Nitrogen-Concentration Dependence on Photocatalytic Activity of TiO$_{2-x}$N$_x$ Powders

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Received: January 31, 2003

The oxidation power of the TiO$_{2-x}$N$_x$ powders with low nitrogen concentrations (<0.02) was evaluated by the decomposition of gaseous 2-propanol (IPA) under the same absorbed photon number, 1.4×10^{14} quanta·cm^{-2}·s^{-1}, of visible (Vis) or ultraviolet (UV) light. Regardless of the x value, the quantum yield values from irradiating with Vis light was lower than with UV light, which suggests that the isolated narrow band formed above the valence band is responsible for the Vis light response in the present nitrogen doped TiO$_2$. In addition, increasing the nitrogen concentration when irradiating with UV light lowered the quantum yields, indicating that the doping sites could also serve as recombination sites.

1. Introduction

Titanium dioxide (TiO$_2$) is an efficient photocatalyst[1−3] but is activated only by irradiating with ultraviolet (UV) light. A current area of research in this field is to modify TiO$_2$ so that it is sensitive to visible (Vis) light. One approach is to substitute Cr, Fe, or Ni, etc., for a Ti site.[4−6] Anpo et al.[5,6] substituted Cr^{3+} or V^{3+} (V^{4+}) at lattice positions of Ti^{4+} in TiO$_2$ by a metal ion-implantation method. They showed that the absorption band of the Cr^{3+}-doped TiO$_2$ shifted to the visible light region and that irradiating with Vis light (wavelength > 450 nm) photocatalytically decomposed NO into N$_2$, O$_2$, and N$_2$O. Another approach is to form Ti^{3+} sites by introducing an oxygen vacancy in TiO$_2$.[7,8] Ando et al.[8] reported the "oxygen vacancy-typed visible light sensitive TiO$_2$" in which anatase TiO$_2$ was fabricated and treated under a reductive plasma (H$_2$ plasma).

In 1986, Sato[9] reported that the calcination of NH$_4$Cl or NH$_4$-OH involving titanium hydroxide caused the photocatalytic sensitization of TiO$_2$ into the Vis light region. He concluded that the prepared powders were NO$_x$-doped TiO$_2$ and that the sensitization of these TiO$_2$ powders was due to the NO$_x$ impurity. Similarly, Noda et al.[10] prepared yellow-colored anatase TiO$_2$ powders from a (NH$_2$)$_2$·H$_2$O and TiCl$_4$ solution and concluded that the Vis light absorption was due to the oxygen vacancies. Recently, several groups reported Vis light sensitive TiO$_2$-based powders and thin films.[11−14] Sakatani et al.[11] prepared nitrogen-doped TiO$_2$ powders by a hydrolytic process, using a TiCl$_3$ solution and an ammonia solution, and reported that irradiating with Vis light in the presence of the powdered photocatalyst caused the photocatalytic decomposition of acetaldehyde to CO$_2$. They concluded that the nitrogen atoms (or ions) were doped at the interstitial sites and that these interstitial nitrogens were responsible for the Vis light response. Ihara et al.[12] also prepared a Vis light sensitive TiO$_2$ photocatalyst by a hydrolytic process, using a Ti(SO$_4$)$_2$ solution and an ammonia solution. They found that irradiating with Vis light in the presence of the prepared powder caused the photocatalytic decomposition of 2-propanol to CO$_2$ and asserted that the oxygen vacancies were responsible for the Vis light response.

Sakatani et al. and Ihara et al. insisted on a different conclusion for Vis light response, although they reported similar fabrication methods for Vis light sensitive TiO$_2$-based photocatalysts. Asahi et al.[13,14] theoretically calculated the band structure of the nitrogen-doped TiO$_2$ and its Vis light induced photocatalysis for powders and thin films. Asahi insisted that the oxygen sites were substituted by nitrogen atoms and that these nitrogens were responsible for the Vis light sensitivity. In addition, Asahi concluded that the Vis light sensitivity of the nitrogen-doped TiO$_2$ was due to the narrowing of the band gap by mixing the N 2p and O 2p states. We have previously reported[15] that nitrogen-doped TiO$_2$ powders irradiated with Vis light photocatalytically decomposed CH$_3$CHO and 2-propanol into CO$_2$ with different product distributions than irradiating with UV light. These experimental results suggested that the isolated N 2p narrow band that forms above the O 2p valence band was responsible for the visible light response and in the nitrogen-doped TiO$_2$ the oxygen sites were substituted by nitrogen.

In the present paper, the band structure of the TiO$_{2-x}$N$_x$ with small values of x (<0.02) was experimentally investigated by comparing the quantum efficiency of decomposing gaseous 2-propanol (IPA) under the same absorbed photon number of Vis or UV light.

2. Experimental Section

TiO$_{2-x}$N$_x$ powders were prepared by annealing anatase TiO$_2$ powder (ST01, Ishihara Sangyo Kaisha Ltd.) under NH$_3$ flow at 550, 575, and 600 °C for 3 h. TiO$_2$ powder (ST01) was also annealed under an airflow at 550 °C for 3 h as a reference sample.

An X-ray diffractometer (XRD), X-ray photoemission spectroscopy (XPS), and UV−Vis light absorbance spectroscopy using the diffuse reflection method characterized the samples. The N 1s and O 1s core levels on the surface were measured by XPS in order to investigate the initial states of the NH$_3$ and air annealed powders. According to Saha et al.,[16] the peak at 396 eV is derived from Ti−N bonds. Therefore, the x values (nitrogen concentrations) were estimated by comparing the product of the 396 eV peak area multiplied by the nitrogen sensitive factor to the product of the 531 eV peak area (O 1s, Ti−O bonds) multiplied by the oxygen sensitive factor.

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TABLE 1: Vis and UV Lights Intensity[a]

x in $TiO_{2-x}N_x$	Vis light/ (mW·cm^{-2})	UV light/ (mW·cm^{-2})	x in $TiO_{2-x}N_x$	Vis light/ (mW·cm^{-2})	UV light/ (mW·cm^{-2})
0	0.645*	0.102	0.011	0.304	0.102
0.0050	0.645	0.110	0.019	0.102	0.095

[a] Absorbed photon number = 1.0×10^{14} quanta/(cm^2·s)(for the value marked with an asterisk, 0 quanta/(cm^2·s)).
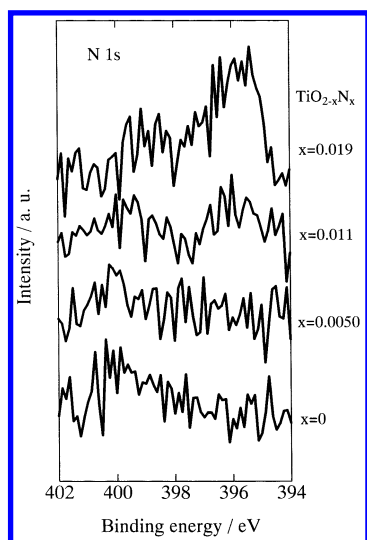
Figure 1. N 1s XPS spectra of $TiO_{2-x}N_x$ and TiO_2 powders.

The photocatalytic oxidation activities were evaluated by the decomposition of gaseous IPA when irradiating with Vis (400–530 nm) or UV (300–400 nm) light. The Vis and UV lights were obtained by a Xe lamp (Hayashi Tokei, Luminar Ace 210) with glass filters (Toshiba Glass, B-47, L-42 and C-40C) and by a black fluorescent light bulb (Toshiba Lighting & Technology) with a glass filter (Toshiba Glass, UV-D36B), respectively. Except when TiO_2 was irradiated with Vis light, the Vis or UV light intensity was calibrated for all the other sample powders to absorb 1.4×10^{14} quanta·cm^{-2}·s^{-1}, as shown in Table 1.

The irradiation area was approximately 4.9 cm^2. A 300 mg sample of either $TiO_{2-x}N_x$ or TiO_2 powders was uniformly spread over the irradiation area in a quartz-made vessel, which had a volume of 500 mL. About 300 ppm of the reactant gas was injected. The samples were kept in the dark once the gas concentration remained constant, which implied that the IPA gas finished absorbing onto the powder surface. The component gas concentrations were measured using a gas chromatograph (Shimadzu model GC-8A).

3. Results

3.1. Sample Characterization. The powders annealed under NH$_3$ flow at 550, 575, and 600 °C were pale yellow, yellow, and dark green, respectively. The XRD patterns indicated that all the powders were a homogeneous anatase (TiO$_2$) phase because only the peaks from the anatase phase and not TiN were observed. The powder annealed under airflow was white and identified as the homogeneous anatase phase.

Figure 1 shows the N 1s XPS spectra of $TiO_{2-x}N_x$ and TiO_2 powders. Since peaks at 396 eV, which have previously been found to result from Ti−N bonds,[16] are observed for the powders annealed under NH$_3$, it was determined that the oxygen sites were substituted by nitrogen atoms. Since the XRD did not indicate the formation of TiN bonds, it was determined that O−Ti−N bonds formed.[15] Therefore, these powders were described as $TiO_{2-x}N_x$. In contrast, the air annealed samples

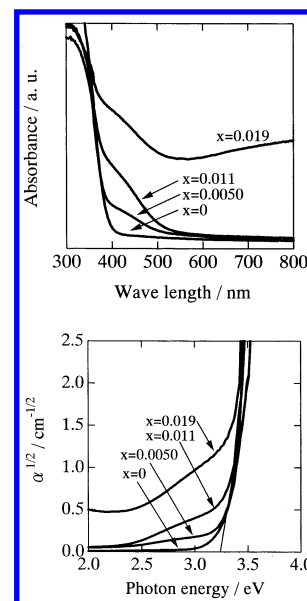**Figure 2.** (a, upper) Optical absorbance spectra of $TiO_{2-x}N_x$ and TiO_2 powders. (b, lower) Plots of the square root of the Kubelka−Munk function against the photon energy of $TiO_{2-x}N_x$ and TiO_2 powders.

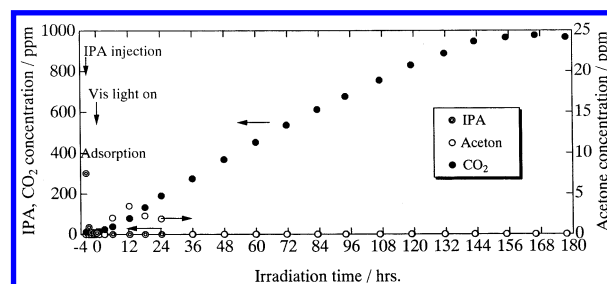**Figure 3.** Changes of IPA, acetone, and CO$_2$ concentrations as a function of time in the presence of $TiO_{1.995}N_{0.005}$ powders under Vis light irradiation (0.645 mW·cm^{-2}).

TABLE 2: x Values in $TiO_{2-x}N_x$

annealing condition	x in $TiO_{2-x}N_x$	annealing condition	x in $TiO_{2-x}N_x$
air 550 °C	0	NH$_3$ 575 °C	0.011
NH$_3$ 550 °C	0.0050	NH$_3$ 600 °C	0.019

did not display a peak at 396 eV and is TiO$_2$. The peak around 400 eV is the chemisorbed N$_2$ molecules, which absorbs onto the surface.[16−19] The estimated x values are listed in Table 2.

Figure 2a shows the optical absorbance spectra obtained by the diffuse reflection of the $TiO_{2-x}N_x$ and TiO_2. Noticeable shifts of the absorption shoulders into the Vis light region were observed for $TiO_{2-x}N_x$. For $x = 0.019$, the increase in absorbance at wavelengths greater than 550 nm corresponds to Ti^{3+} [10] since NH$_3$ decomposes into N$_2$ and H$_2$ at around 550 °C [20] and H$_2$ is a reducing gas. TiO$_2$ is an indirect gap semiconductor,[21] and the band gaps of the $TiO_{2-x}N_x$ and TiO_2 can be estimated from the tangent lines in the plots of the square root of the Kubelka−Munk functions against the photon energy,[22] as shown in Figure 2b. The tangent lines, which are extrapolated to $\alpha^{1/2} = 0$, indicate the band gaps of the $TiO_{2-x}N_x$ and TiO_2 are Eg = 3.2 eV, as shown in Figure 2b.

3.2. Photocatalytic Activity. Figure 3 shows the changes of IPA, acetone, and CO$_2$ concentrations as a function of time in the presence of $TiO_{1.995}N_{0.005}$ powders while irradiating with Vis light (0.645 mW·cm^{-2}). Both acetone and CO$_2$ were produced when irradiating with Vis light, but the acetone further decomposed into CO$_2$. It was concluded that irradiating with
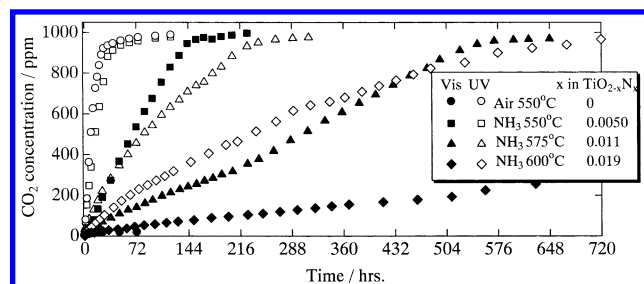
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Figure 4. CO$_2$ concentration changes for the TiO$_{2-x}$N$_x$ ($x = 0$, 0.0050, 0.011, 0.019) powders under Vis or UV light irradiation.
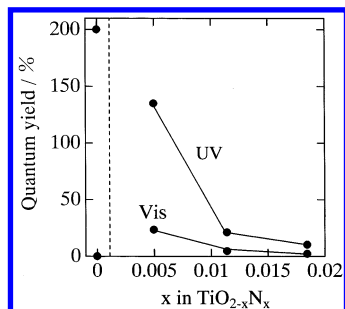

Figure 5. x value dependence of the quantum efficiency.

Vis light in the presence of the photocatalyst completely decomposed the injected IPA because the evolved CO$_2$ concentration was 900 ppm, which was three times the initial IPA concentration.

Similar experiments were conducted with the other photocatalysts. Figure 4 shows the CO$_2$ concentration changes for the TiO$_{2-x}$N$_x$ ($x = 0$, 0.0050, 0.011, 0.019) powders under Vis or UV irradiation, as listed in Table 1. As shown in Figure 4, irradiating TiO$_2$ (TiO$_{2-x}$N$_x$, $x = 0$) with Vis light did not generate CO$_2$ as TiO$_2$ is not Vis light sensitive. CO$_2$, however, was evolved from all the other sample powders by irradiating with Vis light. The CO$_2$ concentration, 900 ppm, indicated that irradiating with Vis light in the presence of the photocatalysts completely decomposed IPA.[23] Irradiating the TiO$_{2-x}$N$_x$ ($x = 0.0050$, 0.011, 0.019) powders with Vis light initially caused a lower CO$_2$ generation rate. As the x values increased, a longer exposure to Vis light was required to decompose IPA. Irradiating with either UV or Vis light in the presence of TiO$_{2-x}$N$_x$ ($x = 0.0050$, 0.011, 0.019) powders completely decomposed IPA.

Figure 5 shows the x value dependence on the quantum efficiency. Assuming that C$_3$H$_8$O + 5H$_2$O + 18h$^+$ → 3CO$_2$ + 18H$^+$, the quantum efficiency (QY) was calculated[24] using the following the equation, QY = (initial CO$_2$ generation rate)/(calculated CO$_2$ generation rate). The absorbed photon numbers were equivalent, 1.4×10^{14} quanta·cm^{-2}·s^{-1}, for all the samples. The calculated CO$_2$ generation rate was determined to be 1.9×10^{-10} mol·s^{-1}. The initial CO$_2$ generation rate was calculated using the conventional least-squares method and the data in Figure 4. When irradiating with either Vis or UV light, the QY values decreased as x increased. The reason will be discussed later.

4. Discussion

Irradiating TiO$_{2-x}$N$_x$ with UV light resulted in a higher QY value than irradiating with Vis light. This trend is plausible because the TiO$_2$ oxygen lattice sites substituted by nitrogen atoms form an isolated narrow band above the valence band. Irradiating with UV light excites electrons in both the valence band and the narrow band, but irradiating with Vis light only excites electrons in the narrow band. If substituting nitrogen

for the oxygen sites in TiO$_2$ narrows the band gap, then the QY values would be the same whether irradiating with Vis or UV light. The observations and Figure 2b do not support the narrowing of the band gap but are consistent with an isolated narrow band above the valence band, which produces the Vis light sensitive photocatalyst. Asahi et al.[13] calculated the band structure of TiO$_{2-x}$N$_x$, where $x = 0.25$ and 0.12, i.e., when 12.5 and 6 at. % of the oxygen sites were substituted by nitrogen, and reported that mixing the N 2p and O 2p states narrowed the band gap. In our studies the x value in the TiO$_{2-x}$N$_x$ powders was much lower and at most was 0.02 (1 at. %). It is plausible that the band structure of the TiO$_{2-x}$N$_x$ with lower values of x (<0.02) should differ from higher x values (>0.12).

The QY values of the TiO$_{2-x}$N$_x$ ($x = 0.0050$, 0.011, 0.019) powders when irradiating with Vis light decreased as the x values increased. When annealing TiO$_2$ powder under an NH$_3$ atmosphere, the oxygen sites were partially replaced with nitrogen atoms while TiO$_2$ was simultaneously reduced.[20] These changes caused an increase in oxygen vacancy and the amount of Ti^{3+}. The oxygen vacancy state in anatase TiO$_2$ is below the lower end of the conduction band at 0.75−1.18 eV [7] and acts as a recombination center for holes and electrons.[25] As the NH$_3$ annealing temperature was increased (with increasing x values), the more TiO$_2$ reduction was reduced and the greater the number of oxygen vacancies, which explains why the QY values were lower as x increased. In fact, TiO$_{1.981}$N$_{0.019}$ powders had an absorbance greater than 550 nm, which corresponds to Ti^{3+} [10] (Figure 2a). The same trend was also observed when TiO$_{2-x}$N$_x$ ($x = 0.0050$, 0.011, 0.019) powders were irradiated with UV light because the oxygen vacancies acted as recombination centers for holes and electrons.

5. Conclusion

TiO$_{2-x}$N$_x$ ($x = 0$, 0.0050, 0.011, 0.019) powders were prepared by annealing under an NH$_3$ flow at 550, 575, and 600 °C. XRD and XPS confirmed that the prepared powders had nitrogen substituted at some of the oxygen sites in TiO$_2$, which formed a narrow N 2p band above the valence band. It was determined that the narrow N 2p band was responsible for the visible light sensitivity by considering the QY values, which were calculated by the CO$_2$ generation rate by decomposing IPA in Vis or UV light at a constant photon number (1.4×10^{14} quanta·cm^{-2}·s^{-1}). When irradiating with Vis light, the QY values decreased as x increased. This is because the oxygen vacancies, which promote the recombination of holes and electrons, increased with x. When irradiating with UV light, the QY values decreased as the nitrogen concentration increased, indicating that the doping sites could serve as recombination centers, too.

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(23) The CO_2 concentration in the presence of $TiO_{1.981}N_{0.019}$ powder is around 300 ppm in Figure 4, but the complete IPA decomposition and the formation of 900 ppm of CO_2 was confirmed.

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(25) The oxygen vacancy state (Ti 3d impurity level) is not visible light sensitive. In fact, hydrogen-reduced TiO_2 (TiO_{2-x}) powders, which have gray color, are not visible light sensitive. The N 2p narrow band exists much deeper than the Ti 3d donor level, and the N 2p level has a lot more oxidation power than the oxygen vacancy level. Therefore, the origin of visible light sensitivity in $TiO_{2-x}N_x$ is the N 2p narrow band level and not the oxygen vacancy level.