Photocatalytic properties of perovskite-type oxynitride solid solutions containing niobium

Hideki Kato,* Ryosuke Aoyagi, Makoto Kobayashi, Masato Kakihana
[a]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan*
**Corresponding author: +81-22-217-5651, hideki.kato.e2@tohoku.ac.jp*

Abstract: In this study, photocatalytic activity of oxynitride solid solutions containing niobium was investigated. Band gap of the $LaNbON_2$-$ATiO_3$ (A = Ca, Sr, Ba) solid solution system varied with the A-site elements. Although the solid solutions had wider band gaps than known Nb-based oxynitride photocatalysts ($SrNbO_2N$ and $BaNbO_2N$), they showed activity for hydrogen evolution. This feature is interesting because $SrNbO_2N$ and $BaNbO_2N$ are inactive for hydrogen evolution.
Keywords: Oxynitride, Solid solution, Band tuning.

1. Introduction

Photocatalytic water splitting gathers attention because of its potential for applications of solar energy conversion. Many factors such as particle size, crystallinity, defect, band potential, and co-catalyst affect photocatalytic properties and activities. Among them, potentials of valence and conduction bands are regarded as very important factors for photocatalysts because they determine band gaps of photocatalysts and the reactivity of photogenerated electrons and holes. Oxynitrides are one of the promising groups for visible-light-driven photocatalysts due to high potential of valence band maximum (VBM) formed by N2p in comparison with those formed by O2p.[1] However, excessively high potential of VBM is not favorable for water oxidation reaction because the driving force, which is potential difference between VBM and water oxidation potential, becomes small. We have achieved band potential tuning of oxynitrides based on $LaTaON_2$ by formation of solid solutions with oxide perovskites, $NaTaO_3$ and $SrTiO_3$.[2,3] In this study, we expand solid solution systems to niobium-based oxynitrides.

2. Experimental

Powders of oxynitride solutions were obtained by nitridation of oxide precursors prepared by a polymerizable complex method employing anhydrous citric acid and propylene glycol as chelating and polymerizing reagents, respectively.[2,3] Pentaethoxy niobium, tetrabutoxy titanium, lanthanum nitrate, and alkaline earth carbonates are used as metal sources. The amorphous oxide precursors obtained were heated under ammonia stream to convert oxides to oxynitrides. For hydrogen evolution reaction, Pt-loaded samples, which were prepared by an impregnation method involving reduction by hydrogen, were employed. For oxygen evolution reaction, bare and CoOx-modified samples were used. Deposition of the CoOx cocatalyst was also performed by the impregnation method coupled with heating under ammonia stream at 773 K.

Photocatalytic activities were examined for hydrogen or oxygen evolution using methanol or silver nitrate as an electron donor or acceptor, respectively, using a gas-closed circulation system. La_2O_3 powder was added into the reactant solution as buffering pH around 8. A 300 W xenon lamp was used as a light source and visible light irradiation was achieved using a cut-off filter ($\lambda > 420$ nm). Evolved gases were analyzed by an online gas chromatograph (Ar carrier, MS-5A column, TCD detector).

3. Results and discussion

Solid solutions examined in this work were obtained as a single phase of perovskite compounds. Absorption properties of solid solutions varied with kinds of combination as shown in Figure 1. In the $LaNbON_2$-$ATiO_3$ (A = Ca, Sr, Ba) system, band gap energy became smaller with the sequence of Ba < Sr < Ca. It would be due to distortion of perovskite framework.[4] When the A-site of perovskite structure is occupied by small cations, the perovskite framework distorts, meaning that connection angle of MX_6

octahedra deviates from 180º. Such distortion in M-X-M bond angles make degree of energy localization high, resulting in expansion of band gaps. Photocatalytic activities of solid solutions are summarized in Table 1. Although $BaNbO_2N$ showed the narrowest band gap among oxynitride examined in this study, it was almost inactive as reported.[5] $SrNbO_2N$ was also inactive for hydrogen evolution besides relatively high activity for oxygen evolution as reported.[6] Among the solid solutions, $La_{0.5}Ca_{0.5}Nb_{0.5}Ti_{0.5}O_2N$ exhibited the highest activity for oxygen evolution irrespective of modification with a CoOx cocatalyst although this photocatalyst showed the shortest absorption edge. $La_{0.5}Ca_{0.5}Nb_{0.5}Ti_{0.5}O_2N$ also showed meaningful activity for oxygen evolution even without the CoOx cocatalyst. Interestingly, all solid solutions produced hydrogen while known Nb-based oxynitrides, $SrNbO_2N$ and $BaNbO_2N$ are inactive.

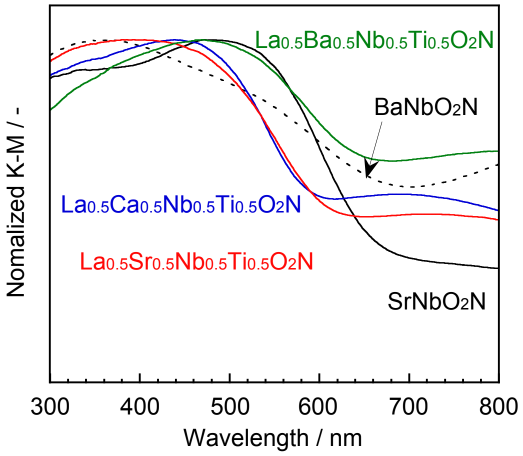

Figure 1. UV-.vis spectra of Nb-based oxynitride solid solutions

Table 1. Photocatalytic activities of Nb-based oxynitride solid solutions.

Sample	Activity / µmol h^{-1}		
	H_2	O_2 (bare)	O_2 (CoOx)
$SrNbO_2N$	0	11.7	73.8
$BaNbO_2N$	0	0.1	1.4
$La_{0.5}Ca_{0.5}Nb_{0.5}Ti_{0.5}O_2N$	0.4	41.3	205
$La_{0.5}Sr_{0.5}Nb_{0.5}Ti_{0.5}O_2N$	0.3	14.3	68.5
$La_{0.5}Ba_{0.5}Nb_{0.5}Ti_{0.5}O_2N$	0.5	0.4	24.6

4. Conclusions

A series of oxynitride solid solutions was successfully synthesized. The solid solutions exhibited activity for hydrogen evolution using methanol as an electron donor although the reported Nb-based oxynitride photocatalysts are inactive for hydrogen evolution. Thus, formation of solid solutions is one of the attractive methods to fabricate new photocatalysts possessing preferred reaction properties.

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