

Article



Oxygen Evolution Activity of LaNbN₂O-Based Photocatalysts Obtained from Nitridation of a Precursor Oxide Structurally Modified by Incorporating Volatile Elements

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Abstract: The perovskite-type oxynitride LaNbN₂O is a photocatalyst that can evolve oxygen from aqueous solutions in response to long-wavelength visible light. However, it is challenging to obtain active LaNbN₂O because of the facile reduction of Nb⁵⁺ during the nitridation of the precursor materials. The present study attempted to synthesize a perovskite-type oxide La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃, containing equimolar amounts of La³⁺ and Nb⁵⁺ in addition to volatile Na⁺ and Zn²⁺, followed by the nitridation of this oxide to generate LaNbN₂O. The obtained oxide was not the intended single-phase material but rather comprised a cuboid perovskite-type oxide similar to La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O₃ along with spherical LaNbO₄ particles and other impurities. A brief nitridation was found to form a LaNbN₂O-like shell structure having a light absorption onset of approximately 700 nm on the cuboid perovskite-type oxide particles. This LaNbN₂O-based photocatalyst, when loaded with a CoO_x cocatalyst, exhibited an apparent quantum yield of 1.7% at 420 nm during oxygen evolution reaction from an aqueous AgNO₃ solution. This was more than double the values obtained from the nitridation products of LaNbO₄ and LaKNaNbO₅. The present work demonstrates a new approach to the design of precursor oxides that yield highly active LaNbN₂O and suggests opportunities for developing efficient Nb-based perovskite oxynitride photocatalysts.

Keywords: oxynitride; visible light; water splitting; crystal structure; nitridation

1. Introduction

Photocatalytic water splitting is an attractive approach to addressing issues related to energy and the environment by converting renewable solar energy into chemical energy stored in the form of hydrogen [1,2]. However, this requires developing efficient semiconductor photocatalysts capable of using visible light, which accounts for close to 54% of solar energy to achieve sufficient solar-to-hydrogen energy conversion efficiencies with reasonable quantum efficiencies [1]. Perovskite-type semiconducting oxynitrides with the general formula AB(N,O)₃ (where A and B represent relatively large twelve-coordinated cations, such as Ca²⁺, Sr²⁺, Ba²⁺ and La³⁺ and smaller six-coordinated cations, such as Ti⁴⁺, Nb⁵⁺ and Ta⁵⁺, respectively) are promising visible-light-driven photocatalysts. These materials exhibit intense visible light absorption, tunable compositions and band structures, and stable crystal structures [3–6]. In particular, Nb-based perovskite-type oxynitrides have long absorption edge wavelengths (λ_{max}) [6,7]. Among these, LaNbN₂O exhibits an especially high λ_{max} of approximately 750 nm, [7] corresponding to bandgap energy of 1.65 eV, that is superior to the values for CaNbNO₂ ($\lambda_{max} = 600$ nm), [8] SrNbNO₂



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). $(\lambda_{max} = 690 \text{ nm})$ [9,10] and BaNbNO₂ ($\lambda_{max} = 740 \text{ nm}$), [11–13] and so has been the subject of research and development efforts.

The oxygen evolution reaction is a half-reaction within the water splitting process, and many AB(N,O)₃ oxynitrides show decent activity in terms of promoting this reaction by photocatalysis [5,14–16]. Despite this, LaNbN₂O has rarely been applied to photocatalytic water oxidation. This is primarily because it is difficult to synthesize LaNbN₂O having suitable semiconducting characteristics. LaNbN₂O is typically obtained by heating oxides containing La and Nb under an NH₃ flow [7,17]. During this nitridation process, Nb⁵⁺ ions are more readily reduced to Nb^{4+,} and Nb³⁺ than are their Ta analogs, such that anion defects are generated [6]. This leads to the formation of mid-gap defect states and the frequent formation of impurity phases, such as rock-salt-type Nb(N,O). Hence, it is necessary to apply moderate nitridation conditions, such as lowering the temperature and shortening the duration, to limit the reduction of Nb⁵⁺. Unfortunately, these adjustments also produce an oxynitride with a low degree of crystallinity, increasing the extent of charge carrier recombination. Thus, it is necessary to investigate reduced nitridation times as an approach to producing LaNbN₂O with properties suitable for efficient photocatalytic O₂ evolution.

Recently, the engineering of precursor oxides based on tuning both the crystal structure and composition has been studied extensively to synthesize active oxynitride photocatalysts. Wang et al. prepared LaNbN₂O exhibiting a remarkable apparent quantum yield (AQY) of 0.82% at 420 nm during oxygen evolution from an aqueous AgNO₃ solution after being loaded with CoO_x as an oxygen evolution cocatalyst [18]. This material was obtained by nitriding the layered oxide LaKNaNbO5, which rapidly generated a plate-like LaNbN₂O shell with exposed (010) facets surrounding a LaKNaNbO₅ core. Both K and Na species were volatilized during the nitridation, and the matching of the La³⁺ and Nb⁵⁺ ion arrangements of the LaKNaNbO₅ and LaNbN₂O yielded highly crystalline LaNbN₂O having a low defect density. In other work, BaTaNO₂ that was highly active during the oxygen evolution reaction was prepared by nitriding a perovskite-type oxide having the nominal formula $(Na_{1/4}Ba_{3/4})(Zn_{1/4}Ta_{3/4})O_3$ (in which the Ba/Ta ratio was unity), with the concurrent volatilization of Na and Zn [15]. This material displayed a high AQY of 11.9% at 420 nm during the photocatalytic oxygen evolution reaction. The benefits of matching the arrangements of cationic components during the nitridation of oxides to oxynitrides have also been reported for other material systems [19–21]. Hence, designing a stoichiometric and isostructural oxide precursor for conversion into an oxynitride photocatalyst has attracted significant attention as a possible means of enhancing the photocatalytic activity of Nb-based oxynitrides.

Based on the above, the present work designed a stoichiometric, isostructural precursor oxide having the nominal formula $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ to prepare $LaNbN_2O$ via nitridation. The volatilization of Na and Zn species from this precursor was expected to promote the nitridation to a greater extent than using $LaNbO_4$. The precursor oxide synthesized in this study was found to consist of a cuboid perovskite-type oxide resembling $La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O_3$, together with spherical $LaNbO_4$ particles and several other impurities. Despite this lack of purity, when modified with a CoO_x cocatalyst, the $LaNbN_2O$ -based material obtained from nitridation of this precursor exhibited more than five times greater photocatalytic evolution activity during the oxygen evolution reaction under visible light (with an AQY of 1.7% at 420 nm) as compared with $LaNbN_2O$ made by the nitridation of $LaNbO_4$. These results demonstrate the possibility of using structurally modified precursor oxides to prepare oxynitride photocatalysts with enhanced activity based on reduced nitridation durations.

2. Results and Discussion

Figure 1A,B respectively presents the X-ray powder diffraction (XRD) patterns and diffuse-refrectance specopy (DRS) data obtained from the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and $LaNbO_4$ and their products generated by nitridation at 1198 K for 2 h. Reference patterns

for La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O₃ (International Centre for Diffraction Data—powder diffraction file (ICDD-PDF): 00-043-0109), [22] LaNbO₄ (ICDD-PDF: 01-071-1405), [23] La₃NbO₇ (ICDD-PDF: 01-071-1345) [24] and LaNbN₂O (ICDD-PDF: 01-078-7116) [25] are also presented for comparison purposes in Figure 1A. The LaNbO₄ sample was found to comprise a single-phase, and its pattern exhibits intense peaks at 27.4° and 28.9° that are attributable to the (-121) and (121) planes of LaNbO₄, respectively. The elemental analysis data obtained using inductively coupled plasma optical emission spectroscopy (ICP-OES), presented in Table 1, indicate that the La/Nb molar ratio in the product was 1.0, consistent with the chemical formula of LaNbO₄. This material showed a light absorption edge at approximately 350 nm. The main XRD peaks produced by the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ resemble that of the perovskite-type compound La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O₃, with a characteristic intense peak at 32.2° that is absent in the LaNbO₄ pattern. However, the peaks produced by the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ are positioned at lower diffraction angles compared to those in the La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O₃ pattern. As shown in Table 1, the La:Na:Zn:Nb molar ratio in the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ sample was 1.16:0.39:0.73:1.00, indicating a greater than 10% surplus and shortage, respectively, of La and Na in the material. The specimen also contained a slight excess of Zn. The XRD pattern and the light absorption onset at approximately 350 nm both suggest that the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ sample included a significant amount of LaNbO₄ as a byproduct. Moreover, the spectrum of the material contains an absorption shoulder tailing to approximately 400 nm that is characteristic of ZnO, even though this compound was not detected in the XRD pattern. Changing the calcination time did not have any significant effect on the XRD pattern of the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ synthesized by the flux method, and LaNbO₄ remained as a byproduct in each case. Therefore, it was impossible to determine the composition or crystal structure of the perovskitetype phase in the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ specimens. Nevertheless, we refer to this oxide herein as La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ based on the nominal molar ratio in the starting mixture for simplicity.



Figure 1. (**A**) XRD patterns and (**B**) DRS data obtained from (**a**) the as-synthesized $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$, (**b**) the product from nitridation at 925 °C for 2 h, (**c**) the LaNbO₄, and (**d**) the product from nitridation at 925 °C for 2 h. Reference patterns for (**e**) LaNbN₂O, (**f**) $La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O_3$, and (**g**) LaNbO₄ are included in (**A**) for comparison. Asterisks (*) represent peaks from La_3NbO_7 . The specimens shown in (**a**) and (**c**) were synthesized by the flux method.

	Nitridation		Molar Ratio to Nb			O. F. aladaa
Sample	Temperature (K)	Time (h)	La	Na	Zn	$(\mu mol h^{-1})$
"La _{0.6} Na _{0.4} Zn _{0.4} Nb _{0.6} O ₃ "	-	-	1.16	0.39	0.73	n.a. ^a
LaNbN ₂ O	1198	1.0	1.13	0.31	0.16	38
LaNbN ₂ O	1198	1.5	1.14	0.29	0.10	74
LaNbN ₂ O	1198	2.0	1.14	0.27	0.07	117
LaNbN ₂ O	1198	2.5	1.14	0.21	0.04	113
LaNbN ₂ O	1198	3.0	1.13	0.17	0.03	48
LaNbN ₂ O	1173	2.0	1.16	0.27	0.14	45
LaNbN ₂ O	1223	2.0	1.13	0.14	0.04	64
LaNbN ₂ O	1248	2.0	1.13	0.08	0.00	21
LaNbO ₄	-	-	1.02	0.00	0.00	n.a. ^a
LaNbN2O from LaNbO4	1198	2.0	1.03	0.01	0.00	21

Table 1. Compositions and photocatalytic oxygen evolution activities of LaNbN2O samples obtainedfrom nitriding either $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ or LaNbO4.

^a not measured because of no visible light absorption.

Scanning electron microscope (SEM) observations showed that the addition of Na and Zn precursors during the preparation of the oxide material significantly changed the particle morphology. The images obtained from the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ and LaNbO₄ and their products following nitridation at 1198 K for 2 h are presented in Figure 2. The LaNbO₄ sample consisted of spherical particles with unclear edges and had particle sizes primarily in the range of $2-4 \mu m$. In contrast, the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ was made of cuboid particles with clear surfaces and edges, 2-4 µm in size, in addition to spherical particles similar to those observed in the LaNbO₄ sample. The cuboid particles were confirmed to include Na and Zn by SEM-EDS and thus were attributed to a perovskite-type oxide similar to La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O₃. A scanning transmission electron miscroscope (STEM) image of one such cuboid $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ particle is presented in Figure 3 and shows clear lattice fringes over a wide range, indicating the single-crystalline nature of the particle. In fact, an selected area electron diffraction (SAED) pattern for one of these particles showed clear diffraction spots that provided further evidence for the single-crystalline nature of the material. Notably, when the heating duration to prepare the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ was shortened from 25 to 10 h, the product appeared to include more agglomerated cuboid particles. This presumably occurred because sufficient dissolution and recrystallization did not occur during the shorter heating time in the molten salt flux.

As shown in Figure 1, the XRD pattern for the nitrided La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ contains a peak at approximately 31°, attributable to the (002) and (200) planes of LaNbN₂O [25]. Some peaks related to the original $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ are also present, but their intensity is significantly weaker following nitridation, whereas the peaks ascribed to LaNbO₄ are essentially unchanged. Similar results were observed following the nitridation of LaNbO₄, in that peaks attributable to the LaNbN₂O phase were generated, but the LaNbO₄ peaks were barely weakened. These observations indicate the high reactivity of the perovskite-type oxide phase during the nitridation. Elemental analysis by ICP-OES established that La:Na:Zn:Nb molar ratio for the product obtained from nitridation of the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ at 1198 K for 2 h was 1.14:0.27:0.07:1.00. Therefore, the La component was preserved, and the Zn component was volatilized to a greater extent than the Na component during nitridation. It should also be noted that the La/Nb ratio was maintained during nitridation of LaNbO₄, and so the volatilization of La was evidently negligible. The excess of La species resulted in the formation of LaNbO₄ as a byproduct. La₃NbO₇ also accounted for a portion of the excess La species because small peaks attributable to La_3NbO_7 were observed after the nitridation. The remaining Na and Zn were presumably doped into the LaNbN₂O material, which may have affected the semiconducting properties of the nitridation product. The absorption edge wavelength as estimated from the onset of light absorption was approximately 700 nm. This wavelength was somewhat shorter

than the value of 750 nm reported for LaNbN₂O and the light absorption onset observed for the nitridation product obtained from LaNbO₄ [17,18]. Notably, the nitridation product resulting from La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ exhibited a brighter color than that produced by LaNbO₄. It is suspected that the nitridation of LaNbO₄ into LaNbON₂ was too slow because it required significant rearrangement of the ions, such that anion vacancies and reduced Nb species were present in the product.



Figure 2. SEM images of (**a**) the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$, (**b**) the product from nitridation at 1198 K for 2 h, (**c**) the LaNbO₄, and (**d**) the product from nitridation at 1198 K for 2 h. The samples in (**a**) and (**c**) were synthesized by the flux method.



Figure 3. STEM images of (**a**,**b**) a cuboid particle in the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ specimen, and (**c**) an SAED pattern of this sample. (**d**,**e**) STEM images of the $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ after nitridation at 1198 K for 2 h.

As shown in Figure 2, the products resulting from nitridation of both $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and $LaNbO_4$ exhibited roughened surfaces, although the sizes and contours of the original particles were fairly well preserved. These results are attributed to the volatilization of the constituent elements in $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and to the increased density of the material obtained from $LaNbO_4$. Such effects are commonly observed following the nitridation of transition metal oxides [12,13,16,18,19]. The structure of the nitridation product of $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ was closely inspected using STEM. As shown in Figure 3e, the product particles had characteristic dense solid cores and porous shells, although the entire particles became porous when the particle size was sufficiently small. In contrast, the nitridation product generated from LaNbO₄ maintained the initial dense structure. Evidently, the formation of a porous structure due to the volatilization of the Na and Zn components effectively promoted nitridation to LaNbN₂O. However, it is arguable if Na and Zn species' volatilization is a driving force to promote the nitridation because the composition of the starting oxide and the rates of Na and Zn evaporation and the exchange of O and N were not controlled.

Nb 3d X-ray photoelectron spectroscopy (XPS) data were acquired to study the surface chemical states of the Nb species in these materials, and Figure 4 provides the XPS spectra for La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ and LaNbO₄ and for their products following nitridation at 1198 K for 2 h. The Nb 3d spectra of the oxide samples were deconvoluted to give a single doublet peak (representing Nb $3d_{5/2}$ and $3d_{3/2}$, with a peak separation of 2.75 eV) attributed to Nb^{5+} . In contrast, the Nb 3d XPS spectra of the nitrided samples could be deconvoluted into two doublet peaks, and the Nb species associated with higher and lower binding energies are attributable to Nb⁵⁺ and reduced Nb (Nb⁴⁺ or Nb³⁺) species, respectively. The Nb⁵⁺ peaks produced by the nitrided samples were also positioned at lower binding energies than those generated by the oxide materials because the Nb⁵⁺ ions formed bonds to less electronegative N^{3-} ions rather than to O^{2-} [26]. The incorporation of N^{3-} in the material was confirmed based on the N 1s peak at a binding energy of approximately 396 eV (Figure S1). The proportions of reduced Nb species relative to the total Nb were almost the same for the samples obtained from nitridation of La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ and LaNbO₄. Therefore, using $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ did not have a unique effect in terms of suppressing the reduction of Nb⁵⁺ during the nitridation.



Figure 4. Nb 3*d* XPS spectra obtained from (**a**) $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$, (**b**) the product from nitridation at 1198 K for 2 h, (**c**) $LaNbO_4$, and (**d**) the product from nitridation at 1198 K for 2 h.

Based on the above characterizations, it is clear that the addition of volatile Na and Zn components can modify the structure of LaNbO₄ to provide a perovskite-type oxide and also promote nitridation to give a LaNbN₂O phase although La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ was not obtained as a pure material and the reduction of Nb⁵⁺ species during the nitridation was not suppressed. Subsequently, the effect of the nitridation conditions of La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ on the properties of the products was investigated to gain additional insights concerning the nitridation process.

The XRD patterns and DRS spectra obtained from the products generated from La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ by nitridation at 1198 K for varying durations are presented in Figures 5 and 6, respectively. Following the initial hour of nitridation, the diffraction peak associated with the perovskite-type oxide weakened significantly, while peaks attributed to the LaNbN₂O phase emerged, and the peaks related to LaNbO₄ also became more intense. In addition, peaks assigned to La_3NbO_7 became observable. As the nitridation time was prolonged, the diffraction peaks from the LaNbN₂O phase became more prominent and sharper, indicative of improved crystallinity, while those ascribed to the perovskite-type oxide were diminished. Both LaNbO₄ and La₃NbO₇ remained in the product after nitridation for 3 h. Elemental analysis by ICP-OES indicated that most Zn in La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ was vaporized during the initial hour of nitridation, whereas the evaporation of Na was slow, and approximately half of the initial quantity of Na remained after 3 h. This difference in the evaporation rates of Na^+ and Zn^{2+} species would be expected to generate a La-rich byproduct (La_3NbO_7) in the initial stage of nitridation. In contrast, the change in the La amount was less than 3%. The nitridation product at 1 h exhibited an onset of light absorption at approximately 700 nm and continuous background absorption beyond the onset. As the heating duration was extended, the absorption onset remained largely unchanged, but the background absorption became stronger. These results suggest that the LaNbN₂O phase was produced during the very early stage of the nitridation process. Background absorption beyond the absorption edge wavelength is commonly associated with the presence of reduced Nb species and anion vacancies [6,7]. Similar trends were observed when the heating time was fixed at 2 h, and the nitridation temperature was varied (Figures S2 and S3). The quantity of the perovskite-type oxide was reduced at higher temperatures, with the concurrent emergence of the LaNbN₂O phase, and byproducts, such as LaNbO₄ and La₃NbO₇ persisted even when the nitridation temperature was increased to 1248 K. The product showed a light absorption onset of approximately 700 nm and the background light absorption became pronounced at higher nitridation temperatures. The volatilization of Na and Zn components also proceeded, although the pace of the former was slower.



Figure 5. XRD patterns obtained from (**a**) $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and (**b**–**f**) products obtained from nitridation at 1198 K for (**b**) 1.0, (**c**) 1.5, (**d**) 2.0, (**e**) 2.5, and (**f**) 3.0 h. Reference patterns for (**g**) LaNbN₂O, (**h**) $La_{0.5}Na_{0.5}Zn_{0.33}Nb_{0.67}O_3$, and (**i**) LaNbO₄ are shown for comparison. Asterisks (*) represent peaks from La_3NbO_7 .



Figure 6. DRS data obtained from (**a**) La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ and (**b**–**f**) products generated from nitridation at 1198 K for (**b**) 1.0, (**c**) 1.5, (**d**) 2.0, (**e**) 2.5, and (**f**) 3.0 h.

The oxygen evolution activity of the LaNbN₂O-based samples produced via nitridation of the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ at 1198 K for 2 h was examined after loading a CoO_x cocatalyst. The cocatalyst-loading amount and loading temperature were initially optimized, as depicted in Figures S4 and S5. The oxygen evolution rate was maximized to be 115–117 µmol h⁻¹ at a Co-loading of 0.5 wt % and loading temperature of 773 K. This CoO_x cocatalyst is thought to provide active sites for oxygen evolution and to facilitate the extraction of photoexcited holes from the photocatalyst [16]. However, excessive loading can result in aggregation of the cocatalyst and shading of the photocatalyst from incident light, both of which can lower activity. The CoO_x-loading temperature window that resulted in the most effective improvement of the O₂ evolution activity was found to be quite narrow, presumably reflecting the tendency of Nb-based oxynitride photocatalysts to react with NH₃.

Figure 7 shows the time courses of gas evolution during the oxygen evolution reaction using the products obtained from $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and $LaNbO_4$ after nitridation at 1198 K for 2 h. The nitridation product from La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ exhibited an oxygen evolution rate of 117 μ mol h⁻¹, which was more than five times produced from LaNbO₄. The corresponding AQY value was 1.7% at 420 nm, which is twice the highest previously reported yield for LaNbN₂O synthesized via the nitridation of LaKNaNbO₅ [18]. The gradual decrease in the O_2 evolution rate over time seen in these data is ascribed to the photodeposition of Ag, which blocked the surface of the photocatalyst and shielded it from the incident light. A small quantity of nitrogen (at most 10 µmol) was also found to be produced due to oxidation of the sample surface during the first hour of the reaction, but this nitrogen evolution dropped to almost zero in the following reaction. These phenomena are typically observed during photocatalytic water oxidation reactions using (oxy)nitrides [5,27]. The significant improvement in the oxygen evolution rate of the LaNbN₂O-based photocatalyst synthesized via nitriding La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ demonstrates the importance of designing a suitable precursor oxide for LaNbN₂O. The matching of the crystal structure allowed for the prompt conversion of the starting oxide into the oxynitride phase during the nitridation. As a result, the density of defects generated during the rearrangement of the constituent elements of LaNbN₂O could be suppressed. However, the extent of Nb⁵⁺ reduction was not appreciably lowered. Moreover, the remaining Na and Zn may have been doped into the LaNbN2O material and have affected the photocatalytic

activity. Further investigation is needed to verify the origin of the activity enhancement of the present LaNbN₂O-based photocatalyst.



Figure 7. Time courses of gas evolution during the oxygen evolution reaction from aqueous AgNO₃ solutions using the products generated from nitridation of (**a**) $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ and (**b**) $LaNbO_4$ at 925 °C for 2 h. Reaction conditions: sample, 0.30 g; cocatalyst, CoO_x (0.5 wt % as Co, loaded at 773 K); solution, 150 mL (50 mM AgNO₃ and 0.20 g La_2O_3); light source, Xe lamp ($\lambda > 420$ nm). Open and closed symbols represent O₂ and N₂, respectively.

The photocatalytic oxygen evolution rates observed when using the nitridation products produced by $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ employing various conditions are presented in Table 1. When using a fixed nitridation temperature of 1198 K, the rate of oxygen evolution increased with increases in the nitridation time from 1 to 2 h, presumably because of increases in the amount and degree of crystallinity of the LaNbN₂O phase. Interestingly, the oxygen evolution rate dropped drastically when the nitridation duration was extended to 3 h, even though the crystallinity of the LaNbN₂O phase was increased. This effect was likely associated with increases in the concentrations of reduced Nb species and anion vacancies, as is evident from the DRS data and Nb 3*d* XPS spectra in Figure 6 and Figure S6, respectively. At a fixed nitridation duration of 2 h, the rate of oxygen evolution was increased markedly by increasing the nitridation temperature from 1173 to 1198 K but then decreased rapidly with the further elevation of the temperature, likely for similar reasons (see Figures S3 and S6).

3. Methods

 $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$ samples were synthesized by a flux method using Na_2CO_3 (2 mmol, Wako Pure Chemicals, 99.8%), La_2O_3 (3 mmol, Kanto Chemicals, 99.99%), ZnO (4 mmol, Kanto Chemicals, 99%) and Nb_2O_5 (3 mmol, High Purity Chemical Laboratory, 99.9%) as raw materials, with a NaCl (50 mmol, Wako, 99.5%) flux. The precursors were first combined and ground in an alumina mortar for 30 min before being transferred to alumina crucibles. The mixture was subsequently heated in air to 1373 K with a temperature ramp of 10 K min⁻¹, held at that temperature for 25 h (unless otherwise noted), and then cooled at 10 K min⁻¹. The product was washed with distilled water to remove the flux and then dried in a vacuum oven at 313 K overnight. This precursor oxide is denoted herein as $La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O_3$, based on the nominal molar ratios in the starting mixture, even though it was a combination of several oxides. For comparison purposes, LaNbO₄

was also synthesized from La_2O_3 (3 mmol) and Nb_2O_5 (3 mmol) as precursors in a NaCl flux (50 mmol) following a similar procedure, but without using Na and Zn sources. The precursors were each calcined at 1373 K for 25 h.

The as-prepared La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ was subjected to nitridation to produce LaNbN₂O. In this process, a quantity (0.5 g) of the La_{0.6}Na_{0.4}Zn_{0.4}Nb_{0.6}O₃ was transferred to an alumina tube and nitrided at 1173–1248 K for 1–3 h under a 200 mL min⁻¹ flow of gaseous NH₃. A quantity (0.5 g) of LaNbO₄ was also nitrided in a similar manner, with heating at 1198 K for 2 h, to produce a control sample made without employing Na₂CO₃ or ZnO.

The CoO_x cocatalyst was deposited by impregnation followed by heating under a flow of NH₃ gas [16]. During this impregnation, a quantity of the photocatalyst powder (0.3 g) was dispersed in a specific volume of an aqueous Co(NO₃)₂.6H₂O solution, followed by a 5 min sonication. The amount of Co added was 0.5 wt % concerning the mass of the photocatalyst powder. Subsequently, the material was completely dried by heating on a water bath at approximately 353 K, after which the powder was collected and heated at 773 K for 1 h in a 200 mL min⁻¹ flow of NH₃.

The photocatalyst samples were analyzed by XRD (MiniFlex 300, Rigaku (Tokyo, Japan); Cu K α) over the 2 θ range of 10° to 60°, and UV-visible DRS (V-670, JASCO, Nagano, Japan) data were acquired over the range of 200–1000 nm. The total reflectance was converted into Kubelka–Munk function $(f(r_{\infty}) = \frac{(1-r_{\infty})^2}{2r_{\infty}})$, where r_{∞} stands for the diffuse-reflectance measured concerning the standard. Spectralon was used as a standard white material. SEM images were acquired with a Phenom ProX desktop scanning electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) and JSM-7600 F microscopes (JEOL, Tokyo, Japan). EDS data were acquired using a Phenom ProX (Thermo Fisher Scientific); STEM images were obtained with an HD2300A instrument (Hitachi High-Tech, Tokyo, Japan). High-resolution transmission electron microscopy (TEM) images and SAED patterns were acquired using a JEM-2010 (JEOL, Japan). XPS data were acquired with a PHI Quantera II spectrometer (ULVAC-PHI. INC, Chigasaki, Japan) incorporating an Al K α X-ray source and the binding energy for the C 1s peak at 285.0 eV was used for calibration purposes. The elemental composition of each specimen was determined by ICP-OES (ICPS-8100, Shimadzu, Kyoto, Japan). Before analysis, the sample was transferred into a platinum crucible and heated with a molten salt mixture composed of K₂CO₃ and H₃BO₃. This material was then dissolved in a mixture of tartaric acid, hydrochloric acid and hydrogen peroxide and then diluted to a concentration suitable for analysis.

The photocatalytic reactions were carried out in a Pyrex top-irradiation type reaction vessel connected to a closed gas circulation system. In each trial, a quantity of the photocatalyst (0.3 g) loaded with the CoO_x cocatalyst was dispersed in 150 mL of a 50 mM aqueous AgNO₃ solution containing 0.20 g of La_2O_3 , with the AgNO₃ and La_2O_3 serving as a sacrificial electron acceptor and a pH buffer, respectively [27]. In this reaction, Ag⁺ ions are reduced into metallic Ag by photoexcited electrons and water is oxidized into oxygen by photoexcited holes. Because of the deposition of Ag particles, the used photocatalyst cannot be reused. However, it is a common practice to use $AgNO_3$ in the photocatalytic material development stage, and developed materials can be utilized in overall water splitting reactions with improvement in the material synthesis and cocatalyst-loading technologies [2,5]. Successful examples include TaON and Ta₃N₅ [20,28]. Before photoirradiation, the suspension in the reaction system was evacuated to completely remove air, after which Ar was introduced as a circulation gas. Following this, the suspension was irradiated from overhead using a 300 W xenon lamp equipped with a dichroic mirror and a cutoff filter ($\lambda \ge 420$ nm). The reactant solution was maintained at 288 K using a cooling water system during the reaction. The evolved gaseous products were analyzed using an integrated gas chromatography system consisting of a GC-8A chromatograph (Shimadzu, Japan) equipped with molecular sieve 5 Å columns and a thermal conductivity detector, with argon as the carrier gas.

The AQY for the oxygen evolution reaction was calculated as:

AQY (%) =
$$[4 \times n(O_2)]/n(\text{photons}) \times 100$$

where $n(O_2)$ and n(photons) are the number of oxygen molecules generated and the number of incident photons, respectively. The number of photons at 420 nm from a 300 W xenon lamp equipped with a bandpass filter was measured to be 3.9×10^{20} photon h⁻¹ using an LS-100 spectroradiometer (EKO Instruments, Tokyo, Japan) by integrating the photon flux at different positions at the height of the suspension surface. The oxygen evolution was found to decrease over time due to the ongoing deposition of Ag, and so the AQY was calculated using $n(O_2)$ and n(photons) values determined during the first hour of irradiation.

4. Conclusions

This work demonstrates a new approach to the synthesis of LaNbN₂O from a perovskitetype La and Nb mixed oxide. The addition of volatile Na and Zn species caused the original oxide to be partly converted into cuboid perovskite-type oxide particles along with spherical LaNbO₄ particles and other byproducts. The cuboid particles were found to undergo nitridation more rapidly than the spherical LaNbO₄ particles due to the volatilization of the Na and Zn species, forming porous LaNbN₂O-like shells on perovskite-type oxide cores. The LaNbN₂O-based photocatalyst obtained in this manner, when loaded with CoO_x as a cocatalyst, exhibited oxygen evolution activity from an aqueous AgNO₃ solution almost twice that of existing LaNbN₂O-based photocatalysts, with an AQY of 1.7% at 420 nm. It is expected that the activity of this material could be further improved by effectively synthesizing a pure perovskite-type mixed oxide with a controlled La/Nb molar ratio. This work demonstrates a novel approach to designing precursor oxides that yield highly active LaNbN₂O. This study also provides new opportunities for developing efficient Nb-based perovskite oxynitride photocatalysts capable of absorbing long-wavelength visible light but highly susceptible to reduction during nitridation.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/catal11050566/s1, XRD patterns, DRS spectra, photocatalytic activity data and XPS spectra.

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References

- 1. Hisatomi, T.; Domen, K. Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts. *Nat. Catal.* **2019**, *2*, 387–399. [CrossRef]
- 2. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chem. Soc. Rev. 2009, 38, 253–278. [CrossRef]

- 3. Ahmed, M.; Xinxin, G. A review of metal oxynitrides for photocatalysis. Inorg. Chem. Front. 2016, 3, 578–590. [CrossRef]
- 4. Wang, W.; Tadé, M.O.; Shao, Z. Research progress of perovskite materials in photocatalysis- and photovoltaics-related energy conversion and environmental treatment. *Chem. Soc. Rev.* **2015**, *44*, 5371–5408. [CrossRef] [PubMed]
- Maeda, K.; Domen, K. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. J. Phys. Chem. C 2007, 111, 7851–7861. [CrossRef]
- Kim, Y.-I.; Woodward, P.M.; Baba-Kishi, A.K.Z.; Tai, C.W. Characterization of the Structural, Optical, and Dielectric Properties of Oxynitride Perovskites AMO2N (A = Ba, Sr, Ca; M = Ta, Nb). *Chem. Mater.* 2004, *16*, 1267–1276. [CrossRef]
- Siritanaratkul, B.; Maeda, K.; Hisatomi, T.; Domen, K. Synthesis and Photocatalytic Activity of Perovskite Niobium Oxynitrides with Wide Visible-Light Absorption Bands. *ChemSusChem* 2010, *4*, 74–78. [CrossRef] [PubMed]
- Haydous, F.; Si, W.; Guzenko, V.A.; Waag, F.; Pomjakushina, E.; el Kazzi, M.; Sévery, L.; Wokaun, A.; Pergolesi, D.; Lippert, T. Improved Photoelectrochemical Water Splitting of CaNbO₂N Photoanodes by CoPi Photodeposition and Surface Passivation. *J. Phys. Chem.* C 2019, 123, 1059–1068. [CrossRef]
- Sun, X.; Liu, G.; Xu, X. Defect management and efficient photocatalytic water oxidation reaction over Mg modified SrNbO₂N. J. Mater. Chem. A 2018, 6, 10947–10957. [CrossRef]
- Maeda, K.; Higashi, M.; Siritanaratkul, B.; Abe, R.; Domen, K. SrNbO₂N as a Water-Splitting Photoanode with a Wide Visible-Light Absorption Band. J. Am. Chem. Soc. 2011, 133, 12334–12337. [CrossRef]
- Seo, J.; Hisatomi, T.; Nakabayashi, M.; Shibata, N.; Minegishi, T.; Katayama, M.; Domen, K. Efficient Solar-Driven Water Oxidation over Perovskite-Type BaNbO₂N Photoanodes Absorbing Visible Light up to 740 nm. *Adv. Energy Mater.* 2018, *8*, 1800094. [CrossRef]
- Yamada, T.; Murata, Y.; Suzuki, S.; Wagata, H.; Oishi, S.; Teshima, K. Template-Assisted Size Control of Polycrystalline BaNbO₂N Particles and Effects of Their Characteristics on Photocatalytic Water Oxidation Performances. *J. Phys. Chem. C* 2018, 122, 8037–8044. [CrossRef]
- Hisatomi, T.; Katayama, C.; Moriya, Y.; Minegishi, T.; Katayama, M.; Nishiyama, H.; Yamada, T.; Domen, K. Photocatalytic oxygen evolution using BaNbO2N modified with cobalt oxide under photoexcitation up to 740 nm. *Energy Environ. Sci.* 2013, 6, 3595–3599. [CrossRef]
- 14. Cui, J.; Luo, Y.; Dong, B.; Qi, Y.; Jia, M.; Zhang, F.; Li, C. Investigation on the Influence of Sc Ions Doping on the Structure and Performance of Ta₃N₅ Photocatalyst for Water Oxidation under Visible Light Irradiation. *Sol. RRL* **2019**, *4*, 1900445. [CrossRef]
- Jadhav, S.; Hasegawa, S.; Hisatomi, T.; Wang, Z.; Seo, J.; Higashi, T.; Katayama, M.; Minegishi, T.; Takata, T.; Peralta-Hernández, J.M.; et al. Efficient photocatalytic oxygen evolution using BaTaO₂N obtained from nitridation of perovskite-type oxide. *J. Mater. Chem. A* 2020, *8*, 1127–1130. [CrossRef]
- Zhang, F.; Yamakata, A.; Maeda, K.; Moriya, Y.; Takata, T.; Kubota, J.; Teshima, K.; Oishi, S.; Domen, K. Cobalt-Modified Porous Single-Crystalline LaTiO₂N for Highly Efficient Water Oxidation under Visible Light. *J. Am. Chem. Soc.* 2012, 134, 8348–8351. [CrossRef] [PubMed]
- 17. Wan, L.; Xiong, F.-Q.; Zhang, B.; Che, R.; Li, Y.; Yang, M. Achieving photocatalytic water oxidation on LaNbON₂ under visible light irradiation. *J. Energy Chem.* **2018**, *27*, 367–371. [CrossRef]
- 18. Wang, X.; Hisatomi, T.; Liang, J.; Wang, Z.; Xiang, Y.; Zhao, Y.; Dai, X.; Takata, T.; Domen, K. Facet engineering of LaNbON₂ transformed from LaKNaNbO₅ for enhanced photocatalytic O₂ evolution. *J. Mater. Chem. A* **2020**, *8*, 11743–11751. [CrossRef]
- 19. Wang, X.; Hisatomi, T.; Wang, Z.; Song, J.; Qu, J.; Takata, T.; Domen, K. Core–Shell-Structured LaTaON₂ Transformed from LaKNaTaO₅ Plates for Enhanced Photocatalytic H₂ Evolution. *Angew. Chem. Int. Ed.* **2019**, *58*, 10666–10670. [CrossRef]
- Wang, Z.; Inoue, Y.; Hisatomi, T.; Ishikawa, R.; Wang, Q.; Takata, T.; Chen, S.; Shibata, N.; Ikuhara, Y.; Domen, K. Overall water splitting by Ta₃N₅ nanorod single crystals grown on the edges of KTaO₃ particles. *Nat. Catal.* 2018, 1, 756–763. [CrossRef]
- Fu, J.; Skrabalak, S.E. Enhanced Photoactivity from Single-Crystalline SrTaO₂N Nanoplates Synthesized by Topotactic Nitridation. Angew. Chem. Int. Ed. 2017, 56, 14169–14173. [CrossRef]
- 22. Novitskaya, G.; Belous, A.; Polyanetskaya, S.; Yanchevskii, O. Russ. J. Inorg. Chem. 1990, 35, 1419. (In English)
- 23. Vullum, F.; Nitsche, F.; Selbach, S.M.; Grande, T. Solid solubility and phase transitions in the system LaNb_{1-x}Ta_xo₄. *J. Solid State Chem.* **2008**, *181*, 2580–2585. [CrossRef]
- 24. Rossell, H.J. Fluorite-related phases Ln₃MO₇, Ln = rare earth, Y or Sc, M = Nb, Sb, or Ta: II. Structure determination. *J. Solid State Chem.* **1979**, *27*, 115–122. [CrossRef]
- Logvinovich, D.; Ebbinghaus, S.G.; Reller, A.; Marozau, I.; Ferri, D.; Weidenkaff, A. Synthesis, Crystal Structure and Optical Properties of LaNbON2. Z. Anorg. Allg. Chem. 2010, 636, 905–912. [CrossRef]
- Chun, W.-J.; Ishikawa, A.; Fujisawa, H.; Takata, T.; Kondo, J.N.; Hara, M.; Kawai, M.; Matsumoto, A.Y.; Domen, K. Conduction and Valence Band Positions of Ta₂O₅, TaON, and Ta₃N₅ by UPS and Electrochemical Methods. *J. Phys. Chem. B* 2003, 107, 1798–1803. [CrossRef]
- 27. Kasahara, A.; Nukumizu, K.; Takata, T.; Kondo, J.N.; Hara, M.; Kobayashi, A.H.; Domen, K. LaTiO₂N as a Visible-Light (≤600 nm)-Driven Photocatalyst (2). *J. Phys. Chem. B* **2003**, 107, 791–797. [CrossRef]
- 28. Maeda, K.; Lu, D.; Domen, K. Direct Water Splitting into Hydrogen and Oxygen under Visible Light by using Modified TaON Photocatalysts with d0Electronic Configuration. *Chem. Eur. J.* **2013**, *19*, 4986–4991. [CrossRef]