Water Splitting into H_2 and O_2 over $Ba_5Nb_4O_{15}$ Photocatalysts with Layered Perovskite Structure Prepared by Polymerizable Complex Method

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Photophysical and photocatalytic properties of $Ba_5Nb_4O_{15}$ with four-layered perovskite structure were investigated. The band gap of $Ba_5Nb_4O_{15}$ was 3.9 eV. A broad emission band of green photoluminescence was observed at 77 K. NiO/$Ba_5Nb_4O_{15}$ pretreated by H_2 reduction followed by O_2 oxidation showed a high activity for water splitting under UV light irradiation.

Photocatalytic water splitting into H_2 and O_2 in a stoichiometric ratio, an uphill reaction, is an important topic. The construction of the library of photocatalysts is important to obtain a guiding principle to design highly active photocatalysts. It has been reported that many metal oxide photocatalysts can decompose water into H_2 and O_2 in a stoichiometric ratio under UV irradiation.[1–14] In particular, many tantalates are highly active photocatalysts for water splitting.[2,6–9,12–14] The band gaps of niobates are usually narrower than those of tantalates. Therefore, it is expected that niobates can work as photocatalysts at longer wavelength than tantalates. However, only $A_4Nb_6O_{17}$ (A = K and Rb),[1] $ZnNb_2O_6$,[4] $Sr_2Nb_2O_7$,[5,6] and $Cs_2Nb_4O_{11}$[11] have been reported as niobate photocatalysts for water splitting. Many active photocatalysts possess perovskite-related structures.[1,2,5–10,12–15] $Ba_5Nb_4O_{15}$ possesses a four-layered perovskite structure, in which a plane in parallel with (111) of a perovskite structure is exposed at interlayer.[16] Thus, the exposed plane of $Ba_5Nb_4O_{15}$ is different from those of other layered perovskite photocatalysts, $K_2La_2Ti_3O_{10}$[1] and $RbLaTa_2O_7$[7] with a (100) plane and $Sr_2M_2O_7$ (M = Nb and Ta)[6] with a (110) plane. Recently, $A_5Ta_4O_{15}$ (A = Sr and Ba) possessing the same structure as $Ba_5Nb_4O_{15}$ has been reported as an efficient photocatalyst.[12,13] Therefore, photocatalytic function of $Ba_5Nb_4O_{15}$ is also expected. In the present paper, we investigated photophysical properties and photocatalytic activity of $Ba_5Nb_4O_{15}$ for water splitting.

$Ba_5Nb_4O_{15}$ powder was prepared by a conventional solid-state reaction (SSR) and a polymerizable complex method (PC).[15] In the case of a SSR method, $Ba_5Nb_4O_{15}$ was prepared from $BaCO_3$ (Kanto Chemical; 99.0%) and Nb_2O_5 (Kanto Chemical; 99.95%). The starting materials were mixed in a mortar, and the mixture was calcined at 1473 K in air using an alumina crucible. In the case of a PC method, the precursor was obtained by pyrolysis of a citrate-complexes containing Ba^{2+} and Nb^{5+} and was calcined at 973–1273 K. Phase purity of the obtained powder was confirmed by X-ray diffraction (Rigaku; MiniFlex). NiO cocatalysts were loaded by an impregnation method from an aqueous $Ni(NO_3)_2$ solution. The powder was calcined at 543 K for 1 h in air. Pretreatment of reduction with 26.6 kPa of H_2 at 773 K for 2 h followed by oxidation with 13.3 kPa of O_2 at 473 K for 1 h was carried out for NiO/$Ba_5Nb_4O_{15}$, if necessary. Diffuse reflection spectra were obtained using a UV–vis–NIR spectrometer (Jasco; UbestV-570) and were converted from reflectance to absorbance by the Kubelka–Munk method. Photoluminescence spectra were measured at 77 K (HORIBA JOBIN YVON: SPEX Fluorolog-3). Water-splitting reactions were carried out in a gas-closed circulation system. The photocatalyst powder (0.5 g) was dispersed in pure water (380 mL) by a magnetic stirrer in an inner irradiation reaction cell made of quartz equipped with a 400-W high-pressure mercury lamp. The amounts of evolved H_2 and O_2 were determined using on-line gas chromatography (Shimadzu; MS-5A column, TCD, Ar carrier).

Figure 1 shows photoluminescence spectra at 77 K and a diffuse reflection spectrum of $Ba_5Nb_4O_{15}$ prepared by a SSR method. The band gap was estimated to be 3.9 eV from the onset of absorption (322 nm). $Ba_5Nb_4O_{15}$ showed a broad green emission with a maximum at 532 nm as previously reported.[17] The onset of the excitation spectrum agreed with that of the absorption spectrum. All of the niobate photocatalysts for water splitting show photoluminescence at 77 K.[11] The observation of photoluminescence indicates that nonradiative transition between photogenerated carriers is suppressed. This property is advantageous for showing photocatalytic activity.

Table 1 shows photocatalytic activities of $Ba_5Nb_4O_{15}$ prepared by SSR and PC methods. Native $Ba_5Nb_4O_{15}$ prepared by the SSR method produced H_2 and O_2. The activity was increased when a NiO cocatalyst was loaded. Moreover, the activity of NiO/$Ba_5Nb_4O_{15}$ was improved one order of magnitude by activation pretreatment of H_2 reduction followed by O_2 oxidation. It indicates that the conduction band level of $Ba_5Nb_4O_{15}$ is not negative enough to inject into NiO cocatalysts without

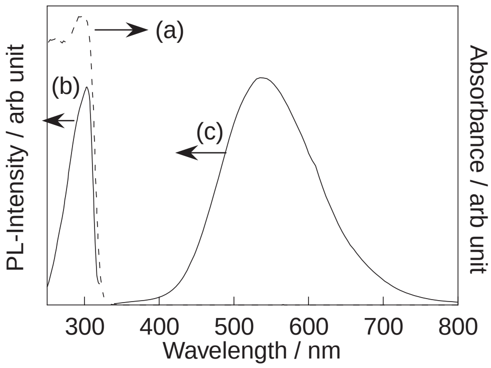

Figure 1. (a) A diffuse reflection spectrum at room temperature, (b) excitation, and (c) emission spectra at 77 K of $Ba_5Nb_4O_{15}$.

Table 1. Photocatalytic water splitting over $Ba_5Nb_4O_{15}$[a]

Preparation method	Calcination condition	S.A. /$m^2\,g^{-1}$	NiO /wt %	Pre-treatment[b]	Activity /μmol h^{-1}	
					H_2	O_2
SSR	1473 K, 10 h	0.7	None	No	10	3
			0.2	No	70	35
			0.2	Yes	650	245
PC	973 K, 10 h	14.5	None	No	3	0
			0.1	Yes	1393	669
			0.7	Yes	2366	1139
	1073 K, 5 h	7.2	0.1	Yes	1041	497
			0.7	Yes	2229	1106
	1273 K, 5 h	1.9	0.1	Yes	939	453

[a]Catalyst (0.5 g), pure water (380 mL), inner irradiation cell made of quartz, 400-W high-pressure mercury lamp. [b]H_2 reduction at 773 K for 2 h and subsequent O_2 oxidation at 473 K for 1 h.

activation pretreatment.[2]

The activity of $NiO/Ba_5Nb_4O_{15}$ prepared by the PC method was higher than that prepared by the SSR method when the calcination condition and the amount of NiO were optimized for each method. Figure 2 shows SEM images of $Ba_5Nb_4O_{15}$ prepared by SSR and PC methods. The particle size of $Ba_5Nb_4O_{15}$ prepared by the SSR method was a few micrometers while that by the PC method was about 100–200 nm. Thus, it was revealed that the particle size of $Ba_5Nb_4O_{15}$ was remarkably reduced by the PC method. The photogenerated carriers have to arrive at the external surface to induce a photocatalytic reaction, except for photocatalysts possessing hydrated interlayer spaces, such as $K_4Nb_6O_{17}$ and $K_2La_2Ti_3O_{10}$.[1] Although $Ba_5Nb_4O_{15}$ possesses a layered structure, its interlayer space is not hydrated as well as $Sr_2Nb_2O_7$. Therefore, the small particle size obtained by the PC method is favorable for photocatalytic performance because photogenerated carriers easily reach the surface. Moreover, plate-like crystals were dominantly obtained by the PC method, implying selective growth of slanted perovskite sheets along a (111) plane. Therefore, the activity of the sample prepared by the PC method was higher than that by the SSR method.

The optimized NiO (0.7 wt %)/$Ba_5Nb_4O_{15}$ photocatalyst steadily produced H_2 and O_2 at the rates of 2.4 and 1.2 mmol/h, respectively, as shown in Figure 3. After 4.5 h of irradiation, 10.9 mmol of H_2 and 5.3 mmol of O_2 produced. The turnover number of the amount of reacted electrons/holes to the molar quantity of $Ba_5Nb_4O_{15}$ was 51. It clearly indicated that the reaction proceeded photocatalytically. The apparent quantum yield was 8% at 270 nm.

In conclusion, $Ba_5Nb_4O_{15}$ with a characteristic perovskite structure and a green photoluminescent property at 77 K was found to be a new niobate photocatalyst material for water splitting. $NiO/Ba_5Nb_4O_{15}$ was a highly efficient photocatalyst among niobates when the activation pretreatment was carried out. The PC-method was superior to the SSR method for preparation of the $Ba_5Nb_4O_{15}$ photocatalyst. The framework of the perovskite structure is distorted,[16] resulting in appearance of polarization as observed for $Sr_2Nb_2O_7$.[6] It is considered that this characteristic structure of the perovskite layer brings out the high photocatalytic ability.

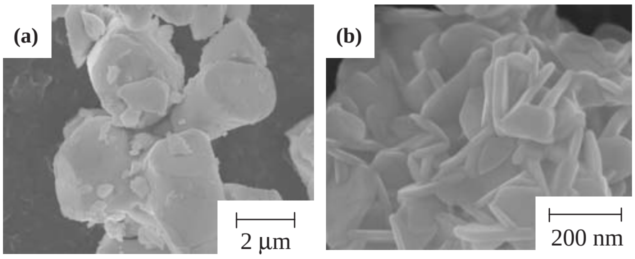

Figure 2. Scanning electron microscope photographs of $Ba_5Nb_4O_{15}$ prepared by (a) SSR and (b) PC methods (1073 K, 5 h).

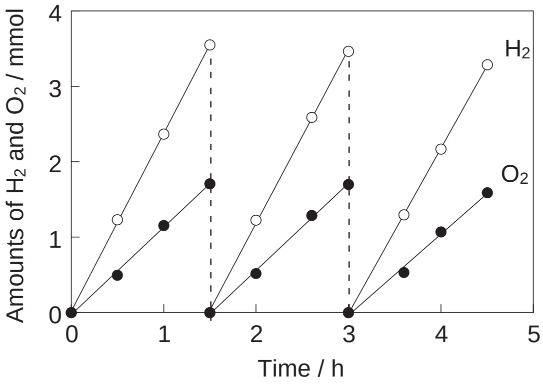

Figure 3. Photocatalytic water splitting over pretreated NiO (0.7 wt %)/$Ba_5Nb_4O_{15}$. Catalyst (0.5 g), pure water (380 mL), inner irradiation cell made of quartz, 400-W high-pressure mercury lamp.

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