Ta$_3$N$_5$ and TaON Thin Films on Ta Foil: Surface Composition and Stability

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Thin films of Ta$_3$N$_5$ and TaON prepared on Ta foils are examined in terms of surface composition and stability in air and in water to evaluate the effectiveness of these materials as visible light-responsive photocatalysts for water oxidation and reduction. The Ta$_3$N$_5$/Ta film is formed by nitridation of Ta$_2$O$_5$ on Ta foil at 1123 K under NH$_3$ flow ($\geq$20 mL min^{-1}), while the TaON/Ta film is formed from the same precursor but with heating at 1073−1123 K under an NH$_3$ flow of 10 mL min^{-1}. The surface of the Ta$_3$N$_5$ film is found to contain oxygen species including hydroxyl groups, and TaON exhibits a higher oxygen content than the stoichiometric amount. X-ray photoelectron spectroscopy reveals that the surface of the Ta$_3$N$_5$ thin film becomes partially hydrolyzed in water, while the TaON film surface remains stable with respect to hydrolysis even in water.

Introduction

Many oxide photocatalysts have been developed for energy problem and the increasingly stringent standards of environmental regulations. Among these, metal oxide photocatalysts such as TiO$_2$ and NaTaO$_3$ work as highly active photocatalysts and can even decompose water efficiently, with proper modification.[1] Most of these metal oxides have band gap energies that are too large to efficiently use solar radiation, however. In these metal oxides, the valence bands predominantly consist of O2p orbitals whose potential energy levels are located at a deep position of about 3 V vs NHE (or about −7.44 V vs vacuum level).[2] Due to this fact, it is generally not feasible to find a transition metal oxide photocatalyst that functions under visible light irradiation.

Recently, the present authors have been investigating (oxy)nitrides of early transition metals, e.g., Ta, Nb, and Ti, as visible light-driven photocatalysts.[3−7] (Oxy)nitrides containing Ta^{5+} or Ti^{4+}, such as TaON, Ta$_3$N$_5$, and LaTiO$_2$N, can be prepared by nitridation of metal oxide powders such as Ta$_2$O$_5$ and La$_2$Ti$_2$O$_7$ under flowing NH$_3$ at above 973 K.[3−8] Through band gap excitations under visible-light irradiation, these (oxy)nitrides function as photocatalysts for the reduction of H$^+$ to H$_2$ and oxidation of water to O$_2$ in the presence of an appropriate sacrificial electron donor (methanol) or acceptor (AgNO$_3$).[9] Among such (oxy)nitrides, TaON and Ta$_3$N$_5$ exhibit high photocatalytic activities for oxidation of water, with quantum efficiencies for oxidation of water to O$_2$ of 34 and 10%, respectively, under visible-light irradiation.[3,4] According to density functional theory (DFT) calculations,[6,10] the conduction band edges of these (oxy)nitrides, as well as transition metal oxide photocatalysts, consist predominantly of empty transition metal d orbitals. The tops of the valence bands of the (oxy)nitrides are constituted by only N2p or a hybridization of N2p and O2p orbitals, respectively. The potential energies of the valence band edges composed of N2p orbitals are higher than those of O2p orbitals in metal oxide photocatalysts, resulting in smaller band gap energies of these (oxy)nitrides.

These (oxy)nitrides prepared previously are apparently stable in air and in water at room temperature, and decomposition by hydrolysis—often observed for metal nitrides—does not appear to proceed in the bulk even during photocatalytic reaction in water. The stabilities of the outermost layers of these materials, however, have not yet been examined in detail. In the present study, Ta$_3$N$_5$ and TaON thin films are prepared on Ta foil, and the surface compositions and stabilities in air and in water are investigated.

Experimental Section

Ta$_3$N$_5$ and TaON thin films (Ta$_3$N$_5$/Ta, TaON/Ta) were prepared by NH$_3$-nitridation of a Ta$_2$O$_5$ layer formed on Ta foil (Ta$_2$O$_5$/Ta).[7] The Ta$_2$O$_5$/Ta precursor was obtained by heating Ta foil (10 × 10 × 0.2 mm^3, 99%, Nilaco Co.) in air at 773 K for 30 min. The thickness of the Ta$_2$O$_5$ layer was estimated to be ca. 3 μm by scanning electron microscopy (SEM). In the previous study, nitridation of Ta$_2$O$_5$/Ta was performed in an alumina tube.[7] However, under such nitridation conditions, it was impossible to completely prevent contamination from air, and transferring the prepared sample to the spectroscopy chambers for analysis hindered the observation of native surfaces. In this study, nitridation of Ta$_2$O$_5$/Ta was carried out in a stainless steel preparation chamber connected directly to the XPS chamber via a gate valve. A schematic of the preparation chamber is shown in Figure 1. The preparation chamber consisted of a turbo molecular pump, a quartz reaction cell, and two transport manipulators. A Ta$_2$O$_5$/Ta sample in the quartz reaction cell was heated under a flow of NH$_3$ (99.999%, 5−120 mL min^{-1}, ca. 1 hPa) at 923−1173 K for 10−120 min. After nitridation, the sample was cooled to room temperature and the chamber was evacuated down to a base pressure of less than 1 × 10^{-6} Pa. The sample was then transferred to the

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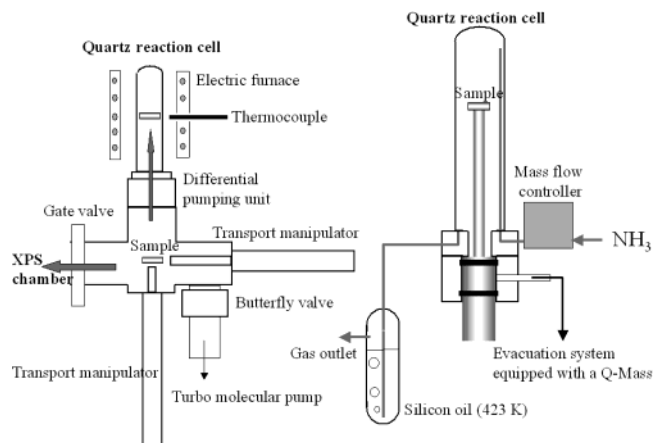‡ Core Research for Evolutional Science and Technology, Japan Science and Technology Co. (CREST, JST).

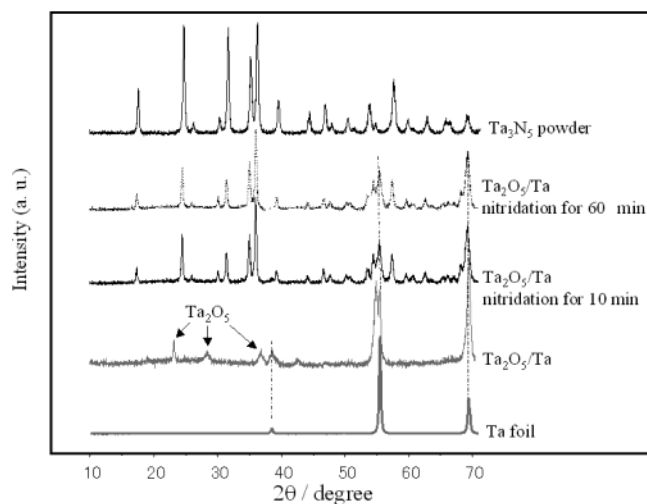**Figure 1.** Preparation chamber equipped with a quadrupole mass spectrometer.

Figure 2. XRD patterns of Ta_3N_5 powder, Ta foil, and Ta_2O_5/Ta before and after nitridation at 1123 K (NH_3 flow rate: 40 mL min^{-1}).

spectroscopy chamber for X-ray photoelectron spectroscopy (XPS) analysis without coming into contact with air. The binding energy determined by XPS was corrected in reference to the C1s peak (284.3 eV) for each sample.

Results and Discussion

Formation of Ta_3N_5/Ta. Figure 2 shows the X-ray diffraction (XRD) patterns of samples after nitridation for 10 and 60 min. For comparison, the XRD patterns of Ta_3N_5 powder and Ta foil are also shown. The diffraction peaks of the samples after nitridation were assigned to those of Ta_3N_5 and metallic Ta in the Ta foil, and no other impurity phase was observed. No significant differences in the XRD patterns could be seen between samples after nitridation for 10 and 60 min, indicating that the Ta_2O_5 layer on the Ta foil is readily converted into Ta_3N_5 under the present nitridation condition. Heating the as-purchased metallic Ta foil for 10 min to 12 h under flowing NH_3 in a similar manner as above did not produce any nitride species according to XRD and XPS analysis, indicating that Ta_3N_5 is not formed by the nitridation of metallic Ta.

Figure 3 shows the XPS spectra for O1s, N1s, and Ta4f regions of Ta_2O_5/Ta before and after nitridation at 1123 K at an NH_3 flow rate of 40 mL min^{-1}. Nitridation under these conditions resulted in the formation of a red film on the foil. For Ta_2O_5/Ta, Ta4f7/2 and 4f5/2, peaks were observed at 26.6 and 28.5 eV, respectively, in good agreement with those for
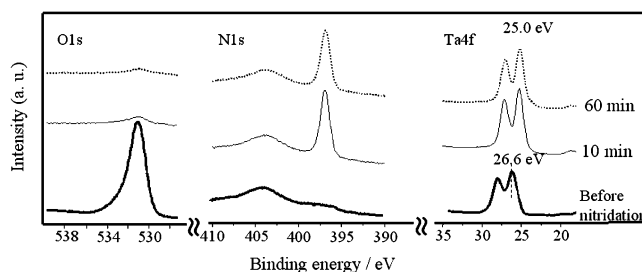

Figure 3. XPS spectra of Ta_2O_5/Ta before and after nitridation at 1123 K (NH_3 flow rate: 40 mL min^{-1}).
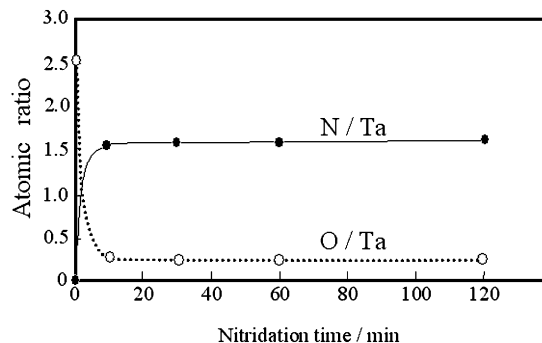

Figure 4. Variation in surface atomic ratios (N/Ta, O/Ta) of the samples with nitridation time (1123 K, NH_3 flow rate: 40 mL min^{-1}).
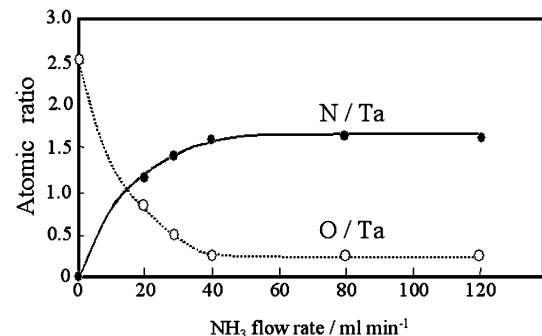

Figure 5. Variation in surface atomic ratios of the samples (1123 K, 60 min) with NH_3 flow rate.

Ta_2O_5 in the literature.[11] The Ta4f7/2 peaks of the samples after nitridation appeared at ca. 25.0 eV, indicating that the Ta4f7/2 peak of Ta^{5+} is shifted to lower binding energies by nitridation.[7] This can be attributed to the bond polarities of Ta−N and Ta−O bonds: Ta−N bonding is more covalent than Ta−O bonding. Such a phenomenon is observed in many metal oxides. Nitridation resulted in the appearance of a N1s peak and a weakening of the O1s peak. However, the O1s peak did not disappear completely, even after nitridation for 60 min.

Figure 4 correlates the surface atomic ratios (N/Ta and O/Ta) with the nitridation time at 1123 K. The surface atomic ratios were estimated using the Ta4f (24−30 eV), N1s (394−398 eV) and O1s (528−534 eV) peaks in the XPS spectra (Figure 3). An increase in the N/Ta ratio and a decrease in O/Ta due to nitridation can be observed after 10 min, after which both atomic ratios remained unchanged. After 120 min, the O/Ta ratio of the sample surfaces was 0.3, indicating that the surface of the prepared Ta_3N_5 thin film contained a considerable amount of oxygen.

The surface composition of Ta_3N_5/Ta was also examined for various NH_3 flow rates. Figure 5 shows the dependence of the surface atomic ratios of the samples on the NH_3 flow rate. The samples were prepared by nitridation for 60 min at 1123 K. In the range of 20 to 120 mL min^{-1} NH_3 flow rate, the surface
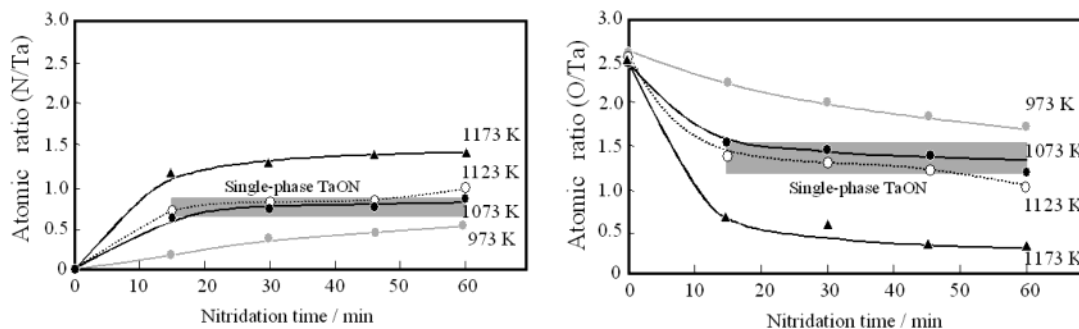
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Figure 6. Variation in surface atomic ratios (N/Ta, O/Ta) of Ta_2O_5/Ta with nitridation at 973−1173 K (NH_3 flow rate: 10 mL min⁻¹).

composition had reached a constant after 30 min, and it was confirmed by XRD analysis that only single-phase Ta_3N_5 was present on all samples. The atomic ratios of N/Ta and O/Ta for the sample prepared at 20 mL min⁻¹ were 1.2 and 0.9, respectively, and the atomic ratio of N/Ta increased with increasing NH_3 flow rate, reaching a plateau at 40 mL min⁻¹. These results demonstrate that nitridation at higher NH_3 flow rates increases the surface N content, but cannot remove all surface O species. One of the possible reasons for this situation is contamination with water in the NH_3 flow during nitridation. It was confirmed by a quadrupole mass spectroscopy (using an instrument connected to the preparation chamber) that there the gas flow during nitridation held less than 1 ppm water. Although a very small amount, the presence of this water may prevent complete nitridation of the surface. It is noted that regardless of the O/Ta ratio (0.3−0.9), the Ta4f7/2 peaks for these samples appeared at 25.0 eV. Therefore, only the exposed surface layer of the films contains large amounts of O, with stoichiometric Ta_3N_5 forming in the subsurface region.

Formation of TaON/Ta. As TaON is an intermediate compound in the process of the formation of Ta_3N_5 by nitridation of Ta_2O_5, the formation of single-phase TaON requires milder nitridation conditions than Ta_3N_5.[4] To form single-phase TaON on Ta foil, nitridation of Ta_2O_5/Ta was attempted at a low NH_3 flow rate (10 mL min⁻¹). Figure 6 shows the progression of the surface atomic ratios (N/Ta and O/Ta) on Ta_2O_5/Ta heated at 973−1173 K under flowing NH_3. The XRD patterns for some samples after nitridation are shown in Figure 7. When nitridation of Ta_2O_5/Ta was carried out at an NH_3 flow rate of over 10 mL min⁻¹, single-phase Ta_3N_5 or a mixture of Ta_3N_5 and TaON was formed on the Ta foil. The surface of the sample prepared by nitridation at 973−1173 K at an NH_3 flow rate of 10 mL min⁻¹ was yellow-orange. At 973 K, N was slowly substituted for O as nitridation progressed, whereas at 1173 K, nitridation proceeded rapidly even at low NH_3 flow rates. Single-phase TaON thin films were finally formed on Ta foils by nitridation for 15−45 min at 1073−1123 K under NH_3 flow at 10 mL min⁻¹.

XRD and XPS revealed that the surface atomic ratios of O/Ta and N/Ta for the single-phase TaON film were 1.2−1.5 and 0.7−0.8, respectively. Thus, the surface of the TaON/Ta samples also had large amounts of O species, with more O than that in stoichiometric TaON. At ratios of O/Ta ≥ 1.9 and N/Ta ≤ 0.5, a mixture of Ta_2O_5 and TaON was observed (Figure 7A), while single-phase Ta_3N_5 or a mixture of TaON and Ta_3N_5 was formed at ratios of O/Ta ≤ 1.0 and N/Ta ≥ 1.0.

Figure 8 shows the XPS spectra for TaON/Ta samples, with the spectra for Ta_2O_5/Ta and Ta_3N_5/Ta shown for comparison. The Ta4f7/2 peaks for the TaON/Ta samples appeared at 26.0 eV, located between the peaks for Ta_2O_5/Ta and Ta_3N_5/Ta. The SEM images of Ta_2O_5/Ta, TaON/Ta, and Ta_3N_5/Ta are shown
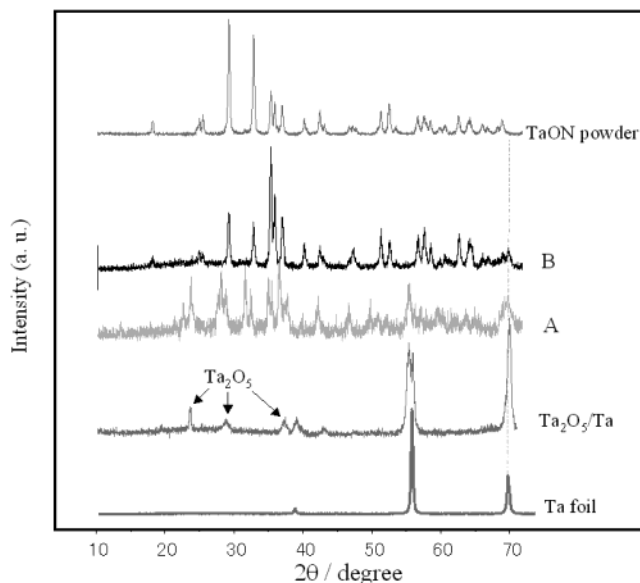

Figure 7. XRD patterns of TaON powder and Ta_2O_5/Ta before and after nitridation (NH_3 flow rate: 10 mL min⁻¹): (A) 973 K, 45 min, N/Ta = 0.5, O/Ta = 1.9, (B) 1073 K, 45 min, N/Ta = 0.8, O/Ta = 1.2
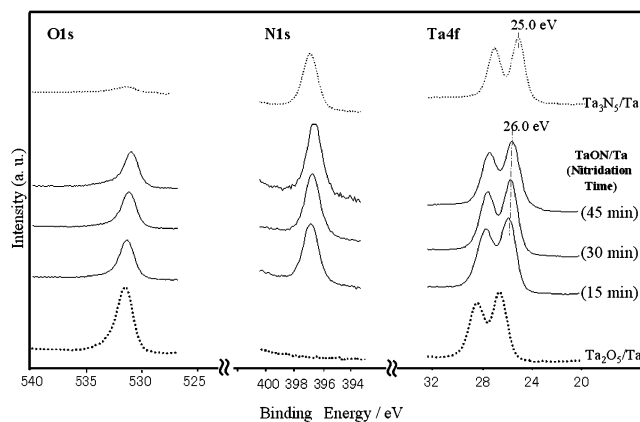

Figure 8. XPS spectra of TaON, Ta_2O_5/Ta, and Ta_3N_5/Ta. TaON/Ta samples were prepared by nitridation for 15−45 min at 1123 K. NH_3 flow rate for all samples was 10 mL min⁻¹.

in Figure 9. The surfaces of Ta_2O_5/Ta, TaON/Ta and Ta_3N_5/Ta were essentially flat, with several cracks.[7] The thickness determined from these observations was ca. 3 μm for all film samples.[7]

Stability of Ta_3N_5/Ta and TaON/Ta in Air and Water. The stabilities of Ta_3N_5/Ta and TaON/Ta were examined in air and in distilled water. Figure 10 shows XPS spectra for Ta_3N_5/Ta samples after contact with air and/or water, and Table 1 summarizes the surface atomic ratios of N/O of these samples. The Ta_3N_5/Ta sample (N/Ta = 1.5, O/Ta = 0.3) obtained by
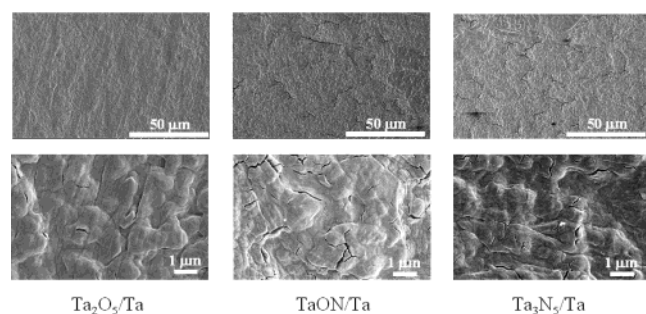
Figure 9. SEM images of Ta_2O_5/Ta, $TaON/Ta$ (N/Ta = 0.8, O/Ta = 1.2) and Ta_3N_5/Ta. (N/Ta = 1.5, O/Ta = 0.3).

TABLE 1: Atomic Ratios of N/O of Ta_3N_5/Ta after Contact with Air and Water

	surface atomic ratio N/O
as prepared	5.0
10 days in air	5.0
2 h in water	5.0
2 days in water	1.5
10 days in water	0.9
20 days in water	0.9

nitridation for 60 min at 1123 K (NH$_3$ flow rate: 40 mL min^{-1}) was allowed to stand in air at room temperature (humidity: 20−40%, temperature: 291−295 K) for 10 days, followed by soaking in distilled water at room temperature for 2 h to 20 days. The color change of the red film was not observed even after soaking in distilled water for 20 days. The surface atomic ratio of N/O was estimated from the N1s and O1s peaks assigned to lattice oxygen (530.9 eV).[12] Although exposure of Ta_3N_5/Ta to air resulted in a small increase in the O1s peak at 532.5 eV,

assignable to surface hydroxyl groups by analogy to surface hydroxyl groups on various transition metal oxides, the ratio of lattice O/N remained unchanged in air as shown in Table 1. In distilled water, N was gradually substituted for O.

Taking into account the surface atomic ratios in Table 1, one-third of the surface N was estimated to be hydrolyzed after 10 days in distilled water. However, hydrolysis slowed with time, and almost stopped after 10 days. The Ta4f7/2 peak of $Ta_3N_5/$ Ta did not shift even after 20 days in water (25.0 eV), and there was no difference in the XRD patterns of the Ta_3N_5/Ta sample immediately after preparation and the same sample after immersion in water for 20 days. The results indicate that a total of approximately one-third of the top surface of the Ta_3N_5 was hydrolyzed by immersion in distilled water for any length of time. Therefore, Ta_3N_5 is essentially stable even in water. The appearance of surface hydroxyl groups suggests that the formation of a protecting oxide/hydroxide (oxynitride) layer prevents further hydrolysis of Ta_3N_5. Such a layer does not have a bad influence on the photocatalysis of Ta_3N_5 because there was no noticeable difference in photocatalytic activities for H$_2$ or O$_2$ evolution before and after soaking Ta_3N_5 powder in distilled water for 20 days.

The results of stability measurements for TaON/Ta are shown in Figure 11 and Table 2. Although the abundance of surface hydroxyl groups on TaON/Ta increased in both air and water, the atomic ratio of N/O remained unchanged, even after immersion in water for 10 days. TaON/Ta is therefore not susceptible to hydrolysis, even on the exposed surface, and as such is much more stable to hydrolysis than Ta_3N_5/Ta.

Although most nitrides are not sufficiently stable, undergoing oxidation and hydrolysis in air and in aqueous solutions, Ta^{5+}-
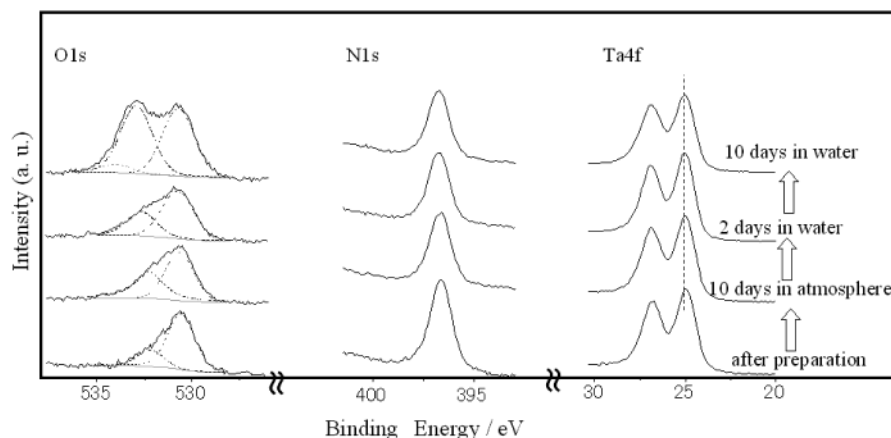

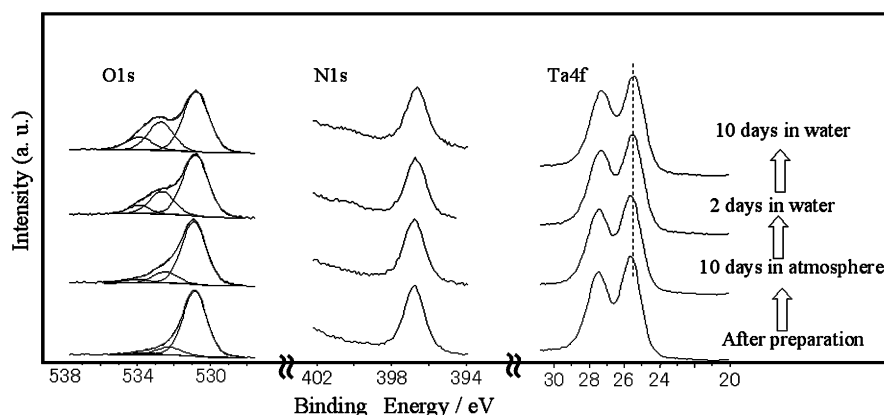**Figure 10.** XPS spectra of Ta_3N_5/Ta after contact with air and water.

Figure 11. XPS spectra of TaON/Ta after contact with air and water.

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TABLE 2: Atomic Ratios of N/O of TaON/Ta after Contact with Air and Water

	surface atomic ratio N/O
as prepared	0.7
10 days in air	0.7
2 h in water	0.7
2 days in water	0.7
10 days in water	0.7
20 days in water	0.7

based (oxy)nitrides are known to exhibit high stability even in aqueous solutions compared to other (oxy)nitrides. For example, it has been reported that CaTaO$_2$N, a perovskite-type oxynitride, is stable even in a concentrated acid solution.[13] Although the stabilities of the exposed surfaces of such (oxy)nitrides have not been examined in detail, the present study reveals that the surfaces of simple Ta^{5+}-based (oxy)nitrides, i.e., TaON and Ta$_3$N$_5$, are stable in water as well as in air.

As mentioned above, both TaON and Ta$_3$N$_5$ function as stable visible light-driven photocatalysts for water decomposition. The high stability of these materials in water is a necessary feature for the continued development of more efficient photocatalytic systems and to accomplish overall water splitting under visible-light irradiation.

Conclusions

Ta$_3$N$_5$ and TaON thin films were prepared on Ta foil by nitridation of Ta$_2$O$_5$/Ta. Nitridation of Ta$_2$O$_5$/Ta at 1123 K under NH$_3$ flow at more than 20 mL min^{-1} resulted in the rapid formation of a single-phase Ta$_3$N$_5$ thin film on the Ta foil. Single-phase TaON/Ta was formed by nitridation for 15−45 min at 1073−1123 K under NH$_3$ flow at 10 mL min^{-1}. The exposed surfaces of both Ta$_3$N$_5$/Ta and TaON/Ta contained larger amounts of O species than the stoichiometric amounts. The surface of Ta$_3$N$_5$/Ta was partially hydrolyzed in water, whereas only negligible hydrolysis proceeded on TaON/Ta even when immersed in water for a long period. The stability of TaON and Ta$_3$N$_5$ films is a favorable characteristic for application to photocatalytic reactions in aqueous solutions.

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(9) In the photocatalytic reaction in the presence of methanol (sacrificial electron donor), excited electrons reduce H$^+$ into H$_2$, and holes oxidize methanol into CO$_2$. The total reaction is represented by the following reaction: H$_2$O + CH$_3$OH $\rightarrow$ 3H$_2$ + CO$_2$ (ΔG° = 5 kJ mol^{-1}). In aqueous AgNO$_3$ solution (sacrificial electron acceptor), reduction of Ag$^+$ into metallic Ag and oxidation of water into O$_2$ proceed by excited electrons and holes, respectively (AgNO$_3$ + ^{1}/$_2$H$_2$O $\rightarrow$ Ag + ^{1}/$_4$O$_2$ + H$^+$ + NO$_3^-$ (ΔG° = 72 kJ mol^{-1})). Neither of these reactions proceeds in dark, under visible light irradiation without the photocatalysts, or by heat due to light irradiation.

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