Water Splitting into H_2 and O_2 over $Cs_2Nb_4O_{11}$ Photocatalyst

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Photophysical and photocatalytic properties of $Cs_2Nb_4O_{11}$ consisting of NbO_6 octahedra and NbO_4 tetrahedra were investigated. The band gap of $Cs_2Nb_4O_{11}$ was 3.7 eV. Broad blue photoluminescence was observed at 77 K. Pretreated NiO-loaded $Cs_2Nb_4O_{11}$ showed a high activity for water splitting under UV-light irradiation.

It has been reported that some oxides based on d^0 and d^{10} metal ions can decompose water into H_2 and O_2 in a stoichiometric ratio under UV irradiation.[1–7] In particular, many tantalates are highly active photocatalysts for water splitting.[2,5,6] For example, $NiO/NaTaO_3$ doped with lanthanum shows a remarkably high activity, and its apparent quantum yield is 56% at 270 nm.[6] In the case of niobates of the same group as tantalates, $A_4Nb_6O_{17}$ (A = K and Rb),[1] $ZnNb_2O_6$,[8] and $Sr_2Nb_2O_7$[9] have been reported as active photocatalysts for water splitting. The band gaps of niobates are usually narrower than those of tantalates, because the levels of conduction bands consisting of Nb4d are more positive than those of Ta5d. Therefore, niobates can respond to longer wavelength than tantalates. On the other hand, there are some reports that the oxides with characteristic structures such as $A_4Nb_6O_{17}$ (A = K and Rb) with a layer structure,[1] $BaTi_4O_9$ with a tunneling structure,[10] and $K_3Ta_3Si_2O_{13}$ with a one dimensional structure[5] function as photocatalysts for water splitting. $Cs_2Nb_4O_{11}$ possesses a unique structure consisting of NbO_6 octahedra and NbO_4 tetrahedra as shown in Figure 1.[11] The unique structure interests us in its photophysical and photocatalytic properties. In the present paper, we report photophysical properties and photocatalytic activity for water splitting on $Cs_2Nb_4O_{11}$.

$Cs_2Nb_4O_{11}$ powder was prepared from Cs_2CO_3 (Kanto Chemical; 98.0%), and Nb_2O_5 (Kanto Chemical; 99.95%) by a conventional solid state reaction. The starting materials were mixed in a mortar and the mixture was calcined at 1173 K in air using a platinum crucible. The excess amount of cesium was added to compensate the volatilization. The excess cesium was washed out with water after the synthesis. 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 200 Torr of H_2 at 773 K for 2 h followed by oxidation with 100 Torr of O_2 at 373–673 K for 1 h was carried out for $NiO/Cs_2Nb_4O_{11}$, 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 (Spex; Fluorolog). Water splitting reactions were carried out in a gas-closed circulation system. The photocatalyst powder (0.5 g) was dispersed in pure water (360 mL) or an aqueous CsOH solution by a magnetic stirrer in an inner irradiation reaction cell made of Pyrex or quartz equipped with a 400-W high-pressure mercury lamp. The amounts of evolved H_2 and O_2 were determined using online gas chromatography (Shimadzu; MS-5A column, TCD, Ar carrier).

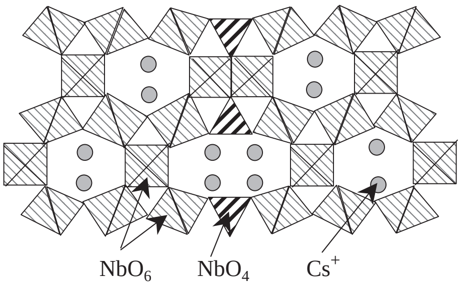

Figure 1. Crystal structure of $Cs_2Nb_4O_{11}$.[11]

Figure 2 shows a diffuse reflection and photoluminescence spectra of $Cs_2Nb_4O_{11}$. The band gap was estimated to be 3.7 eV from the onset of absorption (340 nm). The energy gap between HOMOs and LUMOs of NbO_6 units would be narrower than that of NbO_4. Therefore, although the energy state of NbO_6 is mixed with that of NbO_4, the Nb4d orbital of the NbO_6 unit predominantly contributes to the formation of the conduction band minimum. $Cs_2Nb_4O_{11}$ showed broad blue emission with a maximum at 440 nm. The onset of the excitation spectrum agreed with that of the absorption spectrum. Niobate photocatalysts reported for water splitting show photoluminescence at 77 K.[8,9,12] Moreover, many tantalate photocatalysts for water splitting also show photoluminescence.[5] Therefore, the photoca-

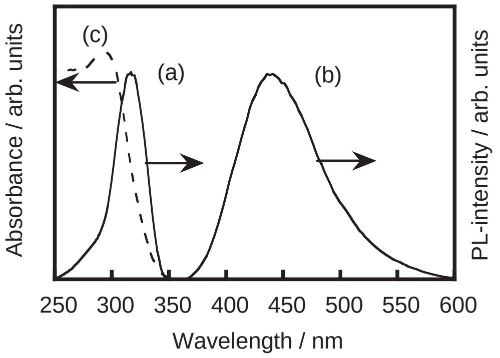

Figure 2. Photoluminescence spectra at 77 K (solid line): (a) an excitation spectrum monitored at 442 nm and (b) an emission spectrum excited at 315 nm, and (c) a diffuse reflection spectrum (broken line) of $Cs_2Nb_4O_{11}$.

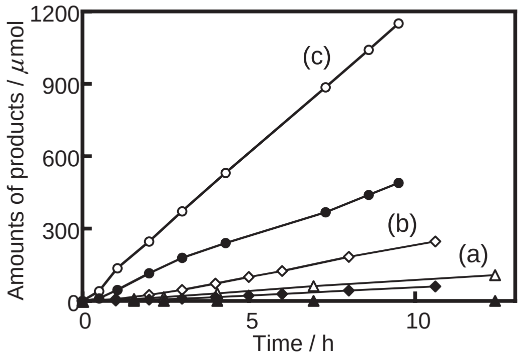

Figure 3. Photocatalytic water splitting over $Cs_2Nb_4O_{11}$: (a) native $Cs_2Nb_4O_{11}$, (b) nontreated NiO (1.5 wt %)/$Cs_2Nb_4O_{11}$, and (c) pretreated NiO (1.5 wt %)/$Cs_2Nb_4O_{11}$. Catalyst (0.5 g), 1 mmol/L of an aqueous CsOH (360 mL), inner irradiation reaction cell made of Pyrex, 400-W high-pressure mercury lamp. Open marks: H_2 and closed marks: O_2.

talytic activity of $Cs_2Nb_4O_{11}$ for water splitting was expected.

Figure 3 shows photocatalytic water splitting on $Cs_2Nb_4O_{11}$ using an inner irradiation reaction cell made of Pyrex. NiO/$Cs_2Nb_4O_{11}$ produced H_2 and O_2 even without activation pretreatment although native $Cs_2Nb_4O_{11}$ showed no activity. The activity of the NiO/$Cs_2Nb_4O_{11}$ photocatalyst was increased by 5 times when the pretreatment was carried out. Thus, $Cs_2Nb_4O_{11}$ was found to be a new niobate photocatalyst for water splitting.

The activation pretreatment is generally necessary for NiO-loaded titanate and niobate photocatalysts to obtain high activities.[1] The pretreatment of reduction followed by reoxidation forms double layered NiO/Ni particles which facilitate the electron transfer from the photocatalyst material to the NiO cocatalysts of the H_2 evolution sites. The pretreatment conditions, especially of the reoxidation process, significantly affect the activity. The present NiO/$Cs_2Nb_4O_{11}$ photocatalyst also required the pretreatment to obtain high activities as well as usual niobate photocatalysts. We examined the effect of the reoxidation temperature following the reduction treatment at 773 K on the photocatalytic activity of the NiO/$Cs_2Nb_4O_{11}$ photocatalyst as shown in Figure 4. All pretreated NiO/$Cs_2Nb_4O_{11}$ photocatalysts produced H_2 and O_2 in a stoichiometric ratio. The optimum reoxidation temperature was 573 K. It would be due to that the NiO layers in the NiO/Ni particles got suitable thickness and good crystallinity when NiO/$Cs_2Nb_4O_{11}$ was reoxidized at 573 K.

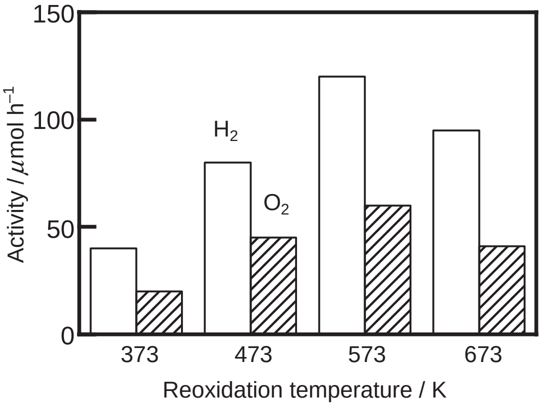

Figure 4. Effect of reoxidation temperature on the photocatalytic water splitting on NiO (0.3 wt %)/$Cs_2Nb_4O_{11}$ reduced at 773 K. Catalyst (0.5 g), 1 mmol/L of an aqueous CsOH (360 mL), inner irradiation reaction cell made of Pyrex, 400-W high-pressure mercury lamp.

In the next step, we investigated the optimum amount of NiO. The NiO (0.2 wt %)/$Cs_2Nb_4O_{11}$ photocatalyst showed the highest activity. As the amount of loaded NiO was increased, an active site to produce H_2 should be increased, resulting in an increase in the activities. On the other hand, extra loading of NiO should cause the shielding of the light and undesirable covering of oxidation sites.

The optimized NiO/$Cs_2Nb_4O_{11}$ photocatalyst produced H_2 and O_2 at the rates of 212 and 98.3 μmol/h at the initial stage, respectively. After 22 h of irradiation, 3.3 mmol of H_2 and 1.5 mmol of O_2 were produced. The turnover number of the amount of reacted electrons/holes to the molar quantity of $Cs_2Nb_4O_{11}$ was 11 at 22 h of the reaction time. It clearly indicated that the reaction proceeded photocatalytically. On the other hand, when a quartz cell was used, the rates of H_2 and O_2 evolution were increased by an increase in the number of absorbed photons and were 1.7 and 0.8 mmol/h, respectively. The activity of $Cs_2Nb_4O_{11}$ was as high as that of $K_4Nb_6O_{17}$ (H_2: 1.8 and O_2: 0.9 mmol/h),[1] and much higher than those of $ZnNb_2O_6$ (H_2: 54 and O_2: 21 μmol/h)[8] and $Sr_2Nb_2O_7$ (H_2: 110 and O_2: 36 μmol/h),[9] which were measured under similar experimental conditions to that of the present study.

In conclusion, $Cs_2Nb_4O_{11}$ with a unique structure and a blue photoluminescent property at 77 K was found to be a new niobate photocatalyst material for water splitting. It is reported that $K_4Nb_6O_{17}$ also possesses a high photocatalytic activity and a blue photoluminescence property.[12] These results suggest that there is the relationship between the photocatalytic activity and the blue photoluminescence property for niobate photocatalysts.

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References

1 K. Domen, J. N. Kondo, M. Hara, and T. Takata, *Bull. Chem. Soc. Jpn.*, **73**, 1307 (2000).
2 K. Shimizu, Y. Tsuji, M. Kawakami, K. Toda, T. Kodama, M. Sato, and Y. Kitayama, *Chem. Lett.*, **2002**, 1158.
3 A. Kudo, H. Kato, and I. Tsuji, *Chem. Lett.*, **33**, 1534 (2004), and references therein.
4 V. R. Reddy, D. W. Hwang, and J. S. Lee, *Catal. Lett.*, **90**, 39 (2003).
5 H. Kato and A. Kudo, *Catal. Today*, **78**, 561 (2003), and references therein.
6 H. Kato, K. Asakura, and A. Kudo, *J. Am. Chem. Soc.*, **125**, 3082 (2003).
7 J. Sato, H. Kobayashi, K. Ikarashi, N. Saito, H. Nishiyama, and Y. Inoue, *J. Phys. Chem. B*, **108**, 4369 (2004), and references therein.
8 A. Kudo, S. Nakagawa, and H. Kato, *Chem. Lett.*, **1999**, 1197.
9 A. Kudo, H. Kato, and S. Nakagawa, *J. Phys. Chem. B*, **104**, 571 (2000).
10 S. Ogura, K. Sato, and Y. Inoue, *Phys. Chem. Chem. Phys.*, **2**, 2449 (2000).
11 P. M. Gasperin, *Acta Crystallogr.*, **B37**, 641 (1981).
12 A. Kudo and T. Sakata, *J. Phys. Chem.*, **100**, 17323 (1996).

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