Morphological change and enhanced photocatalytic activity of tantalum nitride (Ta_3N_5) by ammonothermal treatment with mineralizer

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In this study, we succeeded, for the first time, in changing the particle morphology of a transition metal nitride using ammonothermal post-treatment with a mineralizer. Tantalum (V) nitride (Ta_3N_5) was post-treated using NaI as a mineralizer under ammonothermal conditions with an ammonia pressure of 100 MPa at 673–973 K for 24 h. Post-treatment above 873 K changed the particle morphology of Ta_3N_5 markedly; the particle size was reduced, the crystallite size was increased, and the specific surface area was decreased compared to the as-prepared Ta_3N_5 , suggesting the dissolution of particle surface during post-treatment. In addition, all treated Ta_3N_5 samples showed enhanced photocatalytic activity for hydrogen evolution from an aqueous methanol solution under visible light irradiation compared to untreated Ta_3N_5 . However, the hydrogen evolution activity for the samples post-treated above 873 K was less than that of the samples post-treated at lower temperatures due to the increase in lattice defects in Ta_3N_5 resulting from thermal decomposition.

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1. Introduction

Overall water splitting by photocatalysts utilizing sunlight can produce clean hydrogen. It has attracted attention as a possible technique for artificial photosynthesis. Since the report on the Honda–Fujishima effect in 1972,¹⁾ to develop highly active photocatalysts, significant effort has been given on the exploration of novel photocatalysts and the elucidation of factors affecting photocatalytic activity. In general, highly active photocatalysts have large surface areas and high crystallinity. Thus, the utilization of milder synthetic processes is key to the development of highly active photocatalysts, because when using conventional solid-state reactions involving high-temperature processes, the preparation of materials with these powder characteristics is difficult.

The hydrothermal method is recognized as an effective technique for the preparation of highly active oxide photocatalysts under mild conditions. Compounds such as TiO_2 ,²⁾ Nb_2O_5 ,³⁾ Ta_2O_5 ,⁴⁾ WO_3 ,⁵⁾ BiVO_4 ,⁶⁾ SrNb_2O_6 ,⁷⁾ $\text{Sr}_2\text{Nb}_2\text{O}_7$,⁷⁾ NaTaO_3 ,⁸⁾ and Bi_2WO_6 ⁹⁾ synthesized via hydrothermal processes have large surface areas, high crystallinity, or special morphologies, resulting in higher photocatalytic activities compared with those of corresponding materials obtained using conventional solid-state reactions. In addition, the hydrothermal method has been applied not only to the synthesis of oxides but also as post-treatment for as-synthesized oxides. The hydrothermal treatment of crystalline TiO_2 at 423 K or 473 K enhanced the photocatalytic activity without changing the particle morphology.^{10),11)} By contrast, Kasuga et al.^{12),13)} reported that the hydrothermal treatment

of TiO_2 in aqueous NaOH solution at 383 K resulted in TiO_2 nanotubes with large surface areas. Since then, other research groups have reported that hydrothermally treated TiO_2 in aqueous NaOH solution exhibits enhanced photocatalytic activity.¹⁴⁾ These studies demonstrate that the hydrothermal method is effective not only as a synthetic method for oxides but also as post-treatment for as-synthesized oxides to provide special morphologies and enhance the photocatalytic activity.

Oxynitrides and nitrides are promising as photocatalysts for water splitting due to their visible light absorption properties.¹⁵⁾ Tantalum (V) nitride (Ta_3N_5) has an absorption edge at approximately 600 nm and a band structure suitable for water splitting. It can photocatalytically produce hydrogen and oxygen in the presence of appropriate sacrificial reagents under visible light.^{16),17)} However, Ta_3N_5 is usually prepared via a solid–gas reaction between Ta_2O_5 and NH_3 gas, resulting in low photocatalytic activity due to lattice defects generated during calcination at high temperatures. In recent years, utilizing the characteristics of gas–solid reaction resulting in products that maintain the morphologies of starting solid powders, Ta_3N_5 with various morphologies, such as nanosized,¹⁸⁾ macroporous,¹⁹⁾ mesoporous,²⁰⁾ hollow spherical,²¹⁾ and hollow urchin-like²²⁾ particles, and enhanced photocatalytic activity has been prepared. In contrast, heat treatment under high-pressure ammonia, i.e., ammonothermal treatment, has been reported only as a post-treatment method for enhancing the photocatalytic activity of Ta_3N_5 without altering the crystallinity, morphology, and specific surface area.^{23),24)} The ammonothermal method uses ammonia instead of water, similar to that in the hydrothermal method, thus providing the advantages that the hydrothermal method offers in oxide preparation to nitride synthesis. That is, using a suitable mineralizer, the ammonothermal treatment can change the morphology of nitrides as

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effectively as hydrothermal treatment of TiO_2 with NaOH .

In this study, Ta_3N_5 prepared via a gas–solid reaction was post-treated under ammonothermal conditions with sodium iodide (NaI) as the mineralizer to change its morphology. Here we reported the influence of the ammonothermal post-treatment with NaI on the crystallinity, morphology, and photocatalytic hydrogen evolution activity of Ta_3N_5 .

2. Experimental

2.1 Preparation and ammonothermal post-treatment of Ta_3N_5

In a manner similar to that previously reported,¹⁷⁾ Ta_3N_5 powder was prepared by heating Ta_2O_5 (Kojundo Chemical Laboratory Co., Ltd., 99.9%) in a horizontal alumina tube (80 cm length, 3.4 cm inner diameter) furnace under an ammonia (Taiyo Nippon Sanso, 99.999%) gas flow (500 ml min^{-1}) at 1123 K for 15 h. As the mineralizer for post-treatment, NaI was selected among mineralizers used in the ammonothermal growth of GaN single crystals after consideration of the potential for corrosion of the reaction vessel and the production of insoluble compounds.²⁵⁾ Thus, for the ammonothermal post-treatment, Ta_3N_5 (0.35 g) was mixed with NaI (Kanto Chemical, 99.5%) at a molar ratio of $\text{Ta}:\text{Na} = 1:3$, and then the mixture was placed in a nickel tube (12.5 cm length, 4 mm outer diameter, 0.125 mm thickness) with one end welded. The tube was then placed in a test-tube-type pressure vessel (20 cm length, 5 mm inner diameter), and the vessel was evacuated and subsequently filled with liquid ammonia and sealed. The sample in the vessel was then heated to 673–973 K at a rate of 5 K min^{-1} using an electric furnace, and the temperature was maintained for 24 h at an ammonia pressure of 100 MPa. After treatment, the sample was naturally cooled to room temperature in the furnace, washed several times with pure water, and then dried in air at 353 K.

2.2 Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2200 X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 40 mA. The average crystallite size of the Ta_3N_5 samples was estimated from the broadening of the 023 diffraction peaks using Scherrer's equation.²⁶⁾ Scanning electron microscopy (SEM) images were obtained using a Hitachi S-5200 field-emission scanning electron microscope. UV–vis diffuse reflectance spectra (DRS) were measured on a Jasco V-550 spectrometer equipped with an integrating sphere and using BaSO_4 as the reflectance reference. The diffuse reflectance was converted to absorbance using the Kubelka–Munk method. Specific surface areas were calculated using the Brunauer–Emmet–Teller single-point method at 77 K with a Shimadzu Micromeritics FlowSorb III 2305 surface area analyzer.

2.3 Measurement of photocatalytic activity for hydrogen evolution

Photocatalytic reactions were conducted in a Pyrex side-irradiation-type reaction vessel connected to a closed gas circulation system. The hydrogen evolution reactions were conducted using 300 ml of 80 vol.% aqueous methanol solution containing 0.3 g of the sample and an appropriate amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical, 97%) as the precursor for the Pt co-catalyst. Before the reaction, the system was degassed and filled with Ar gas (100 Torr). A 70 W ceramic metal halide lamp ($\lambda > 380 \text{ nm}$) was used as the light source. The evolved gas was analyzed by gas chromatography (GC-8A, TCD, MS-5A column; Shimadzu; Ar carrier gas).

Fig. 1. XRD patterns of Ta_3N_5 (a) as-prepared and post-treated with NaI at (b) 673 K, (c) 773 K, (d) 823 K, (e) 873 K, and (f) 973 K for 24 h under ammonothermal conditions. Enlarged view of the 023 diffraction peaks of Ta_3N_5 shows a decrease in the full widths at half maximum.

3. Results and discussion

3.1 Crystal phase and crystallinity

Figure 1 shows the XRD patterns of the as-prepared Ta_3N_5 and Ta_3N_5 ammonothermally post-treated with NaI . From the XRD patterns of the samples treated above 773 K, it can be seen that TaON and an unknown phase were formed. These impurity phases are considered to be oxynitride and the intermediate phase formed by the reaction of Ta_3N_5 with infinitesimal amounts of H_2O introduced with NaI . Moreover, from enlarged view of the 023 diffraction peaks of Ta_3N_5 , we observed a decrease in the full widths at half maximum of the peaks that suggests an increase in the crystallite size of treated samples. **Figure 2** shows the dependence of the average crystallite size of Ta_3N_5 ammonothermally post-treated with NaI on treatment temperature. We previously reported that after ammonothermal post-treatment without mineralizers, the crystallite size of Ta_3N_5 remains nearly unchanged.²⁴⁾ By contrast, as can be seen in Fig. 2, ammonothermal post-treatment with NaI monotonically increased the crystallite size of Ta_3N_5 with the treatment temperature. This result indicates that NaI contributes to the enhancement of the crystallinity of Ta_3N_5 during ammonothermal post-treatment. To the best of our knowledge, there are no studies on the ammonothermal post-treatment that enhances the crystallinity of a transition metal nitride.

3.2 Particle morphology

Figure 3 shows the SEM images of the as-prepared Ta_3N_5 and the Ta_3N_5 ammonothermally post-treated with NaI . The as-prepared sample [Fig. 3(a)] consisted of porous particles with sizes of 300–500 nm. The samples treated below 823 K [Figs. 3(b)–3(d)] remained unchanged compared with the as-prepared sample. In contrast, the particle sizes in the sample treated at 873 K [Fig. 3(e)] ranged from 50 to 200 nm. Furthermore, the sample treated at 973 K [Fig. 3(f)] consisted of non-porous particles that were slightly larger than those in the sample treated at 873 K. These morphological changes are caused by the dissolution of Ta_3N_5 particles into the supercritical ammonia

Fig. 2. Dependence of average crystallite size of Ta_3N_5 ammonothermally post-treated with NaI on treatment temperature.

Fig. 4. UV-vis DRS of Ta_3N_5 ammonothermally post-treated with NaI at various temperatures.

Fig. 3. SEM images of Ta_3N_5 (a) as-prepared and post-treated with NaI at (b) 673 K, (c) 773 K, (d) 823 K, (e) 873 K, and (f) 973 K for 24 h under ammonothermal conditions.

promoted by NaI, followed by recrystallization of smaller Ta_3N_5 particles. Judging from the result of XRD, these morphologically changed particles are considered to be a mixture of Ta_3N_5 and a small amount of impurity phases but not pure Ta_3N_5 . Post-calcination in air, which is a general post-treatment to enhance photocatalytic activity, leads to increased crystallite size, that is, enhanced crystallinity, along with increased particle size. In contrast, for samples morphologically changed, ammonothermal post-treatment increased the crystallite size but decreased the particle size compared to the as-prepared sample. Moreover, if particles dissolved by the treatment recrystallized as single crystals, the crystallite size should be generally consistent with

the particle size. However, even for samples with morphological changes, the particle sizes estimated from the SEM images were larger than the crystallite sizes estimated using Scherrer's equation. These results suggest that samples treated above 873 K contain more crystalline, small and polycrystalline particles generated via recrystallization as well as low-crystallinity, large particles for which only the surface dissolved. That is, even the treatments above 873 K are assumed to dissolve only the surface of Ta_3N_5 . The specific surface areas of samples treated at 673, 773, 823, 873, and 973 K were 11.1, 11.3, 11.0, 9.4, and $5.6 \text{ m}^2 \text{ g}^{-1}$, respectively. Only the samples with morphological changes had smaller specific surface areas compared with the as-prepared sample ($9.8 \text{ m}^2 \text{ g}^{-1}$). The decrease in the specific surface areas of the samples with morphological changes is attributed to the disappearance of pores due to dissolution of particle surfaces. Takata et al.²⁷⁾ and Ma et al.²⁸⁾ reported that the use of alkali metal salts in pre-treatment, synthesis, and post-treatment of Ta_3N_5 led to morphological changes at temperatures above the melting points of the salts (at least 1123 K). In contrast, in this study, ammonothermal post-treatment with NaI as the mineralizer changed the morphology of Ta_3N_5 even at 873 K, which is below the melting point of NaI (924 K).

3.3 Optical properties

Figure 4 shows the UV-vis DRS of the as-prepared Ta_3N_5 and Ta_3N_5 ammonothermally post-treated with NaI. As can be seen, there was no significant difference in the absorption edge between the as-prepared and treated samples. However, for the samples treated above 823 K, the intensity of absorption in the longer wavelength region increased due to the presence of reduced Ta species¹⁸⁾ at higher treatment temperatures. Similar increases in the absorption intensity of Ta_3N_5 have been previously observed following ammonothermal post-treatment at 823 K²⁴⁾ and high-pressure N_2 post-treatment above 873 K,²⁹⁾ suggesting that Ta_3N_5 partially decomposes even under high-pressure conditions. Therefore, on the basis of the results of the UV-vis DRS analysis, it was concluded that Ta_3N_5 is partially decomposed during the ammonothermal post-treatment with NaI above 823 K.

Fig. 5. Dependence of photocatalytic activity for hydrogen evolution of Ta₃N₅ ammonothermally post-treated with NaI on treatment temperature. Reaction conditions: catalyst, 0.3 g; 80 vol.% aqueous methanol solution, 300 ml; light source, 70 W ceramic metal halide lamp ($\lambda > 380$ nm); reaction vessel, Pyrex side-irradiation-type.

3.4 Photocatalytic activity for hydrogen evolution

Figure 5 shows the dependence of photocatalytic activity for hydrogen evolution of the Ta₃N₅ samples ammonothermally post-treated with NaI on treatment temperature. All of post-treated Ta₃N₅ showed increased hydrogen evolution activity in comparison with as-prepared Ta₃N₅. As in the case without mineralizers,²⁴⁾ this increase in photocatalytic activity may result from decrease in surface defects by exposure to high-pressure ammonia and the accompanying improvement in electron transfer from the surface of Ta₃N₅ to the loaded Pt co-catalyst. The hydrogen evolution activity initially increased with the treatment temperature, reaching a maximum value at 823 K, and then decreased above 873 K. Although the Ta₃N₅ samples treated above 873 K showed obvious changes in their morphologies, as observed in the SEM images [Figs. 3(e) and 3(f)], the photocatalytic activity were lower than that of the samples treated at 823 K, which did not experience a morphology change. The decrease in the photocatalytic activity of the samples treated above 873 K is attributed to the facilitation of the undesirable recombination of the photogenerated carriers due to an increase in the quantity of reduced Ta species, as suggested in the UV–vis DRS spectrum (Fig. 4). Previously,²³⁾ the photocatalytic activity of Ta₃N₅ ammonothermally post-treated without NaI was also enhanced to maximum at 823 K, which is consistent with the temperature dependence observed in this study. In addition, there was no significant difference in the maximum activity between Ta₃N₅ treated with (22.1 μmol h⁻¹) and without (21.1 μmol h⁻¹) NaI. Therefore, it can be inferred that the photocatalytic activity of ammonothermally post-treated Ta₃N₅ is affected by the presence of reduced Ta species generated due to partial thermal decomposition, regardless of the addition of NaI.

4. Conclusion

We revealed that the addition of NaI in the ammonothermal post-treatment of Ta₃N₅ leads to morphological changes in the Ta₃N₅ particles at relatively low temperatures (873–973 K) by

promoting the dissolution of Ta₃N₅ into supercritical ammonia. This result is the first successful demonstration that ammonothermal post-treatment is capable of changing the particle morphology of transition metal nitrides when using a mineralizer. Obvious changes in the morphology following post-treatment were initially observed at 873 K, such as a decrease in the Ta₃N₅ particle size, an increase in the crystallite size, and a decrease in the specific surface area. In comparison with the as-prepared Ta₃N₅, all treated Ta₃N₅ samples showed enhanced photocatalytic activity for hydrogen evolution. However, the maximum activity was observed for Ta₃N₅ post-treated at 823 K, and the activity decreased for samples post-treated above 873 K due to an increase in lattice defects in Ta₃N₅ resulting from partial thermal decomposition during treatment. Notably, the maximum activity as well as the dependence of photocatalytic activity on treatment temperature were nearly unchanged when using NaI. These results suggest that the enhanced photocatalytic activity of Ta₃N₅ was dominated by lattice defects, rather than the changes in crystallinity and morphology.

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