# Energy Structure and Photocatalytic Activity of Niobates and Tantalates Containing Sn(II) with a $5s^2$ Electron Configuration

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$SnNb_2O_6$ (BG = 2.3 eV) containing $Sn^{2+}$ with a $5s^2$ electron configuration showed the photocatalytic activity for $H_2$ evolution from an aqueous methanol solution under visible light irradiation ($\lambda > 420$ nm) in the presence of a Pt cocatalyst. The energy structure calculation by the plane wave based density functional method revealed that the conduction and valence bands consisted of Nb4d and Sn5s orbitals, respectively. The valence band level consisting of the Sn5s orbitals was more negative than that consisting of O2p orbitals resulting in $SnNb_2O_6$ being responsive to visible light.

Photocatalytic water splitting is an important theme in terms of a light energy conversion to a chemical energy. Some metal oxide photocatalysts which can split water into $H_2$ and $O_2$ in a stoichiometric amount with high efficiencies under UV light irradiation have been reported.[1–3] Some metal sulfides such as CdS and $AgInZn_7S_9$ have also been reported as photocatalysts which can efficiently reduce water to form $H_2$ under visible light irradiation in the presence of sacrificial reagents.[4,5] Recently, metal oxynitride and oxysulfide have also been found to be active photocatalysts.[6,7] However, metal oxide photocatalysts efficiently working for $H_2$ evolution under visible light irradiation have not been developed even in the presence of sacrificial reagents.

Valence bands of many oxide semiconductor photocatalysts consist of O2p orbitals and their potentials (ca. 3 eV) are considerably more positive than an oxidation potential of water to form $O_2$ ($E^\circ O_2/H_2O = 1.23$ eV at pH 0). If a conduction band of a photocatalyst has a potential enough for $H_2$ formation by the reduction of water ($E^\circ H_2O/H_2 = 0$ eV at pH 0), the band gap is inevitably larger than 3 eV. It results in that the oxide photocatalyst responds to only UV light. Therefore, the valence band of which the potential is more negative than that consisting of O2p orbitals has to be formed with some other orbitals.

$BiVO_4$ (BG = 2.4 eV) shows the high activity for $O_2$ evolution from an aqueous $AgNO_3$ solution under visible light irradiation.[8] The visible light response is due to the band structure in which the valence band consists of $Bi^{3+}$ with a $6s^2$ electron configuration. Therefore, the present auothors have paid attention to Sn(II) with a $5s^2$ electron configuration, similarly to $Bi^{3+}$, as an element which could form a valence band. In the present paper, photocatalytic $H_2$ evolution from an aqueous methanol solution on niobates and tantalates containing Sn(II) were studied.

$Sn_2Nb_2O_7$, $Sn_2Ta_2O_7$, $SnNb_2O_6$, and $SnTa_2O_6$ were prepared by solid-state reactions. Starting materials used were as follows; SnO (Wako Pure Chemical, purity; 99.9%), $Nb_2O_5$ (Kanto Chemical, purity; 99.95%), and $Ta_2O_5$ (Rare Metallic, purity; 99.99%). Mixtures of the starting materials were calcined at 973–1273 K for 6–40 h in a nitrogen flow using an alumina boat. Diffuse reflectance spectra were measured using a UV–vis NIR spectrometer with an integrating sphere (JASCO, Ubest-570). Photocatalytic reactions of $H_2$ evolution from an aqueous methanol solution (10 vol %) were conducted in a gas-closed circulation system. The photocatalyst powder (0.3 g) was dispersed in the solution (150 mL) by a magnetic stirrer in a cell with a top-window made of Pyrex. Pt cocatalysts were loaded in situ by a photodeposition method using $H_2PtCl_6$. The light source was a 300 W Xe illuminator (ILC technology; CERMAX, LX300F) attached with cut-off filters (Kenko). The amounts of $H_2$ evolved were determined using gas chromatography (Shimadzu; GC-8A, TCD, Ar carrier). The plane wave based density functional method was carried out for $SnNb_2O_6$ employing the CASTEP program.[9] The core electrons were replaced with the ultrasoft core potentials, and the valence electronic configurations for Sn, Nb, and O atoms were $5s^25p^2$, $4s^24p^65s^14d^4$, and $2s^22p^4$, respectively. The calculations were carried out using the primitive unit cell of $(SnNb_2O_6)_2$, and the number of occupied molecular orbital was 66.

Table 1 shows photocatalytic $H_2$ evolution from an aqueous methanol solution under visible light irradiation ($\lambda > 420$ nm) or UV light irradiation ($\lambda > 300$ nm) on $Sn_2Nb_2O_7$, $Sn_2Ta_2O_7$, $SnNb_2O_6$, and $SnTa_2O_6$. $Pt/Sn_2Ta_2O_7$ showed the photocatalytic activity for $H_2$ evolution under UV light irradiation. In contract, $Pt/Sn_2Nb_2O_7$ didn't show the photocatalytic activity even if $Sn_2Nb_2O_7$ has the same pyrochlore structure as $Sn_2Ta_2O_7$. This difference in the photocatalytic activity between niobates and tantalates is probably due to the difference in their conduction band levels. $Pt/SnNb_2O_6$ showed the photocatalytic activity for $H_2$ evolution under visible light irradiation. On the other hand, $Pt/SnTa_2O_6$ didn't show the activity. The non-activity would be due to defects working as recombination centers between photogenerated electrons and holes because $SnTa_2O_6$ was prepared at higher temperature (1273 K) and for longer time (40 h) than other niobates and tantalates. In fact, preparation at higher temperature and for longer time for $SnNb_2O_6$ and $Sn_2Ta_2O_7$ gave low activities.

The rate of $H_2$ evolution was about 18 $\mu mol\,h^{-1}$ at the initial stage over the optimized $Pt/SnNb_2O_6$ photocatalyst as shown in Figure 1. The turnover number of the amount of reacted elec-

**Table 1.** Photocatalytic activities of niobates and tantalates containing Sn(II) for $H_2$ evolution from an aqueous methanol solution

| Photocatalyst | Preparation condition | Band gap/eV | Incident light/nm | Activity /µmol h$^{-1}$ |
|---|---|---|---|---|
| $Sn_2Ta_2O_7$ | 1073 K/5 h | 3.0 | $\lambda > 300$ | 2.1 |
| $Sn_2Nb_2O_7$ | 1073 K/7 h | 2.3 | $\lambda > 420$ | 0 |
| $SnTa_2O_6$ | 1273 K/40 h | 3.1 | $\lambda > 300$ | 0 |
| $SnNb_2O_6$ | 1173 K/6 h | 2.3 | $\lambda > 420$ | 18 |

trons to the number of Sn on the surface was 180 at 10 h of the reaction time. The employed number of Sn was calculated by taking 1.3 m$^2$/g of a BET surface area and a (011) plane of the $SnNb_2O_6$ crystal into account. The X-ray diffraction pattern was unchanged after the reaction. The $H_2$ evolution was not observed under dark condition. These results concluded that the $H_2$ evolution proceeded photocatalytically. In contrast, the $SnNb_2O_6$ photocatalyst didn't show the activity for overall water splitting or $O_2$ evolution from an aqueous $AgNO_3$ solution.

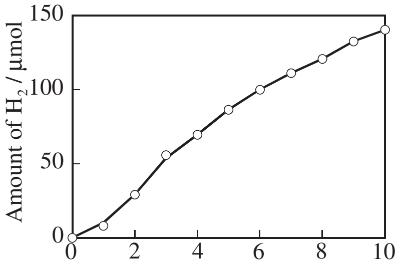

**Figure 1.** Photocatalytic $H_2$ evolution from an aqueous methanol solution (150 ml) under visible light irradiation ($\lambda >$ 420 nm) over Pt (0.3 wt%)/$SnNb_2O_6$ powder (0.3 g).

Figure 2 shows the wavelength dependency for the $H_2$ evolution and a diffuse reflectance spectrum of $SnNb_2O_6$ which showed the photocatalytic activity under visible light irradiation. The wavelength was controlled with cut-off filters. A wide absorption band with an onset around 540 nm and a sharp absorption edge were observed. The shape of the spectrum indicated that the absorption band was due to not an impurity level but a band gap transition. The band gaps of oxide photocatalysts in which the conduction and valence bands consist of Nb4d and O2p orbitals, respectively, are usually larger than 3 eV. In contrast, the band gap of $SnNb_2O_6$ was estimated to be 2.3 eV; that was a small value for niobates. The calculation of the band structure by the density functional method indicated that the conduction band of the $SnNb_2O_6$ photocatalyst consisted of Nb4d orbitals while the valence band was formed with a hybrid orbital of Sn5s and O2p. This valence band level was more negative than that consisting of only O2p orbitals. It has been clarified that the wide absorption band in the visible light region of the $SnNb_2O_6$ photocatalyst was due to the transition from the valence band formed with Sn5s orbitals to the conduction band consisting of Nb4d orbitals. The onset of the wavelength dependency agreed with that of the diffuse reflectance spectrum indicating that the photocatalysts reaction proceeded with the band gap excitation.

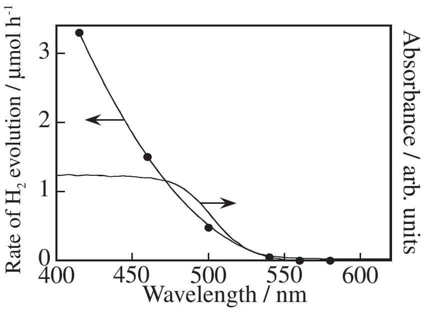

**Figure 2.** Wavelength dependency for the $H_2$ evolution and a diffuse reflection spectrum of $SnNb_2O_6$ photocatalyst.

In conclusion, the rare oxide photocatalyst which is active for $H_2$ evolution under visible light irradiation $SnNb_2O_6$, has been developed as an active photocatalyst for $H_2$ evolution from an aqueous methanol solution under visible light irradiation ($\lambda > 420$ nm). It is noteworthy that the valence band was formed with Sn5s orbitals resulting in the decrease in the band gap of oxide photocatalysts. $Sn^{2+}$ with a $5s^2$ electron configuration is an effective element for forming a valence band in oxide photocatalysts as well as previously reported $Bi^{3+}$.[8]

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