TiO$_x$N$_y$/TiO$_2$ Photocatalyst for Hydrogen Evolution under Visible-Light Irradiation. I: Characterization of N in TiO$_x$N$_y$/TiO$_2$ Photocatalyst

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Abstract: TiO$_x$N$_y$/TiO$_2$ was synthesized by nitriding of TiO$_2$ in NH$_3$ gas. TiO$_x$N$_y$/TiO$_2$ generated hydrogen from methanol aqueous solution under visible-light irradiation. It was revealed by N K-edge XANES and N 1s XPS measurements that the N species contributing to visible-light responsiveness was the O-Ti-N species. The structure of TiO$_x$N$_y$/TiO$_2$ showing the photocatalytic activity was a double shell type with thin layers of TiO$_2$-N$_y$ that covers the TiO$_2$ core. Although N content on the surface decreased during the photocatalytic reaction, N was supplied from the deeper side to keep the TiO$_2$-N$_y$ phase at the surface and the activity as well.

Introduction

TiO$_2$ is the most widely studied photocatalyst in water splitting or photodecomposition of organic pollutants in air and water.\textsuperscript{1,2} However, the band gap of TiO$_2$ is too wide (3.2 eV) to use visible light that is a major part of sunlight. Therefore, narrowing its band gap is necessary to increase energy efficiency of utilization of solar light. Many studies for the band gap narrowing of TiO$_2$ have been reported such as doping of transition-metal cations and partly reducing TiO$_2$.\textsuperscript{3,4}

Recently, oxynitrides of Ti have attracted attention as visible-light responsive photocatalysts because of their narrower band gap than TiO$_2$.\textsuperscript{5} Zheng et al. have reported that the TiO$_x$N$_y$/TiN core–shell structure synthesized by quick oxidation of TiN showed photocatalytic activity for hydrogen evolution under visible-light irradiation.\textsuperscript{6} Since TiN is basically metallic, some modification is mandatory to be an active photocatalyst.\textsuperscript{7} Li et al. have proposed to use mesoporous TiN microspheres with an egg-shaped shell type structure.\textsuperscript{8} Yang et al. have demonstrated that the heterojunction of TiO$_2$ and TiN on the TiO$_x$N$_y$/TiN composite enhanced photocatalytic activity.\textsuperscript{9}

In these previous reports, the role and/or chemical state of N in TiO$_x$N$_y$/TiN or TiO$_x$N$_y$/TiO$_2$ (referred to as oxynitride composites) having photocatalytic activity has not been discussed in detail.

In addition, the stability of the oxynitride composites under photocatalytic water splitting or other reductive reactions is discussed.\textsuperscript{10–12} One is loss of activity caused by N removal during photocatalytic reactions, and the other is the stability of the oxynitride composites under some oxidation required for their industrial use such as calcination or heat treatment in air. These research situations of the oxynitride composites as photocatalysts motivate us to investigate the chemical state of N in the oxynitride and its role for the photocatalytic water splitting and to examine the stability of N in mild oxidation conditions.

Results are reported in two series of papers. In this paper (referred to as paper I) entitled as “Characterization of N in TiO$_x$N$_y$/TiO$_2$ Photocatalyst”, we have performed nitriding of TiO$_2$ in NH$_3$ gas to synthesized TiO$_x$N$_y$/TiO$_2$ which was used as a photocatalyst to generate hydrogen from methanol aqueous solution under visible-light irradiation. TiO$_x$N$_y$/TiO$_2$ was also subjected to detailed characterization with a particular focus on the chemical state of N by means of XANES and XPS. In a succeeding paper (referred to as paper II) entitled as “Degradation of Photocatalytic Activity of TiO$_x$N$_y$/TiO$_2$ with Mild Oxidation”, the stability of N in TiO$_x$N$_y$/TiO$_2$ and/or TiO$_x$N$_y$/TiO$_2$ itself under mild oxidation conditions was examined. To investigate the role of N in TiO$_x$N$_y$/TiO$_2$, the results of papers I and II were used comprehensively in each discussion section.

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RESULTS

Water Splitting. Figure 1 shows an integrated hydrogen amount produced by the water splitting for all samples. As seen in the figure, all samples except Pt/JRC-TIO-7 (original anatase TiO$_2$ sample) showed catalytic activity. TON-850 showed an induction period of 1 h to detect hydrogen evolution. This is probably because the electrons generated by photocatalysis during the first hour were used to reduce deposited nano-Pt particles to be metallic. Since the activity of TON-950 or TON-1050 was higher than that of TON-850, no induction period appeared. The nitriding samples continued their catalytic activity for 5 h, showing a nearly constant hydrogen production rate with larger rates for higher nitriding temperature. Hydrogen evolution over TiN was negligible.

Characterization. Before Use (As-Prepared). XRD patterns and TEM images of all samples are shown in Figures 2 and 3, respectively. As seen in Figure 3a, the starting material of anatase (JRC-TIO-7) was very fine particles, and accordingly, its XRD pattern consisted of broad peaks of the anatase crystalline. In XRD patterns, TON-850 exhibited only the anatase phase (ICSD #202243), while TON-950 and -1050 showed an fcc phase of TiO$_2$N$_x$ (ICSD #426340) additionally. XRD patterns of the anatase phase became intense and sharper with increasing nitriding temperature, indicating an improvement of crystallinity and grain growth of the anatase phase.

Both are evidenced by TEM observations in Figure 3. Growth of the particle sizes is clear together with the appearance of lattice fringes corresponding to a lattice spacing of 3.4 Å for the (101) plane of the anatase in Figure 3a–d. It should be noted that strong contrast appeared at the edges of the particles in the TEM images of nitriding samples and the edge became darker with increasing nitriding temperature. The edge of particles on TON-950 consisted of a dark small particle (see Figure 3c). Considering that TEM images become darker with the increase of electron density, the darker small particles are likely TiO$_2$N$_x$ particles. Actually, TON-1050 (Figure 3d,e) shows a different lattice fringe with a lattice spacing of 2.4 Å, corresponding to the (111) plane of TiO$_2$N$_x$ with the fcc phase in addition to the (101) anatase fringe.

All the above results are summarized in Table 1 together with the specific surface areas of the samples after Pt loading. The surface area decreased with increasing nitriding temperature, which well corresponds to the growth of the particle sizes. This also supports that the nitriding and the grain growth simultaneously proceeded.

Figure 4 shows the UV–vis diffuse reflectance spectra for all samples. The original TiO$_2$ (JRC-TIO-7) shows a clear cutoff at around 380 nm, corresponding to the band gap of TiO$_2$, while all nitriding samples show absorption above 380 nm with its intensity stronger for the higher nitriding temperature. The absorption in the wavelength region from 500 to 800 nm has been attributed to Ti$^{3+}$. This suggests that Ti$^{4+}$ was reduced by the nitriding corresponding to the formation of TiO$_2$N$_x$.

Figure 5i,ii shows the N 1s and O 1s XPS spectra, respectively, of TON-850, -950, -1050, and TiN. In N 1s XPS spectra, a peak that appeared at 396 eV for TON-950 and -1050 is attributed to N bonded to Ti (Ti–N bond formation). The O 1s XPS spectrum of JRC-TIO-7 shows three O 1s peaks at 530.1, 532.3, and 534.0 eV. The first and second peaks are assigned to Ti–O–Ti bonding of lattice oxygen (O$_L$) and OH groups on the surface (O$_{OH}$), respectively. The third peak is most likely caused by C–O bonding (O$_C$) in some surface contaminants in air. With increasing nitriding temperature, O$_L$ shifted to higher binding energy, which is the indication of an increase in N content. Actually, O$_C$ of TON-1050 showed almost the same binding energy as that of commercial TiN whose surface was oxidized. The intensities of (O$_{OH}$) and (O$_C$) increased until the nitriding temperature was 950 K, and the intensity decreased in TON-1050. Such intensity changes of (O$_{OH}$) and (O$_C$) are probably due to the fluctuations of the intensity of the C 1s peak given by the surface contaminants. All above characterization can be summarized as follows. TON-950 included the fcc phase of TiO$_2$N$_x$ which covered most of its surface. TiO$_2$N$_x$ was not well crystallized and hence easily adsorbed surface contaminants. In contrast, the TiO$_2$N$_x$ phase on TON-1050 was more stabilized making thicker layers with less surface contaminants.

The formation of TiO$_2$N$_x$ on TON-950 and TON-1050 is also confirmed in normalized N K-edge XANES spectra of TON-950 and TON-1050 given in Figure 6, in which appeared a double peaked structure specific to the formation of O–Ti–N.

Thus, the formation of TiO$_2$N$_x$ on TiO$_2$ is very likely the cause of photocatalytic activities of TON-950 and TON-1050 on the water splitting under visible-light irradiation as will be discussed later.

After Use of the Highest Active Sample (TON-1050) for 5 h. Figure 7a–c shows the XRD patterns, UV–vis diffuse reflectance spectra, and N K-edge XANES spectra before and after the photocatalytic reaction for the highest active sample of TON-1050, respectively. In Figure 7a,b, differences between the two samples were small. In contrast, N K-edge XANES changed significantly (see Figure 7c). In the TON-1050 after...
use, the intensity of the spectrum decreased while maintaining the peak structure. The difference was also appreciable in the N 1s XPS spectra of TON-1050 as shown in Figure 8a,b for before and after use, respectively. In the figures, sequential changes of the spectra with Ar ion sputtering time corresponding to depth are given. Although the peak intensity and structure did not change in TON-1050 before and after use, in TON-1050 after use, the intensity decreased with Ar sputtering time without changing peak shape. Converting the Ar sputtering time to sputtered depth, the XPS peak intensity ratios of N 1s to Ti 2p (not shown here) are plotted against the sputtered depth in Figure 8c. In TON-1050 before use, N distributed homogeneously into a depth of over 30 nm with an atomic ratio of N/Ti of around 0.35, while N concentration within 20 nm from the surface decreased in TON-1050 after use. Considering no appreciable change in the shape of N 1s XPS spectra, the surface of TON-1050 after use still kept the TiO$_x$N$_y$ phase with the same chemical state of N as that before use, and hence, the photocatalytic activity was kept for a reaction time of over 5 h.

**DISCUSSION**

**N Species Contributing to Visible-Light Responsiveness.** As described above, nitriding of TiO$_2$ under NH$_3$ formed TiO$_x$N$_y$ on the surface of TiO$_2$. The N content in TiO$_x$N$_y$ reached about 0.3 N/Ti ratio in TON-1050. The nitriding probably proceeds as follows. At first, some O atoms in TiO$_2$ are removed by H$_2$ generated by decomposition of NH$_3$ followed by substitution of a remaining oxygen vacancy by N (Figure 5ii). With increasing amount of substituting N atoms, nucleation or precipitation of fcc-phase TiO$_x$N$_y$ starts.
N K-edge XANES spectra of the samples: (a) TON-850, (b) TON-950, and (c) TON-1050. The arrows indicate the features of double peak structures, which are attributed to O−Ti−N species.

Figure 7. Comparison of TON-1050 before and after the photocatalytic reaction: (a) XRD, (b) UV−vis diffuse reflectance spectra, and (c) N K-edge XANES spectra.

Figure 8. N 1s XPS spectra of TON-1050 (a) before and (b) after the reaction. (c) The atomic ratio of N/ Ti in the depth direction measured by XPS after stepwise sputtering by Ar ions in TON-1050 before and after the reaction.

on the surface of TiO2 because of quite small solubility of N in TiO2 and followed by growth of the TiO2N 

y layers with growth of particle size as seen in Figure 3d,e. Further nitriding at higher temperature proceeds to substitution of O atoms in TiO2N 

y by N, which finally changes to TiN.18

In these nitriding processes, three types of bonding of N have been reported: two types of N occupying the lattice site of TiO2N 

y and/or TiN as N−Ti−N and O−Ti−N accompanying some lattice distortion and one molecular type as O−N−O species (NO2) and/or N2 substituting an O site or enlarged interstitial sites. In addition, a very tiny amount of N could be retained in the anatase phase. As expected from the metallic nature of TiN, it was not active for the water splitting. Therefore, contribution of N−Ti−N bonding for visible-light responsiveness must be very low. In paper II, we have observed that oxidation of TiO2N 

y produced NOx-like molecular species, which inhibit photocatalytic activity rather than providing visible-light responsiveness. In our previous study, we have found that O−Ti−N species in TiO2 contributed to visible-light responsiveness.19−21 Thus, the formation of O−Ti−N bonding in TiO2N 

y is most likely the origin of the photocatalytic water splitting under visible-light irradiation. Actually, as shown in Figures 1 and 2, higher nitriding temperature led to higher photocatalytic activity with the increase in the intensity of the peak due to TiO2N 

y in XRD. However, full nitriding at higher temperature to make TiN suppress the activity.

Stability of O−Ti−N Species in TiO2N 

y. The prepared samples kept H2 evolution more than 5 h, while Pan et al. reported that N in oxyxnitride was unstable during the photocatalytic reaction.17 Therefore, we have characterized the most active sample of TON-1050 before and after use. As seen in Figure 7a,b, the crystalline structure and optical absorption of TON-1050 hardly changed; that is, the bulk state hardly changed before and after the reaction. However, the N content (given in N/Ti ratio) in near surface regions decreased to 0.1 after use from 0.3 before use. This is a clear indication of N removal as already reported by Abe et al.12 The cause was attributed to N2 evolution by the reaction of the photo-generated hole (h+) and N in the surface region. Nevertheless, catalytic activity was kept for at least 5 h. Considering the observation that N kept the initial chemical state after use and that the appearance of the concentration gradient of N from the deeper side to the surface, N must be supplied by diffusion from the deeper side. Namely, as far as the TiO2N 

y phase remains at the near surface region, the photocatalytic activity would remain. This behavior is completely different from the deactivation of TiO2N 

y given by oxidation in mild oxidation conditions reported in paper II in which N was oxidized to form O−N−O species (NOx) and remained near the surface resulting in the deactivation. In the present work, there was no indication of NOx formation and the catalytic activity remained over 5 h. Nevertheless, loss of N would continue, and some stabilization of TiO2N 

y is necessary for its practical use.

■ CONCLUSIONS

We have succeeded to prepare the N-doped TiO2 photocatalyst with activity for water splitting in methanol solution under visible light and investigated the role of N on water splitting with various characterization techniques. N doping was done by nitriding of anatase (TiO2) under NH3 gas flow at...
a temperature ranging from 850 to 1050 K. The N-doped TiO$_2$, which shows the catalytic activity for water splitting, exhibits two phase structures: the anatase phase probably containing some N and the cubic structure of TiO$_2$N$_x$ that grew on the surface of the anatase.

The content of the TiO$_2$N$_x$ phase in the samples increased with nitriding temperature accompanying the increase of hydrogen evolution. This indicates that TiO$_2$N$_x$ works as visible-light responsiveness species for photocatalytic hydrogen evolution. The chemical state of N in TiO$_2$N$_x$ is characterized by N K-edge XANES and found to be bonded directly to Ti and O atoms making N–Ti–O species.

From depth profiling of N, N in the as-prepared samples was homogeneously contained more than 30 nm in depth, while the N content within 10 nm from the surface was reduced after 5 h of photocatalytic water splitting; even at that time, the catalytic activity was maintained. Nevertheless, loss of N would continue, and the photocatalytic activity would reduce for a longer reaction time. Therefore, some stabilization of TiO$_2$N$_x$ is necessary for its practical use.

In conclusion, N making O–Ti–N species in TiO$_2$N$_x$ provided the visible-light responsiveness for the water splitting. However, N is removed from the surface during the reaction. If some N were supplied from the inside to keep the cubic TiO$_2$N$_x$ phase at the surface, the photocatalytic activity would be continued.

**EXPERIMENTS**

**Synthesis of TiO$_2$N$_x$/TiO$_2$ Photocatalyst Samples.** Synthesis of TiO$_2$N$_x$/TiO$_2$ N doping in TiO$_2$ and nitriding of TiO$_2$ were done under NH$_3$ gas flow at 850, 950, and 1050 K for 3 h, respectively. As a starting material, anatase-type TiO$_2$ (JRC-TIO-7, Japan Reference Catalyst) was used. Thus, obtained samples are referred to as TON-X (X denotes nitriding temperature). Commercially available TiN (Mitsuwa Chemicals) was also examined as one of the samples.

**Characterization of the Samples.** Diffuse reflectance spectra of the samples were measured by 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 with BaSO$_4$ as a standard. Crystal structures of the samples were identified by X-ray diffraction analysis (RIGAKU, RINT-TTRIII). Morphology of the samples was observed by a transmission electron microscope (JEOL, JEM-2100F). The concentration and chemical state of N in the samples were investigated by XPS (X-ray photoelectron spectroscopy) (Shimadzu, ESCA-3400HSE). N K-edge XANES spectra of the samples were measured by a UV–vis spectrometer (JASCO, V-670) in the wavelength range of 200–850 nm. The reflectance was converted to the absorbance by the Kubelka–Munk function with BaSO$_4$ as a standard.

**Water Splitting under Visible-Light Irradiation.** In order to evaluate the photocatalytic activity of the samples, the half reaction of water splitting under visible light using methanol aqueous solution was carried out. The reaction is referred simply to as hydrogen evolution hereafter. 1 wt % Pt nanoparticles as a cocatalyst was deposited on the samples by a photodeposition method. The sample (0.1 g) was put into 10 mL of 20 vol % methanol aqueous solution in a quartz cell under He gas flow with a flow rate of 3 mL/min. Methanol was used as a hole acceptor. The cell was irradiated with visible light ($\lambda > 440$) given off by a 300 W xenon lamp with cutting UV light by a cutoff filter, L-44 (Opto Sigma, SCF-50S-44Y). The produced hydrogen gas was analyzed with a gas chromatograph (Shimadzu, TCD-GC, GC-8A).

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**Notes**

The authors declare no competing financial interest.

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