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Investigation on nitridation processes of $\text{Sr}_2\text{Nb}_2\text{O}_7$ and SrNbO_3 to SrNbO_2N for photoelectrochemical water splitting

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The processes involved in the nitridation of $\text{Sr}_2\text{Nb}_2\text{O}_7$ and SrNbO_3 to SrNbO_2N were assessed by varying the nitridation time, and the related effects on the physical and photoelectrochemical properties of the nitrated products were investigated. In the case of the layered perovskite-type oxide $\text{Sr}_2\text{Nb}_2\text{O}_7$, the introduction of nitrogen and the extraction of oxygen took place concurrently, leading to lattice shrinkage and a porous structure. In contrast, during nitridation of the perovskite-type oxide SrNbO_3 , nitrogen was initially introduced without any loss of oxygen, which caused phase separation as a result of a lattice expansion and a charge compensation. The photoelectrochemical properties of obtained SrNbO_2N under simulated sunlight were found to vary with the oxide precursor used and with the nitridation process.

Hydrogen produced from water using sunlight is an attractive candidate as a next-generation clean fuel. For this reason, the photoelectrochemical (PEC) water splitting reaction has been the subject of significant research following the initial report of the Honda-Fujishima effect¹. In order to utilize sunlight effectively during PEC water splitting, various oxynitrides and oxysulfides capable of absorbing a wide range of visible wavelengths have been developed². At present, Ta-based (oxy)nitrides such as TaON , Ta_3N_5 , $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$, and BaTaO_2N are being intensively investigated both in powder suspensions and PEC systems, and have exhibited relatively high efficiencies^{3–6}. In contrast, studies regarding Nb-based materials remain limited, even though such compounds actually have longer absorption edge wavelengths than the analogous Ta-based materials. It is also notable that Nb is potentially preferable to Ta both with regard to the lower cost and ready supply of the former, although the efficiencies reported for Nb-based catalysts remain very low^{7,8}.

Among Nb-based oxynitrides, SrNbO_2N is a potential candidate for photoanodes in PEC cells. SrNbO_2N has a perovskite-type structure and an absorption edge at approximately 690 nm⁹. It has been reported that SrNbO_2N modified with a CoPi cocatalyst functions as a photoanode, generating a current density of 1.5 mA cm^{-2} at 1.23 V vs. a reversible hydrogen electrode (RHE)¹⁰. Typically, SrNbO_2N is synthesized from the layered perovskite-type compound $\text{Sr}_2\text{Nb}_2\text{O}_7$ or from amorphous oxide precursors by heating these materials under an ammonia flow. $\text{Sr}_5\text{Nb}_4\text{O}_{15}$, $\text{Sr}_4\text{Nb}_2\text{O}_9$ and SrNb_2O_6 are all possible oxide precursors, although the Sr/Nb ratios in these materials are not the ideal value of unity, thus requiring an additional washing step to remove excess Sr or Nb species after nitridation. Recently, $\text{Sr}_{1-x}\text{NbO}_3$, having a slightly distorted perovskite-type structure, has been reported as a photocatalyst with an absorption edge of 650 nm, and has been found to work as a photoanode¹¹, albeit with very limited PEC performance. Very recently, our own group determined that ANbO_2N compounds ($A = \text{Ba}, \text{Sr}$) synthesized from ANbO_3 ($A = \text{Ba}, \text{Sr}$) function as photoanodes in conjunction with a loaded cocatalyst¹². As an

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example, SrNbO_2N synthesized from SrNbO_3 has exhibited a current density of 0.4 mA cm^{-2} at 1.2 V vs. RHE under simulated sunlight irradiation. The perovskite-type compound SrNbO_3 can therefore be used as the oxide precursor for the synthesis of this catalyst.

One of the key factors associated with improving Nb-based oxynitride photocatalysts is control over the nitridation conditions. Although the nitridation conditions for the oxynitrides have already been largely optimized in each material, our understanding of the nitridation mechanism and the relationship between the nitridation processes and PEC properties remains very limited. In the case of $\text{Sr}_2\text{Nb}_2\text{O}_7$, the overall nitridation reaction can be summarized according to the theoretical equation:

It is considered that the active species during nitridation is NH , NH_2 or N radical species¹³. In this process, at the same time, the decomposition of ammonia partly produces hydrogen as:

meaning that a reductive atmosphere is present during nitridation¹⁴. Nitridation typically changes the crystal structure of the oxide due to the exchange of O^{2-} with N^{3-} . As an example, $\text{Sr}_2\text{Nb}_2\text{O}_7$, initially having a layered perovskite structure, transitions to the perovskite-type material SrNbO_2N . On the other hand, SrNbO_3 is believed to undergo nitridation to SrNbO_2N via the reaction:

In this case, both the oxide precursor and the resulting oxynitride have a perovskite-type structure. Another feature of this process is that Nb^{4+} is evidently oxidized to Nb^{5+} in spite of the reductive atmosphere during the nitridation. Although the total nitridation reactions from $\text{Sr}_2\text{Nb}_2\text{O}_7$ or SrNbO_3 to SrNbO_2N apparently seems to be relatively simple, as summarized in Eqs (1) and (3), the details of these nitridation processes are not yet known.

In the current work, nitridation of $\text{Sr}_2\text{Nb}_2\text{O}_7$ and SrNbO_3 were investigated for various reaction times. The results demonstrate that the nitridation mechanisms for these two oxide precursors are greatly different, resulting in different optical, morphological and PEC properties for the end products.

Experimental

Preparation of SrNbO_2N . $\text{Sr}_2\text{Nb}_2\text{O}_7$ was synthesized using a flux method¹⁰. SrCO_3 , Nb_2O_5 , and RbCl (as a flux) were mixed in a molar ratio of $\text{Sr}:\text{Nb}:\text{Rb} = 1:1:5$ and then heated in an alumina crucible for 5 h at 1423 K in air. The mixture was subsequently cooled to 1073 K at a rate of 1 K min^{-1} and then allowed to cool to room temperature, followed by washing using a copious amount of distilled water.

To obtain SrNbO_3 , $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ was first synthesized by calcining a mixture of SrCO_3 and Nb_2O_5 (at a $\text{Sr}:\text{Nb}$ molar ratio of 5:4) at 1423 K for 48 h in air. The resulting $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ particles were mixed with Nb metal powder at a $\text{Sr}_5\text{Nb}_4\text{O}_{15}:\text{Nb}$ molar ratio of 1:1 in an agate mortar, and then calcined under an Ar flow of 100 mL min^{-1} at 1773 K for 20 h to synthesize SrNbO_3 ^{11,15}. During this calcination, the sample was wrapped in a 5 cm square sheet of Nb foil and placed on an alumina boat.

In a typical nitridation, approximately 0.5 g of the oxide precursor was placed on an alumina boat, heated at 10 K min^{-1} to 1173 K and then held for 1, 5, 10, 20, 30, or 40 h at 1173 K under a 250 mL min^{-1} NH_3 flow. Finally, samples were allowed to cool naturally to room temperature.

Preparation of photoelectrodes. Photoelectrodes composed of SrNbO_2N were prepared by a particle transfer method¹⁶. The photocatalyst powder was first suspended in 2-propanol and then dropped onto a glass plate, after which the solution was dried at room temperature. A layer of Nb (approximately 300 nm thick) was then deposited on the dried particles using radio-frequency (RF) magnetron sputtering, followed by the sputtering of a thick Ti layer ($>5 \mu\text{m}$). The resulting film incorporating the photocatalyst powder was transferred to another glass plate using double sided carbon tape and ultrasonicated in distilled water to remove particles that were not firmly held by the metal film.

Photoelectrochemical measurements. Current-potential curves for the SrNbO_2N photoanodes were acquired using a typical three-electrode configuration under intermittent illumination with simulated sunlight provided by a Xe lamp equipped with an air mass (AM) 1.5G filter (San'ei Denki, XES-40S2-CE). Ag/AgCl in a saturated KCl solution and Pt wire were employed as the reference and counter electrodes, respectively. The electrolyte was a 0.2 M aqueous sodium phosphate solution adjusted to a pH of 13 by NaOH addition. In all cases, a CoPi cocatalyst was deposited by electrodeposition at 1.7 V vs. RHE for 200 s¹⁷.

Characterization. Samples were characterized using X-ray diffraction (XRD; Rigaku, RINT-Ultima III), UV-vis diffuse reflectance spectroscopy (DRS; JASCO, V-670DS), field-emission scanning electron microscopy (FE-SEM; Hitachi, S-4700, and JEOL, JSM-7001F) and field-emission transmission electron microscopy (FE-TEM; JEOL, JEM-2800). The DRS reflectance (R) data were converted to the Kubelka-Munk function using the equation $f(R) = (1-R)^2/(2R)$. The relative weight (W_R) of each specimen was determined from the equation $W_R = (W_a - W_0)/(W_b - W_0)$, where W_a , W_b , and W_0 are the total weight of the powder and the alumina boat after nitridation, the total weight of the powder and alumina boat before nitridation, and the weight of the alumina boat, respectively. Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu, ICPS-8100) and oxygen/nitrogen combustion analysis (ON analysis; Horiba, EMGA-620W/C). Nitrogen adsorption isotherms for the samples were acquired at 77 K with a BELSORP-mini instrument

Figure 1. XRD patterns for SrNbO_2N obtained from nitridation of (A) $\text{Sr}_2\text{Nb}_2\text{O}_7$, and (B) SrNbO_3 . Legend: (a) oxide precursor and (b–f) nitrided samples obtained after nitridation for (b) 1, (c) 5, (d) 10, (e) 20, and (f) 30 h. Closed triangles ($\blacktriangledown$) and closed circles ($\bullet$) indicate $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ and $\text{Sr}_7\text{Nb}_6\text{O}_{21}$, respectively. The inset in (B) is a magnification of the region indicated by the box.

(MicrotracBEL). The relative surface areas of the samples were determined using the Brunauer-Emmett-Teller (BET) model.

Results and Discussion

Structural analysis. The $\text{Sr}_2\text{Nb}_2\text{O}_7$ oxide precursor was synthesized by a flux method and then subsequently nitrided for various nitridation time to investigate the process that generates SrNbO_2N . Figure 1A shows the XRD patterns obtained from the $\text{Sr}_2\text{Nb}_2\text{O}_7$ oxide precursor and the nitridation product SrNbO_2N . It is evident that $\text{Sr}_2\text{Nb}_2\text{O}_7$ with a layered perovskite-type structure was obtained without any impurity phases. As the nitridation time was increased, the diffraction peaks due to the oxide precursor became less intense, while peaks attributed to a perovskite-type SrNbO_2N phase appeared. After 10 h, peaks from the oxide precursor completely disappeared. As shown in Table S1, the full width at half maximum (FWHM) values of the (110) diffraction peaks generated by the SrNbO_2N did not change after 5 h. This result indicates that the crystallinity was not improved by prolonging the nitridation for more than 5 h.

Figure 1B presents XRD patterns for the SrNbO_3 oxide precursor and the nitridation product SrNbO_2N . SrNbO_3 was synthesized by a solid state reaction under an Ar flow, and a small amount of a $\text{Sr}_7\text{Nb}_6\text{O}_{21}$ phase was evidently present as an impurity phase. It has been reported that stoichiometric SrNbO_3 is not readily obtained, while Sr-poor compositions having the formula $\text{Sr}_{1-x}\text{NbO}_3$ are relatively stable¹¹. Moreover, ICP-AES data demonstrated that the Sr/Nb ratio in the oxide precursor was 0.96 (Table S2), most likely due to the vaporization of Sr species during calcination at 1773 K. Therefore, it is probable that the synthesized oxide was a mixture of $\text{Sr}_{1-x}\text{NbO}_3$ and a small amount of $\text{Sr}_7\text{Nb}_6\text{O}_{21}$. Since SrNbO_3 and SrNbO_2N both have a perovskite-type structure and their lattice constants are very similar (the lattice mismatch is only 0.7%), it was anticipated that the nitridation would proceed without any change in the crystal structure. Surprisingly, it was found that, following the initial stage of nitridation, a $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ phase appeared and then gradually disappeared as SrNbO_2N was formed. In addition, the $\text{Sr}_7\text{Nb}_6\text{O}_{21}$ phase disappeared after 1 h of nitridation. As shown in Fig. S1, the diffraction peaks attributed to a perovskite-type structure were shifted to lower angles as the nitridation progressed. It is notable that the diffraction peaks associated with SrNbO_3 and SrNbO_2N could not be separated, indicating that a solid solution of SrNbO_3 and SrNbO_2N was partly formed in this stage. Figure 2 indicates d-values of (211) diffraction peaks. In the case of SrNbO_2N nitrided from $\text{Sr}_2\text{Nb}_2\text{O}_7$, d-values became constant after nitridation for 5 h. On the other hand, in the case of SrNbO_3 series, d-values first became larger then gradually reduced after 10 h. It is expected that the introduction of nitrogen increase the lattice constant since the ionic radius of N^{3-} is larger than that of O^{2-} . Another possibility is the introduction of oxygen vacancies which were produced during nitridation. This effect will be discussed in detail later. The FWHM values for the (110) diffraction peaks resulting from a perovskite structure initially increased and then decreased with increasing nitridation time, although these FWHM values remained larger than those from $\text{Sr}_2\text{Nb}_2\text{O}_7$ as shown in Table S1. These data demonstrate that the SrNbO_2N synthesized from SrNbO_3 had a lower degree of crystallinity than that obtained from $\text{Sr}_2\text{Nb}_2\text{O}_7$. Consequently, nitridation of the perovskite-type material SrNbO_3 to the perovskite-type product SrNbO_2N proceeded to some extent, but with a phase separation during the initial stage of nitridation.

Morphological properties. The SEM images shown in Fig. 3 reveal that the $\text{Sr}_2\text{Nb}_2\text{O}_7$ particles were composed of bundles of columnar crystals. The $\text{Sr}_2\text{Nb}_2\text{O}_7$ particles were typically several micrometers in size but some were also much larger or smaller as shown in Fig. S2. The crystals gradually became more porous as the nitridation time was prolonged (See Fig. 3(b–d)). This trend has also been observed for (oxy)nitrides such as TaON , Ta_3N_5 , and LaTiO_2N ^{18–20}. In most instances of nitridation of oxides to form (oxy)nitrides, a lattice shrinkage occurs. In the case of nitridation of the layered perovskite-type compound $\text{Sr}_2\text{Nb}_2\text{O}_7$, 2 mol of nitrogen is

Figure 2. d-values of (211) peaks for SrNbO₂N nitrided from different oxide precursors. Closed circles and open diamonds indicate Sr₂Nb₂O₇ and SrNbO₃ series, respectively.

introduced while 3 mol of oxygen is extracted, resulting in a structural change from a layered perovskite to a perovskite. Since a layered perovskite structure has a lower density than a cubic perovskite, the lattice will shrink. Based on the observation that the secondary particles retained their original sizes after nitridation, it is most likely that porous oxynitrides were obtained after nitridation due to a lattice shrinkage. This porous structure is also supported by the nitrogen adsorption analysis data shown in Table S3, which indicates that the surface area was doubled following nitridation.

In the case of SrNbO₃, large particles with a size of more than 5 μm were observed, and the average particle size was larger than that for Sr₂Nb₂O₇. As shown in Table S3, the surface area for SrNbO₃ was much less than that for Sr₂Nb₂O₇ due to the presence of smoother surfaces and larger particles. One distinct difference from Sr₂Nb₂O₇ particles was observed in the sample nitrided for 1 h. The SEM image in Fig. 3(f) demonstrates that parallel cracks were present in the sample nitrided for 1 h, probably suggesting the formation of Sr₅Nb₄O₁₅ with a layered perovskite related structure. As the nitridation time increased, the surface morphology became porous and cracked, resulting in a steady increase in surface area, as shown in Table S3. In contrast to Sr₂Nb₂O₇, nitridation from SrNbO₃ did not involve a change in the crystal structure and so the crystals would be expected to expand as nitrogen was introduced. This effect is believed to have expanded the particles, leading to the formation of cracks and a phase separation.

Figure 4A shows the cross-sectional SEM images of SrNbO₂N nitrided from SrNbO₃ with various nitridation time. In this measurement, SrNbO₂N/Nb/Ti photoelectrodes prepared by a particle transfer method were utilized for suppressing charge up during SEM observation. After nitridation for 1 h, some cracks and pores near surface appeared. In the case of nitridation for 20 h, there are obviously two regions like a “core-shell” structure, in which a “core” has smaller pores while a “shell” has larger pores. Even after nitridation for 40 h, some particles remained a “core-shell” structure while others completely became porous. The cross-sectional TEM image more precisely presented porous structure as shown in Fig. 4B. It was revealed that even “core” was porous although the pores were smaller than pores in “shell.” Although EDS analysis shows both “core” and “shell” contain certain amount of nitrogen, it is notable that the “shell” in Fig. 5 has larger N/O ratio of 0.41 than 0.28 in the “core,” indicating that the “core” was less nitrided.

Optical properties. Figure 5 shows the diffuse reflectance (DR) spectra of the oxide precursors and the SrNbO₂N samples obtained at different nitridation times. The original Sr₂Nb₂O₇ particles had a white color and were only able to absorb light up to 320 nm. However, the absorption edge clearly shifted to longer wavelengths as nitridation proceeded. After nitridation for 1 h, the absorption edge was over 600 nm and reached 690 nm after 5 h. Further nitridation did not affect the optical properties. Absorption beyond the absorption edge as observed here is usually attributed to the formation of reduced Nb species or anion defects such as anion vacancies or O_N anti-site defects.

SrNbO₃ exhibited strong absorption up to 650 nm and had a blood red coloration, both of which are consistent with previous results^{11,12}. DR spectra of samples nitrided for less than 10 h did not show clear absorption edges and contained intense background signals over 700 nm. After nitridation for 20 h, an absorption edge appeared at 690 nm, although this edge was not well defined. It is notable that the SrNbO₃ particles showed relatively minimal absorption beyond the absorption edge region in spite of the reduced valency of the Nb in this material, indicating that reduced Nb species were not responsible for the absorption above 700 nm. Therefore, it is probable that this absorption can be primarily attributed to anion defects. Moreover, the absorption above 700 nm decreased with increasing nitridation time more than 1 h, indicating that the number of anion defects first increased and then gradually decreased with progression of the nitridation.

Relative weight analysis. Nitridation of the oxides to the oxynitride was further examined by following trends in the relative weight of the nitrided particles compared to the oxide precursors, using the equation provided in the Experimental section. This method can readily track the extent of nitridation. In the case of the Sr₂Nb₂O₇ series, it was expected that the relative weight would decrease as a function of the nitridation time, reaching a value of 0.958 at complete nitridation. As shown in Fig. 6, the relative weight rapidly decreased over

Figure 3. SEM images of (a) original $\text{Sr}_2\text{Nb}_2\text{O}_7$, and products obtained after nitridation for (b) 1, (c) 5, and (d) 20 h, (e) original SrNbO_3 , and products obtained after nitridation for (f) 1, (g) 5, (h) 20 h, and (i) 40 h. The white arrows in (f) indicate parallel cracks.

Figure 4. (A) Cross sectional SEM images of (a) $\text{SrNbO}_3/\text{Nb}/\text{Ti}$ and subsequently nitrided $\text{SrNbO}_2\text{N}/\text{Nb}/\text{Ti}$ nitrided for (b) 1 h, (c) 20 h and (d) 40 h. The white arrows in (b) indicate cracks. (B) STEM-DF image of SrNbO_2N nitrided from SrNbO_3 for 20 h. The N/O ratio by EDS in area (i) and (ii) is 0.28 and 0.41, respectively.

the initial 5 h, then further decreased up to 10 h, resulting in a plateau value close to the expected value. Thus, these relative weight data provide clear evidence for the progression of the expected nitridation. A similar trend has also been reported for the nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$ -based oxides²¹. The elemental analysis data in Table S2 also support the above discussions. These values show that the O/Nb ratio steadily decreased while the N/Nb ratio increased, indicating that the introduction of nitrogen and the extraction of oxygen occurred simultaneously based on charge compensation.

Interestingly, a completely different trend was observed in the case of the SrNbO_3 series. SrNbO_2N has a formula weight ($226.53 \text{ g mol}^{-1}$) slightly less than that of SrNbO_3 ($228.53 \text{ g mol}^{-1}$), and so it was anticipated that a similar trend to $\text{Sr}_2\text{Nb}_2\text{O}_7$ series in the relative weight would be observed, with a gradual decrease in parallel

Figure 5. Diffuse reflectance spectra for SrNbO_2N obtained by nitridation of (A) $\text{Sr}_2\text{Nb}_2\text{O}_7$ and (B) SrNbO_3 . Legend: (a) oxide precursor and (b–f) samples obtained after nitridation times of (b) 1, (c) 5, (d) 10, (e) 20, and (f) 30 h.

Figure 6. Relative weight of oxide precursors and nitrided samples as a function of nitridation time. Closed circles (●) and open diamonds (◇) indicate SrNbO_2N synthesized from $\text{Sr}_2\text{Nb}_2\text{O}_7$ and SrNbO_3 , respectively. Dashed lines indicate the expected value following complete nitridation.

with the anion exchange. However, as shown in Fig. 6, the relative weight initially increased, followed by a slow decrease. The elemental analysis data in Table S2 also show that the N/Nb ratio increased whereas the O/Nb ratio did not change from that in the oxide precursor after nitridation for 1 h, indicative of an increase in the total anion amount. One unique characteristic of SrNbO_3 is that the Nb^{4+} must be oxidized to Nb^{5+} to form SrNbO_2N during nitridation. In order to compensate for this, the Nb species must be oxidized during this process. Therefore, it appears that nitrogen was introduced during the initial stage of nitridation while oxygen ions remained in the crystals, followed by the subsequent extraction of the oxygen. After nitridation for 1 h, the relative weight became 1.016. When assumed that the increase of relative weight is only due to introduction of N species, the expected composition formula is $\text{SrNbO}_3\text{N}_{0.26}$. The XRD analysis as shown in Fig. 1 presents that $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ has formed at this stage. Therefore, it is more likely that the obtained product was a mixture of $\text{Sr}_5\text{Nb}_4\text{O}_{15-x}\text{N}_x$ and $\text{Sr}_{1-y}\text{NbO}_{3-z}\text{N}_z$. To simplify this, considering the mixture is $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ and $\text{Sr}_{1-x}\text{NbO}_{3-y}\text{N}_y$, it is roughly estimated that 30–40% of SrNbO_3 has changed into $\text{Sr}_5\text{Nb}_4\text{O}_{15}$.

Even after nitridation for 30 h, the relative weight did not reach the expected value, indicating that the nitridation of SrNbO_3 did not proceed to completion. One possible reason is the larger particle size for the SrNbO_3 oxide precursor, although the different crystal structures of SrNbO_3 and $\text{Sr}_2\text{Nb}_2\text{O}_7$ might also be responsible.

Figure 7. Current-potential curves for CoPi/SrNbO₂N/Nb/Ti photoelectrodes synthesized from (A) Sr₂Nb₂O₇ and (B) SrNbO₃. Legend: (a) oxides, and samples nitrided for (b) 1, (c) 5, (d) 10, (e) 20, and (f) 30 h. Data were acquired under intermittent simulated sunlight (AM 1.5G) in an aqueous 0.2 M Na₃PO₄ solution adjusted to pH 13 by NaOH addition. Potentials were swept from positive to negative at a scan rate of 10 mV s⁻¹.

The effect of temperature during the nitridation of SrNbO₃ was also investigated. As shown in Fig. S3, even at 1123 and 1223 K, similar trends were observed in the relative weight data. The application of higher temperatures during nitridation seems to accelerate the process, although the effect was limited.

Photoelectrochemical performance. PEC water splitting was performed using both the oxides and the oxynitrides. Figure 7A shows current-potential curves obtained from photoanodes made of Sr₂Nb₂O₇ and the nitrided product SrNbO₂N, modified using a CoPi cocatalyst. Under simulated sunlight, Sr₂Nb₂O₇ did not show a clear photoresponse because of the minimal photon flux in the UV region. However, the photocurrent at a positive potential increased as the nitridation time was prolonged up to 10 h, reaching 0.77 mA cm⁻² at 1.2 V vs. RHE, and then dropping after 20 h. The onset potential did not exhibit any clear dependence on the nitridation time. Moreover, since it was confirmed by the relative weight analysis that a nitridation time of 10 h was sufficient for Sr₂Nb₂O₇, it is likely that the photocurrent reached maximum after completion of crystal structural change and that excess nitridation led to a degradation of the surface of the SrNbO₂N. It is thus found that the PEC properties were relevant to the extent of nitridation proceeded.

As shown in Fig. 7B, an almost negligible photocurrent was observed when using CoPi/SrNbO₃/Nb/Ti despite the SrNbO₃ was able to absorb light up to 650 nm. This is consistent with our previous results¹². A definite photoanodic current was generated even after nitridation for only 1 h. As the formation of SrNbO₂N proceeded, the photocurrents steadily increased to reach a maximum of 0.75 mA cm⁻² at 1.2 V vs. RHE after nitridation for 20 h, which was the comparable photocurrent to one obtained in Sr₂Nb₂O₇ series. This value is almost twice that previously reported for SrNbO₂N synthesized from SrNbO₃. It is consistent that the optimum nitridation time was longer than that of Sr₂Nb₂O₇ due to the slow nitridation process and a larger particle size. It is worth noting that SrNbO₂N made from SrNbO₃ was less crystalline and had a larger concentration of defects compared to the material prepared from Sr₂Nb₂O₇ but exhibited a similar photocurrent.

Proposed nitridation processes. Based on obtained results, we propose the nitridation processes of Sr₂Nb₂O₇ and SrNbO₃ as follows. In both cases, the nitridation processes via oxygen vacancy were considered. When assumed that active nitrogen species are NH₂, for example, the nitridation process of Sr₂Nb₂O₇ could be explained with equations as:

In the first step, oxygen atoms desorb and oxygen vacancies (V_O) form (Eq. (4)). Next, nitrogen atoms are introduced to V_O and nitrogen anti sites (N_O) are formed (Eq. (5)). Finally, oxygen vacancies disappear by changing the crystal structure (Eq. (6)). In total, 3 mol of oxygen atoms are exchanged by 2 mol of nitrogen. Desorbed O₂ reacts with H₂ to produce H₂O. It is notable that overall nitridation process itself is not an oxidation-reduction reaction. Although the authors did not fully understand the actual active species of nitrogen, above equations

Figure 8. Schematic images of nitridation process of (Left) before and (Right) during nitridation of (A) a layered perovskite $\text{Sr}_2\text{Nb}_2\text{O}_7$ and (B) a perovskite SrNbO_3 .

indicate that the formation of anion vacancies is inevitable when nitridation process includes a crystal structural change.

As shown in Fig. 8A, the layered perovskite-type material $\text{Sr}_2\text{Nb}_2\text{O}_7$ has interlayers between the NbO_6 layers for nitrogen to penetrate into the crystal. It has been reported that, in the case of an $\text{A}_2\text{B}_2\text{O}_7$ oxide, nitrogen is introduced through spaces among layers by a so-called ‘zipper’ like mechanism, in which introduced nitrogen connects the interlayers to transform to the perovskite type structure²². Therefore, nitrogen could be exchanged with oxygen concurrently. Moreover, this anion exchange causes a lattice shrinkage. Considering the apparent particle size does not change during nitridation, it is most likely that this process leads the porous structures.

Contrary, in the case of nitridation of SrNbO_3 , Eq. (6) should be exchanged by the following equation:

This process does not contain any crystal structural changes. Furthermore, this total nitridation process is an oxidation reaction. As a result, reduced Nb^{4+} should be oxidized to Nb^{5+} after nitridation. When step (5) or (6') are slow, oxygen vacancies stimulate in the crystals. It is reasonable that the oxidation of Nb^{4+} was challenging under a reductive atmosphere during nitridation. Therefore, it is most likely that considerable number of oxygen vacancies remain in SrNbO_3 and obtained products, leading to the large absorption over 700 nm (Fig. 5B(b–f)). Since introduction of oxygen vacancies and nitrogen species both expand the lattice constant (the lattice mismatch of oxide and resulting oxynitride is 0.7%), this causes the crack formation (Fig. 3(f)) to solve the stimulated distortion as shown in Fig. 8B. Our group has reported that A site poor perovskite $\text{Ba}_{1-x}\text{NbO}_{3-6}$ was nitrided with maintaining the perovskite type structure¹². In this case, the lattice mismatch reduced to only 0.1% at $\text{Ba}_{0.84}\text{NbO}_{3-6}$. Although 0.7% of the lattice mismatch in SrNbO_3 system is relatively small in terms of solid solution formation, it was seen that the small lattice mismatch played the critical role in this nitridation process. Formation of cracks requires the increase of the total amount of anion species, resulting in a phase separation of $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ and an increase of the relative weight at the initial stage of nitridation (Fig. 6). Additionally, some Nb^{4+} species are supposed to be oxidized to Nb^{5+} in this step. As nitridation proceeded, both SrNbO_3 and $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ are nitrided to the final product, SrNbO_2N .

Judging from the lattice constants, in the nitridation of SrNbO_3 to SrNbO_2N , a lattice shrinkage does not seem to proceed. It is thus likely that the porous structure was inevitably obtained due to exchanging oxygen and nitrogen species regardless of the extent of a lattice mismatch. In contrast to $\text{Sr}_2\text{Nb}_2\text{O}_7$ oxides, a perovskite-type oxide SrNbO_3 does not have interlayers to accelerate the diffusion of nitrogen sources. Therefore, it is more likely that the diffusion of nitrogen is much slower in this material than in $\text{Sr}_2\text{Nb}_2\text{O}_7$. Although the formation of $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ partly contribute to the anion diffusion, SrNbO_3 requires more severe conditions, such as the longer nitridation time and higher nitridation temperature than $\text{Sr}_2\text{Nb}_2\text{O}_7$. These differences in the nitridation process are primarily the result of variations in the crystal structure and the valency of the cations in the oxide precursors. The resulting photocurrents were also affected by the nitridation processes. Photocurrent reached maximum after 10 h in the case of $\text{Sr}_2\text{Nb}_2\text{O}_7$ series while 20 h of nitridation was optimum for SrNbO_3 series. In the case of nitridation of SrNbO_3 , nitridation speed is dominated by a diffusion of nitrogen species. Therefore, particle size should play a critical role in nitridation time and resulting PEC properties. Since, in this paper, SrNbO_3 was synthesized at relatively high temperature, 1773 K, it was challenging to reduce a particle size. Further development of synthesis procedure to control a particle size should improve PEC properties. Moreover, in both nitridation processes, anion vacancies inevitably formed, and this probably lead the limited photocurrent and positive onset potentials. It is therefore a key to develop a nitridation process to reduce the anion vacancies for realizing the solar hydrogen production using oxynitride materials.

Conclusion

In conclusion, the nitridation processes for two oxide precursors, the layered perovskite-type $\text{Sr}_2\text{Nb}_2\text{O}_7$ and the perovskite-type SrNbO_3 , to produce the perovskite-type material SrNbO_2N were examined. The relationship between the PEC properties of the products and the initial oxide were also investigated. Nitridation without any change in crystal structure was partly achieved in nitridation of SrNbO_3 , although formation of an impurity phase was detected. The data also suggest that nitridation from SrNbO_3 proceeds via a different pathway from $\text{Sr}_2\text{Nb}_2\text{O}_7$, with variations in lattice expansion and oxidation of Nb cations. Nitridation models based on the crystal structure were presented, in which nitridation processes triggered by formation of oxygen vacancies were considered. The photocurrent obtained from the products was correlated with the extent of nitridation determined from the relative weight analysis. This study demonstrates the importance of understanding the nitridation mechanism for the oxide precursor, focusing on the crystal structure. The knowledge obtained in this study should be widely applicable to other oxynitrides.

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Author Contributions

K.D. planned and supervised the project. M(asanori). K(odera). performed the synthesis and characterizations for the materials, and M(asao). K(atayama)., T.H. and T.M. supervised these. synthesis and characterizations. Y.M. supervised the synthesis of SrNbO₃. M(asanori). K(odera), M(asao). K(atayama) and K.D. wrote the paper.

Additional Information

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