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Amount of Tungsten Dopant Influencing the Photocatalytic Water Oxidation Activity of LaTiO$_2$N Crystals Grown Directly by an NH$_3$-Assisted Flux Method

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Abstract

Solar water splitting technologies for hydrogen generation using visible-light-active (oxy)nitride photocatalysts have been intensively studied to achieve a greater supply of clean and renewable energy. Here, we have investigated the amount of tungsten dopant influencing the photocatalytic water oxidation activity of LaTiO$_2$N (LTON) crystals grown directly by an NH$_3$-assisted KCl flux method in the absence of cocatalyst. With the maximum amount of tungsten dopant ($x = 0.10$), LaWO$_{0.6}$N$_{2.4}$ was formed as a minor phase to the W-doped LaTiO$_2$N phase (W-LTON). The optimum W-doped LaTiO$_2$N crystals were grown with the tungsten amount of $x = 0.05$, showing the nearly three-fold higher O$_2$ evolution rate (51 µmol·h$^{-1}$) compared to pure LaTiO$_2$N crystals (18 µmol·h$^{-1}$). The improvement in O$_2$ evolution rate of the LaTiO$_2$N crystals was due presumably to the improved conductivity, enhanced light absorption, and efficient charge separation stemmed from tungsten doping. According to the first-principles density function theory (DFT) calculations, although no significant change in band gap by tungsten doping was observed, a slight broadening of valence and conduction bands was noted in W-LTON which may improve the electron/hole conductivity due to reducing the effective mass of electron. Also, tungsten doping was beneficial in creating the effective defects and in enhancing the photocatalytic water oxidation activity of the LaTiO$_2$N crystals.
**Keywords**: LaTiO$_2$N; Water oxidation; Flux Growth; Tungsten doping; Transition Metal; Oxynitride

**Introduction**

Photocatalytic overall water splitting to generate hydrogen and oxygen over (oxy)nitride photocatalysts using solar energy has been studied as one of the potential approaches to fulfill a growing demand for clean and renewable energy as well as to solve serious environmental issues.$^{1,2}$ Having a band gap of about 2.1 eV ($\lambda = \text{ca.} 600$ nm), lanthanum titanium oxynitride (LaTiO$_2$N) is a member of the visible-light-active (oxy)nitride photocatalysts family and has shown a good photocatalytic activity for hydrogen and oxygen generation from water splitting in the presence of suitable sacrificial reagents under visible light because of its appropriate band positions.$^{3,4}$ The achievable theoretical potential of a photocatalyst with a visible light absorption edge of 600 nm is $16.2\%$ solar-energy-conversion efficiency (assuming an overall water splitting quantum yield of unity).$^5$ Recent reports have demonstrated that the solid solution $\left(\text{SrTiO}_3\right)_{1-x}\left(\text{LaTiO}_2\text{N}\right)_x$,$^6$ doping cations $A$ or $B$ site in $\text{ABO}_x\text{N}_y$ ($\left(\text{La},\text{Ca}\right)\text{Ti(O,N)}_3$ and $\text{LaTi}_{1-x}M_x\text{(O,N)}_3\delta^\pm$ ($x = 0$ and 0.1, $M = \text{Nb}^{5+}$, $\text{W}^{6+}$)),$^7,8$ and loading various cocatalysts ($\text{IrO}_x$, $\text{CoO}_x$, $\text{Co}_2\text{O}_4$)$^{9-11}$ were beneficial for the improvement of photocatalytic performance of LaTiO$_2$N. However, various charge carrier recombination paths lead to lower water splitting activity of LaTiO$_2$N.
Flux growth method has been demonstrated as one of the straightforward techniques to improve the photocatalytic activity of inorganic crystals by reducing the density of defects, which act as recombination centers for photogenerated electrons and holes in the crystals.\textsuperscript{12,13} For instance, the LaTiO$_2$N crystals fabricated by nitridation of the La$_2$Ti$_2$O$_7$ precursor under an NH$_3$ flow with and without flux exhibited higher photocatalytic activity for water oxidation\textsuperscript{10,14} Recently, we have also grown the LaTiO$_2$N crystals with less defect density and high crystallinity by a direct NH$_3$-assisted flux method using the KCl flux, and higher photocatalytic activity for water oxidation was achieved.\textsuperscript{15} Furthermore, doping the semiconductor-based photocatalysts with transition-metal cations having partly filled $d$ orbitals has also improved the photocatalytic activity through the effect that the transition-metal cations can behave as a center for absorption of visible light because of the formed donor or acceptor level in the forbidden band of the host material.\textsuperscript{16,17} Particularly, the tungsten doping significantly improved the electron lifetime and enhanced the photocatalytic activity of Ta$_3$N$_5$ and BaTaO$_2$N due to the faster interface charge transfer and the suppressed recombination and photocorrosion of the W-doped Ta$_3$N$_5$ photoelectrode\textsuperscript{18} and the pronounced upward band-bending character of the W-doped BaTaO$_2$N, allowing an easy migration of holes to the surface.\textsuperscript{19} In this work, we report on the direct growth of the W-doped LaTiO$_2$N crystals by an NH$_3$-assisted flux method using the KCl flux, and the photocatalytic activity for water oxidation of pure and W-doped LaTiO$_2$N crystals was comparatively studied with respect to the doping amount of tungsten.
Experimental

An NH₃-assisted flux growth of the W-doped LaTiO₂N (LaTi₁₋ₓWₓ(O,N)₃) crystals was performed using reagent-grade La₂O₃, TiO₂, Na₂WO₄·2H₂O, and KCl (> 98%, Wako Pure Chemical Industries, Ltd.). The well-homogenized mixture of La₂O₃, TiO₂, and Na₂WO₄·2H₂O in stoichiometric ratio was used as a solute, and KCl was employed as a flux. The solute (W-doped La₂Ti₂O₇) concentration was defined as 5 mol%, and the total mass of a solute-flux mixture was approximately 3.0 g for each run. To study the effect of the amount of tungsten dopant on the crystal growth, phase evolution, and photocatalytic water oxidation activity, x was changed from 0.00 to 0.10 in LaTi₁₋ₓWₓ(O,N)₃. After manual dry mixing for 30 min, each solute-flux mixture was placed in a platinum cell with a capacity of 4.0 cm³, heated at 950 °C for 10 h at a heating rate of 600 °C·h⁻¹ under an NH₃ flow (200 mL·min⁻¹), and cooled naturally. The flux-grown crystals were separated from the remaining flux by washing the final crystal products with warm water and dried at 100 °C for 10 h.

The crystalline phases of the flux-grown crystals were identified by X-ray diffraction (XRD, MiniflexII, Rigaku). The morphology and size of the crystals were observed by field-emission scanning electron microscopy (FE-SEM, JSM-7600F, JEOL). The amount of tungsten dopant (Ti:W ratio) in the flux-grown crystals was analyzed by inductively coupled plasma - optical emission spectrometry (ICP-OES, SPS5510, SII Nanotechnology Inc.). The Brunauer, Emmett, and Teller (BET) specific surface areas (S_{BET}) of the flux-grown crystals were obtained from the N₂
adsorption-desorption isotherms at 77 K by using a BELSORP-mini instrument (BEL Japan, Inc.).

The ultraviolet-visible (UV-Vis) diffuse reflectance spectra were recorded on a JASCO V-630 spectrophotometer.

The photocatalytic O₂ evolution experiments were conducted with 100 mg of bare crystals and 200 mg of La₂O₃ (pH buffer) dispersed in 300 mL of 10 mM AgNO₃ (> 99%, Wako Pure Chemical Industries, Ltd.) solution (sacrificial electron scavenger) in a glass cell connected to a closed-circulation system. A 300W Xe lamp fitted with a cold mirror (CM-1) and a cutoff filter (λ > 420 nm) was used as a visible light source. The evolved gases were detected by a gas chromatograph (GC-8A, TCD, Ar gas carrier, Shimadzu).

The structural relaxation for pure LaTiO₂N (LTON), tungsten doped LTON (W-LTON), and non-nitrided oxide (LTO) was performed by first-principles density function theory (DFT) calculations with the Vienna Ab Initio Simulation Package²⁰,²¹ using the modified Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol-GGA)²²,²³ and the projector-augmented wave (PAW) method.²⁴ A spin polarization calculation was used, a kinetic cutoff energy was 500 eV, and k-point mesh was set as satisfying a convergence test (< 5 meV/LaTiO₂N). The initial configuration of LTON was referred to the previous report of combined synchrotron and neutron diffraction and DFT study by Yashima et al.²⁵ For the comparison purpose, we have also investigated the electronic structure of LTO in which all the nitride ions, N³⁻, in LTON were replaced by oxide ion, O²⁻, (O_N⁻), and the total number of electrons in the lattice was
controlled to be $[\text{LaTiO}_3]^+$. A jellium background was used to neutralize the lattice with charged point defects. The exact composition of the calculated cell was $\text{La}_4\text{Ti}_4\text{O}_8\text{N}_4$ and $\text{La}_4\text{Ti}_4\text{O}_{12}$ for LTON and LTO, respectively, and $\sqrt{2} \times 2 \times \sqrt{2}$ against conventional perovskite unit cell was used. For W-LTON, we expanded the simulation cell to a size of $2 \times 2 \times 2$ conventional perovskite unit cell to model the point defect of $\text{W}^{6+}$ ion at $\text{Ti}^{4+}$ site $(\text{W}_{\text{Ti}})$, and two oxide ions were replaced by nitride ions for charge compensation. The resulting composition of the W-LTON cell was $\text{La}_8\text{WTi}_7\text{O}_{14}\text{N}_{10}$ for present computation. W/Ti or O/N was randomly arranged at each cation or anion site, and the total electron energy was computed for 8 candidates. The cell with the lowest total energy was chosen for further electronic structure analysis. Because the band gaps of both compounds were underestimated, which is typical of the GGA functional, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was used to estimate the band gaps of LTON, W-LTON, and LTO. The details are described in Refs. 27, 28. Due to the large computational cost for HSE06 functional, the relaxed ionic configuration by GGA functional was used in this study.

Results and discussion

Figure 1 shows the XRD patterns of pure and W-doped $\text{LaTiO}_2\text{N}$ crystals grown by an NH$_3$-assisted KCl flux method with different amounts of tungsten dopant $(\text{LaTi}_{1-x}\text{W}_x\text{O}_3\text{N}_3$: $x = 0.00, 0.01, 0.02, 0.05, \text{and} 0.10)$. The XRD patterns of the crystals grown with the tungsten amounts of $x = 0.00 - 0.05$ were identical to the International Centre for Diffraction Data Powder Diffraction File (ICDD
PDF 48-1230) data for LaTiO$_2$N with the orthorhombic crystal structure. A further increase in the amount of tungsten dopant to $x = 0.10$ caused the formation of LaWO$_{0.6}$N$_{2.4}$ (ICDD PDF 84-1682) as an impurity phase to LaTiO$_2$N. In accordance with increasing the amount of tungsten dopant from $x = 0.00$ to $x = 0.05$, the main $112$ diffraction peak at 32.08° in the XRD patterns of the flux-grown crystals shifted slightly to a lower angle due possibly to the presence of the substitutional tungsten species in the LaTiO$_2$N crystal lattice. In this case, Ti$^{4+}$ can be replaced with W$^{4+}$, W$^{5+}$ or W$^{6+}$ because of similar ionic radius of Ti$^{4+}$ (0.61 Å) with that of W$^{4+}$ (0.66 Å), W$^{5+}$ (0.62 Å), and W$^{6+}$ (0.60 Å) under such a condition that each coordination number is 6. In previous reports on W-doped and W–N-codoped TiO$_2$, Ti$^{4+}$ was substituted with W$^{6+}$; therefore, the diffraction peaks of the crystals were shifted to a higher angle due to the fact that the ionic radius of W$^{6+}$ is smaller than that of Ti$^{4+}$. On the contrary, the main $112$ diffraction peak shifted slightly to a lower angle in the present study. The shift of the $112$ diffraction peak to a lower angle is associated with the expansion of the lattice volume caused by the substituted tungsten species (W$^{4+}$ and W$^{5+}$) and the mild lattice strain caused by the repulsion between interstitial tungsten dopants.

With the tungsten amount of $x = 0.10$, the main $112$ peak shifted slightly to a higher angle with respect to that of other W-doped LaTiO$_2$N crystals ($x = 0.01 - 0.05$) due to the reason that all tungsten source could not be doped in the LaTiO$_2$N crystal structure because of the separation of the LaWO$_{0.6}$N$_{2.4}$ crystal phase during the flux growth.
Figure 1. XRD patterns of LaTi$_{1-x}$W$_x$(O,N)$_3$: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$, and (e) $x = 0.10$ crystals directly grown by an NH$_3$-assisted KCl flux method.

Figure 2 shows the SEM images and EDS spectra of pure and W-doped LaTiO$_2$N crystals grown directly by an NH$_3$-assisted KCl flux method. As shown in the SEM images, with increasing the amount of tungsten dopant from $x = 0.00$ to $x = 0.05$, the flux-grown crystals with a rounded shape have the average crystal sizes of about 178, 234, 227, and 206 nm, respectively. However, when the amount of tungsten dopant reached $x = 0.10$, the flux-grown crystals possess two different morphologies: small rounded (about 210 nm in size) and large cuboid (about 396 nm in size). According to the EDS results (not shown here), small rounded crystals belong to the W-doped LaTiO$_2$N phase and large cuboid crystals to the LaWO$_{0.6}$N$_{2.4}$ phase. Moreover, the amount of incorporated tungsten species in the flux-grown crystals was monotonously increased with increasing the amount of tungsten source in the starting mixture, as judged from the EDS spectra.
Also, the exact amount of tungsten species doped in the LaTi\textsubscript{1-x}W\textsubscript{x}(O,N)\textsubscript{3} crystals grown with \( x = 0.01, 0.02, 0.05, \) and 0.10 was analyzed by ICP-OES and found to be 0.014, 0.021, 0.053 and 0.101, respectively, which are closer to the starting compositions. However, the exact amount of tungsten species in the LaTi\textsubscript{1-x}W\textsubscript{x}(O,N)\textsubscript{3} crystals grown with \( x = 0.10 \) could not be decided due to the presence of two phases (LaTiO\textsubscript{2}N and LaWO\textsubscript{0.6}N\textsubscript{2.4}).

According to our previous report,\textsuperscript{15} the small rounded W-doped LaTiO\textsubscript{2}N crystals could be grown through the following processes: (i) the formation of the W-doped La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} crystals at lower temperatures and shorter times of nitridation due to the lack of atomic nitrogen, (ii) the conversion of the W-doped La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} crystals into the W-doped LaTiO\textsubscript{2}N crystals under an NH\textsubscript{3} flow with the assistance of the KCl flux, and (iii) the growth of the W-doped LaTiO\textsubscript{2}N crystals through the dissolution-precipitation processes and due to the Gibbs-Thomson effect.\textsuperscript{35} Meantime, with the maximum amount of tungsten dopant (\( x = 0.10 \)), large cuboid LaWO\textsubscript{0.6}N\textsubscript{2.4} crystals with tetragonal symmetry could also be grown along with the W-doped LaTiO\textsubscript{2}N crystals because the crystal faces with lower surface energy became prominent.\textsuperscript{36,37}
Figure 2. SEM images and EDS spectra of LaTi$_{1-x}$W$_x$(O,N)$_3$: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$, and (e) $x = 0.10$) crystals directly grown by an NH$_3$-assisted KCl flux method. The scale bar is 1 µm.
Figure 3. UV-Vis diffuse reflectance spectra of LaTi$_{1-x}$W$_x$(O,N)$_3$ (x = 0.00, 0.01, 0.02, 0.05, and 0.10) crystals directly grown by an NH$_3$-assisted KCl flux method.

Figure 3 shows the UV-Vis diffuse reflectance spectra of pure and W-doped LaTiO$_2$N crystals grown directly by an NH$_3$-assisted KCl flux method. The absorption-edge wavelength of pure LaTiO$_2$N crystals is approximately 589 nm, and the estimated band-gap energy is 2.11 eV. In contrast, the absorption-edge wavelengths of the W-doped LaTiO$_2$N crystals shifted slightly toward the red end of the spectrum (λ = 589 - 610 nm) with increasing the amount of tungsten dopant, resulting in slightly narrower band-gap energies ($E_g = 2.03$ - 2.11 eV) compared to that of pure LaTiO$_2$N crystals. With increasing the amount of tungsten dopant, the color of the flux-grown crystals altered from light brown to dark brown, as shown in Figure 3. In previous reports on W-doped and W–N-codoped TiO$_2$, the red-shifted absorption-edge wavelength for the tungsten-doped crystals was related to the charge transfer between the valence (N 2p or/and O 2p) to conduction (Ti 3d) bands of TiO$_2$ and tungsten dopant level.$^{31,34,38,39}$ In W–N-codoped TiO$_2$, the synergistic doping effect of tungsten and nitrogen increased the solubility limits of tungsten and nitrogen.$^{33}$ In our case, the tungsten doping made a slight red shift of the absorption-edge wavelength and narrowed the band gap energy of the LaTiO$_2$N crystals. Presumably, the tungsten doping could promote the inclusion of more interstitial nitrogen in the lattice of the LaTiO$_2$N crystals compared to pure LaTiO$_2$N crystals. It is known that the conduction and valence bands of LaTiO$_2$N are mainly consisted of the orbital of Ti 3d and the hybrid orbital of O 2p and N 2p,
respectively, and the potential of N 2p orbital is higher than that of O 2p orbital by using normal hydrogen electrode (NHE) as a standard potential.\textsuperscript{40} As a result, the top of valence band becomes higher with increasing the amount of interstitial nitrogen in the W-doped LaTiO\textsubscript{2}N crystals, narrowing the band-gap energy of the flux-grown crystals.\textsuperscript{41} Therefore, it can be concluded that a slight shift in the absorption-edge wavelength for the W-doped LaTiO\textsubscript{2}N crystals was possibly stemmed from two factors: the charge transfer between the valence band or conduction band and tungsten dopant level in the W-doped LaTiO\textsubscript{2}N crystals and the narrowing of the band-gap energy with an increased amount of interstitial nitrogen.

![Graph](image)

**Figure 4.** Reaction time courses of photocatalytic O\textsubscript{2} evolution of LaTi\textsubscript{1-x}W\textsubscript{x}(O,N)\textsubscript{3} (x = 0.00, 0.01, 0.02, 0.05, and 0.10) crystals directly grown by an NH\textsubscript{3}-assisted KCl flux method. Photocatalytic reaction conditions: 100 mg photocatalyst loaded with CoO\textsubscript{x} cocatalyst (2 wt\% Co); aqueous solution of AgNO\textsubscript{3} (10 mM, 300 mL); 200 mg La\textsubscript{2}O\textsubscript{3} (pH buffer); light source – 300W Xe lamp fitted with a cold mirror (CM-1) and a cutoff filter (\textlambda > 420 nm); a side-irradiation-type reaction vessel was used in this study.
Figure 4 shows the reaction time courses of the photocatalytic O₂ evolution over pure and W-doped LaTiO₂N crystals grown directly by an NH₃-assisted KCl flux method. Within the first 2 h of the photocatalytic O₂ evolution reaction, the maximum O₂ evolution rate (51 µmol·h⁻¹) was achieved by the W-doped LaTiO₂N crystals with the tungsten amount of x = 0.05 which is nearly three-fold greater than that of pure LaTiO₂N (18 µmol·h⁻¹). Probably, this improvement in photocatalytic O₂ evolution is attributed to the enhanced conductivity of the W-doped LaTiO₂N crystals and an effective separation of the photogenerated charge carriers due to tungsten doping.⁸,¹⁸,³⁴ However, with the maximum amount of tungsten dopant (x = 0.10), the O₂ evolution rate abruptly decreased to 31 µmol·h⁻¹. This decrease can be related to the presence of a large amount of defect states, which were generated due to the superfluous tungsten doping in the forbidden band of LaTiO₂N.¹⁸,¹⁹ Those defect states would likely act as the recombination centers for the photogenerated electrons and holes.¹⁸,¹⁹ The O₂ evolution rate was slightly decreased with increasing the reaction time because of the deposition of metallic silver nanoparticles on the surfaces of the flux-grown photocatalyst crystals, and the metallic silver nanoparticles hinder light absorption and cover surface active sites.¹⁹ With an increase in the amount of tungsten dopant from x = 0.00 to x = 0.10, the specific surface areas of the flux-grown crystals decreased in the following order: 9.5 (x = 0.00), 7.7 (x = 0.01), 7.3 (x = 0.02), 7.1 (x = 0.05), and 6.1 (x = 0.10) m²·g⁻¹. With the maximum amount of tungsten dopant (x = 0.10), the lower specific surface area may additionally contribute to the lowered photocatalytic activity for O₂ evolution.⁴² Due to the
photodecomposition of the flux-grown oxynitride crystals, a negligible amount of N₂ gas (< 12 µmol) was evolved after 2 h of photocatalytic reaction. The N₂ evolution rate was drastically diminished with the progress of photocatalytic reaction, indicating the stability of the flux-grown oxynitride crystals under the current experimental conditions.

![Diagram](image)

**Figure 5.** Schematic representation of photocatalytic O₂ evolution over (a) pure LaTiO₂N and (b) W-doped LaTiO₂N crystals directly grown by an NH₃-assisted KCl flux method.

On the basis of the results obtained in this study and previous reports, the schematic diagrams of the AgNO₃-assisted O₂ evolution over pure and W-doped LaTiO₂N crystals under visible light irradiation at pH = 7 is shown in Figure 5. Generally, the W 5d orbital of WO₃ is more positive potential as compared to the reduction potential of H₂O to generate H₂. Presumably, the W 5d orbital existing in the W-doped LaTiO₂N crystals can hybridize with Ti 3d orbital and lower the bottom of conduction band, as shown in Figure 5b. The tungsten dopant and interstitial nitrogen species are expected to significantly contribute to the change in band gap energy of the W-doped LaTiO₂N. However, according to the previous theoretical calculations, the incorporation of tungsten in the titanium site led to the shift of Fermi level into the conduction band due to the strong...
hybridization of Ti 3d states with W 5d states, causing the broadening of the band gap energy of W-doped TiO$_2$. Based on this phenomenon, it is possible that the W-doped LaTiO$_2$N can act as a degenerate semiconductor. Moreover, the isolated N 2p narrow band, which consists of interstitial nitrogen and is located just above the O 2p + N 2p valence band, can additionally contribute to the improvement of photocatalytic water oxidation activity of the W-doped LaTiO$_2$N because of the enhanced light absorption and narrowed band gap.

Figure 6 shows the local densities of states (LDOS) for (a) LTON, (b) W-LTON, and (c) LTO calculated by HSE06 functional, and the estimated band gaps are 2.3, 2.3, and 3.4 eV, respectively. The calculated band gaps for LTON and W-LTON (about 2.3 eV) are in accordance with the band gaps experimentally obtained in this study (2.03 – 2.11 eV). Note that the conventional GGA functional is prone to underestimate the band gap, indicating about 1.3 eV for LTON in the present calculation (not shown here). Therefore, the calculated electronic structure based on the HSE06 calculations is discussed hereinafter unless specially mentioned. Obviously, the band gap of pure oxide (LTO) is much larger than that of oxynitrides (LTON, W-LTON). In detail, the top of valence band of LTO is mainly formed by O 2p orbital, whereas N 2p orbital is visible at the top of valence band followed by O 2p orbital at lower energy level in oxynitrides. A significant decrease in band gap achieved by introducing the nitride ions into the LTO framework is primarily due to the elevation of the top of valence band by N 2p orbital. Figure 7a shows the partial electron density for the top of valence band (ranging from -1 eV to 0 eV in Figure 6b) for W-LTON, and the partial
electron densities are mainly distributed around the nitride ions. The bottom of conduction band is mainly composed of Ti 3d orbital for the three models of LTON, W-LTON, and LTO. Note that W 5d and 6s orbitals are also located at the bottom of conduction band, but no significant change in band gap is indicated. The partial electron density distribution at the bottom of conduction band (ranging from 2.3 eV to 3 eV in Figure 6b for W-LTON also indicates that the conduction band is mainly composed of both Ti and W t_{2g} orbitals, as shown in Figure 7b. Although no significant change in band gap by W doping was observed, a slight broadening of valence and conduction bands was noted in W-LTON which may improve the electron/hole conductivity due to reducing the effective mass of electron.

![Figure 6. Local density of states (LDOS) for (a) LaTiO_2N (LTON), (b) W-doped LTON (W-LTON), and (c) [LaTiO_3]^+ (LTO) obtained by first-principles calculations using HSE06 hybrid](image)

Figure 6. Local density of states (LDOS) for (a) LaTiO_2N (LTON), (b) W-doped LTON (W-LTON), and (c) [LaTiO_3]^+ (LTO) obtained by first-principles calculations using HSE06 hybrid
functional. Black, dark blue, red, green, and light blue lines represent the LDOS of La, Ti, O, N, and W, respectively. The energy scale is aligned so that the Fermi level is to be zero.

**Figure 7.** Calculated partial electron density distribution for W-doped LaTiO$_2$N (W-LTON). Panels (a) and (b) represent the partial electron density at the top of valence band (from -1 to 2 eV in Figure 6b) and the bottom of conduction band (from 2.3 to 3 eV), respectively. The isosurface level is set to be 0.02 Å$^{-3}$. In panel (a), N 2p orbital is clearly visible due to its dumbbell shape orbital. In panel (b), the orbital is not directed to the ligands (oxide or nitride ion), indicating that the bottom of conduction band, both at W and Ti sites, is mainly composed of $t_{2g}$ type orbital.

**Conclusions**
To conclude, LaTi$_{1-x}$W$_x$(O,N)$_3$ ($x = 0.00 - 0.10$) crystals were directly grown by an NH$_3$-assisted flux method using the KCl flux. With the maximum amount of tungsten dopant ($x = 0.10$), LaWO$_{0.6}$N$_{2.4}$ was formed as an impurity phase to the W-doped LaTiO$_2$N phase. The W-doped LaTiO$_2$N crystals grown with $x = 0.00 – 0.05$ in a rounded shape had average sizes of ca. 178, 234, 227, and 206 nm, respectively, whereas the crystals grown with $x = 0.10$ possessed two different morphologies: small rounded (ca. 210 nm in size) and large cuboid (ca. 396 nm in size). An increase in the amount of tungsten dopant resulted in a slight decrease in the specific surface area from 9.5 to 6.1 m$^2$·g$^{-1}$. From the first-principles density function theory (DFT) calculations, a slight broadening of valence and conduction bands was observed in W-LTON which may improve the electron/hole conductivity due to reducing the effective mass of electron. Considering the first 2 h of the photocatalytic water oxidation reaction, the W-doped LaTiO$_2$N crystals grown with $x = 0.05$ showed higher O$_2$ evolution rate (51 µmol·h$^{-1}$) compared with pure LaTiO$_2$N crystals (18 µmol·h$^{-1}$) due to the improved conductivity, enhanced light absorption, and efficient charge separation.

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**References**


Effect of tungsten dopant on photocatalytic water oxidation activity of LaTiO$_2$N crystals grown by an NH$_3$-assisted flux method was studied.