

Visible Light Sensitive Photocatalysts, Nitrogen-Doped Ta₂O₅ Powders

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The photocatalytic activities of nitrogen-doped Ta₂O₅ powders, Ta₂O_{5-x}N_x ($x = 0.10, 0.17, 0.24, 0.35$) were evaluated by the decomposition of gaseous 2-propanol (IPA) under visible (Vis) and ultraviolet (UV) light irradiations with the same absorbed photon number (1.4×10^{14} quanta·cm⁻²·sec⁻¹). Ta₂O_{5-x}N_x could decompose IPA under both Vis and UV light irradiations, and its photocatalytic activity depended on the dopant concentration and the wavelength of the irradiated light. The values of photonic efficiency decreased with increasing the degree of x when irradiating with both Vis and UV lights.

1. Introduction

Titanium dioxide (TiO₂) has been extensively studied as a photocatalytic material because of its high oxidation power and its photoinduced high hydrophilicity.^{1–3} However, since TiO₂ shows the photocatalytic activity only under ultraviolet (UV) light irradiation, highly active and visible (Vis) light sensitive photocatalytic materials have been sought for an effective use of solar energy and an application of photocatalysts to indoor condition where UV light intensity is insufficient.

The Vis light sensitive photocatalysts studied so far can be classified into two categories from the viewpoints of their application fields: one is for water-splitting, and the other is for the decomposition of mostly organic compounds. For water-splitting materials under Vis light irradiation, oxynitrides, containing Ti or Ta, have been studied by Domen and co-workers.^{4–6} They reported tantalum oxynitride, TaON, as a water-splitting material under UV and Vis light irradiations.⁵ Especially this TaON is excellent for the oxidation of water into O₂ with a sacrificial electron acceptor. For organic compounds decomposing materials under Vis light irradiation, the modification of TiO₂ has been attempted. For example, Anpo et al. reported that Cr³⁺-doped TiO₂ prepared by ion-implantation method absorbed Vis light and showed the photocatalytic activity under Vis light irradiation.^{7,8} Recently, nitrogen-doped TiO₂ (TiO_{2-x}N_x) was reported as a Vis light sensitive photocatalyst, and it could decompose organic compounds under UV and Vis light irradiations.⁹ We have also investigated the nitrogen-concentration dependence on the photocatalytic activity using TiO_{2-x}N_x powders¹⁰ and films.¹¹ In addition to nitrogen, sulfur^{12–14} or carbon^{15–17}-doped TiO₂ as Vis light sensitive photocatalysts were reported one after another. However, to the best of our knowledge, there have been few reports on Vis light sensitive photocatalytic materials for the decomposition of organic compounds, except for TiO₂-based photocatalysts.¹⁸

Ta₂O₅, similarly to TiO₂, shows photocatalytic activity under UV light irradiation.¹⁹ Accordingly, it is expected that the nitrogen-doped Ta₂O₅ can decompose organic compounds under not only UV but also Vis light irradiations, as in nitrogen-doped TiO₂.

In the present study, we have fabricated nitrogen-doped Ta₂O₅ and evaluated the photocatalytic oxidation activity by the decomposition of gaseous 2-propanol (IPA) under the same absorbed photon number of Vis and UV lights.

2. Experimental Section

Nitrogen-doped Ta₂O₅ powders were prepared by annealing commercial Ta₂O₅ powders (Wako Chemical; 99.9%) under NH₃ atmosphere at 600–850 °C for 3 h. Ta₂O₅ powder was also annealed under air atmosphere at 600 °C for 3 h as a reference sample.

The crystal phases of the prepared samples were determined by X-ray diffraction (XRD) with CuK_α rays (Rigaku, RINT-2100). UV–Vis absorption spectra using the diffuse reflection method were obtained by a spectrometer (Shimadzu, UV-3100). The nitrogen concentrations in the powders were estimated using X-ray photoelectron spectroscopy (XPS: Perkin-Elmer, 5600). The X-ray source was MgK_α. To correct the Fermi level of the XPS peaks, the peaks were calibrated with C 1s peak, derived from a surface-contaminant hydrocarbon that had a binding energy of 284.8 eV. To refresh the surface of the samples, the surface was etched several nanometers deep by Ar⁺ ion bombardment with the accelerating voltage of 3.0 kV. It was reported that the peak at 397 eV corresponds to N 1s, derived from Ta–N bonds.^{20–23} However, because the peak area of N 1s was partly overlapped with that of Ta 4p_{3/2}, a peak separation method was applied to calculate the peak area of N 1s. The nitrogen concentrations were estimated by comparing the product of the 397 eV peak area multiplied by the nitrogen concentration sensitive factor to the product of the 531 eV peak area (O 1s, Ta–O bonds) multiplied by the oxygen concentration sensitive factor.

The photocatalytic oxidation activity was evaluated by the decomposition of gaseous IPA under Vis (400–530 nm) or UV (300–400 nm) light irradiation. The Vis and UV lights were obtained by a Xe lamp (Hayashi Tokei, Luminar Ace 210) with a combination of glass filters (Asahi-technoglass, B-47, L-42 and C-40C) for Vis light and with a glass filter (Asahi-technoglass, UV-D36B) for UV light, respectively. The Vis and UV light intensities were adjusted so that all samples, except for the Vis light irradiation to Ta₂O₅ and TaON, could absorb the photon flux of 1.4×10^{14} quanta·cm⁻²·sec⁻¹. The light

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TABLE 1: Vis and UV Light Intensities^a

x in $\text{Ta}_2\text{O}_{5-x}\text{N}_x$	Vis light/ $\text{mW}\cdot\text{cm}^{-2}$	UV light/ $\text{mW}\cdot\text{cm}^{-2}$
0	4.0 ^b	5.0
0.10	4.0	0.23
0.17	0.56	0.17
0.24	0.23	0.11
0.35	0.12	0.098

^a Absorbed photon number = 1.4×10^{14} quanta $\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$. ^b ~ 0 quanta $\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ (theoretical).

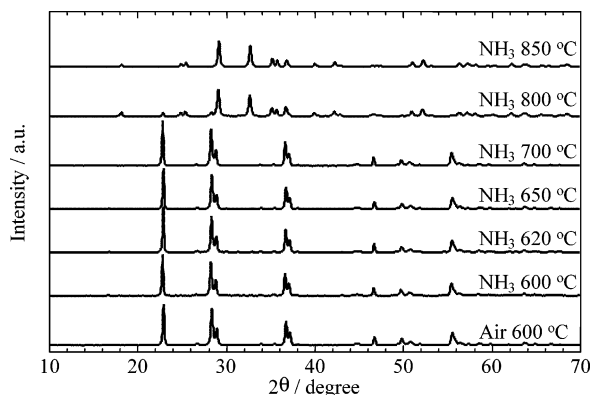


Figure 1. X-ray powder diffraction patterns of NH_3 or air annealed Ta_2O_5 powders. Annealing temperature: 600–850 °C (NH_3) and 600 °C (air). The crystal phases of the obtained powders were Ta_2O_5 at 600–700 °C, the mixture of TaON and Ta_2O_5 at 800 °C, and TaON at 850 °C.

intensities for all samples are listed in Table 1. In some cases, the light intensities were turned up after a long period of irradiation time so that the photocatalytic reaction proceeded more quickly.

A 300-mg sample (Ta_2O_5 , nitrogen-doped Ta_2O_5) was evenly and uniformly spread without open spaces in the sample over the irradiation area (a circular laboratory dish with a radius of 1.7 cm, approximately 9.1 cm^2) in a 500-mL vessel. So, in this experimental condition, irradiated light was absorbed only on the outer geometric surface of the powder. About 300 ppm of reactant gas (IPA) was injected into the vessel and then the samples were stored in the dark condition. After the confirmation that the IPA gas concentration was kept constant, which implied that the reactant gas finished adsorbing onto the powder surface, the light irradiation started. It is well known that the photocatalytic oxidation of IPA proceeds through acetone as an intermediate, followed by the slow oxidation of acetone to final products, CO_2 and H_2O .²⁴ The amounts of IPA, acetone, and CO_2 were determined using gas chromatography (Shimadzu model GC-8A) to evaluate the photocatalytic activity.

3. Results and Discussion

3.1. Sample Characterization. The powders annealed under NH_3 atmosphere became deeper yellow with higher annealing temperature and finally became green. The XRD patterns of the obtained samples are shown in Figure 1. The samples, annealed at the temperatures below 700 °C, maintained the crystal structure of Ta_2O_5 , and neither TaON nor Ta_3N_5 phases were observed. When annealed at 800 °C, however, the crystal structure changed from Ta_2O_5 to TaON form, and the sample finally became a homogeneous TaON phase by annealing at 850 °C under NH_3 atmosphere. The powder annealed under air atmosphere was white and identified as a homogeneous Ta_2O_5 phase.

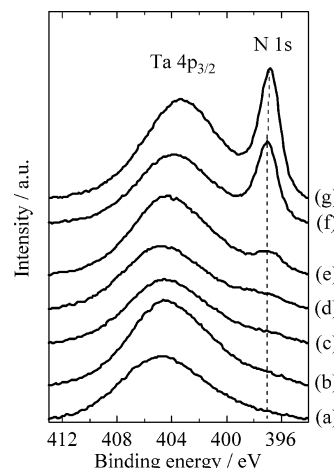


Figure 2. N 1s XPS spectra of Ta_2O_5 , $\text{Ta}_2\text{O}_{5-x}\text{N}_x$, and TaON powders. (a) $x = 0$ (600 °C, air), (b) $x = 0.10$ (600 °C, NH_3), (c) $x = 0.17$ (620 °C, NH_3), (d) $x = 0.24$ (650 °C, NH_3), (e) $x = 0.35$ (700 °C, NH_3), (f) mixture of TaON and Ta_2O_5 (800 °C, NH_3), and (g) TaON phase, $\text{TaO}_{1.40}\text{N}_{0.60}$ (850 °C, NH_3).

TABLE 2: x Values in $\text{Ta}_2\text{O}_{5-x}\text{N}_x$

annealing condition	x in $\text{Ta}_2\text{O}_{5-x}\text{N}_x$
air 600 °C	0
NH_3 600 °C	0.10
NH_3 620 °C	0.17
NH_3 650 °C	0.24
NH_3 700 °C	0.35

Figure 2 shows the N 1s XPS spectra of the prepared powders. The peaks at 397 eV, which have previously been found to result from Ta–N bonds,^{20–23} were observed for the powders annealed under NH_3 . Considering the XRD patterns and the XPS spectra below 700 °C, it was determined that the O–Ta–N bonds were formed and that nitrogen atoms were located at some of the oxygen sites in Ta_2O_5 . Accordingly, these powders, which were annealed at the temperatures below 700 °C, could be described as $\text{Ta}_2\text{O}_{5-x}\text{N}_x$. The estimated nitrogen concentrations, x values, are listed in Table 2.

The composition of the TaON (850 °C, 3 h, NH_3 annealing) was nonstoichiometric $\text{TaO}_{1.40}\text{N}_{0.60}$. Hitoki et al. reported that the composition of their prepared “TaON” was also nonstoichiometric $\text{TaO}_{1.24}\text{N}_{0.84}$.⁵ They prepared TaON by heating Ta_2O_5 powder in an atmosphere of NH_3 flow at 850 °C for 15 h. The nitrogen concentration of TaON in the present study was lower than that of their powders because of the short annealing time.

Figure 3 shows UV–Vis absorption spectra of the prepared powders. $\text{Ta}_2\text{O}_{5-x}\text{N}_x$ powders obviously absorbed Vis light (>400 nm) and the absorption area in the Vis region increased with increasing annealing temperature, that is, with increasing the x values in $\text{Ta}_2\text{O}_{5-x}\text{N}_x$. It is hence considered that nitrogen atoms at oxygen sites are responsible for the Vis light absorption.

3.2. Photocatalytic Activity. **3.2.1. Photocatalytic Activities of $\text{Ta}_2\text{O}_{5-x}\text{N}_x$ Powders ($x = 0, 0.10, 0.17, 0.24, 0.35$) under Vis Light Irradiation.** Figure 4 shows the changes of IPA, acetone, and CO_2 concentrations as a function of time in the presence of $\text{Ta}_2\text{O}_{4.83}\text{N}_{0.17}$ powders under Vis light irradiation, as an example. As for $\text{Ta}_2\text{O}_{4.83}\text{N}_{0.17}$ powders (NH_3 620 °C), both acetone and CO_2 were produced when irradiating with Vis light. It can be considered that this photocatalyst could completely decompose the injected IPA to the final product CO_2 under Vis light irradiation because the concentration of acetone, which is the intermediate of the IPA oxidative decomposition,

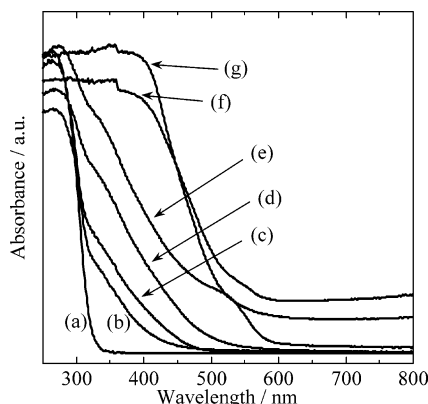


Figure 3. UV-Vis absorption spectra of Ta₂O₅, Ta₂O_{5-x}N_x, and TaON powders. (a) $x = 0$ (600 °C, air), (b) $x = 0.10$ (600 °C, NH₃), (c) $x = 0.17$ (620 °C, NH₃), (d) $x = 0.24$ (650 °C, NH₃), (e) $x = 0.35$ (700 °C, NH₃), (f) mixture of TaON and Ta₂O₅ (800 °C, NH₃), and (g) TaON phase, TaO_{1.40}N_{0.60} (850 °C, NH₃).

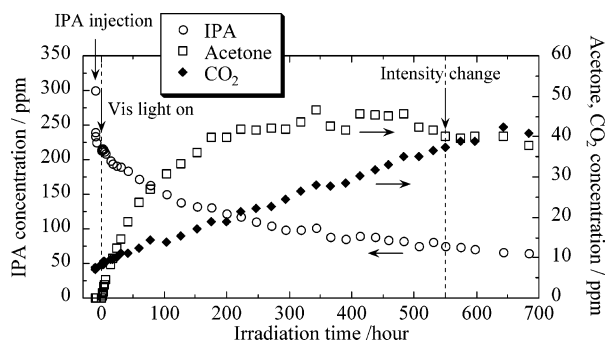


Figure 4. Changes of IPA, acetone, and CO₂ concentrations as a function of time in the presence of Ta₂O_{4.83}N_{0.17} powder under Vis light irradiation (0.56 mW·cm⁻²). After 550 hours of irradiation, Vis light intensity was changed to 1.12 mW·cm⁻² to accelerate the photocatalytic reaction.

reached the maximum and then decreased with time, indicating that the acetone was further decomposed to CO₂ by this photocatalyst. Similar experiments were conducted for the other samples, and the changes of acetone and CO₂ concentrations by the IPA decomposition for all Ta₂O_{5-x}N_x powders ($x = 0.10, 0.17, 0.24, 0.35$) are summarized in Figure 5a and b, respectively. It is obvious from Figure 5 that the photocatalytic activity of Ta₂O_{5-x}N_x samples decreased with increasing x values. As for Ta₂O_{4.90}N_{0.10} powders (NH₃ 600 °C), as the acetone concentration once increased and then decreased, a similar conclusion to the Ta₂O_{4.83}N_{0.17} case was deduced. The CO₂ generation rate in the presence of Ta₂O_{4.90}N_{0.10} was much faster than that in the presence of Ta₂O_{4.83}N_{0.17}.

As for Ta₂O_{4.76}N_{0.24} powders (NH₃ 650 °C), the acetone concentration increased very slowly, and the decrease of the acetone concentration was not observed even when the light intensity was turned up (** in Figure 5a), while it was observed in Ta₂O_{4.83}N_{0.17} (* in Figure 5a). As for the heavily doped Ta₂O_{5-x}N_x powders, Ta₂O_{4.65}N_{0.35} (NH₃ 700 °C), acetone was not generated at all in 150 h of Vis light irradiation. These phenomena will be discussed in the next section.

Photocatalytic activity of Ta₂O_{4.90}N_{0.10} powders was compared with that of Ta₂O₅ (calcined in air at 600 °C) to make sure that Ta₂O_{4.90}N_{0.10} was Vis light sensitive photocatalyst (Figure 6), as glass filters could not cut off UV light completely. The Vis light intensity irradiated to Ta₂O₅ was the same as that to Ta₂O_{4.90}N_{0.10} and was 4.0 mW/cm². Figure 6 elucidated that the photocatalytic activity of Ta₂O_{4.90}N_{0.10} under Vis light

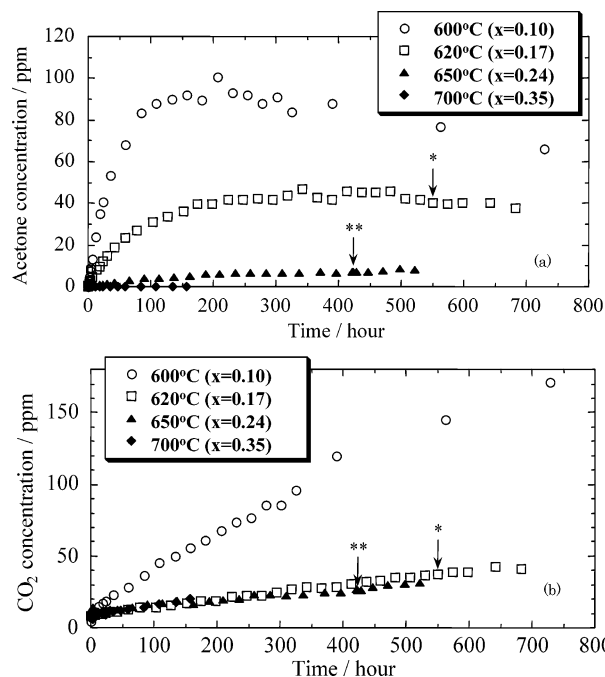


Figure 5. Acetone (a) and CO₂ (b) concentration changes for NH₃-annealed Ta₂O_{5-x}N_x powders ($x = 0.10, 0.17, 0.24, 0.35$) under Vis light irradiation. *: The light intensity was changed from 0.56 mW·cm⁻² to 1.12 mW·cm⁻² ($x = 0.17$). **: The light intensity was changed from 0.23 mW·cm⁻² to 1.15 mW·cm⁻² ($x = 0.24$).

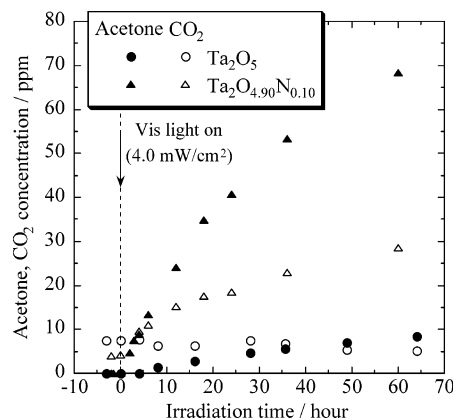


Figure 6. Acetone and CO₂ concentration changes for Ta₂O₅ and Ta₂O_{4.90}N_{0.10} powders under Vis light irradiation (4.0 mW·cm⁻²).

irradiation was far superior to that of Ta₂O₅ and that Ta₂O_{4.90}N_{0.10} made effective use of Vis light.

3.2.2. Photocatalytic Activity of TaON Powder under Vis Light Irradiation. The photocatalytic activity of TaON (TaO_{1.40}N_{0.60}) powder under Vis light irradiation was also evaluated as a reference (Figure 7). Here, the Vis light intensity and the absorbed photon number for TaON were 1.0 mW/cm² and 1.7×10^{15} quanta·cm⁻²·sec⁻¹, respectively. It is apparent from Figure 7 that TaON had little photocatalytic activity for the decomposition of IPA under Vis light irradiation despite the absorbed photon number for TaON was approximately 10 times as large as that for Ta₂O_{5-x}N_x. We concluded that TaON was not proper for the decomposition of organic compounds under Vis light irradiation, though it absorbs a lot of Vis light and is regarded as the Vis light sensitive photocatalyst for the oxidation of water into O₂ with a sacrificial electron acceptor.⁵

3.3. Photonic Efficiency (PE). Initial acetone and CO₂ generation rates by IPA decomposition were calculated using the conventional least-squares method and the data are listed

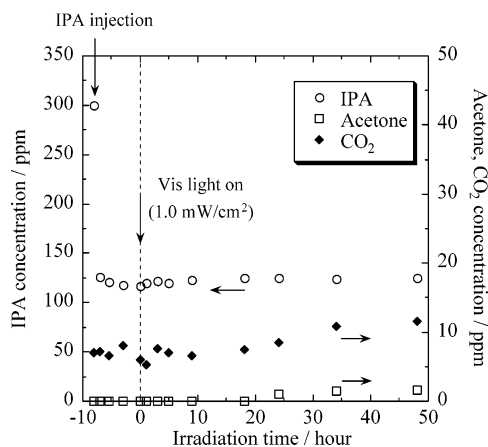


Figure 7. Changes of IPA, acetone, and CO₂ concentrations as a function of time in the presence of TaON (TaO_{1.40}N_{0.60}) powder under Vis light irradiation (1.0 mW·cm⁻²). The absorbed photon number was 1.7×10^{15} quanta·cm⁻²·sec⁻¹.

TABLE 3: Initial Acetone and CO₂ Generation Rates and Apparent Total PE Values in Ta₂O_{5-x}N_x under Vis (a) and UV (b) Light Irradiations

(a) Vis Light Irradiation			
x in Ta ₂ O _{5-x} N _x	acetone/ 10 ⁻¹² ·mol·sec ⁻¹	CO ₂ / 10 ⁻¹² ·mol·sec ⁻¹	PE _{total} /%
0	1.1 ^a	0 ^a	N. D. ^b
0.10	11	2.9	1.3
0.17	3.3	0.51	0.30
0.24	0.40	0.15	0.061
0.35	0	0	0
(b) UV Light Irradiation			
x in Ta ₂ O _{5-x} N _x	acetone/ 10 ⁻¹² ·mol·sec ⁻¹	CO ₂ / 10 ⁻¹² ·mol·sec ⁻¹	PE _{total} /%
0	23	16	5.5
0.10	4.8	1.8	0.74
0.17	0.27	1.1	0.31
0.24	0.81	0.38	0.15
0.35	0	0	0

^a These values were calculated from Figure 6. ^b PE_{total} could not be determined because the absorbed photon number for Ta₂O₅ was virtually zero under Vis light irradiation.

in Table 3. Only one photon participates in the decomposition process of IPA to acetone;^{25,26} therefore, the apparent PE values for acetone generation were calculated using the following equation:²⁷

$$PE_{\text{acetone}} = \frac{\text{initial acetone generation rate}}{\text{the absorption rate of incident photon}} \quad (1)$$

The absorbed photon numbers were equivalent, 1.4×10^{14} quanta·cm⁻²·sec⁻¹, for all the samples; therefore, the absorption rate of incident photons was 1.3×10^{15} quanta·sec⁻¹ ($9.1 \text{ cm}^2 \times 1.4 \times 10^{14} \text{ quanta} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} = 1.3 \times 10^{15} \text{ quanta} \cdot \text{sec}^{-1}$). Here, the absorption rate for photons was estimated at most, as it was assumed that sample powders absorbed all incident photons. Consequently, the PE values were estimated at least. Compared to the mechanism of acetone generation, that of CO₂ generation is complex and it is difficult to decide the number of photons participating in the reaction because there are two reaction paths in it.^{28,29} Assuming the following formula: $\text{C}_3\text{H}_8\text{O} + 5\text{H}_2\text{O} + 18\text{h}^+ \rightarrow 3\text{CO}_2 + 18\text{H}^+$, that is, six photons are needed for producing one CO₂ molecule,¹⁰ the apparent PE

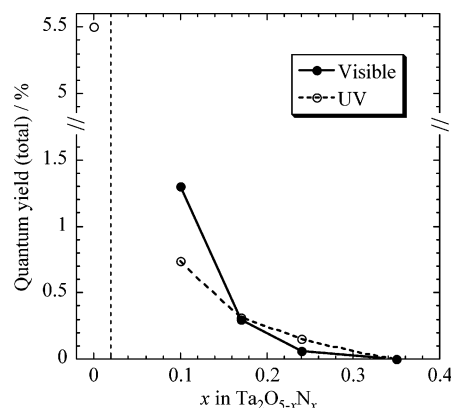


Figure 8. Dependence of PE_{total} on x values.

values for CO₂ generation were calculated using the following equation:

$$PE_{\text{CO}_2} = 6 \times \frac{\text{initial CO}_2 \text{ generation rate}}{\text{the absorption rate of incident photon}} \quad (2)$$

The apparent total PE values, $PE_{\text{total}} = PE_{\text{acetone}} + PE_{\text{CO}_2}$, versus doped nitrogen concentration are plotted in Figure 8. When irradiating with either Vis or UV light, the PE values decreased with increasing x values. The same tendency was observed in nitrogen-doped TiO₂, TiO_{2-x}N_x.¹⁰ The following two reasons can be considered. One is the formation of oxygen vacancies. When annealing Ta₂O₅ powder under NH₃ atm, the oxygen sites were partially substituted by nitrogen atoms while Ta₂O₅ was simultaneously reduced because NH₃ gas was decomposed thermally to H₂ and N₂ gases.³⁰ The oxygen vacancies act as recombination centers for holes and electrons, and these vacancies increase with increasing annealing temperature under NH₃ atm. The other is that the uppermost valence band of Ta₂O_{5-x}N_x, which determines the oxidation power of a photogenerated hole, shifted upward to be negative with increasing dopant nitrogen concentration, resulting in the decrease of the oxidation power. It can be assumed that the oxidation of acetone to CO₂ does not proceed in high dopant concentration because the strong oxidation power is necessary to promote it. Therefore, it is plausible that Ta₂O_{4.76}N_{0.24} (NH₃ 650 °C) could not decompose acetone to CO₂ under Vis light irradiation before and even after turning up the light intensity (Figure 5). The further decrease of the oxidation power should be caused in Ta₂O_{4.65}N_{0.35} (700 °C). Accordingly, it is reasonable that acetone was not produced when irradiating with Vis light because Ta₂O_{4.65}N_{0.35} could not decompose the injected IPA at all (Figure 5).

Figure 8 indicates that in the region of high nitrogen concentrations, the UV light activity was superior to the Vis one, in the region of low nitrogen concentrations, vice versa. This trend was different from TiO_{2-x}N_x, because the UV activity in TiO_{2-x}N_x was superior to the Vis one all over the region of nitrogen concentrations.¹⁰ The reason for this is still unclear, but it was confirmed that the activity of nitrogen-doped photocatalysts depended on the nitrogen concentration.

4. Conclusion

Ta₂O_{5-x}N_x ($x = 0.10, 0.17, 0.24, 0.35$) powders were fabricated by annealing Ta₂O₅ powders under NH₃ atmosphere at 600, 620, 650, and 700 °C, respectively. TaON powders were obtained by annealing Ta₂O₅ under NH₃ at 850 °C. When Ta₂O₅ was doped heavily by nitrogen, the Ta₂O₅ structure changed to TaON, accompanied by the crystal structure change. The

fabricated Ta₂O_{5-x}N_x and TaON powders could absorb Vis light, and it was found by XRD and XPS that in Ta₂O_{5-x}N_x nitrogen atoms were located partially at the oxygen sites in Ta₂O₅ structure. The photocatalytic activity of Ta₂O_{5-x}N_x was evaluated by the decomposition of IPA under both UV and Vis light irradiations at a constant absorbed photon number (1.4×10^{14} quanta·cm⁻²·sec⁻¹), so was TaON under Vis light irradiation (1.7×10^{15} quanta·cm⁻²·sec⁻¹). Ta₂O_{5-x}N_x ($x = 0.10, 0.17, 0.24$) could decompose IPA under Vis light irradiation, and the activity depended on the nitrogen concentration and the wavelength of the irradiated light, whereas TaON could not. In the present study, the UV light sensitive photocatalyst, Ta₂O₅, could be the Vis light sensitive one by nitrogen doping at the oxygen sites with keeping its mother structure. Not showing the data in this report, we have prepared nitrogen-doped Nb₂O₅ (Nb₂O_{5-x}N_x) and confirmed the Vis light activity by the decomposition of IPA. Therefore, it is certain that nitrogen doping is a promising method for preparing Vis light sensitive photocatalysts.

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