Article

Photocatalytic Activities of Protonated Layered Perovskite Compounds, HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$, Formed by Ion-exchange/intercalation Reaction

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Abstract

Protonated layered perovskite compounds, HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$, were prepared from $n = 1$ Ruddlesden-Popper phase, NaLaTiO_4 , by the ion-exchange/intercalation reaction. Photocatalytic activities of HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ for H_2 evolution from aqueous methanol solutions were studied. Anhydrous protonated form, HLaTiO_4 , showed higher photocatalytic activity than hydrous protonated form, $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$. In a series of $\text{H}_x\text{Na}_{1-x}\text{LaTiO}_4 \cdot y\text{H}_2\text{O}$, it was considered that the influence of the distortion of TiO_6 octahedra in the perovskite layer on the photocatalytic activities was greater than that of the presence of interlayer water molecules.

Key words: ion-exchange, intercalation, layered perovskite, photocatalyst, crystal structure

1 Introduction

Much attention has been paid to the photocatalytic water splitting, because the clean energy carrier, H_2 , could be obtained from renewable water.[1] The photocatalytic reaction involves the migration step of photoexcited electrons and holes from the inside of the solid sample to the surface in addition to the surface reaction. The lattice defect in the crystal facilitates the charge recombination. Therefore, not only high surface area, i.e., lots of reaction sites, but also high crystallinity of the sample is necessary for active photocatalysts. However, it is difficult to satisfy both conditions by a conventional solid-state reaction. In such a background, soft chemical processing such as an ion-exchange reaction has been expected as an effective photocatalyst synthesis method to satisfy these conflicting conditions. For example, hydrous layered perovskite, $\text{Rb}_2\text{La}_2\text{Ti}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$, prepared by the soft chemical processing reportedly shows a reasonable activity for splitting water into H_2 and O_2 in a stoichiometric ratio under UV irradiation.[2] This high photocatalytic activity has been considered to be due to the presence of water molecules in the interlayer. That is, the interlayer space functions as the reaction site. Consequently, the interlayer modification of layered perovskite compounds improves the photocatalytic activity.

Recently, we have reported the syntheses of anhydrous protonated layered perovskite, HLaTiO_4 , and hydrous protonated layered perovskite, $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$, by an ion-exchange/intercalation reaction of sodium typed layered perovskite, NaLaTiO_4 . [3] Because $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ contains the interlayer water molecule, a high photocatalytic activity is expected as well as $\text{Rb}_2\text{La}_2\text{Ti}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$. Furthermore, the crystal structure of $\text{H}_x\text{Na}_{1-x}\text{LaTiO}_4 \cdot y\text{H}_2\text{O}$ is unique in the series of layered perovskite compounds, which typically consists of multiple perovskite layers. That is, the structure of $\text{H}_x\text{Na}_{1-x}\text{LaTiO}_4 \cdot y\text{H}_2\text{O}$ consists of (a) single TiO_6

octahedral layer, (b) an interlayer and (c) single LaO_9 polyhedral layer ordered with a sequence of $-(a)-(b)-(a)-(c)-(a)-$ along the c -axis.[3] Moreover, neutron diffraction has revealed the precise structural difference caused by the ion-exchange/intercalation reaction between HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ in our previous reports.[4, 5] Because it has been known that the difference of crystal structure brings the difference of the charge separation efficiency in the crystal, the Comparison of photocatalytic activities for both compounds could give new information on the interlayer modification of layered perovskite by soft chemical processing.[6] In this paper, we report the photocatalytic activities of HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ for H_2 evolution from an aqueous methanol solution under UV irradiation, and characterize the difference from the view point of the crystal structure.

2 Experimental

The compounds, HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$, were prepared, according to the procedures in the previous papers.[3-5] The starting compound, NaLaTiO_4 , was prepared by the conventional solid-state reaction. Prior to the preparation, La_2O_3 was predehydrated at 900°C for 9 h, because La_2O_3 agent contains a small amount of $\text{La}(\text{OH})_3$. Stoichiometric amounts of TiO_2 and La_2O_3 and 50 % excess of Na_2CO_3 were mixed, and heated at 900°C for 30 min after preheating at 700°C for 2 h in the air. The product was washed to remove excess Na_2O with distilled water and dried at 160°C . The ion-exchange/intercalation reactions of proton and water molecule were carried out in HCl solution of 10^{-1} and 10^{-5} M (mol dm^{-3}) at room temperature for 12 and 72 h, respectively. The HCl solution was refreshed everyday during the reaction. The resulting samples were washed with distilled water and dried at room temperature. The products were identified by powder X-ray diffraction (XRD), using a Rigaku RINT2100/PC diffractometer with monochromated $\text{Cu K}\alpha$ radiation, and ion-exchange ratio was determined by measuring pH value and Na^+ ion concentration in filtrate, using a TOA HM-5S pH meter and a Shimadzu AA6800 atomic absorption spectrometer, respectively. Thermogravimetric analysis (TGA) was performed on a Rigaku TAS100 instrument at a heating rate of $10^\circ\text{C min}^{-1}$ in the air. Diffuse reflectance spectra were measured using a Shimadzu UV-2100PC spectrophotometer. Nitrogen adsorption measurement was performed to estimate the BET surface area of the samples, using a BEL BELSORP 18SP. Pt-cocatalyst (0.1 wt %) were loaded in situ by a photoreduction method, using an aqueous H_2PtCl_6 solution.

The behavior of photocatalytic H_2 evolution from an aqueous methanol solution was examined using a closed gas-circulation system. The photocatalyst powder (0.3 g) was dispersed in a 10 vol% aqueous methanol solution (370 mL) in quartz-glass cell under an Ar atmosphere. The dispersion was irradiated by a 400-W high pressure Hg lamp. The amount of H_2 was measured by gas chromatography, using a Shimadzu GC-8A.

3 Results and Discussion

The powder XRD patterns of the compounds prepared by the ion-exchange/intercalation reaction of NaLaTiO_4 were identical to those of HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ in the previous study, respectively.[3] Furthermore, the chemical compositions of the resulting samples characterized by the pH meter, atomic absorption and TGA instrument were also consistent with the results in the previous study.[3] Thus, the resulting samples were employed in the measurement for photocatalytic H_2 evolution from an aqueous methanol solution.

Figure 1 shows the diffuse reflectance spectra of HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$. Both compounds showed similar absorption behavior each other and the absorption edge of about 370 nm. Figure 2 shows the time course of H_2 evolution on HLaTiO_4 and $\text{H}_{0.34}\text{Na}_{0.66}\text{LaTiO}_4 \cdot 0.59\text{H}_2\text{O}$ from an aqueous methanol

solution under UV irradiation. No reaction took place in the dark. In subsequent reaction, after evacuation, H₂ evolution proceeded again, accompanied by no significant decrease of activity. Moreover, the XRD patterns of the samples after the reactions were same as those before the reactions, respectively. These results indicate that HLaTiO₄ and H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O function as photocatalyst for photoreduction of H₂O into H₂ under UV irradiation.

Table 1 shows photocatalytic activities of H₂ evolution on HLaTiO₄ and H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O from an aqueous methanol solution under UV irradiation together with the BET surface area estimated by the N₂ adsorption measurement. Hydrous protonated form, H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O, was expected to show a high photocatalytic activity, because the water molecules exist in the interlayer space. However, the activity was lower than

Fig. 1 Diffuse reflectance spectra of (a) H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O and (b) HLaTiO₄.

Fig. 2 H₂ evolution from aqueous methanol solutions on (a) H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O and (b) HLaTiO₄. Catalyst; 0.3 g, cocatalyst; Pt (0.1 wt%), reaction solution; a 10 vol% aqueous methanol solution of 370 mL, and light source; a 400 W high pressure Hg lamp.

Table 1 Photocatalytic activities of H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O and HLaTiO₄ for H₂ evolution^a

catalyst	surface area / m ² ·g ⁻¹	rate of H ₂ evolution / μmol·h ⁻¹
H _{0.34} Na _{0.66} LaTiO ₄ ·0.59H ₂ O	2.8	20
HLaTiO ₄	11.7	170

^aCatalyst; 0.3 g, cocatalyst; Pt (0.1 wt%), reaction solution; a 10 vol% aqueous methanol solution of 370 mL, and light source; a 400 W high pressure Hg lamp.

that of anhydrous protonated form, HLaTiO₄. Furthermore, the activity of hydrous protonated form was under 50 % of that of anhydrous protonated form, though the activities were normalized by the BET surface area. The light absorption properties of both compounds were almost same, and the XRD patterns suggested that the crystallinity of both compounds was not different so much. Therefore, it was considered that the difference of the photocatalytic activity was concerned with the structural difference between HLaTiO₄ and H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O as follows: Kudo et al. reported that the charge separation efficiency of perovskite compound, ATaO₃ (A = Li, Na and K), improved with deviating O-Ta-O bond angle from the ideal value of 180 °.[6] That is, the distorted perovskite structure is favorable for the high photocatalytic activity. Neutron diffraction has revealed the precise crystal structure of HLaTiO₄ and H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O in our previous reports, and the degree of distortion of TiO₆ octahedra in the perovskite layer of HLaTiO₄ was revealed to be higher than that of H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O.[4, 5] Consequently, anhydrous protonated form, HLaTiO₄, showed higher photocatalytic activity than hydrous protonated form, H_{0.34}Na_{0.66}LaTiO₄·0.59H₂O. This result indicates 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, in a series of H_xNa_{1-x}LaTiO₄·yH₂O. Furthermore, the degree of distortion of TiO₆ octahedra in the perovskite layer of HLaTiO₄ was also higher than that of parent compound, NaLaTiO₄. [5] While the photocatalytic activity of NaLaTiO₄, which was unstable in the aqueous methanol solution, could not be characterized, the protonation bringing the structural distortion could be one of the effective interlayer modification of layered perovskite compounds for high photocatalytic activities as well as the hydration in Rb₂La₂Ti₃O₁₀·xH₂O.

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