

Preparation of LaTiO₂N Using Hydrothermally Synthesized La₂Ti₂O₇ as a Precursor and Urea as a Nitriding Agent

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Abstract: A facile method was successfully developed to prepare perovskite-type metal oxynitrides, LaTiO₂N, from La₂Ti₂O₇ as a precursor in an atmosphere of N₂. Urea was employed as a solid-state nitriding agent, instead of gaseous NH₃, to increase the safety of the reaction. The hydrothermally prepared La₂Ti₂O₇ precursor had a nanosheet morphology and contained La(OH)₃ as a by-product. Through the optimization of reaction conditions including heat-treatment temperature and content of urea, single-phase LaTiO₂N could be obtained. In addition, we revealed that the La(OH)₃ present in the La₂Ti₂O₇ precursor played an important role in the nitriding process using urea. La₂O₂CN₂ was generated by the reaction of La(OH)₃ with the thermal decomposition products of urea at the medium temperature range. This indicated that the NH₃ gas released from the thermal decomposition of urea did not directly cause nitridation of the La₂Ti₂O₇ precursor.

1. Introduction

Metal oxynitrides have attracted great attention over the past two decades for their promising applications in many fields, such as visible-light-driven photocatalysts,^[1-9] high-K dielectrics,^[10-13] ferroelectrics,^[14-16] colossal magnetoresistive materials,^[17-19] and environmentally friendly inorganic pigments.^[20-24] Metal oxynitrides with perovskite-type structure are of particular interest because the incorporation of nitrogen into the oxidic perovskite crystalline structure leads to multifunctional properties as a result of band gap reduction.^[10,23,25-27] When O atoms are partially substituted by N atoms, the N 2p states and O 2p states are hybridized, reducing the band gap.^[28,29] Perovskite-type metal oxynitrides commonly contain early transition metals such as Ti, V, Zr, Nb, Ta, Mo, and W. Jansen et al. demonstrated that the solid solutions between CaTaO₂N and LaTaO₂N₂ (i.e., Ca_xLa_{1-x}TaO_{1+x}N_{2-x}) have a range of yellow to red colors and are possible pigments to replace Cd-containing materials.^[20] As a typical perovskite-type oxynitride, LaTiO₂N has been recognized as a candidate for a visible-light-driven photocatalysis because

of its narrow band gap (ca. 2.1 eV) and generates both H₂ and O₂ under irradiation of visible light in the presence of co-catalysts and sacrificial agents.^[30-34] LaTiO₂N has favorable band positions for solar water splitting. In addition, it is composed of relatively cheap and abundant metals, compared with other perovskite-type metal oxynitrides, such as SrNbO₂N and BaTaO₂N. The synthesis of perovskite-type oxynitrides containing LaTiO₂N is generally conducted by nitridation of metal oxide precursors.^[23,30-34] Gaseous NH₃ is the most widely employed nitriding agent to prepare oxynitrides. Normally, the ammonolysis is carried out at temperatures between 800 and 1300 °C and requires a long duration to complete the diffusion of nitrogen. However, the use of gaseous NH₃ at such high temperatures incurs a relatively high risk and makes scaled-up synthesis difficult, and is thus a major drawback of this method. Therefore, development of NH₃-gas-free preparation procedures of metal oxynitrides is a current research goal.^[35-37] Clarke and co-workers achieved the first preparation of SrTaO₂N in N₂ atmosphere by heat-treatment of a mixture of SrO and TaON at 1500 °C.^[35] Kikkawa et al. have also reported a direct preparation procedure of SrTaO₂N by using SrCO₃ and Ta₃N₅ in N₂ atmosphere.^[36] However, the nitrogen-containing precursors, i.e., TaON or Ta₃N₅, have to be prepared via the ammonolysis of Ta₂O₅ beforehand, meaning that these procedures do not exclude the use of NH₃ gas entirely.^[35,36] Recently, the syntheses of nitrides and oxynitrides through the reaction of metal oxide precursors with NaNH₂ molten salt have been reported.^[37-41] Preparation of perovskite metal oxynitrides, such as BaTaO₂N^[40] and BaNbO₂N,^[41] using NaNH₂ as a nitriding agent has also been achieved by the flux method and explosive reactions. Though these processes enable NH₃-gas-free preparation, they are very difficult to carry out on a large scale because NaNH₂ is highly sensitive. Compared with NH₃ and NaNH₂, urea is a possible alternative nitriding agent that is cheap, non-toxic, non-corrosive, and easily handled. The use of urea as a solid-state nitriding agent has been the subject of several studies. Moriga et al. reported synthesis of LaTiO₂N using urea or thiourea.^[42] However, despite the use of urea and thiourea as co-nitriding agents in this approach, NH₃ gas was still also used. Rao et al. reported preparation of various perovskite metal oxynitrides by heating metal carbonates and transition metal oxides with excess urea.^[43] Giordano and co-workers have also achieved the controlled synthesis of TaON and Ta₃N₅ using a method employing Ca²⁺ and urea.^[44] However, the mechanism by which urea induces nitridation was not adequately elucidated in these reports. Very recently, we have achieved a facile synthesis of a solid solution of GaN and ZnO (GaN:ZnO) by using a layered double hydroxide (LDH) containing Zn²⁺ and Ga³⁺ as a precursor, and urea as a nitriding agent.^[45] The nitridation process of the Zn–Ga LDH and urea system was investigated by various spectroscopic techniques.

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We revealed that a ZnCN_2 -like species was generated as an intermediate at the medium temperature range and played important roles in the formation of $\text{GaN}:\text{ZnO}$. However, the preparation of perovskite metal oxynitrides, i.e., ABO_2N and/or ABON_2 ($A = \text{Ca, Sr, Ba, or La}$; $B = \text{Ti, Zr, Nb, or Ta}$) by using corresponding perovskite metal oxides, such as ABO_3 and $\text{A}_2\text{B}_2\text{O}_7$, as precursors, and urea as the nitriding agent, has not been accomplished yet.

In the present study, we have demonstrated a facile synthesis of the $\text{La}_2\text{Ti}_2\text{O}_7$ precursor and its subsequent nitridation to form LaTiO_2N by using urea as a nitriding agent. $\text{La}_2\text{Ti}_2\text{O}_7$ was prepared by a hydrothermal process using a water-soluble titanium complex as a precursor. Attempts to synthesize $\text{La}_2\text{Ti}_2\text{O}_7$ were carried out through several solution techniques. Nanoflake-type $\text{La}_2\text{Ti}_2\text{O}_7$ can be fabricated by the hydrothermal process.^[46–48] We predicted that the nanoflake structure should favor the complete diffusion of nitrogen during the nitriding process because of its high surface area and thinner morphology than bulk- or micropowder-type structures. In addition, $\text{La}(\text{OH})_3$ was generated as a by-product during the hydrothermal process. We have examined the influence of the presence of $\text{La}(\text{OH})_3$ in the precursor on the transformation from $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N . The transformation conditions from $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N , including heat-treatment temperature and duration and mixing ratio of urea to $\text{La}_2\text{Ti}_2\text{O}_7$, have also been optimized. The obtained samples were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (UV-vis DRS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS), and oxygen/nitrogen combustion analysis. In addition, we have investigated the nitridation mechanism of $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N in the presence of urea as a nitriding agent by using XRD and Fourier transform infrared (FT-IR) spectroscopy.

2. Results and Discussion

Preparation of $\text{La}_2\text{Ti}_2\text{O}_7$ as a precursor of LaTiO_2N via the hydrothermal process: Firstly, $\text{La}_2\text{Ti}_2\text{O}_7$, a precursor of LaTiO_2N , was prepared by the hydrothermal method. The XRD pattern of the product obtained by the hydrothermal treatment of a solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and a water-soluble Ti complex, titanium(IV) bis(ammonium lactato) dihydroxide (TALH), at 200°C for 24 h is shown in Figure 1a within the 2θ range of 20° to 70° . Diffraction peaks assignable to a layered perovskite with monoclinic structure (space group: $P2_1$) are found in the pattern. In addition, it also contains peaks attributed to $\text{La}(\text{OH})_3$. A TEM image of the product is shown in Figure S1. Similar to previous reports,^[46–48] rectangular nanosheets with an edge size on the submicrometer scale were observed. In addition, short nanorods with relatively uniform diameters were present in the product. It is well known that $\text{La}(\text{OH})_3$ samples prepared through solution processes have 1D nanostructures, such as nanorods, nanobelts, nanotubes, and nanowires.^[49–52] Therefore, these nanorods co-existing with the main product can be assumed to be $\text{La}(\text{OH})_3$. This by-product can be removed from the main product by exploiting the solubility of $\text{La}(\text{OH})_3$ in acidic solution.^[53] The molar ratio of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ in the pristine product obtained by the hydrothermal method was investigated by ICP-OES. The ratio was 0.425:0.575 ($\text{La}_2\text{Ti}_2\text{O}_7 +$

$\text{La}(\text{OH})_3 = 1$). Actually, the molar ratio of La/Ti in the starting mixture for the hydrothermal process was adjusted to 1:1. The ICP-OES investigation also revealed that negligible La and Ti components were contained in the supernatant aqueous phase after the hydrothermal process. Here, the hydrothermally prepared products were washed with ethanol. It seems that unreacted Ti species were eliminated during this washing process. Therefore, the molar ratio of La is richer than that of Ti in the obtained products ($\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$). Figure 1b shows an XRD pattern of the product after washing with HNO_3 solution and subsequently with deionized water. The peaks indexed to $\text{La}(\text{OH})_3$ disappear and all remaining diffraction peaks match well with the characteristic reflections of the $\text{La}_2\text{Ti}_2\text{O}_7$ crystalline phase. Therefore, $\text{La}_2\text{Ti}_2\text{O}_7$ was obtained in a single phase by the hydrothermal method and subsequent washing with HNO_3 solution. For comparison, $\text{La}_2\text{Ti}_2\text{O}_7$ was also synthesized by the polymerized complex (PC) method.^[30] XRD peaks attributable to the $\text{La}_2\text{Ti}_2\text{O}_7$ crystalline phase were observed in the diffraction pattern, while no other peaks were visible (Figure S2a). Relative to the sample obtained by the PC method, the XRD pattern for the hydrothermally obtained product shows weaker and broader diffraction peaks. This indicates that the hydrothermal product has much smaller crystal sizes and less ideal crystallinity than the PC sample.

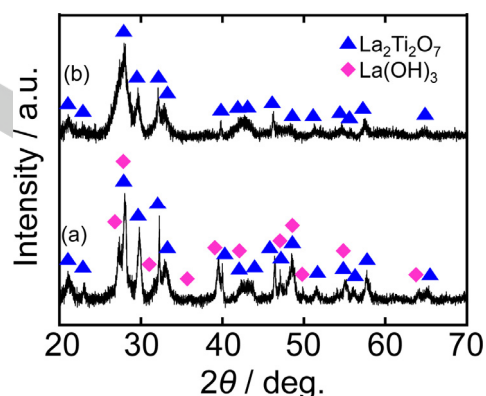


Figure 1. XRD patterns of products obtained from hydrothermal method: (a) as-prepared sample, (b) sample washed with HNO_3 solution and deionized water.

Optimization of transformation conditions from $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N using urea as a nitriding agent: Next, we examined the nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$ using urea to prepare LaTiO_2N . Both the pristine product obtained via the hydrothermal process, i.e., the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$, and the washed product, i.e., the single phase of $\text{La}_2\text{Ti}_2\text{O}_7$, were used as precursors. Figure 2 shows optical photographs of the samples before and after calcination with urea. As depicted in Figure 2a and b, both pristine and washed products were white before calcination. When the washed product was calcined with urea, the color of the sample changed to dark-blue (Figure 2c). The XRD pattern of the sample derived from calcination of the washed product ($\text{La}_2\text{Ti}_2\text{O}_7$ without $\text{La}(\text{OH})_3$) and urea contained only diffraction peaks attributed to $\text{La}_2\text{Ti}_2\text{O}_7$ and no peaks attributed to LaTiO_2N (Figure 3a). The dark-blue color seems to originate from the reduction of Ti species and/or the partial nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$. In contrast, a product with a green-brown color was obtained after calcination of the *unwashed* product (the mixture of

$\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ and urea (Figure 2d). As shown in Figure 3b, the transformation of the $\text{La}_2\text{Ti}_2\text{O}_7$ crystals into LaTiO_2N crystals with orthorhombic structure (space group: *Imma*) by nitridation using urea was successful. Though some diffraction peaks assignable to the La_2O_3 phase also co-existed, these impurities could be removed by washing with acidic solution (details are discussed later).^[54] These results indicated that while pure $\text{La}_2\text{Ti}_2\text{O}_7$ cannot be directly nitrided to LaTiO_2N by urea, this nitridation can be achieved when the precursor contains $\text{La}(\text{OH})_3$. To prove this hypothesis, the washed product of hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ (single phase) was remixed with commercial $\text{La}(\text{OH})_3$ and used as a precursor for preparation of LaTiO_2N using urea as a nitriding agent. Though the color of this sample after calcination was brown (Figure 2d), slightly different from the calcined pristine product, the XRD pattern of this control sample (Figure 3c) was very similar to that of the sample prepared using the pristine product from the hydrothermal process, i.e., the detected peaks were assignable to LaTiO_2N and La_2O_3 . Furthermore, $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by the PC method was also examined as a control experiment. When nitridation using urea was carried out for this $\text{La}_2\text{Ti}_2\text{O}_7$, the XRD pattern retained the peaks indexed to $\text{La}_2\text{Ti}_2\text{O}_7$ and no reflection peak attributed to LaTiO_2N was found (Figure S2b). However, when $\text{La}(\text{OH})_3$ was added to the $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by the PC method, LaTiO_2N was obtained by nitridation using urea (Figure S2c). These results revealed that the co-existence of $\text{La}(\text{OH})_3$ in the hydrothermal product of $\text{La}_2\text{Ti}_2\text{O}_7$ plays important roles for the nitridation process using urea as a nitriding agent. Therefore, the pristine product obtained by the hydrothermal process was used as a precursor in subsequent experiments.

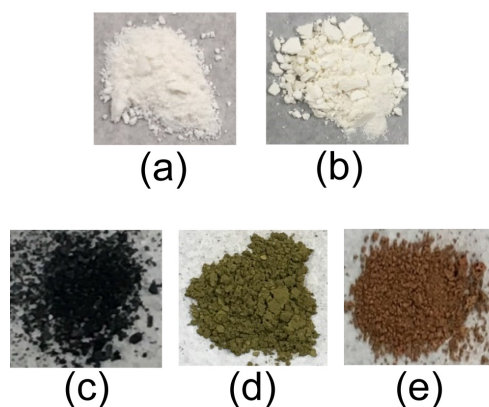


Figure 2. Optical photographs of products obtained after (a) hydrothermal treatment, (b) washing of (a) with aqueous solution of HNO_3 and deionized water, (c) calcination using (b) and urea at 930°C for 2 h, (d) calcination using (a) and urea at 930°C for 2 h, and (e) calcination using (b), commercial $\text{La}(\text{OH})_3$ and urea at 930°C for 2 h.

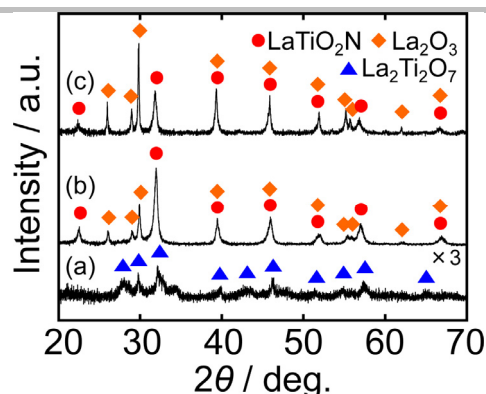


Figure 3. XRD patterns of products obtained after (a) calcination of washed $\text{La}_2\text{Ti}_2\text{O}_7$ (without $\text{La}(\text{OH})_3$) with urea at 930°C for 2 h, (b) calcination of pristine $\text{La}_2\text{Ti}_2\text{O}_7$ obtained by hydrothermal treatment (containing $\text{La}(\text{OH})_3$) with urea at 930°C for 2 h, (c) calcination of washed $\text{La}_2\text{Ti}_2\text{O}_7$ remixed with commercial $\text{La}(\text{OH})_3$ with urea at 930°C for 2 h.

We have optimized the conditions for nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N using urea, i.e., the ratio of $\text{La}_2\text{Ti}_2\text{O}_7$ and urea, reaction time, and reaction temperature. Optical photographs and XRD patterns of the products obtained from mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea with various mixing ratios after calcination are shown in Figure 4 and 5, respectively. We used molar ratios of urea to $\text{La}_2\text{Ti}_2\text{O}_7$ ($[\text{urea}] / [\text{La}_2\text{Ti}_2\text{O}_7] = R$) of 3.0, 4.5, 6.0, and 7.5. The calcination temperature and duration were fixed at 950°C and 8 h, respectively. In the case of $R = 3.0$, the sample maintained a white color even after calcination (Figure 4). The XRD pattern of this sample indicated that $\text{La}_2\text{Ti}_2\text{O}_7$ was generated in addition to the remnant of $\text{La}_2\text{Ti}_2\text{O}_7$ (Figure 5). In contrast, the color of the sample after calcination was brown in the case of $R \geq 4.5$ (Figure 4). In addition, the color became darker with increasing R value. Diffraction peaks assignable to LaTiO_2N and La_2O_3 were found in the XRD patterns for these samples. In addition, XRD peaks attributable to $\text{La}_2\text{O}_2\text{CN}_2$ crystals with tetragonal structure (space group: *I4/mmm*) were also observed for the samples prepared with $R \geq 7.5$. $\text{La}_2\text{O}_2\text{CN}_2$ is difficult to remove by washing with acidic solutions or organic solvents, whereas La_2O_3 can be removed by an acidic solution. Therefore, the optimal mixing ratio to obtain LaTiO_2N is $R = 4.5$; we used this ratio in subsequent experiments.

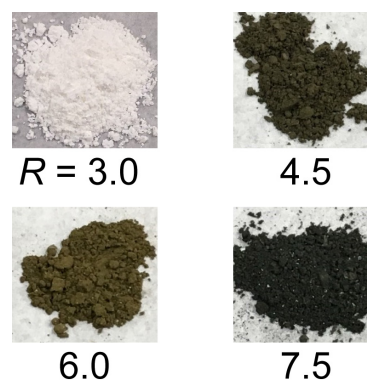


Figure 4. Optical photographs of products obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea with various mixing ratios ($R = 3.0, 4.5, 6.0$, and 7.5) after calcination at 950°C for 8 h.

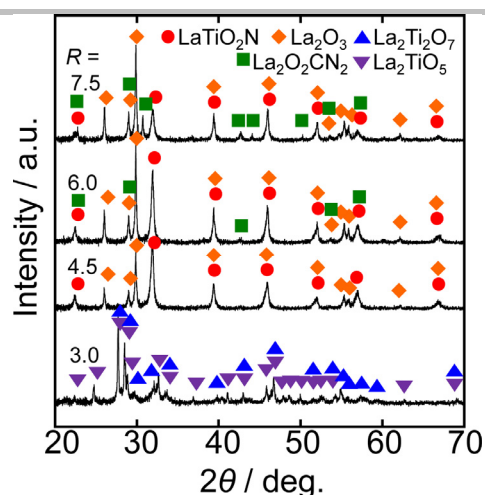


Figure 5. XRD patterns of products obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea with various mixing ratios ($R = 3.0, 4.5, 6.0$, and 7.5) after calcination at 950°C for 8 h.

Figure 6 displays the XRD patterns of the products obtained from mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 950°C for various durations (0.5–8 h). The diffraction peaks of the product obtained after calcination for 0.5 h were assignable to LaTiO_2N , La_2O_3 , $\text{La}_2\text{O}_2\text{CN}_2$, and $\text{La}_2\text{Ti}_2\text{O}_7$. The diffraction peaks for $\text{La}_2\text{Ti}_2\text{O}_7$ disappeared when the calcination duration was elongated to 1 h. Furthermore, the peaks indexed to $\text{La}_2\text{O}_2\text{CN}_2$ were not detected when the reaction time was longer than 2 h and only diffraction peaks of LaTiO_2N and La_2O_3 were found. The intensity of the peaks of La_2O_3 increased with increasing calcination duration. From the viewpoint of the energy consumption during calcination, we determined that the optimal calcination duration was 2 h and used this duration in subsequent experiments.

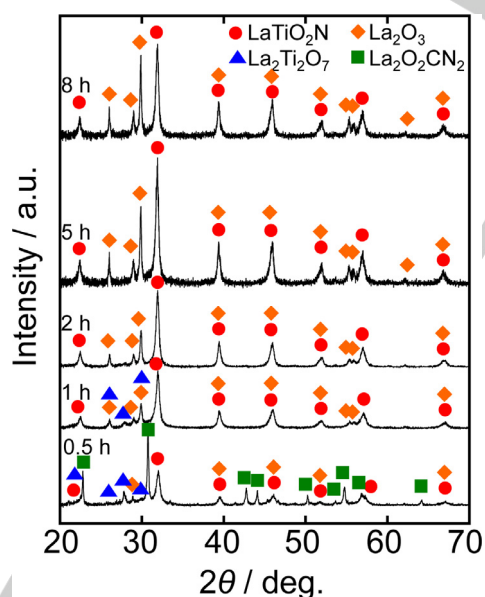


Figure 6. XRD patterns of products obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 950°C for 0.5, 1, 2, 5, and 8 h.

The influence of calcination temperature on the transformation of $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N was also investigated. Figure 7 presents the XRD patterns of the products obtained from mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at various reaction temperatures (900 – 1000°C) for 2 h. Even in the case of the sample prepared at 900°C , diffraction peaks attributable to LaTiO_2N were found. This indicates that the nitridation reaction from $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N could be initiated at 900°C . However, the remnant of the precursor, $\text{La}_2\text{Ti}_2\text{O}_7$, and the formation of a by-product, $\text{La}_2\text{O}_2\text{CN}_2$, were also indicated by this pattern. Therefore, a calcination temperature higher than 930°C should be used to obtain single-phase LaTiO_2N . The intensity of the peaks of La_2O_3 was increased with increasing calcination temperature. Therefore, we determined that the optimal calcination temperature was 930°C . Combining all these results, the optimal conditions to obtain single-phase LaTiO_2N by using hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ as a precursor and urea as a nitriding agent can be summarized as follows: (1) The pristine product of $\text{La}_2\text{Ti}_2\text{O}_7$ (containing $\text{La}(\text{OH})_3$) prepared via the hydrothermal method should be employed as a precursor without any purification (such as washing with acidic solution); (2) The optimal mixing ratio of $\text{La}_2\text{Ti}_2\text{O}_7$ and urea (R) is 4.5; (3) The optimal calcination temperature and duration are 930°C and 2 h, respectively; (4) After calcination, the by-product, i.e., La_2O_3 , should be removed by washing with acidic solution, such as aqueous HCl . Figure 8 shows the XRD pattern of LaTiO_2N obtained by these optimal conditions. A single phase of LaTiO_2N crystals with orthorhombic structure can be seen, with no other peaks.

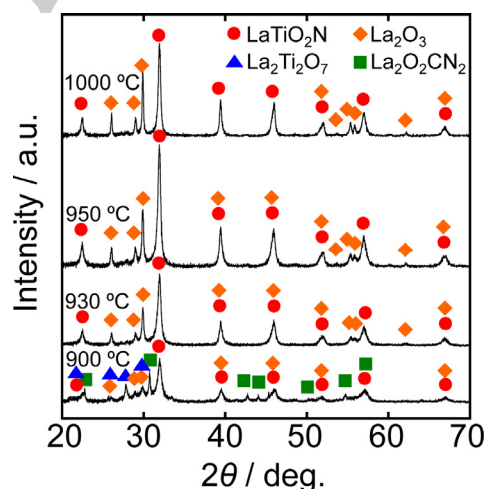


Figure 7. XRD patterns of products obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at $900, 930, 950$, and 1000°C for 2 h.

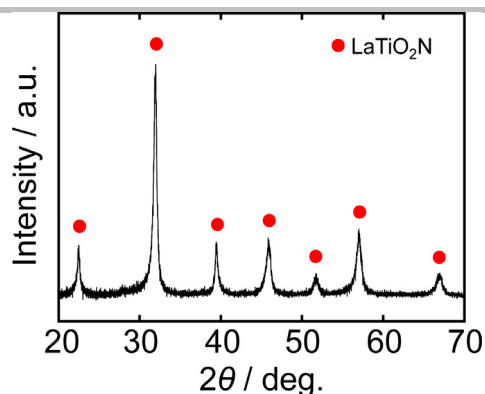


Figure 8. XRD patterns of LaTiO_2N obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 930°C for 2 h and washing with aqueous solution of HCl .

Nitridation mechanism of $\text{La}_2\text{Ti}_2\text{O}_7$ to form LaTiO_2N : The synthesis of metal oxynitrides using urea as a nitriding agent has been achieved by several research groups.^[43,44] In the previous reports, it was postulated that the NH_3 generated by decomposition of urea around 140°C ^[55] reacts with the precursor, i.e., metal oxides, to yield metal oxynitrides. However, as mentioned above, the nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N occurs at temperatures above 900°C in the current system. Therefore, it is unlikely that the NH_3 generated by decomposition of urea remained in the reaction furnace at such a high temperature, because the reaction was carried out under a N_2 flow. To exclude the possibility that the NH_3 generated by the decomposition of urea directly nitrided $\text{La}_2\text{Ti}_2\text{O}_7$, we carried out a control experiment in which the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ obtained by the hydrothermal method was placed in a separate position from urea in an alumina crucible boat (a photographic image is given in Figure S3.) The boat was heated under N_2 flow at 930°C for 2 h. After calcination, urea disappeared from the alumina boat and a white powder remained in the position where the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ was placed (Figure S3). This white powder was a mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and La_2TiO_5 , as shown by the XRD pattern in Figure S4. In addition, as shown in Figure 3, the nitridation of pure $\text{La}_2\text{Ti}_2\text{O}_7$ did not take place even when $\text{La}_2\text{Ti}_2\text{O}_7$ was well mixed with urea. These results revealed that the NH_3 generated at ca. 140°C does not directly induce nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$. Recently, we have reported the preparation of $\text{GaN}:\text{ZnO}$ solid solution from a Zn-Ga LDH using urea as a nitriding agent.^[45] We discovered that ZnCN_2 -like intermediate species were generated at the medium temperature range in this previous study. Furthermore, in the current system, $\text{La}_2\text{O}_2\text{CN}_2$ was generated as a by-product when the calcination was carried out at relatively low temperature (900°C) and/or for short duration (0.5 h) (see Figure 6 and 7). In addition, $\text{La}_2\text{O}_2\text{CN}_2$ was obtained in a single phase when a mixture of $\text{La}(\text{OH})_3$ and urea was heated at 800°C for 2 h (Figure S5). These facts suggest that generation of metal cyanamide or metal oxycyanamide as intermediate species is related to the nitridation process using urea. We performed heat-treatment of the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea at temperatures between 100 and 800°C to examine the intermediate species during calcination. XRD patterns of the samples obtained from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea after heating at 100, 200, 500, 600, and 800°C for 2 h are

shown in Figure 9. For comparison, the XRD pattern of the mixture before calcination is also given in Figure 9. In the pattern of the sample heat-treated at 100°C , diffraction peaks attributed to $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea were observed and no other peaks were found. This suggests that no decomposition of urea occurred under 100°C , consistent with the fact that the decomposition temperature of urea is 140°C .^[55] For the sample heat-treated at 200°C , only diffraction peaks indexed to $\text{La}_2\text{Ti}_2\text{O}_7$ were observed while those of $\text{La}(\text{OH})_3$ and urea disappeared. When the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ (without urea) was heated at 200°C for 2 h, the diffraction peaks of $\text{La}(\text{OH})_3$ clearly remained (Figure S6). These results suggest that the presence of $\text{La}(\text{OH})_3$ is a dominant factor in the formation of $\text{La}_2\text{O}_2\text{CN}_2$, and in the reaction between $\text{La}(\text{OH})_3$ in the mixture and urea initiated at temperatures between 100 and 200°C . For the samples heat-treated at 300 – 500°C , only negligible changes in the XRD patterns were found compared with the product obtained after heating at 200°C . When the mixtures were heated at 600 – 800°C , diffraction peaks indexed to $\text{La}_2\text{O}_2\text{CN}_2$ were found in addition to those of $\text{La}_2\text{Ti}_2\text{O}_7$. The intensity of the diffraction peaks of $\text{La}_2\text{O}_2\text{CN}_2$ increased with increasing reaction temperature. As shown in Figure 7, diffraction peaks of LaTiO_2N were observed, while the intensity of those of $\text{La}_2\text{O}_2\text{CN}_2$ was drastically decreased, for the product obtained by heat-treatment at 900°C compared with the mixture heated at 800°C . These results suggest that formation of $\text{La}_2\text{O}_2\text{CN}_2$ was involved in the nitridation reaction in the current system and in the generation of LaTiO_2N initiated between 800 and 900°C . The involvement of $\text{La}_2\text{O}_2\text{CN}_2$ in the nitridation process is clearly implicated by the XRD pattern of the sample obtained by heat-treatment of the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{O}_2\text{CN}_2$ at 930°C , which includes peaks assignable to LaTiO_2N (Figure S7).

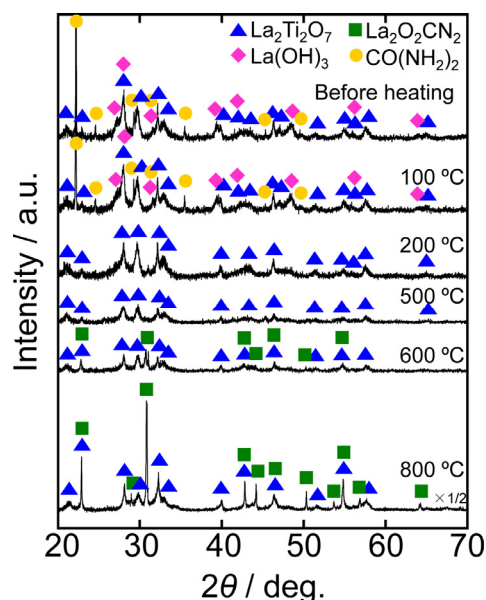


Figure 9. XRD patterns of the mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) before and after heat-treatment at 100, 200, 500, 600, and 800°C for 2 h.

The formation of a metal cyanamide, $\text{La}_2\text{O}_2\text{CN}_2$, was further confirmed by FT-IR spectroscopy, as shown in Figure 10. The mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea heat-treated at 100, 200,

300, 600, 800, and 930 °C were analyzed by diffuse-reflectance FT-IR spectroscopy (Figure 10a). For reference, the FT-IR spectra of the $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ mixture, urea, and $\text{La}_2\text{O}_2\text{CN}_2$ are also given in Figure 10b. Pure $\text{La}_2\text{O}_2\text{CN}_2$ displayed a sharp absorption peak around 2000 cm^{-1} corresponding to the asymmetric stretching mode of $[\text{NCN}]^{2-}$. This peak is consistent with previous reports of $\text{La}_2\text{O}_2\text{CN}_2$ ^[56] and also with the IR spectra of various metal cyanamides, such as ZnCN_2 ,^[57] CoCN_2 , NiCN_2 ,^[58] and MnCN_2 .^[59]

When the mixture was heat-treated at 100 °C, the spectrum was superimposable on that of the mixture before heat-treatment, which did not contain a peak around 2200 cm^{-1} . However, a strong absorption peak was found in the spectrum for the sample heat-treated at 200 °C. A similar peak was observed in the IR spectrum of the sample after heat-treatment at 200 °C in our previous study of the Zn–Ga LDH and urea system.^[45] The IR spectra for the samples heat-treated at 300 and 800 °C also displayed the bands around $1800\text{--}2200\text{ cm}^{-1}$. On decomposition at 140 °C, urea was transformed into cyanamide species. Therefore, during heat-treatment, oxycyanamide species presented as intermediates. The spectra of samples heat-treated at 930 °C did not show any characteristic absorption bands of $[\text{NCN}]^{2-}$. This suggests that the intermediate oxycyanamide species decomposed over 800 °C to form LaTiO_2N , which was consistent with the XRD analyses. Considering the results of the XRD and FT-IR investigations, we proposed a mechanism for the nitridation of $\text{La}_2\text{Ti}_2\text{O}_7$ to LaTiO_2N using urea as a nitrogen source. First, the $\text{La}(\text{OH})_3$ contained in the hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ reacts with urea around 140 °C. At this stage, intermediate species containing $[\text{NCN}]^{2-}$ react with the HCNO and/or H_2CN_2 generated by urea decomposition. When the temperature exceeds 600 °C, $\text{La}_2\text{O}_2\text{CN}_2$ is generated. Decomposition of the $\text{La}_2\text{O}_2\text{CN}_2$ occurs over 800 °C. Finally, crystallization of LaTiO_2N is completed around 930 °C.

We have also carried out a control experiment using a mixture of $\text{La}(\text{OH})_3$ and TiO_2 as a precursor for preparation of LaTiO_2N via the urea-nitriding process. However, the XRD pattern of the sample obtained from this control experiment contained only diffraction peaks attributed to La_2O_3 , TiO_2 , and $\text{La}_2\text{O}_2\text{CN}_2$, and no peaks attributed to LaTiO_2N (figure not shown). Therefore, the mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$ should be employed as a precursor of LaTiO_2N for the urea-nitriding process.

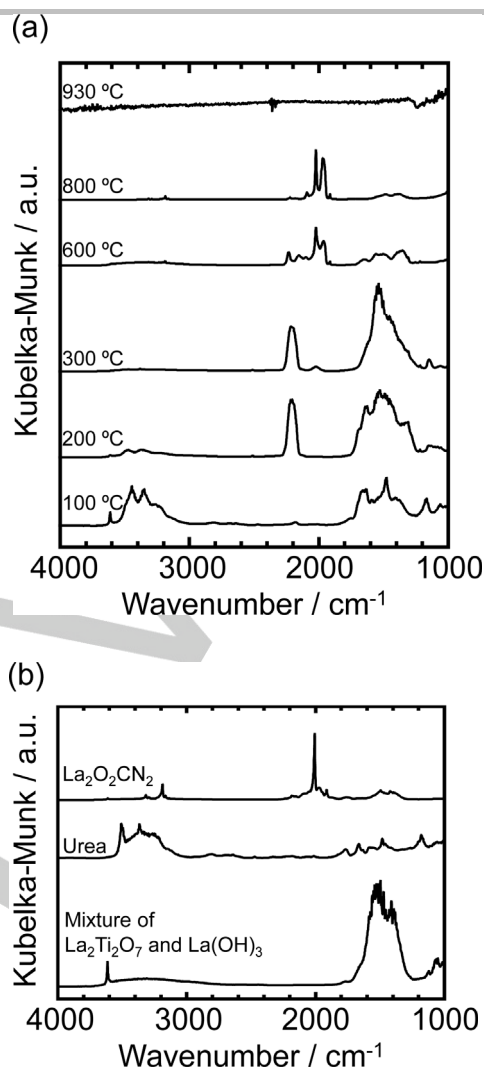


Figure 10. FT-IR spectra of the mixtures of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea before and after heat-treatment at 100, 200, 300, 600, 800, and 930 °C for 2 h (a) and standard samples ($\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{La}(\text{OH})_3$, urea, and $\text{La}_2\text{O}_2\text{CN}_2$) (b).

Characterization of LaTiO_2N synthesized from hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ and urea: A TEM image of LaTiO_2N synthesized from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 930 °C for 2 h is given as Figure S8. Comparison of this image with the TEM image of hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ in Figure S1 reveals that the sheet-like shape of $\text{La}_2\text{Ti}_2\text{O}_7$ was maintained to a slight extent. Figure 11 shows the UV-vis diffuse reflectance spectrum of LaTiO_2N synthesized from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 930 °C for 2 h. The absorption edge of LaTiO_2N is located at approximately 570 nm. The band gap (E_g) of the obtained LaTiO_2N was roughly estimated to be 2.2 eV, a value close to that of a previously reported LaTiO_2N prepared through nitridation using gaseous NH_3 .^[30] The background absorption was observed in the longer wavelength region above the adsorption edge ($>600\text{ nm}$). This is attributed to reduced cationic species (Ti^{3+}) and/or vacant anion sites in the crystal structure of LaTiO_2N . The atomic composition of the synthesized LaTiO_2N was investigated by ICP-OES and oxygen/nitrogen combustion analysis. The ICP-OES investigation revealed that the molar ratio of cations, i.e., La and

Ti, was 0.96:1.04 ($\text{La} + \text{Ti} = 2$), which was close to the ideal ratio ($\text{La}:\text{Ti} = 1:1$). However, the molar ratio of anions, which was determined by oxygen/nitrogen combustion analysis, was $\text{O}:\text{N} = 2.23:0.77$ ($\text{O} + \text{N} = 3$), which deviated from the ideal ratio ($\text{O}:\text{N} = 2:1$). XPS was performed on the prepared LaTiO_2N . The $\text{Ti } 2p_{3/2}$ XPS spectrum is presented in Figure 12. The peak is located between the literature positions of Ti^{4+} and Ti^{3+} .^[42] This supports the presence of Ti^{3+} in addition to Ti^{4+} in the prepared LaTiO_2N . It is well known that Ti^{3+} species in LaTiO_2N may act as recombination centers when the material is applied as a photocatalyst. Therefore, we are currently attempting the elimination of Ti^{3+} species by a post-annealing process.

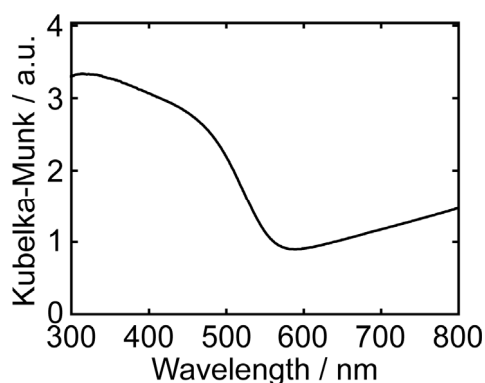


Figure 11. UV-vis diffuse reflectance spectrum of LaTiO_2N synthesized from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 930°C for 2 h and washing with aqueous solution of HCl and deionized water.

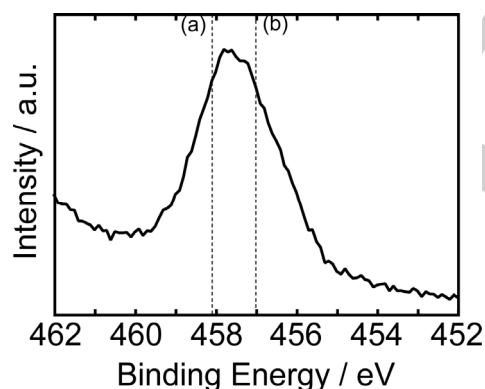


Figure 12. $\text{Ti } 2p_{3/2}$ XPS spectrum of LaTiO_2N synthesized from the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) after calcination at 930°C for 2 h and washing with aqueous solution of HCl and deionized water. The dashed lines of (a) and (b) show the literature^[42] values of Ti^{4+} and Ti^{3+} , respectively.

3. Conclusions

We have successfully developed a facile synthetic method to prepare LaTiO_2N without ammonolysis. Instead of gaseous NH_3 , urea was employed as a solid-state nitriding agent. $\text{La}_2\text{Ti}_2\text{O}_7$ was prepared as a precursor via the hydrothermal process using a water-soluble Ti complex. The hydrothermally obtained products were composed of nanosheet-type $\text{La}_2\text{Ti}_2\text{O}_7$, with $\text{La}(\text{OH})_3$ as a by-product. LaTiO_2N could be obtained by heat-treatment of the mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea in a flow of N_2 , whereas it could not be obtained by heat-treatment of a mixture of only

$\text{La}_2\text{Ti}_2\text{O}_7$ and urea (without $\text{La}(\text{OH})_3$). XRD and FT-IR investigations revealed that an $\text{La}_2\text{O}_2\text{CN}_2$ -like intermediate was generated by the reaction of $\text{La}(\text{OH})_3$ with the thermal decomposition products of urea, such as HCNO and/or H_2CN_2 , at temperatures above 150°C . This oxycyanamide intermediate species remained until around ca. 800°C and decomposed to form LaTiO_2N above 800°C . In this system, therefore, the nitriding agent is not ammonia released from the decomposition of urea. After optimizing parameters such as the heat-treatment temperature and the urea: $\text{La}_2\text{Ti}_2\text{O}_7$ ratio, single-phase LaTiO_2N was efficiently obtained by calcination at 930°C for 2 h using a mixture of $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}(\text{OH})_3$, and urea ($R = 4.5$) and washing with HCl solution. The nitridation process using urea will surely offer a new opportunity for facile synthesis of various metal oxynitrides with good safety, low cost, and operational simplicity. The LaTiO_2N obtained from urea-induced nitridation of the $\text{La}_2\text{Ti}_2\text{O}_7$ precursor in this study showed an optical absorption above 600 nm, which is attributed to oxygen and/or nitrogen deficiencies associated with reduced Ti^{3+} species. ICP-OES, oxygen/nitrogen analysis, and XPS investigations also supported this finding. When the obtained LaTiO_2N is applied as a photocatalyst, such Ti^{3+} reduced species will provide a donor level just below the conduction band minimum, which will act as a recombination center of photogenerated electrons and holes and thereby induce the decrease of photocatalytic activity. Therefore, the elimination of reduced Ti^{3+} species and oxygen and/or nitrogen deficiencies is currently being investigated by our research group.

4. Experimental Section

4.1. Materials: Lanthanum(III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; $\geq 99.0\%$) and titanium(IV) bis(ammonium lactato) dihydroxide (TALH) ($\text{C}_6\text{H}_{18}\text{N}_2\text{O}_8\text{Ti}$; 50% (w/w) in water) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Urea ($\text{CO}(\text{NH}_2)_2$, 99%), sodium hydroxide (NaOH) solution (5 mol dm^{-3}), hydrochloric acid (HCl) solution (1 mol dm^{-3}), and nitric acid (HNO_3) solution (60 wt%) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Lanthanum hydroxide ($\text{La}(\text{OH})_3$, 99.9%) was purchased from Strem Chemicals, Inc. (Newburyport, MA, USA). All reagents were used as received without further purification. The water used in all experiments was deionized with a Milli-Q system (Merck Millipore, Billerica, MA, USA).

4.2. Preparation of $\text{La}_2\text{Ti}_2\text{O}_7$: $\text{La}_2\text{Ti}_2\text{O}_7$ was prepared by the hydrothermal method.^[46] Firstly, TALH solution was diluted to 0.05 mol dm^{-3} by addition of deionized water. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.6 mmol) was added into the diluted solution of TALH. The molar ratio of La/Ti in this mixture was adjusted to 1:1. Then, aqueous solution of NaOH (10 mL; 5.0 mol dm^{-3}) was added to this solution. After stirring for 30 min, the mixture was placed in a 50 mL polytetrafluoroethylene (PTFE) vessel. The vessel was sealed and placed inside a stainless steel autoclave, which was heated in an oven. The heating temperature and duration were set at 200°C and for 24 h, respectively. The products obtained were collected by centrifugation and washed with ethanol three times and dried overnight in an oven at 50°C . To obtain $\text{La}_2\text{Ti}_2\text{O}_7$ without any impurities, the by-product, i.e., $\text{La}(\text{OH})_3$, was removed from the products by washing with HNO_3 solution once and deionized water twice. For comparison, $\text{La}_2\text{Ti}_2\text{O}_7$ was also synthesized by the polymerized complex (PC) method, as referred to in a previous report (details are given in the Supporting Information).^[30]

4.3. Preparation of LaTiO_2N : Hydrothermally prepared $\text{La}_2\text{Ti}_2\text{O}_7$ was employed as a precursor of LaTiO_2N . Both the pristine product (containing $\text{La}(\text{OH})_3$) and washed product (without $\text{La}(\text{OH})_3$) were used.

The $\text{La}_2\text{Ti}_2\text{O}_7$ was mixed with urea using an agate mortar and pestle. The mixture was heated under a nitrogen stream (300 mL min^{-1}) in a horizontal tube furnace using an alumina crucible boat. The final heat-treatment temperature was varied from 900 to 1000°C . The temperature of the furnace was raised to the final temperature at a heating rate of $15^\circ\text{C min}^{-1}$. The reaction time at the final temperature was varied from 0.5 to 8 h. A mixture of washed $\text{La}_2\text{Ti}_2\text{O}_7$ and commercial $\text{La}(\text{OH})_3$ was used for a control experiment. In addition, a mixture of $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by the PC method and commercial $\text{La}(\text{OH})_3$ was also used for comparison.

4.4. Characterization: Structural analysis of the obtained samples was conducted by XRD (D8 Advance, Bruker AXS, Germany) using $\text{Cu-K}\alpha$ radiation. TEM images were captured with a JEOL JEM-2010 microscope operating at 200 kV. Samples were prepared by depositing a droplet of each dispersion on carbon-coated copper grids covered with elastic carbon films and drying in vacuum overnight. UV-vis DRS spectra were measured by a spectrophotometer (V-670, JASCO, Tokyo, Japan). The band gap (E_g) of the synthesized LaTiO_2N was estimated using the conventional equation:^[60]

$$E_g (\text{eV}) = 1240 / \lambda (\text{nm})$$

where λ represents an absorption edge wavelength of the material. The La and Ti contents were measured via ICP-OES using a Thermo Scientific iCAP 6500. FT-IR spectra were collected over the range of $4000\text{--}1000 \text{ cm}^{-1}$ with a JASCO FT/IR-4200 spectrometer fitted with a diffuse reflectance accessory. The O and N contents were measured by an oxygen/nitrogen combustion analyzer (EMGA-620W, HORIBA Ltd., Kyoto, Japan). The valence state of Ti in the synthesized LaTiO_2N was evaluated by XPS (ESCA-3400, Shimadzu Co., Kyoto, Japan).

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Keywords: Metal oxynitrides • Mixed-anion compounds • Solid state nitriding agents • Hydrothermal process • Urea

- [1] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* **2005**, *127*, 8286–8287.
- [2] X. Chen, Y.-B. Lou, A. C. S. Samia, C. Burda, J. L. Gole, *Adv. Funct. Mater.* **2005**, *15*, 41–49.
- [3] K. Maeda, T. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* **2006**, *440*, 295.
- [4] Y. Moriya, T. Takata, K. Domen, *Coord. Chem. Rev.* **2013**, *257*, 1957–1969.
- [5] A. Fuertes, *Mater. Horiz.* **2015**, *2*, 453–461.
- [6] K. Maeda, K. Domen, *Bull. Chem. Soc. Jpn.* **2016**, *89*, 627–648.
- [7] M. Ahmed, G. Xinxin, *Inorg. Chem. Front.* **2016**, *3*, 578–590.
- [8] T. Takata, K. Domen, *Dalton Trans.* **2017**, *46*, 10529–10544.
- [9] D. Abeyasinghe, S. E. Skrabalak, *ACS Energy Lett.* **2018**, *3*, 1331–1344.
- [10] Y. I. Kim, P. M. Woodward, K. Z. Baba-Kishi, C. W. Tai, *Chem. Mater.* **2004**, *16*, 1267–1276.
- [11] V. Petrovsky, A. Manohar, F. Dogan, *J. Appl. Phys.* **2006**, *100*, 014102.
- [12] G. He, L. D. Zhang, M. Liu, Z. Q. Sun, *Appl. Phys. Lett.* **2010**, *97*, 062908.
- [13] H. H. Lu, J. P. Xu, L. Liu, L. S. Wang, P. T. Lai, W. M. Tang, *Microelectron. Reliab.* **2005**, *127*, 8286–8287.
- [14] A. Rousseau, V. Laur, S. Deputier, V. Bouquet, M. Guilloux-Viry, G. Tanne, P. Laurent, F. Huret, A. Perrin, *Thin Solid Films*, **2008**, *516*, 4882–4888.
- [15] D. Oka, Y. Hirose, H. Kamisaka, T. Fukumura, K. Sasa, S. Ishii, H. Matsuzaki, Y. Sato, Y. Ikuhara, T. Hasegawa, *Sci. Rep.* **2014**, *4*, 4987.
- [16] S. Kikkawa, S. Sun, Y. Masubuchi, Y. Nagamine, T. Shibahara, *Chem. Mater.* **2016**, *28*, 1312–1317.
- [17] M. Yang, J. Oro-Sole, A. Kusmartseva, A. Fuertes, J. P. Attfield, *J. Am. Chem. Soc.* **2010**, *132*, 4822–4829.
- [18] D. Oka, Y. Hirose, M. Kaneko, S. Nakao, T. Fukumura, K. Yamashita, T. Hasegawa, *J. Am. Chem. Soc.* **2005**, *127*, 8286–8287.
- [19] A. Fuertes, *Prog. Solid State Chem.* **2018**, *51*, 63–70.
- [20] M. Jansen, H. P. Letschert, *Nature* **2000**, *404*, 980–982.
- [21] F. Chevire, F. Tessier, R. Marchand, *Eur. J. Inorg. Chem.* **2006**, *2006*, 1223–1230.
- [22] R. Aguiar, D. Lopinovich, A. Weidenkaff, A. Rachel, A. Reller, S. G. Ebbinghaus, *Dyes Pigm.* **2008**, *76*, 70–75.
- [23] S. G. Ebbinghaus, H. P. Abicht, R. Dronskowski, T. Muller, A. Reller, A. Weidenkaff, *Prog. Solid State Chem.* **2009**, *37*, 173–205.
- [24] R. J. Xie, H. T. Hintzen, *J. Am. Ceram. Soc.* **2013**, *96*, 665–687.
- [25] S. J. Clarke, B. P. Guino, C. W. Michie, M. J. C. Calmont, M. J. Rosseinsky, *Chem. Mater.* **2002**, *14*, 288–294.
- [26] A. Fuertes, *J. Mater. Chem.* **2012**, *22*, 3293–3299.
- [27] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun.* **2018**, *9*, 772.
- [28] F. Tessier, P. Maillard, F. Chevire, K. Domen, S. Kikkawa, *J. Ceram. Soc. Jpn.* **2009**, *117*, 1–5.
- [29] O. Ruzimuradov, S. Nurmanov, M. Hojamberdiev, R. M. Prasad, A. Gurlo, J. Broetz, K. Nakanishi, R. Riedel, *J. Eur. Ceram. Soc.* **2014**, *34*, 809–816.
- [30] A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Phys. Chem. A* **2002**, *106*, 6750–6753.
- [31] A. Kasahara, K. Nukumizu, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Phys. Chem. B* **2003**, *107*, 791–797.
- [32] A. E. Maegli, E. H. Otal, T. Hisatomi, S. Yoon, C. M. Leroy, N. Schauble, Y. Lu, M. Grätzel, A. Weidenkaff, *Energy Proc.* **2012**, *22*, 61–66.
- [33] M. Matsukawa, R. Ishikawa, T. Hisatomi, Y. Moriya, N. Shibata, J. Kubota, Y. Ikuhara, K. Domen, *Nano Lett.* **2014**, *14*, 1038–1041.
- [34] M. Hojamberdiev, A. Yamaguchi, K. Yubuta, S. Oishi, K. Teshima, *Inorg. Chem.* **2015**, *54*, 3237–3244.
- [35] S. J. Clarke, K. A. Hardstone, C. W. Michie, M. J. Rosseinsky, *Chem. Mater.* **2002**, *14*, 2664–2669.
- [36] S.-K. Sun, T. Motohashi, Y. Masubuchi, S. Kikkawa, *J. Eur. Ceram. Soc.* **2014**, *34*, 4451–4455.
- [37] A. Miura, T. Takei, N. Kumada, *Cryst. Growth Des.* **2012**, *12*, 4545–4547.
- [38] A. Miura, T. Takei, N. Kumada, *Inorg. Chem.* **2013**, *52*, 11787–11791.
- [39] A. Miura, C. Rosero-Navarro, Y. Masubuchi, M. Higuchi, S. Kikkawa, K. Tadanaga, *Angew. Chem., Int. Ed.* **2016**, *55*, 7963–7967.
- [40] Y. Setsuda, Y. Maruyama, C. Izawa, T. Watanabe, *Chem. Lett.* **2017**, *46*, 987–989.
- [41] J. Odahara, A. Miura, N. C. Rosero-Navarro, K. Tadanaga, *Inorg. Chem.* **2018**, *57*, 24–27.
- [42] N. G. Sarda, M. Omune, T. Hayashi, A. Chan, S. Kataoka, K. Murai, G. I. N. Waterhouse, T. Moriga, *J. Eur. Ceram. Soc.* **2015**, *35*, 3311–3317.
- [43] A. Gomathi, S. Reshma, C. N. R. Rao, *J. Solid State Chem.* **2009**, *182*, 72–82.
- [44] C. Giordano, C. Erpen, W. Yao, B. Milke, M. Antonietti, *Small* **2011**, *7*, 3334–3340.
- [45] K. Katagiri, Y. Hayashi, R. Yoshiyuki, K. Inumaru, T. Uchiyama, N. Nagata, Y. Uchimoto, A. Miyoshi, K. Maeda, *Inorg. Chem.* **2018**, *57*, 13953–13962.
- [46] X. Lin, H. Wang, H. Du, X. Xiong, B. Qu, Z. Guo, D. Chu, *ACS Appl. Mater. Interfaces* **2016**, *8*, 1486–1492.
- [47] D. Chen, R. Xu, *Mater. Res. Bull.* **1998**, *33*, 409–417.
- [48] H. Song, T. Peng, P. Cai, H. Yi, C. Yan, *Catal. Lett.* **2007**, *113*, 54–58.
- [49] X. Ma, H. Zhang, Y. Ji, J. Xu, D. Yang, *Mater. Lett.* **2004**, *58*, 1180–1182.

- [50] F. Khosrow-pour, M. Aghazadeh, B. Arhami, *J. Electrochem. Soc.* **2013**, *160*, D150-D155.
- [51] F. Niu, A.-M. Cao, W.-G. Song, L.-J. Wan, *J. Phys. Chem. C* **2008**, *112*, 17988–17993.
- [52] J. Feng, X. Li, M. Wang, X. Zheng, J. Bai, L. Wang, Y. Peng, *RSC Adv.* **2015**, *5*, 16093–16100.
- [53] E. V. Shkol'nikov, *Russ. J. Appl. Chem.* **2009**, *82*, 2098–2014.
- [54] K. Kawashima, M. Hojamberdiev, H. Wagata, K. Yubuta, S. Oishi, K. Teshima, *Cryst. Growth Des.* **2015**, *15*, 333–339.
- [55] S. Podsiadlo, *Thermochim. Acta* **1995**, *256*, 367–373.
- [56] Y. Hashimoto, M. Takahashi, S. Kikkawa, F. Kanamaru, *J. Solid State Chem.* **114**, 592–594 (1995).
- [57] K. M. Kaye, W. Grantham, G. A. Hyett, *Chem. Vap. Deposition* **2015**, *21*, 281–287.
- [58] M. Krott, X. Liu, B. P. T. Fokwa, M. Speldrich, H. Lueken, R. Dronskowski, *Inorg. Chem.* **2007**, *46*, 2204–2207.
- [59] X. Liu, M. Krott, P. Müller, C. Hu, H. Lueken, R. Dronskowski, *Inorg. Chem.* **2005**, *44*, 3001–3003.
- [60] A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253–278..

Entry for the Table of Contents

FULL PAPER

Perovskite-type metal oxynitrides, LaTiO_2N , were prepared using hydrothermally synthesized $\text{La}_2\text{Ti}_2\text{O}_7$ as a precursor and urea as a solid-state nitriding agent. The $\text{La}(\text{OH})_3$ present in the $\text{La}_2\text{Ti}_2\text{O}_7$ precursor formed $\text{La}_2\text{O}_2\text{CN}_2$ as an intermediate species by reaction with urea and played an important role in the nitriding process in this system.

**Metal oxynitride***

R. Okada, K. Katagiri, * Y. Masubuchi,
K. Inumaru

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**Preparation of LaTiO_2N Using
Hydrothermally Synthesized
 $\text{La}_2\text{Ti}_2\text{O}_7$ as a Precursor and Urea as
a Nitriding Agent**

Keywords:

Metal oxynitrides; Mixed-anion compounds; Solid state nitriding agents; Hydrothermal process; Urea