TiO$_x$N$_y$/TiO$_2$ Photocatalyst for Hydrogen Evolution under Visible Light Irradiation II Degradation of Photocatalytic Activity of TiO$_x$N$_y$/TiO$_2$ with Mild Oxidation

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**ABSTRACT:** We have studied degradation of photocatalytic activity of TiO$_x$N$_y$ for water splitting under visible light irradiation with heat treatment in O$_2$/N$_2$ mixed gas. The reduction of the N content by oxidation through the formation of O—N—O species (NO$_x$) was confirmed as the result of the reduction of the catalytic activity. The catalytic activity is not simply related to the amount of N remained but that of N taking the chemical state of O—Ti—N in TiO$_x$N$_y$ which is the active species for visible light responsiveness on hydrogen evolution. N in TiO$_x$N$_y$ is first oxidized to NO$_x$ species during the oxidation, which reduces the activity. Then, O—N—O species (NO$_x$) is removed as NO$_x$ gas from the surface. Because the formation of O—N—O in TiO$_x$N$_y$ could induce an impurity energy level to enhance charge recombination, the loss of catalytic activity might be influenced by the formation of O—N—O species (NO$_x$) rather than the loss of the N content from TiO$_x$N$_y$.

**INTRODUCTION**

In recent days, the oxynitride of Ti (TiO$_{1−x}$N$_x$) has been extensively studied as photocatalysts for the water splitting and decomposition of organic pollutants. However, the role and/or chemical state of N doped in TiO$_x$N$_y$ on photocatalytic activity has not been examined in detail. In addition, there are concerns on the stability of N in TiO$_x$N$_y$ under photocatalytic water splitting or other reductive reactions and also stability of N in TiO$_x$N$_y$ under some heat treatments required for its industrial use such as calcination or heat treatment in air. This research situation motivates us to investigate the chemical state of N in TiO$_x$N$_y$ and its role for photocatalytic water splitting and to examine the stability of N in TiO$_x$N$_y$ or TiO$_x$N$_y$ itself under mild oxidation conditions.

The results are reported in two series of papers. In paper I, entitled as “Characterization of N in TiO$_x$N$_y$/TiO$_2$ photocatalyst”, we have given results that TiO$_x$N$_y$ consisting of the fcc phase on the TiO$_2$ core (TiO$_x$N$_y$/TiO$_2$) shows photocatalytic activity to generate hydrogen from methanol aqueous solution under visible light irradiation, in particular, formation of N—Ti—O species is critical to have the catalytic activity. In the present paper, referred as paper II, entitled as “Degradation of photocatalytic activity of TiO$_x$N$_y$ with mild oxidation”, stability of N in TiO$_x$N$_y$/TiO$_2$ or TiO$_x$N$_y$/TiO$_2$ itself under mild oxidation condition was examined. The results of papers I and II were used comprehensively in the Discussion section.

For industrial use of photocatalysts, some engineering processes are required to make the configuration or shape of the catalysts to attain efficient use of photon. For evaluation of photocatalytic activity, micrometer- to nanometer-sized catalysts are often used as dispersion or suspension of them in water including reactants. However, the photocatalysts used in industries are generally fixed on a substrate shaped as a board, panel, and so forth for the following two reasons: (1) in case of surface contamination of the photocatalysts, periodic cleaning is required. The cleaning of fixed photocatalysts on a substrate is easier than that of dispersion or suspension and (2) a fixed panel array has an advantage in cost compared to a particle suspension system on water splitting. The fixation of the photocatalysts to the substrate is usually performed by calcination or heat treatment in air. Considering a report by Tajima et al., in which annealing of N-doped TiO$_2$ in the presence of oxygen gas decreased its N content and photocatalytic activity, TiO$_x$N$_y$/TiO$_2$ would be unstable at high temperature in the presence of oxygen. However, details of chemical state changes in TiO$_x$N$_y$ under mild oxidation and relationship between the chemical state change and photocatalytic activity have not been examined yet. Hence, in this...
paper, we have investigated the effect of the mild oxidation of TiO\textsubscript{N}/TiO\textsubscript{2} on photocatalytic hydrogen evolution in methanol aqueous solution under visible light irradiation with detailed analysis of the oxidation of TiO\textsubscript{N}/TiO\textsubscript{2} and characterization of N in it.

### RESULTS

Figure 1 shows the integrated amount of hydrogen evolution as the function of reaction time for three samples [(a) TON, (b) O\textsubscript{2}TON-573 K (2%), and (c) O\textsubscript{2}TON-673 K (2%)]. All samples were deposited with 1 wt % Pt as the cocatalyst.

![Figure 1](image1.png)

Figure 1. Hydrogen production in water splitting with methanol aqueous solution under visible light irradiation over (a) TON, (b) O\textsubscript{2}TON-573 K (2%), and (c) O\textsubscript{2}TON-673 K (2%). All samples were deposited with 1 wt % Pt as the cocatalyst.

O\textsubscript{2}TON-573 K (2%), and (c) O\textsubscript{2}TON-673 K (2%)]. No hydrogen evolution was observed in the sample without nitriding (JRC-TIO-7), as described in paper I. As seen in Figure 1, TON showed photocatalytic activity and continued its activities for 5 h showing nearly a constant hydrogen production rate. This is consistent with the results of the paper I. Among the oxidized samples, only O\textsubscript{2}TON-573 K (2%) remained the activity of nearly half of TON, and the others showed no photocatalytic activity.

X-ray diffraction patterns of the samples are compared in Figure 2. As noted in the paper I, TON was consisted of the fcc phase of TiO\textsubscript{N}/TiO\textsubscript{2} showing anatase. Although some N could be doped in the anatase phase, the diffraction patterns of the anatase phase in Figure 2 are quite similar to anatase crystalline. The oxidation reduced the peaks of the TiO\textsubscript{N}/TiO\textsubscript{2} phase, and the heavier oxidation made most of the sample to be of fully the anatase phase. The oxidation resulted in appreciable changes in the diffraction patterns, that is, a peak appeared at around 43° because (200) diffraction of TiO\textsubscript{2}N\textsubscript{y} decreased its intensity and shifted to a higher angle with heating at higher temperature and higher oxygen concentration. This indicates that N was removed by the oxidation, and the average distances of Ti–N and Ti–O in TiO\textsubscript{N} phase decreased because the lattice spacing of (200) in TiO\textsubscript{N} corresponds to the average distance of a mixture of Ti–O and Ti–N. On the other hand, peaks at 25 and 48° corresponding to (101) and (200) diffractions of the anatase phase hardly changed. This suggests that even if some N were doped in the anatase phase, its influence on the hydrogen evolution should be quite small.

![Figure 2](image2.png)

Figure 2. X-ray diffraction patterns of (a) JRC-TIO-7, (b) TON, (c) O\textsubscript{2}TON-573 K (2%), (d) O\textsubscript{2}TON-673 K (2%), and (e) O\textsubscript{2}TON-673 K (21%). Right side figures are enlarged views at around 43° and 48°.

UV–vis diffuse reflectance spectra of the samples are shown in Figure 3. The original TiO\textsubscript{2} (JRC-TIO-7) showed a clear cut-off at around 380 nm, corresponding to its band gap, while TON showed large and broad absorption in the wavelength region from 500 to 800 nm, which has been attributed to the existence of Ti\textsuperscript{3+} corresponding to the formation of the TiO\textsubscript{N} phase.\textsuperscript{12,13} Oxidation at 673 K reduced the broad absorption because of the oxidation of Ti\textsuperscript{3+} to Ti\textsuperscript{4+}. As given in Table 1, little change was observed in specific surface area with the oxidation, maintaining at around 30 m\textsuperscript{2}/g. N K-edge X-ray absorption near-edge spectroscopy (XANES) spectra also showed significant changes with the oxidation, as given in Figure 4. The characteristic double-peak structure appeared at around 396–402 eV in TON is a typical indication of the existence of the TiO\textsubscript{N} phase. The oxidation clearly reduced the double peaks and gave a new single peak at around 400 eV. However, the 400 eV peak mostly disappeared with the heavier oxidation condition. N 1s and O 1s X-ray photoelectron spectroscopy (XPS) spectra of the samples are shown in Figure 5. In the N 1s spectra, TON had a single peak at 396 eV, while O\textsubscript{2}TON-673 K (2%) had double peaks at 396 and 402 eV. The double peaks are assigned to N bonded to Ti (N\textsubscript{Ti}) and O–N–O (ONO) species (N\textsubscript{ONO}).\textsuperscript{14,15} The intensity of N\textsubscript{Ti} significantly decreased after the oxidation, showing a decrease in the N content. The O 1s XPS spectrum in TON is divided into three species, Ti–O–Ti bonding of lattice oxygen (O\textsubscript{L}) at 530.1 eV, OH groups on the surface (O\textsubscript{OH}) at 532.3 eV, and C–O bonding (O\textsubscript{C}) at 534 eV caused by surface contaminants in air, respectively.\textsuperscript{16} On the other hand, the spectrum in O\textsubscript{2}TON-673 K (2%) shows four kinds of oxygen species, (O\textsubscript{L}, O\textsubscript{OH}, and O\textsubscript{C}) and O–N–O species at 533.6 eV (O\textsubscript{N=O}).\textsuperscript{17} In addition, O\textsubscript{O} in O\textsubscript{2}TON-673 K (2%) shifted lower binding energy rather than that in TON, indicating a decrease in the N content. Both N 1s and O 1s XPS spectra showed the formation of O–N–O species and decrease in the N content by the oxidation of TON.
The present results clearly show that TiO$_2$N$_x$-TiO$_2$ giving high photocatalytic activity on the hydrogen evolution was oxidized under rather mild oxidation conditions and lost its catalytic activity. Oxidation must result in the removal of N in TiO$_2$N$_x$, and even doped N in TiO$_2$. In the following, details of N removal process in the oxidation are discussed. As concluded in paper I, active species for visible light responsiveness is most likely O−Ti−N species in the TiO$_2$N$_x$ phase. Therefore, either or both the removal of N from TiO$_2$N$_x$/TiO$_2$ or changes of the chemical state of N in TiO$_2$N$_x$/TiO$_2$ could be the cause for the loss of the activity.

### DISCUSSION

The present results clearly show that TiO$_2$N$_x$/TiO$_2$ giving high photocatalytic activity on the hydrogen evolution was oxidized under rather mild oxidation conditions and lost its catalytic activity. Oxidation must result in the removal of N in TiO$_2$N$_x$, and even doped N in TiO$_2$. In the following, details of N removal process in the oxidation are discussed. As concluded in paper I, active species for visible light responsiveness is most likely O−Ti−N species in the TiO$_2$N$_x$ phase. Therefore, either or both the removal of N from TiO$_2$N$_x$/TiO$_2$ or changes of the chemical state of N in TiO$_2$N$_x$/TiO$_2$ could be the cause for the loss of the activity.

### Table 1. Peak Positions in X-ray Diffraction Patterns and the BET Surface Area of Samples

| sample name (oxygen concentration) | peak position around 43° corresponding to atomic distance Ti−O or Ti−N in TiO$_2$N$_x$ (in deg.) | peak position around 48° corresponding to atomic distance of Ti−O or Ti−N in TiO$_2$ (in deg.) | specific surface area (m$^2$/g) |
|-----------------------------------|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------|-------------------------------|
| JRC-TIO-7                         | no peak                                                                          | 48.1                                                                            | 270                           |
| TON                               | 43.16                                                                            | 48.1                                                                            | 30                            |
| O$_2$TON-573 K (2%)               | 43.22                                                                            | 48.08                                                                          | 29.8                          |
| O$_2$TON-673 K (2%)               | 43.3                                                                             | 48.08                                                                          | 29.8                          |
| O$_2$TON-673 K (21%)              | 43.32                                                                            | 48.08                                                                          | 29.5                          |

Considering a higher angle shift of the 43° peak corresponding to lattice spacing of (200) in TiO$_2$N$_x$, the oxidation induced the replacement of the N atom with an O atom to make the average distance of Ti−O and Ti−N shorter because the ionic radius of O$^2-$ is smaller than that of N$^-$ (see Table 1). On the other hand, in (200) in anatase TiO$_2$, no peak shift was observed. If N atoms were doped in TiO$_2$ by nitriding, the oxidation should change the (200) peak in TiO$_2$ to higher angle corresponding to the decrease in photocatalytic activity. However, no such change was observed. Thus, we concluded that the anatase phase, even if they contained some N, was hardly contributing to the hydrogen evolution. This indicates that the removal of N from TiO$_2$N$_x$ by heavy oxidation actually caused the loss of the photocatalytic activity.

In milder oxidation, it is found that changes of the chemical state of N in TiO$_2$N$_x$ also reduced the photocatalytic activity, as discussed in the following. As shown in Figure 3, the oxidation reduced the absorption in the visible region drastically. However, referring the absorption spectra of the samples reported in paper I, the loss of photocatalytic activity caused by the oxidation was more appreciable than that expected from the reduction in optical absorption. This suggests some changes in the chemical state of N in TiO$_2$N$_x$ before its removal.

The oxidation gave significant changes in the UV-vis diffuse reflectance, as seen in Figure 3 and N K-edge XANES, as seen in Figure 4b−d. The characteristic double-peaked structure appeared around 396−402 eV in TiO$_2$N$_x$, decreased with the oxidation temperature. Instead, a sharp single peak at 400 eV appeared which was attributed to the formation of O−N−O in TiO$_2$N$_x$. With higher temperature oxidation (see O$_2$TON-673 K (2%) in Figure 4), the double-peaked structure changed to the single peak. As N K-edge XANES in the total electron yield mode gives information on depth within 10 nm from the surface, the oxidation changed the bonding of O−Ti−N near the surface of TiO$_2$N$_x$ to O−N−O. If many O−N−O were formed in the bulk of TiO$_2$N$_x$, the lower angle shift of (200) diffraction of TiO$_2$N$_x$ should be observed because O−N−O is larger than the N atom. Nevertheless, the higher angle shift was observed (see Figure 2). Hence, under milder oxidation condition, before the removal of N, O−N−O species (or bonding) appeared near the surface region of TiO$_2$N$_x$.

The formation of O−N−O (NO$_x$) species was also confirmed in N 1s and O 1s XPS spectra of the oxidized samples (Figure 5). Because of limited analyzing depth of XPS, the formation of these species in the deeper region over 10 nm from the surface was not clear.

Thus, in milder oxidation, the formation of O−N−O near the surface region of TiO$_2$N$_x$ is likely the main cause for the reduction of the photocatalytic activity on the hydrogen evolution. Also, the oxidation process seems to proceed as following; first, O attacks N in O−Ti−N−Ti to break Ti−N bonding to make O−N−O in surface layers, and further
oxidation makes N a fully oxidized state to be released. Asahi and Morikawa\textsuperscript{11} calculated density of states of TiO\textsubscript{2} with various nitrogen complex species including substitutional NO\textsubscript{2}-doping. Their calculation showed that substitutional NO\textsubscript{2}-doping species created an impurity energy state between the conduction band and the valence band. An impurity energy state has been known to trap the photogenerated carriers and conduction band and the valence band. An impurity energy dopant species created an impurity energy state between the doping. Their calculation showed that substitutional NO \textsubscript{2}- the amount N possibly doped in TiO\textsubscript{2} is quite small, the TiO\textsubscript{2} done far below 573 K.

condition is necessary, for example, calcination in air must be done at far below 573 K; otherwise, we have to develop a new method to synthesize TiO\textsubscript{N}x resistant to oxidation.

**EXPERIMENTS**

Synthesis of TiO\textsubscript{N}x/TiO\textsubscript{2} Photocatalyst Samples. TiO\textsubscript{N}x/TiO\textsubscript{2} photocatalyst samples were prepared in the same way as reported in the paper I; In brief, anatase type TiO\textsubscript{2} (JRC-TiO-7, Japan Reference Catalyst) was nitriled under NH\textsubscript{3} gas flow at 1050 K. The sample used here consisted of the TiO\textsubscript{N}x phase covering the TiO\textsubscript{2} core (referred as TON hereafter) and showed the highest photocatalytic activity for hydrogen evolution from methanol aqueous solution as half reaction of water splitting under visible light irradiation in the synthesized sample.

To investigate the degradation of photocatalytic activity of TON for the hydrogen evolution by heat treatment in the presence of O\textsubscript{2} gas, TON was heat treated at 573 K or 673 K for 2 h in the mixed gases of N\textsubscript{2} and O\textsubscript{2} with two different oxygen contents, that is, 2% for milder oxidation and 21% for air except minor elements. Thus, oxidized samples are referred as O\textsubscript{x} TON-573 K (2%), and O\textsubscript{x} TON-673 K (2%) or O\textsubscript{x} OXTON-673 K (21%).

Characterization of the Samples. Diffuse reflectance spectra of the TON sample and the oxidized ones were obtained by using a UV–vis–NIR spectrometer (JASCO, V-670) in the wavelength range of 200—850 nm. The reflectance was converted to the absorbance by the Kubelka–Munk function referring that of BaSO\textsubscript{4} as a standard. The crystal structure of the samples was identified by X-ray diffraction analysis (Rigaku, RINT-TTRIII). Concentration and the chemical state of nitrogen or oxygen in the samples were investigated by XPS (Shimadzu, ESCA-3400HSE). N K edge XANES spectra of the samples were measured with the BL7U at the Aichi Synchrotron Radiation Center at room temperature in the total electron yield mode. The specific surface area of the samples was determined by the Brunauer–Emmet–Teller (BET) method (Mountech, Maccorb HM-1220).

Photocatalytic Activity. Photocatalytic activities of TON and the oxidized samples were examined by the same way as in the paper I for the half reaction of water splitting under visible light irradiation in methanol aqueous solution. The reaction is referred simply as hydrogen evolution hereafter. Pt nanoparticles (1 wt %) as the cocatalyst was deposited on the samples by a photodeposition method.\textsuperscript{21} The sample (0.1 g) was put into 10 mL of 20 vol % methanol aqueous solution in a quartz cell under He gas flow at a flow rate of 3 mL/min. The cell was irradiated with visible light (λ > 440) given by a 300 W xenon lamp with cutting UV light by a cut-off filter, L-44 (OptoSigma, SCF-50S-44Y). The production of hydrogen was analyzed using a gas chromatograph (Shimadzu, TCD-GC, GC-8A).

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**Notes**

The authors declare no competing financial interest.
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