and sample (cm)	30

vestigate the photocatalytic characteristics of partially reduced TiO$_2$ under visible-light irradiation. Table 1 shows experimental conditions for photocatalytic characteristics in the visible-light region. After evacuation of the reactor using the rotary pump, 2-propanol (10,000 ppm) in the gas phase added to dry-air at 0.1 atm was introduced into the batch-type reactor. The dry-air gas was introduced into the reactor after the adsorption equilibrium of 2-propanol gas had been reached. A 130-W halogen lamp (intensity, 1.8×10^4 lx) was used as the visible-light source. The distance between the halogen lamp and sample boat was about 300 mm. UV cut film (Asone, Japan) was used to exclude UV light, and the irradiation period was set at 80 min. Acetone formation resulting from the oxidation of 2-propanol was measured by using a gas chromatograph (GC-8A; Shimadzu, Japan) equipped with a 2-m PEG-1000 column, with measurements taken every 20 min. Transformation of anatase-type TiO$_2$ to the rutile type and other titanium oxides was observed by X-ray diffraction (XRD). The visible-light absorption of partially reduced TiO$_2$ was measured with a UV-VIS spectrometer (U-3500; Hitachi, Japan).

RESULTS

The photocatalytic characteristics of partially reduced TiO$_2$ (TiO$_{2-x}$) by plasma treatment and plasma-heated treatment were investigated by the photocatalytic oxidation of 2-propanol to acetone under visible-light irradiation. Fig. 2 shows the X-ray diffraction pattern of partially reduced TiO$_2$ by plasma treatment of 90 W and plasmaheated treatment of 90 W at 400 °C. XRD analysis of all the TiO$_{2-x}$ samples in this experiments showed that the transformation of anatase-type TiO$_2$ to the rutile type as well as other titanium oxides was not observed. Acetone formation due to photocatalytic oxidation of raw TiO$_2$ was not observed in the visible-light region. Fig. 3 shows the time-course of acetone production from the photocatalytic oxidation of 2-propanol under visible-light irradiation. The experimental parameter is the discharge input power. The acetone formation was observed and the level of produced acetone increased with the time of visible-light irradiation. The acetone level was measured to facilitate estimation of the kinetic rate constant. The photocatalytic oxidation kinetics of many organic compounds is often modeled using the Langmuir-Hinshelwood (L-H) equation, which is also related
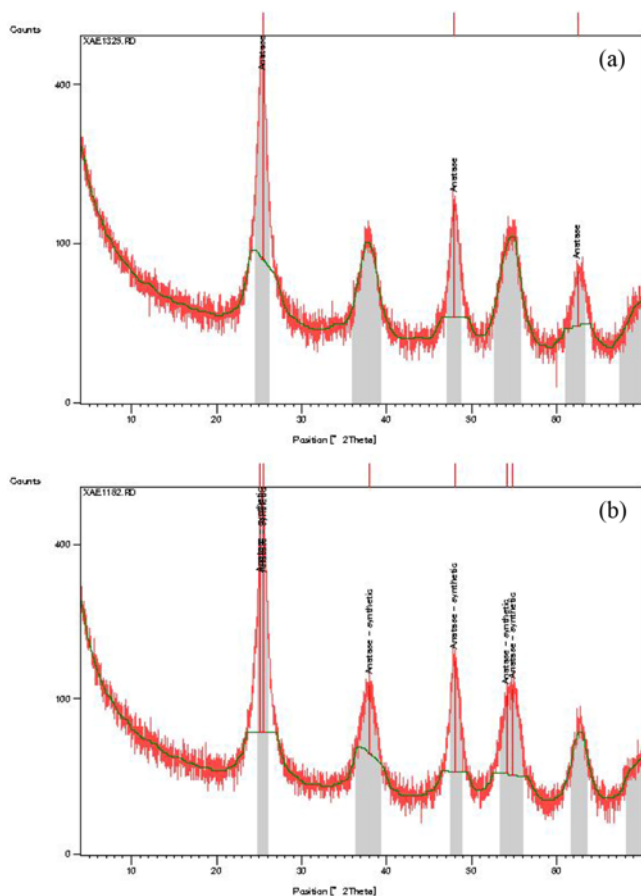
Fig. 2. X-ray diffraction pattern of partially reduced TiO$_2$ by plasma treatment of 90 W (a) and plasma-heated treatment of 90 W at 400 ℃ (b).
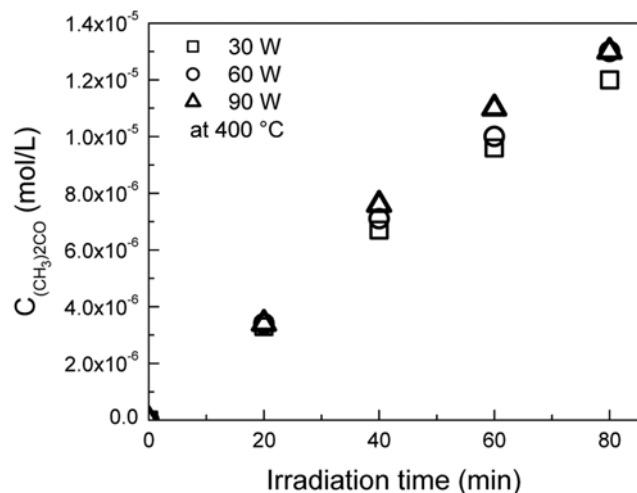

Fig. 3. The time-evolution of concentration of acetone produced by the photocatalytic oxidation of 2-propanol under visible-light irradiation according to discharge input power (No photocatalytic oxidation of 2-propanol to acetone with raw TiO$_2$ was observed under visible-light irradiation).

to the adsorption properties of the substrate on the photocatalyst surface. However, the zero-order model provides a slightly better fit
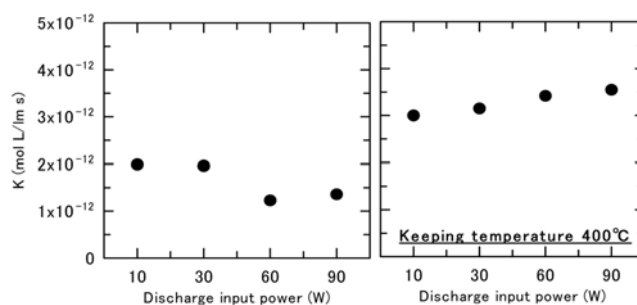
Fig. 4. Kinetic rate constants of visible-light active TiO$_{2-x}$ using plasma treatment and plasma-heated treatment.

than the LHHW (Langmuir-Hinshelwood-Hougen-Watson) model, as shown in Fig. 3. A linearized form of the zero-order kinetic model can be given as:

$$C_A = C_{A0} + K\left(\frac{LT}{2V}\right) \tag{1}$$

where C_A is the concentration of acetone (mol s^{-1}), C_{A0} is the initial concentration of acetone (mol s^{-1}), K is the kinetic rate constant (mol· L lm^{-1}s^{-1}), L is the intensity of visible light (lm), T is time (s), and V is the reactor volume (L). The kinetic rate constant can be determined by performing least-squares regression analysis of C_A versus t.

The photocatalytic reaction of partially reduced TiO$_2$ under visible light irradiation was investigated with comparison of plasma treatment and plasma-heated treatment. Fig. 4 shows the kinetic rate constants of visible-light active TiO$_{2-x}$ using plasma treatment and plasma-heated treatment. The kinetic rate constants for plasma-heated treatment are larger than one for plasma treatment and increased slightly with increasing of discharge input power. The kinetic rate constants for plasma-heated treatment are significantly different from one for plasma treatment due to the acceleration of chemical reaction with H atom and ionized species such as H$^+$, H$_2^+$ in H$_2$ plasma. As shown in Fig. 4, it appears that the effect of chemical reaction for plasma-heated treatment increases more significantly than that for plasma treatment. This explains why the partially reduced TiO$_2$ by plasma-heated treatment shows more decreased band gap energy than one by plasma treatment due to oxygen defects and shows the photocatalytic activity in visible-light region. It was reported that TiO$_2$ powders reduced by hydrogen plasma treatment with elevated temperatures created a new absorption band in the visible light region and showed photocatalytic activity in this region [7]. The new absorption band is based on oxygen vacancies formed in the oxygen ion lattice and the new energy level based on the oxygen vacancies is located to be about 2.0 eV above the valence band [11]. This result suggests that plasma-heated treatment has a stronger effect than plasma treatment for the visible-light photocatalytic activity of TiO$_{2-x}$ and the energy level of the oxygen vacancy for plasma-heated treatment is located higher than one for plasma treatment (see Fig. 5).

Fig. 6 shows the UV-VIS absorption spectra of the partially reduced TiO$_2$ by plasma treatment and plasma-heated treatment. The absorption edge for TiO$_{2-x}$ by plasma treatment and plasma-heated treatment was shifted larger than that for raw TiO$_2$ and it induced a new absorption band at 400-800 nm. As shown in Fig. 6, the absorption bands of partially reduced TiO$_2$ by plasma-heated treat-
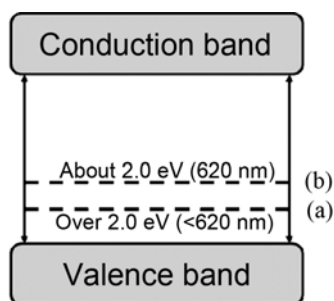
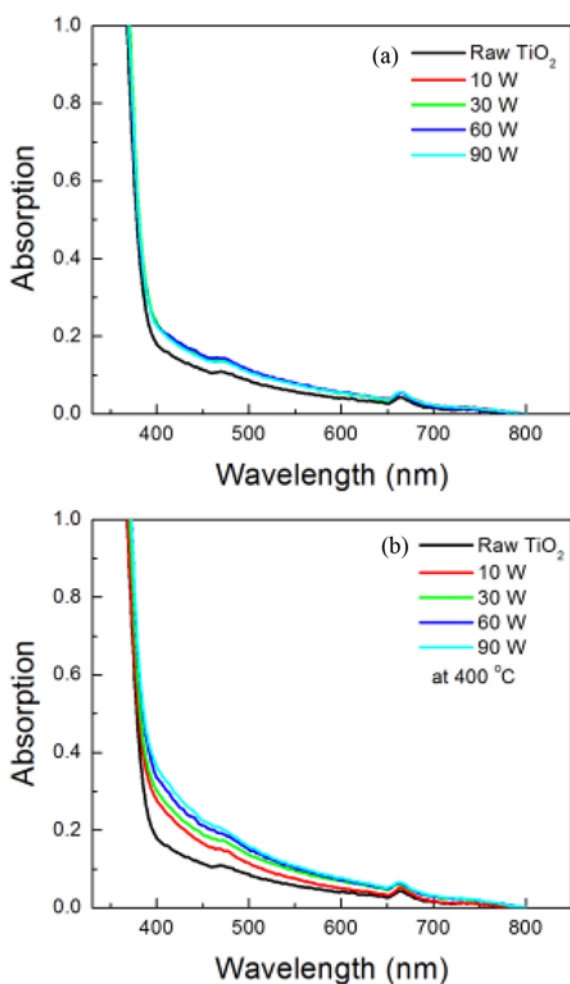**Fig. 5. The new energy state based on oxygen vacancy by plasma treatment (a) and plasma-heated treatment (b).**

Fig. 6. UV-VIS absorption spectra of raw TiO$_2$ and partially reduced TiO$_2$ by plasma treatment (a) and plasma-heated treatment (b).

ment showed significantly broader red-shifted band than one by plasma treatment in the visible-light region. The new energy state based on the oxygen vacancies is located about 2.0 eV above the valence band. And, since the energy state of the oxygen vacancies acts as a donor, light with wavelengths below about 1,030 nm is absorbed by the formation of oxygen vacancies. Therefore, the visible light absorption shown in Fig. 5 originates from the formation of oxygen vacancies (Vo).
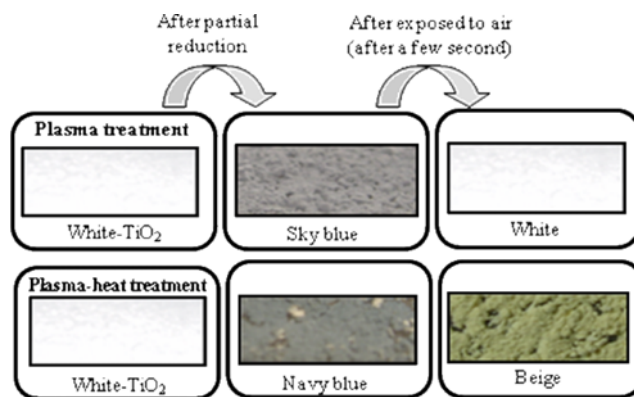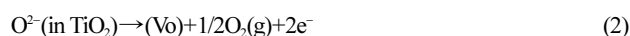

Fig. 7. The surface color change of partially reduced TiO$_2$ by plasma treatment and plasma-heated treatment.

$$O^{2-}(\text{in TiO}_2) \rightarrow (\text{Vo}) + 1/2O_2(g) + 2e^- \quad\quad (2)$$

Ti^{4+} ions in the lattice react with the electron because of their chemical attraction [12]. Ti^{3+} defect states caused by oxygen vacancies are located in the band gap, 0.7-0.9 eV below the Fermi level [13] and the formation of Ti^{3+} species also brings about visible light absorption [14].

$$e^- + Ti^{4+} \rightarrow Ti^{3+} \quad\quad (3)$$

It is assumed that the electrons trapped at Ti^{3+} species move to the oxygen vacancies formed by plasma-heated treatment, since oxygen vacancies act also as the trap sites [15].

$$Vo + e^- \rightarrow Vo^- \qu\quad (4)$$

This indicates that TiO$_{2-x}$ samples by plasma-heated treatment are more able to absorb visible light than one by plasma treatment and have a stronger photocatalytic characteristic than one by plasma treatment in the visible-light region.

Fig. 7 shows the surface color change of partially reduced TiO$_2$ by plasma treatment and plasma-heated treatment, respectively. The surface color of TiO$_{2-x}$ after plasma treatment changed from white to sky blue color. The surface color of TiO$_{2-x}$ changed from white to navy blue after plasma-heated treatment. When TiO$_{2-x}$ samples were exposed to air, the surface color of TiO$_{2-x}$ changed from sky blue to white for plasma treatment and from navy blue to beige for plasma-heated treatment. It is reported that the color of TiO$_2$ treated by H$_2$ plasma changed from white to navy blue due to oxygen defects [16]. Ihara et al. reported that the color change of TiO$_2$ by H$_2$ plasma treatment was from ivory to beige due to oxygen defects [7]. It is reported that the blue color is due to electrons trapped on surface [17]. It is assumed that the surface color change is caused by electron movement at Ti^{3+} species. Thus, the color change of white to navy blue in this experiment may be attributed to the electrons at the surface site, and the disappearance of navy blue coloration may be due to the combination of an electron and oxygen. The surface color of TiO$_{2-x}$ samples by plasma treatment and plasma-heated treatment may be due to oxygen defects.

CONCLUSION

The partially reduced TiO$_2$ by plasma treatment and plasma-heated

treatment showed photocatalytic characteristics in visible-light region. The plasma-heated treatment has a stronger effect than the plasma treatment for the visible-light photocatalytic activity of TiO_{2-x}. The partially reduced TiO_2 by plasma-heated treatment shows broader red-shifted absorption bands than one by plasma treatment in the visible-light region, and appears to have visible-light absorption. The energy level of the oxygen vacancy for plasma-heated treatment is higher than one for plasma treatment. The color change of TiO_{2-x} to blue is due to the oxygen defects, which correlate with the appearance of visible-light absorption and visible-light photocatalytic activity. After being exposed to air, the surface color of TiO_{2-x} changed from blue to beige or white due to the combination of an electron and oxygen. The color change of TiO_{2-x} needs more research.

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