Overall Water Splitting into H_2 and O_2 under UV Irradiation on NiO-loaded $ZnNb_2O_6$ Photocatalysts Consisting of d^{10} and d^0 Ions

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(Received July 19, 1999; CL-990632)

NiO-loaded $ZnNb_2O_6$ photocatalysts showed an activity for decomposition of pure water into H_2 and O_2 under band gap irradiation (hν>4.0 eV). This oxide photocatalyst is a new type of a photocatalyst material from the view point of the component because it consists of d^{10} and d^0 metal ions.

Water splitting on photocatalysts has attracted attention as a photon energy conversion reaction. TiO_2[1-4] and $SrTiO_3$[5] have been employed as photocatalyst materials for the water splitting for a long time. Recently, some new photocatalyst materials with high activities for the water splitting ($K_4Nb_6O_{17}$,[6] $Na_2Ti_6O_{13}$,[7] $BaTi_4O_9$,[8] ZrO_2,[9] Ta_2O_5,[10] $K_2La_2Ti_3O_{10}$,[11] metal tantalates,[12] and $Sr_2Nb_2O_7$[13]) have been found. These oxide photocatalysts consist of d^0 transition metal ions such as Ti^{4+} and Nb^{5+} and their mixed oxides with s-block ions. On the other hand, some oxides consisting of d^{10} metal ions such as Zn^{2+} and In^{3+} show activities for H_2 or O_2 evolution from aqueous solutions containing sacrificial reagents.[14-17] However, they are not active for the water splitting into H_2 and O_2. It is important to investigate photocatalytic activities of mixed oxides consisting of metal ions with various combinations in order to get information for the development of new photocatalyst materials. In the present paper, the water splitting on a new $ZnNb_2O_6$ photocatalyst consisting of d^{10} and d^0 metal ions is reported.

$ZnNb_2O_6$ powder was prepared by a conventional solid state reaction of Nb_2O_5 (Kanto Chemical, purity; 99.95%) with ZnO (Kanto Chemical, purity; 99.0%) by calcination at 1373 K for 20 h in air in a platinum crucible. $ZnNb_2O_6$ with a columbite structure was confirmed by X-ray diffraction (Rigaku, RINT-1400).[18,19] NiO was loaded by an impregnation method from $Ni(NO_3)_2$. Pretreatment of photocatalysts and photocatalytic water splitting were conducted in a closed gas circulation system. H_2 reduction and subsequent O_2 oxidation at appropriate temperatures were carried out as the pretreatment. Photocatalyst powder (1 g) was dispersed in pure water (370 ml) by a magnetic stirrer and irradiated by 450 W high pressure mercury lamp (Ushio, UM-452). Amounts of H_2 and O_2 evolved were determined by using a gas chromatograph (Shimadzu, GC-8A). A diffuse reflectance spectrum was obtained by using a UV-VIS-NIR spectrometer (JASCO, Ubest V-570). Photoluminescence spectra were measured by a fluorospectrometer (Spex, Fluoromax).

Figure 1 shows diffuse reflectance and photoluminescence spectra of $ZnNb_2O_6$ at room temperature. $ZnNb_2O_6$ has been studied as a phosphor which shows blue emission at room temperature.[20,21] The emission spectrum at 450 nm and excitation spectrum with the onset at 305 nm were observed as had been reported.[20,21] The excitation spectrum was similar to the diffuse reflectance spectrum. The band gap was estimated to be 4.0 eV from the onsets of the spectra.

Table 1 shows the activities of photocatalytic decomposition of pure water on native and NiO-loaded $ZnNb_2O_6$ photocatalysts.

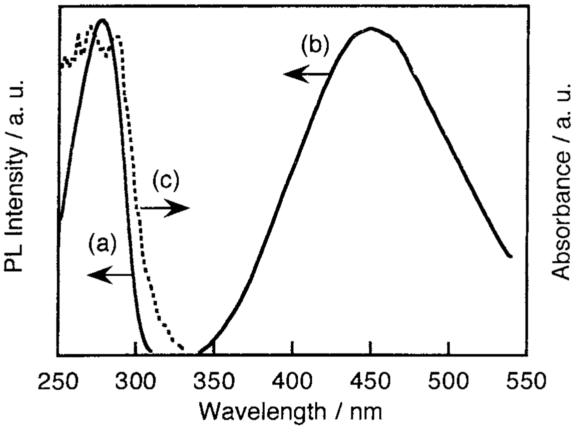

Figure 1. (a) Excitation, (b) emission, and (c) diffuse reflectance spectra of $ZnNb_2O_6$ at 300 K.

Table 1. Photocatalytic water splitting on $ZnNb_2O_6$ powder

Catalyst	Pretreatment	Activity / μmol/h	
		H_2	O_2
$ZnNb_2O_6$	non	0.6	0
$NiO/ZnNb_2O_6$ [a]	non	9	3.4
$NiO/ZnNb_2O_6$ [a]	R573-O473 [b]	54	21
$NiO/ZnNb_2O_6$ [a]	R773-O473 [b]	24	8

[a] The amount of NiO loaded; 0.5 wt%. [b] R and O represent temperature in Kelvin for H_2 reduction and O_2 oxidation on the pretreatment, respectively.

The activity of the native $ZnNb_2O_6$ powder was negligible. The $NiO/ZnNb_2O_6$ catalyst produced H_2 and O_2 from pure water simultaneously even without pretreatment. Moreover, the activity was drastically increased by pretreatment as shown in Figure 2 and Table 1. It is reasonable judging from the flat band potential (-0.4 eV vs. NHE)[22] that the $ZnNb_2O_6$ photocatalyst is active for the water splitting and that the pretreatment is needed for the $NiO/ZnNb_2O_6$ photocatalyst to show the high activity. In general, the optimum pretreatment temperature for H_2 reduction is 773 K for NiO-loaded photocatalysts such as TiO_2 and $SrTiO_3$.[2,5,6,10,11,13] In contrast, 573 K was better than 773 K for the reduction temperature of the $NiO/ZnNb_2O_6$ photocatalyst because the zinc in $ZnNb_2O_6$ was reduced at 773 K to be volatilized and the crystal structure was partly collapsed.

The authors have recently reported photocatalytic activities of various tantalate photocatalysts.[12] Among them, the activity of native $ZnTa_2O_6$ was negligible as well as $ZnNb_2O_6$. However, the $NiO/ZnTa_2O_6$ photocatalyst with a 4.4 eV band gap was active for the water splitting (H_2; 15 μmol/h, O_2; 6 μmol/h). It is noteworthy that, although the crystal structure of $ZnNb_2O_6$ is different from that of $ZnTa_2O_6$,[19] both $ZnNb_2O_6$ and $ZnTa_2O_6$ in

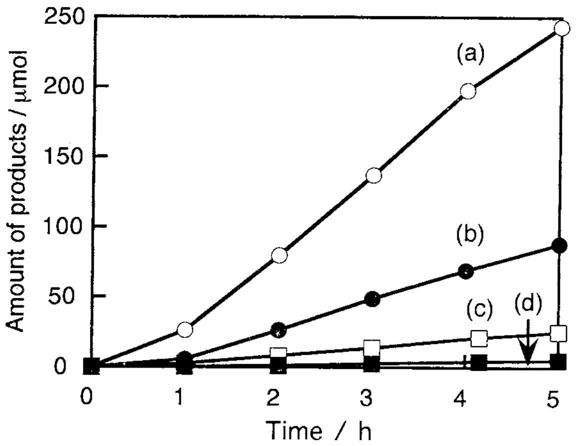

Figure 2. Photocatalytic decomposition of pure water on nontreated and pretreated NiO (0.5 wt%) / $ZnNb_2O_6$ powder. (a) H_2 and (b) O_2 for the pretreated catalyst, (c) H_2 and (d) O_2 for the nontreated catalyst.
Catalyst; 1 g, water; 370 ml, light source; 450 W high pressure mercury lamp, cell; inner irradiation reaction cell made of quartz.

the same family possessed the photocatalytic activities for water splitting.

$K_4Nb_6O_{17}$ with a layered structure has been reported as a niobate photocatalyst which is active for the water splitting.[6] $Sr_2Nb_2O_7$ and $Ca_2Nb_2O_7$ with layered perovskite structures have recently been found to show the high activity for the water splitting.[13] These niobate photocatalysts are layered oxides consisting of Nb^{5+} with d^0 configuration and s-block ions. In contrast, $ZnNb_2O_6$ is a new bulk type of photocatalyst materials from the view point of constituent metal ions as well as $ZnTa_2O_6$ because it consists of d^0 and d^{10} metal ions. Although the $ZnNb_2O_6$ photocatalyst works only under UV irradiation, the result obtained in the present study indicates the possibility of other materials with some combinations of metal cations except for the combination of d^0 and s-block ions for the photocatalytic water splitting.

In mixed oxides of s-block and d^0 transition metal ions such as $SrTiO_3$, in general, the valence band is formed by O_{2p} while the conduction band consists of the vacant d orbital of the transition metal ion. In mixed oxides of d^0 and d^{10} metal ions, the full d orbital in the d^{10} metal ion may form a valence band while the vacant s orbital in the d^{10} metal ion may form the conduction band. In $ZnNb_2O_6$, the full Zn_{3d} orbital seems to form the filled band more deeply (more positive potential) than O_{2p} because Zn^{2+} hardly becomes trivalent. Therefore, the valence band is due to O_{2p}. On the other hand, the vacant Zn_{4s} orbital may take part in the formation of the conduction band with the Nb_{4d} orbital.

This work was supported by New Energy and Industrial Technology Development Organization (NEDO)/Research Institute of Innovate Technology for the Earth (RITE), Core Research for Evolutional Science and Technology (CREST), and a Grant-in-Aid (No. 11640601) from the Ministry of Education, Science, Sports, and Culture, Japan.

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