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Understanding the effect of partial N^{3-} -to- O^{2-} substitution and H^+ -to- K^+ exchange on photocatalytic water reduction activity of Ruddlesden–Popper layered perovskite $KLaTiO_4$

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ABSTRACT

Ruddlesden–Popper perovskites, $HLaTiO_4$ and $HLaTiO_{4-x}N_x$ were prepared by proton exchange of layered $KLaTiO_4$ synthesized by a solid-state reaction and $KLaTiO_{4-x}N_x$ obtained by nitridation, respectively. The influence of nitridation time on crystal structure, morphology, and absorption wavelength and optical band-gap energy of $KLaTiO_4$ crystals was studied. According to the XRD and SEM results, the crystal structure and plate-like morphology of the parent oxide were roughly retained even after nitridation at 800 °C for 10 h. The absorption edge wavelength of the $KLaTiO_4$ crystals was found to be at about 350 nm ($E_g = 3.54$ eV), while the absorption edge wavelength of the $KLaTiO_{4-x}N_x$ crystals (after 10 h nitridation) was about 586 nm ($E_g = 2.12$ eV). To investigate the effect of partial N^{3-} -to- O^{2-} substitution and H^+ -to- K^+ exchange on photocatalytic water reduction activity of Ruddlesden–Popper layered perovskite $KLaTiO_4$, the photocatalytic activity for water reduction half-reaction over Pt-photodeposited $KLaTiO_4$, $KLaTiO_{4-x}N_x$, $HLaTiO_4$, and $HLaTiO_{4-x}N_x$ was evaluated under simulated solar light. Among all the samples, Pt-photodeposited $KLaTiO_4$ exhibited the highest photocatalytic activity for H_2 evolution. In contrast, Pt-photodeposited $KLaTiO_{4-x}N_x$ showed a low photostability and photocatalytic activity for H_2 evolution due to the negative impact of the defective layer and reduced titanium species. In addition, perovskite oxynitride $[LaTiO_{4-x}N_x]^-$ nanosheets were successfully fabricated by a mechanical exfoliation (sonication) of the $KLaTiO_{4-x}N_x$ crystals. The colloidal suspension of the oxynitride nanosheets showed a Tyndall effect, implying their good dispersion and stability in water.

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1. Introduction

In recent decades, artificial photosynthesis for solar water splitting has been studied for the source of clean sustainable fuel and chemical production [1,2]. Previously, several perovskite oxides such as $SrTiO_3$ [3], $NaTaO_3$ [4], $K_2La_2Ti_3O_{10}$ [5], $KLaTiO_4$ [6], etc. have been demonstrated as photocatalysts for overall water splitting under ultraviolet (UV) light irradiation. Among them, the

layered perovskite oxides are considered to be promising candidates for overall water splitting photocatalysts because of their diverse derivatives that can be easily synthesized through an interlayer cation exchange, proton exchange, doping, and anion substitution [7,8].

Potassium lanthanum titanate, $KLaTiO_4$, with the tetragonal space group $P4/nmm$ has single perovskite slabs interleaved by potassium and lanthanum ions, and the perovskite slabs are composed of octahedral TiO_6 sheets (Fig. 1) [9]. Previously, Takata et al. [6] achieved 12.5% quantum yield for water splitting into H_2 and O_2 over $KLaTiO_4$ under UV light irradiation. Furthermore, cocatalyst-loaded and zirconium-doped $KLaTiO_4$ ($Ni-KLaZr_xTi_{1-x}O_4$) was also demonstrated in the same study to improve the photocatalytic activity for overall water splitting under UV light irradiation,

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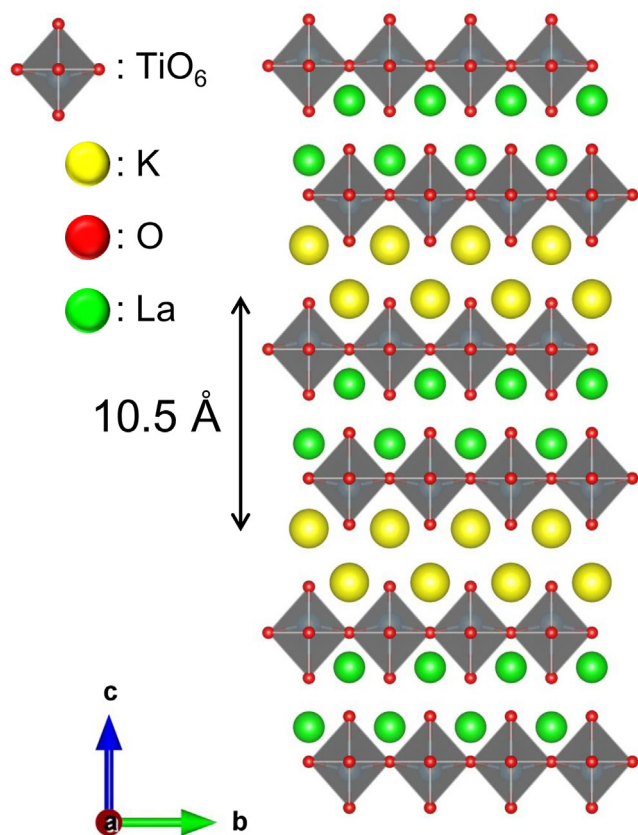


Fig. 1. Schematic illustration of the idealized crystal structure of KLaTiO₄.

and the amount of evolved H₂ was 6.4 times higher than that of pure KLaTiO₄ [6]. However, it is known that the sunlight has much energy (about 54%) to total energy in the visible light region ($\lambda = 400\text{--}700$) [10]. As KLaTiO₄ can only be excited under UV light ($\lambda < 340$ nm) due to its wide band-gap energy ($E_g = 3.6$ eV), it is difficult to achieve high efficiency in solar water splitting over KLaTiO₄.

Regarding to the enhancement of the photocatalytic activity of oxide materials under visible light irradiation, non-metal doping, forming an isolated band just above the valence band, has been considered as one of the effective strategies [11]. For non-metal doping, carbon, nitrogen, fluorine, phosphorus, and sulfur are mainly used as the dopants, and nitrogen doping has particularly received much attention because of giving novel physical properties (i.e. absorption across the visible light region and high stability) to oxides and maintaining innocuity even after decomposing the nitrogen-doped oxides [12,13]. Asahi et al. [13] reported that compared to doping with carbon, fluorine, phosphorus, or sulfur into TiO₂ lattice, the substitutional doping of N into TiO₂ is the most effective for band-gap narrowing because of the formation of the hybrid orbitals of N 2p and O 2p.

For instance, several nitrogen-doped oxides such as TiO_{2-x}N_x [13], Cs_{0.68}Ti_{1.83}O_{4-x}N_x [14], CsCa₂Ta₃O_{10-x}N_x [15], Sr₅Ta₄O_{15-x}N_x [16], CsBa₂Ta₃O_{10-x}N_x [17], etc. exhibited the light absorption in the visible light region. Especially, for the layered oxides, nitrogen doping has shown an extremely high effect on enhancing the visible light absorption due to easy diffusion of nitrogen ions from the surface to the internal structure of crystals through the interlayer, thereby increasing the nitrogen incorporation [14,16]. Thus, the layered CsCa₂Ta₃O_{10-x}N_x, Sr₅Ta₄O_{15-x}N_x, and CsBa₂Ta₃O_{10-x}N_x have shown the improved absorption edges at 582, 565, and 600 nm, respectively [15–17].

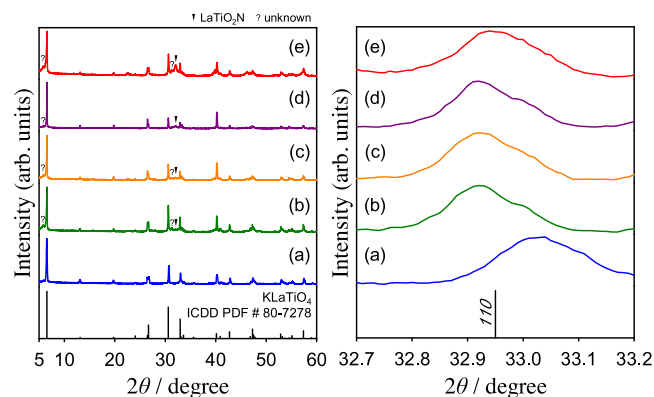


Fig. 2. XRD patterns of the KLaTiO₄ crystals synthesized by solid state reaction (a) and the KLaTiO₄ crystals nitrated at 800 °C for 3 (b), 5 (c), 7 (d), and 10 h (e).

Due to the hydration of the interlayer cations and molecules [18], proton exchange was also reported to be effective in improving water splitting activity of the layered compounds. Nishimoto et al. [19] studied the photocatalytic activities of HLaTiO₄ and H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O for H₂ evolution from aqueous methanol solutions under UV light irradiation and found that the distorted perovskite structure is favorable for the high photocatalytic activity. Also, they pointed out that the influence of the distortion of TiO₆ octahedra in the perovskite layer on the photocatalytic activities is greater than that of the presence of interlayer water molecules. Approximately 80% apparent quantum yield (AQY) at 300 nm was achieved by the perovskite nanosheets of protonated oxide HCa₂Nb₂TaO₁₀ crystals because the nanosheets having high surface area allow a prompt transfer of photogenerated electrons and holes to their surface without a rapid recombination [20]. As protonated layered crystals are also able to utilize their interlayer spaces for the photocatalytic water splitting reaction and decomposition of organic molecules adsorbed into their interlayer gallery, the above-mentioned “nanosheet effect” on the enhancement of photocatalytic activity is expected for the protonated layered crystals.

In this study, we are aimed to study the effect of partial N³⁻-to-O²⁻ substitution and H⁺-to-K⁺ exchange on the photocatalytic water reduction activity of Ruddlesden–Popper layered perovskite KLaTiO₄. The effect of nitridation time at 800 °C under an NH₃ flow on phase stability, morphology and light absorption of KLaTiO₄ crystals was investigated. The photocatalytic water reduction activity of the protonated HLaTiO₄ and HLaTiO_{4-x}N_x crystals were explored under simulated solar light in comparison to unprotonated KLaTiO₄ and KLaTiO_{4-x}N_x crystals. Also, the fabrication of the [LaTiO_{4-x}N_x]⁻ nanosheets by a mechanical exfoliation of the nitrated KLaTiO₄ crystals is demonstrated.

2. Experimental

2.1. Growth of KLaTiO₄ crystals

The layered perovskite KLaTiO₄ crystals were synthesized by a solid-state reaction using a well-homogenized mixture of reagent-grade KNO₃, La₂O₃ and TiO₂ (> 98%, Wako Pure Chemical Industries, Ltd.) in a molar ratio of K:La:Ti = 1.55:1:1 [9]. The synthesis reaction can be expressed, as follows:



An excess amount (55 mol%) of KNO₃ was added in order to compensate for the potassium loss by volatilization at high temperature. The well-homogenized mixture (10 g) was placed in a platinum crucible with a capacity of 30 cm³ and closed loosely

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