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**Relation**

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Preparation of LaTiO$_2$N Using Hydrothermally Synthesized La$_2$Ti$_2$O$_7$ as a Precursor and Urea as a Nitriding Agent

Ryoki Okada[,a] Kiyofumi Katagiri,*[a] Yuji Masubuchi,[b] and Kei Inumaru[a]

Abstract: A facile method was successfully developed to prepare perovskite-type metal oxynitrides, LaTiO$_2$N, from La$_2$Ti$_2$O$_7$ as a precursor in an atmosphere of N$_2$. Urea was employed as a solid-state nitriding agent, instead of gaseous NH$_3$, to increase the safety of the reaction. The hydrothermally prepared La$_2$Ti$_2$O$_7$ 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 LaTiO$_2$N with the thermal decomposition products of urea at the environmentfriendly inorganic pigments. [20-24] Metal oxynitrides commonly contain early transition metals 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] When O atoms are partially substituted by N atoms, the N 2p states and O 2p states are hybridized, reducing the band gap. 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 CaTaO$_2$N and LaTaON$_x$ (i.e., Ca$_{1-x}$La$_x$TaO$_{2-x}$N$_x$) have a range of yellow to red colors and are possible pigments to replace Cd-containing materials.[20] As a typical perovskite-type oxynitride, LaTiO$_2$N has been recognized as a candidate for a visible-light-driven photocatalyst because of its narrow band gap (ca. 2.1 eV) and generates both H$_2$ and O$_2$ under irradiation of visible light in the presence of cocatalysts and sacrificial agents.[30-34] LaTiO$_2$N 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 SrNbO$_2$N and BaTaO$_2$N. The synthesis of perovskite-type oxynitrides containing LaTiO$_2$N is generally conducted by nitridation of metal oxide precursors.[31-33] Gaseous NH$_3$ 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 NH$_3$ 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 NH$_3$-gas-free preparation procedures of metal oxynitrides is a current research goal.[35-37] Clarke and co-workers achieved the first preparation of SrTaO$_2$N in N$_2$ atmosphere by heat-treatment of a mixture of SrO and TaON at 1500 °C.[38] Kikkawa et al. have also reported a direct preparation procedure of SrTaO$_2$N by using SrCO$_3$ and Ta$_2$N$_5$ in N$_2$ atmosphere.[39] However, the nitrogen-containing precursors, i.e., TaON or Ta$_2$N$_5$, have to be prepared via the ammonolysis of Ta$_2$O$_5$ beforehand, meaning that these procedures do not exclude the use of NH$_3$ gas entirely.[36,39] Recently, the syntheses of nitrides and oxynitrides through the reaction of metal oxide precursors with NaNH$_2$ molten salt have been reported.[37,41] Preparation of perovskite metal oxynitrides, such as BaTaO$_2$N$[40]$ and BaNbO$_2$N$[41]$ using NaNH$_2$ as a nitriding agent has also been achieved by the flux method and explosive reactions. Though these processes enable NH$_3$-gas-free preparation, they are very difficult to carry out on a large scale because NaNH$_2$ is highly sensitive. Compared with NH$_3$ and Na$_2$NH$_2$, 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 LaTiO$_2$N using urea or thiourea.[42] However, despite the use of urea and thiourea as co-nitriding agents in this approach, NH$_3$ 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 Ta$_2$N$_5$ using a method employing Ca$^{2+}$ 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 Zn$^{2+}$ and Ga$^{3+}$ 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.
We revealed that a ZnCN₂-like species was generated as an intermediate at the medium temperature range and played important roles in the formation of GaN:ZnO. However, the preparation of perovskite metal oxynitrides, i.e., AB₂O₃N and/or ABON₂ (A = Ca, Sr, Ba, or La; B = Ti, Zr, Nb, or Ta) by using corresponding perovskite metal oxides, such as AB₂O₃ and A₂B₂O₇, 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 La₄Ti₄O₁₁ precursor and its subsequent nitridation to form LaTiO₂N by using urea as a nitriding agent. La₂Ti₂O₇ was prepared by a hydrothermal process using a water-soluble titanium compound as a precursor. Attempts to synthesize La₂Ti₂O₇ were carried out through several solution techniques. Nanoflake-type La₂Ti₂O₇ can be fabricated by the hydrothermal process. 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, La(OH)₃ was generated as a by-product during the hydrothermal process. We have examined the influence of the presence of La(OH)₃ in the precursor on the transformation from La₂Ti₂O₇ to LaTiO₂N. The transformation conditions from La₂Ti₂O₇ to LaTiO₂N, including heat-treatment temperature and duration and mixing ratio of urea to La₂Ti₂O₇, 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 La₂Ti₂O₇ to LaTiO₂N 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 La₂Ti₂O₇ as a precursor of LaTiO₂N via the hydrothermal process: Firstly, La₂Ti₂O₇, a precursor of LaTiO₂N, was prepared by the hydrothermal method. The XRD pattern of the product obtained by the hydrothermal treatment of a solution of La(NO₃)₃·6H₂O 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: P2₁) are found in the pattern. In addition, it also contains peaks attributed to La(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 La(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 La(OH)₃. This by-product can be removed from the main product by exploiting the solubility of La(OH)₃ in acidic solution.[53] The molar ratio of La₂Ti₂O₇ and La(OH)₃ in the pristine product obtained by the hydrothermal method was investigated by ICP-OES. The ratio was 0.425:0.575 (La₂Ti₂O₇ + La(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 eliminate during this washing process. Therefore, the molar ratio of La is richer than that of Ti in the obtained products (La₂Ti₂O₇ and La(OH)₃). Figure 1b shows an XRD pattern of the product after washing with HNO₃ solution and subsequently with deionized water. The peaks indexed to La(OH)₃ disappear and all remaining diffraction peaks match well with the characteristic reflections of the La₂Ti₂O₇ crystalline phase. Therefore, La₂Ti₂O₇ was obtained in a single phase by the hydrothermal method and subsequent washing with HNO₃ solution. For comparison, La₂Ti₂O₇ was also synthesized by the polymerized complex (PC) method.[30] XRD peaks attributable to the La₂Ti₂O₇ 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.

Optimization of transformation conditions from La₂Ti₂O₇ to LaTiO₂N using urea as a nitriding agent: Next, we examined the nitridation of La₂Ti₂O₇ using urea to prepare LaTiO₂N. Both the pristine product obtained via the hydrothermal process, i.e., the mixture of La₂Ti₂O₇ and La(OH)₃, and the washed product, i.e., the single phase of La₂Ti₂O₇, 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 (La₂Ti₂O₇ without La(OH)₃) and urea contained only diffraction peaks attributed to La₂Ti₂O₇ and no peaks attributed to LaTiO₂N (Figure 3a). The dark-blue color seems to originate from the reduction of Ti species and/or the partial nitridation of La₂Ti₂O₇. In contrast, a product with a green-brown color was obtained after calcination of the unwashed product (the mixture of
La$_2$Ti$_2$O$_7$ and La(OH)$_3$ and urea (Figure 2d). As shown in Figure 3b, the transformation of the La$_2$Ti$_2$O$_7$ crystals into LaTiO$_2$N crystals with orthorhombic structure (space group: Imma) by nitridation using urea was successful. Though some diffraction peaks assignable to the La$_2$O$_3$ phase also co-existed, these impurities could be removed by washing with acidic solution (details are discussed later). These results indicated that while pure La$_2$Ti$_2$O$_7$ cannot be directly nitrided to LaTiO$_2$N by urea, this nitridation can be achieved when the precursor contains La(OH)$_3$. To prove this hypothesis, the washed product of hydrothermally prepared La$_2$Ti$_2$O$_7$ (single phase) was remixed with commercial La(OH)$_3$ and used as a precursor for preparation of LaTiO$_2$N 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$_2$N and La$_2$O$_3$. Furthermore, La$_2$Ti$_2$O$_7$ prepared by the PC method was also examined as a control experiment. When nitridation using urea was carried out for this La$_2$Ti$_2$O$_7$, the XRD pattern retained the peaks indexed to La$_2$Ti$_2$O$_7$ and no reflection peak attributed to LaTiO$_2$N was found (Figure S2b). However, when La(OH)$_3$ was added to the La$_2$Ti$_2$O$_7$ prepared by the PC method, LaTiO$_2$N was obtained by nitridation using urea (Figure S2c). These results revealed that the co-existence of La(OH)$_3$ in the hydrothermal product of La$_2$Ti$_2$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.

We have optimized the conditions for nitridation of La$_2$Ti$_2$O$_7$ to LaTiO$_2$N using urea, i.e., the ratio of La$_2$Ti$_2$O$_7$ and urea, reaction time, and reaction temperature. Optical photographs and XRD patterns of the products obtained from mixtures of La$_2$Ti$_2$O$_7$, La(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 La$_2$Ti$_2$O$_7$ ([urea] / [La$_2$Ti$_2$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 La$_2$TiO$_5$ was generated in addition to the remnant of La$_2$Ti$_2$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$_2$N and La$_2$O$_3$ were found in the XRD patterns for these samples. In addition, XRD peaks attributable to La$_2$O$_2$CN$_2$ crystals with tetragonal structure (space group: I41/mmm) were also observed for the samples prepared with $R \geq 7.5$. La$_2$O$_2$CN$_2$ is difficult to remove by washing with acidic solutions or organic solvents, whereas La$_2$O$_3$ can be removed by an acidic solution. Therefore, the optimal mixing ratio to obtain LaTiO$_2$N is $R = 4.5$; we used this ratio in subsequent experiments.
The influence of calcination temperature on the transformation of \( \text{La}_2\text{Ti}_2\text{O}_7 \) to \( \text{LaTiO}_2\text{N} \) was also investigated. Figure 7 presents the XRD patterns of the products obtained from mixtures of \( \text{La}_2\text{Ti}_2\text{O}_7 \), \( \text{La(OH)}_3 \), 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 \( \text{LaTiO}_2\text{N} \) were found. This indicates that the nitridation reaction from \( \text{La}_2\text{Ti}_2\text{O}_7 \) to \( \text{LaTiO}_2\text{N} \) 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 \( \text{LaTiO}_2\text{N} \). The intensity of the peaks of \( \text{La}_2\text{O}_3 \) 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 \( \text{LaTiO}_2\text{N} \) 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 \( \text{La(OH)}_3 \)) 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., \( \text{La}_2\text{O}_3 \), should be removed by washing with acidic solution, such as aqueous HCl. Figure 8 shows the XRD pattern of \( \text{LaTiO}_2\text{N} \) obtained by these optimal conditions. A single phase of \( \text{LaTiO}_2\text{N} \) crystals with orthorhombic structure can be seen, with no other peaks.
Nitridation mechanism of La$_2$Ti$_2$O$_7$ to form LaTiO$_2$N: 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 La$_2$Ti$_2$O$_7$ to LaTiO$_2$N 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 La$_2$Ti$_2$O$_7$, we carried out a control experiment in which the mixture of La$_2$Ti$_2$O$_7$ and La(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 La$_2$Ti$_2$O$_7$ and La(OH)$_3$ was placed (Figure S3). This white powder was a mixture of La$_2$Ti$_2$O$_7$ and La$_2$O$_2$CN$_2$, as shown by the XRD pattern in Figure S4. In addition, as shown in Figure 3, the nitridation of pure La$_2$Ti$_2$O$_7$ did not take place even when La$_2$Ti$_2$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 La$_2$Ti$_2$O$_7$. Recently, we have reported the preparation of GaN: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, La$_2$O$_2$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, La$_2$O$_2$CN$_2$ was obtained in a single phase when a mixture of La(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 La$_2$Ti$_2$O$_7$, La(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 La$_2$Ti$_2$O$_7$, La(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 La$_2$Ti$_2$O$_7$, La(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 La$_2$Ti$_2$O$_7$ were observed while those of La(OH)$_3$ and urea disappeared. When the mixture of La$_2$Ti$_2$O$_7$ and La(OH)$_3$ (without urea) was heated at 200 °C for 2 h, the diffraction peaks of La(OH)$_3$ clearly remained (Figure S6). These results suggest that the presence of La(OH)$_3$ is a dominant factor in the formation of La$_2$O$_2$CN$_2$, and in the reaction between La(OH)$_3$ and 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 La$_2$O$_2$CN$_2$ were found in addition to those of La$_2$Ti$_2$O$_7$. The intensity of the diffraction peaks of La$_2$O$_2$CN$_2$ increased with increasing reaction temperature. As shown in Figure 7, diffraction peaks of LaTiO$_2$N were observed, while the intensity of those of La$_2$O$_2$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 La$_2$O$_2$CN$_2$ was involved in the nitridation reaction in the current system and in the generation of LaTiO$_2$N initiated between 800 and 900 °C. The involvement of La$_2$O$_2$CN$_2$ in the nitridation process is clearly implicated by the XRD pattern of the sample obtained by heat-treatment of the mixture of La$_2$Ti$_2$O$_7$ and La$_2$O$_2$CN$_2$ at 930 °C, which includes peaks assignable to LaTiO$_2$N (Figure S7).
300, 600, 800, and 930 °C were analyzed by diffuse-reflectance FT-IR spectroscopy (Figure 10a). For reference, the FT-IR spectra of the La$_2$Ti$_2$O$_7$ and La(OH)$_3$ mixture, urea, and La$_2$O$_2$CN$_2$ are also given in Figure 10b. Pure La$_2$O$_2$CN$_2$ displayed a sharp absorption peak around 2000 cm$^{-1}$ corresponding to the asymmetric stretching mode of [NCN]$^2$$^-$. This peak is consistent with previous reports of La$_2$O$_2$CN$_2$[56] and also with the IR spectra of various metal cyanamides, such as ZnCN$_2$[57] CoCN$_2$, NiCN$_2$[58] and MnCN$_2$.[59] When the mixture was heat-treated at 100 °C, the spectrum was superimposable on that of the mixture before heat-treatment, which did not contain a peak around 2200 cm$^{-1}$. However, a strong absorption peak was found in the spectrum for the sample heat-treated at 200 °C. A similar peak was observed in the IR spectrum of the sample after heat-treatment at 200 °C in our previous study of the Zn–Ga LDH and urea system.[45] The IR spectra for the samples heat-treated at 300 and 800 °C also displayed the bands around 1800–2200 cm$^{-1}$. On decomposition at 140 °C, urea was transformed into cyanamide species. Therefore, during heat-treatment, oxycyanamide species presented as intermediates. The spectra of samples heat-treated at 930 °C did not show any characteristic absorption bands of [NCN]$^2$$^-$. This suggests that the intermediate oxycyanamide species decomposed over 800 °C to form LaTiO$_2$N, which was consistent with the XRD analyses. Considering the results of the XRD and FT-IR investigations, we proposed a mechanism for the nitridation of La$_2$Ti$_2$O$_7$ to LaTiO$_2$N using urea as a nitrogen source. First, the La(OH)$_3$ contained in the hydrothermally prepared La$_2$Ti$_2$O$_7$ reacts with urea around 140 °C. At this stage, intermediate species containing [NCN]$^2$$^-$ react with the HCNO and/or H$_2$CN$_2$ generated by urea decomposition. When the temperature exceeds 600 °C, La$_2$O$_2$CN$_2$ is generated. Decomposition of the La$_2$O$_2$CN$_2$ occurs over 800 °C. Finally, crystallization of LaTiO$_2$N is completed around 930 °C.

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

Characterization of LaTiO$_2$N synthesized from hydrothermally prepared La$_2$Ti$_2$O$_7$ and urea: A TEM image of LaTiO$_2$N synthesized from the mixture of La$_2$Ti$_2$O$_7$, La(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 La$_2$Ti$_2$O$_7$ in Figure S1 reveals that the sheet-like shape of La$_2$Ti$_2$O$_7$ was maintained to a slight extent. Figure 11 shows the UV-vis diffuse reflectance spectrum of LaTiO$_2$N synthesized from the mixture of La$_2$Ti$_2$O$_7$, La(OH)$_3$, and urea (R = 4.5) after calcination at 930 °C for 2 h. The absorption edge of LaTiO$_2$N is located at approximately 570 nm. The bandgap ($E_g$) of the obtained LaTiO$_2$N was roughly estimated to be 2.2 eV, a value close to that of a previously reported LaTiO$_2$N prepared through nitridation using gaseous NH$_3$.[30] The background absorption was observed in the longer wavelength region above the adsorption edge (<600 nm). This is attributed to reduced cationic species (Ti$^{3+}$) and/or vacant anion sites in the crystal structure of LaTiO$_2$N. The atomic composition of the synthesized LaTiO$_2$N 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 96.01.04 (La + Ti = 2), which was close to the ideal ratio (La:Ti = 1:1). However, the molar ratio of anions, which was determined by oxygen/nitrogen combustion analysis, was O:N = 2:23.0.77 (O + N = 3), which deviated from the ideal ratio (O:N = 2:1). XPS was performed on the prepared LaTiO2N. The Ti 2p3/2 XPS spectrum is presented in Figure 12. The peak is located between the literature positions of Ti 4+ and Ti 3+. This supports the presence of Ti 3+ in addition to Ti 4+ in the prepared LaTiO2N. It is well known that Ti 3+ species in LaTiO2N 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 12. Ti 2p3/2 XPS spectrum of LaTiO2N synthesized from the mixture of La2Ti2O7, La(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.

4. Experimental Section

4.1. Materials: Lanthanum(III) nitrate hexahydrate (La(NO3)3·6H2O; ≥99.9%) and titanium(IV) bis(ammonium lactato) dihydroxide (TALH) (C6H18N2O8Ti; 50% (w/w) in water) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Urea (CO(NH2)2, 99%), sodium hydroxide (NaOH) solution (5 mol dm−3), hydrochloric acid (HCl) solution (1 mol dm−3), and nitric acid (HNO3) solution (60 wt%) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Lanthanum hydroxide (La(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.

4.2. Preparation of La2Ti2O7: La2Ti2O7 was prepared by the hydrothermal method.[46] Firstly, TALH solution was diluted to 0.05 mol dm−3 and adjusting pH to 7 by addition of deionized water. La(NO3)3·6H2O (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 La2Ti2O7 without any impurities, the by-product, i.e., La(OH)3, was removed from the products by washing with HNO3 solution once and deionized water twice. For comparison, La2TiO3 was also synthesized by the polymerized complex (PC) method, as referred to in a previous report (details are given in the Supporting Information).[35]

4.3. Preparation of LaTiO2N: Hydrothermally prepared La2Ti3O7 was employed as a precursor of LaTiO2N. Both the pristine product (containing La(OH)3) and washed product (without La(OH)3) were used.

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[Figure 11. UV-vis diffuse reflectance spectrum of LaTiO2N synthesized from the mixture of La2Ti2O7, La(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. Ti 2p3/2 XPS spectrum of LaTiO2N synthesized from the mixture of La2Ti2O7, La(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.]

3. Conclusions

We have successfully developed a facile synthetic method to prepare LaTiO2N without ammonolysis. Instead of gaseous NH3, urea was employed as a solid-state nitriding agent. La2Ti3O7 was prepared as a precursor via the hydrothermal process using a water-soluble Ti complex. The hydrothermally obtained products were composed of nanosheet-type La2Ti2O7, with La(OH)3 as a by-product. LaTiO2N could be obtained by heat-treatment of the mixture of La2Ti2O7, La(OH)3, and urea in a flow of N2, whereas it could not be obtained by heat-treatment of a mixture of only La2Ti3O7 and urea (without La(OH)3). XRD and FT-IR investigations revealed that an La2O2CN2-like intermediate was generated by the reaction of La(OH)3 with the thermal decomposition products of urea, such as HCN and/or H2CN2, at temperatures above 150 °C. This oxycyanamide intermediate species remained until around ca. 800 °C and decomposed to form LaTiO2N 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/La2Ti3O7 ratio, single-phase LaTiO2N was efficiently obtained by calcination at 930 °C for 2 h using a mixture of La2Ti2O7, La(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 LaTiO2N obtained from urea-induced nitridation of the La2Ti3O7 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 LaTiO2N is applied as a photocatalyst, such Ti 3+ reduced species will provide a donor 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.
The LaTiO$_2$N 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 °C min$^{-1}$. The reaction time at the final temperature was varied from 0.5 to 8 h. A mixture of washed LaTiO$_2$N and commercial La(OH)$_3$ was used for a control experiment. In addition, a mixture of LaTiO$_2$N prepared by the PC method and commercial La(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 Cu-Kα 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 lacey 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$_2$N was estimated using the conventional equation:[30]

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

where $\lambda$ represents an absorption edge wavelength of the material. The La and Ti contents were measured via ICP-OES using a Thermo Jarrell-Ash Spectra AA1 spectrometer fitted with a diffuse reflectance accessory. The O and N contents were measured by an oxygen/nitrogen combustion analyzer (EMGA-620W, HORIBA Ltd., Tokyo, Japan). The valence state of Ti in the synthesized LaTiO$_2$N was estimated using the oxygen/nitrogen combustion analyzer (EMGA-620W, HORIBA Ltd., Tokyo, Japan). The valence state of Ti in the synthesized LaTiO$_2$N was estimated using the oxygen/nitrogen combustion analyzer (EMGA-620W, HORIBA Ltd., Tokyo, Japan). The valence state of Ti in the synthesized LaTiO$_2$N was estimated using the oxygen/nitrogen combustion analyzer (EMGA-620W, HORIBA Ltd., Tokyo, Japan).

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

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

**Keywords:**

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