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## Novel Photocatalyst Based on Metastable ZrSnO<sub>4</sub> Solid for Hydrogen and Oxygen Evolutions

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Photocatalytic activity has been demonstrated for  $ZrSnO_4$  by controlling the bandgap and the bottom of the conduction band of  $ZrO_2$  and  $SnO_2$ . The single-phase with the metastable  $ZrSnO_4$  solid was successfully obtained, and  $ZrSnO_4$  exhibited the photocatalytic activity for hydrogen and oxygen production from water under the UV irradiation.

Keywords: Photocatalyst, Hydrogen production, Oxygen production

In recent years, since emission of carbon dioxide and depletion of fossil fuels are serious problems, clean and renewable energy source is required. Hydrogen has been paid great attention as a new energy carrier, because the emission gas is only water. Especially, fuel cell converts from hydrogen fuel into electric energy effectively, and this device has been already commercialized as a hydrogen fuel cell vehicle. Although the hydrogen gas is generally produced by steam reforming method from fossil fuels involved with the generation of carbon dioxide, this process does not solve the fundamental problems. Electrolysis of water is another method to produce hydrogen without emitting carbon dioxide; however it requires electric power source. Photocatalytic hydrogen production from water by using solar energy is an ideal method, that is, clean, inexhaustible abundant, sustainable, and environmentally harmonious method [1-4]. For the water splitting, both the reduction and oxidation potentials of water have to be located within the bandgap of the photocatalyst. In other words, the bottom of the conduction band has to be more negative than the reduction potential of water to produce hydrogen (0 V vs normal hydrogen electrode [NHE]), and the top of the valence band has to be more positive than the oxidation potential of water to produce oxygen (+1.23 V vs NHE). Since photo-induced water splitting on rutile TiO<sub>2</sub> electrodes was demonstrated in 1972 [5], photocatalytic activity of semiconductor has been extensively studied. Almost efficient photocatalytic materials contain d<sup>0</sup> or d<sup>10</sup> metal ions [3-8], such as Ti<sup>4+</sup>, Zr<sup>4+</sup>, and Nb<sup>5+</sup> for d<sup>0</sup> ions and Ga<sup>3+</sup>, Sn<sup>4+</sup>, and Sb<sup>5+</sup> for d<sup>10</sup> ions. Their metal oxides hold electronic configurations suitable for water splitting, because the top of valence band formed by O 2p orbitals are generally located at ca. +3 V or higher vs. NHE, which exceeds the oxidation potential of water (+1.23 V). Therefore, the level of the conduction band and the bandgap energy are the key factors for the metal oxides to drive the water splitting reaction.

In order to develop a novel photocatalyst for water splitting, we focused on  $Zr^{4+}$  and  $Sn^{4+}$  as the d<sup>0</sup> and d<sup>10</sup> metal ions, respectively.  $ZrO_2$  has large bandgap of 5.0 eV [9], which leads to a high photoreduction ability. Nevertheless, the excitation of electron requires high energy photon, i.e., short-

wavelength light below ca. 248 nm. For SnO<sub>2</sub>, the bandgap (3.1 eV [8]) is narrow compared to  $ZrO_2$  and applied as a photocatalyst for organic compounds decomposition [10]. However, SnO<sub>2</sub> cannot reduce water to hydrogen, because the bottom of the conduction band is more positive than the redox potential of  $H^+/H_2$ . Therefore, the oxides composed of  $Zr^{4+}$ and  $\operatorname{Sn}^{4+}$  is expected to possess both the photoreduction ability and the narrow bandgap. In the previous studies, however, it is difficult to obtain a single-phase of Zr-Sn oxide from the phase diagram of ZrO<sub>2</sub>-SnO<sub>2</sub> binary system due to the high stability of ZrO<sub>2</sub> and SnO<sub>2</sub> crystal structure [11-14]. While only few studies of metastable ZrSnO<sub>4</sub> have been reported [15,16], its crystal structural properties still remain unclear. Therefore, we synthesized the metastable  $ZrSnO_4$  solid by the co-precipitation method, to apply for its crystal structural analysis and photocatalytic activity for water splitting was investigated.

 $ZrSnO_4$  was prepared by the co-precipitation method. The ZrSnO<sub>4</sub> precursor was precipitated from ZrOCl<sub>2</sub> and SnCl<sub>2</sub> mixed solution using ammonia solution, and then calcined at various temperatures. Figure 1 shows the thermogravimetricdifferential thermal analysis (TG-DTA) of the ZrSnO4 precursor. At ca. 100 °C, an endothermic peak was observed with an abrupt weight loss due to the vaporization of the adsorbed solvents, such as water and ammonia. A sharp exothermic peak was explicitly observed at 568 °C. From the X-ray powder diffraction (XRD) measurements (Figure S1), a crystalline phase was observed at 600 °C, while the precursor was amorphous phase, suggesting that the exothermic peak was attributed to the crystallization. When calcining over 800 °C, the additional phase of SnO<sub>2</sub> was observed. In addition, for the sample after the TG-DTA up to 1400 °C, the XRD pattern was assigned to be only ZrO<sub>2</sub> and SnO<sub>2</sub> (Figure S2). Therefore, a broad exothermic peak at ca. 900 °C is considered to be attributed to the decomposition of ZrSnO<sub>4</sub>. A slight weight loss during the crystallization and the decomposition might be affected by the decrease of residual chloride ions, where a slight amount of chlorine species (0.65 at%) was detected for the sample calcined at 600 °C by X-ray fluorescence analysis. From these results, the ZrSnO<sub>4</sub> solid solution is the metastable phase, which decomposes at ca. 800 °C.

For the crystalline  $ZrSnO_4$  solid calcined at 600 °C, the XRD pattern was slightly different from the database [16] (Figure S3), while the prepared  $ZrO_2$  and  $SnO_2$  were single-phases of the monoclinic  $ZrO_2$  and the tetragonal  $SnO_2$  phases, respectively (Figure S3). Although a few studies have reported the single-phase of  $ZrSnO_4$  [15,16], the obvious pattern has not been obtained and the structural analysis has not been performed; e.g. the structure of  $ZrSnO_4$  has been



Figure 1. TG-DTA results for the ZrSnO<sub>4</sub> precursor.

assigned as  $\alpha$ -PbO<sub>2</sub>-type phase from the similarity between the observed Debye-Scherrer ring and that of  $ZrTiO_4$  with  $\alpha$ -PbO<sub>2</sub>-type structure [15]. From this reason, it is considered that the observed pattern of ZrSnO<sub>4</sub> was inconsistent with the database as shown in Figure S3; therefore, the Rietveld refinement was carried out to confirm the single-phase and to determine its structural parameters. The result of the Rietveld analysis using RIETAN-FP program [17] is shown in Figure 2, where the cationic ratio of Zr and Sn was determined by Xray fluorescence analysis. Based on the single-phase orthorhombic  $\alpha$ -PbO<sub>2</sub>-type structure (*Pbcn*), the observed pattern was in good agreement with the calculated one, and no impurity phase was confirmed. The structural parameters are listed in Table S1 and the crystal structure is illustrated in the inset of Figure 2 by VESTA software [18]. ZrSnO<sub>4</sub> holds zigzag chains of edge-sharing (Zr,Sn)O<sub>6</sub> octahedra along the caxis, where  $Zr^{4+}$  and  $Sn^{4+}$  occupy the same 4c site. To our best knowledge, this is the first report to reveal the metastable ZrSnO<sub>4</sub> structure by the crystal structural analysis.

Figure 3(a) shows the absorption spectra of  $ZrSnO_4$ ,  $ZrO_2$ , and  $SnO_2$ , estimated by the Kubelka-Munk function from the UV-vis reflectance spectra. From the absorption edge, the



**Figure 2**. Result of Rietveld refinement for  $ZrSnO_4$ . Crystal structure of  $ZrSnO_4$  is shown in the inset.

band gap energies of ZrO<sub>2</sub> and SnO<sub>2</sub> were calculated to be 5.0 and 3.4 eV, which are consistent with the previous studies [8,9]. The band gap energy of  $ZrSnO_4$  (3.9 eV) was almost the medium value between those of ZrO<sub>2</sub> and SnO<sub>2</sub>. Figure 3(b) shows the band positions of ZrSnO<sub>4</sub>, ZrO<sub>2</sub>, and SnO<sub>2</sub>, where the top level of valence band was estimated from UPS measurement. For ZrSnO<sub>4</sub>, the band gap straddles the reduction and oxidation potential of water, which are 0 and +1.23 V vs. NHE, respectively, indicating that the ZrSnO<sub>4</sub> possesses the water splitting property. In addition, ZrSnO<sub>4</sub> exhibited the photoreduction ability of -0.5 V vs. NHE as high as that of  $ZrO_2$ , while the excitation energy for  $ZrSnO_4$  is lower than that for ZrO<sub>2</sub>. Among these samples, SnO<sub>2</sub> showed the lowest excitation energy; however, the bottom level of the conduction band of SnO<sub>2</sub> is more positive than the reduction potential of  $H^+/H_2$ .

The hydrogen production was evaluated by using methanol (10 vol%) as an oxidizable reagent and 0.7 wt% platinum as a co-catalyst for  $ZrSnO_4$ ,  $ZrO_2$ , and  $SnO_2$  under UV irradiation (400 W Hg lamp; 250 - 577 nm), and the results are shown in Figure 4. For  $ZrSnO_4$ , the hydrogen evolution was considerably higher than those of  $ZrO_2$  and  $SnO_2$ . Here,  $ZrO_2$  did not absorb photon effectively due to its large band gap, corresponding to the light of wavelength shorter than ca. 250 nm. In addition, the photocatalytic ability of  $SnO_2$  was not confirmed, because the bottom of the conduction band was more positive than the reduction potential of proton. Therefore, the high photocatalytic activity for  $ZrSnO_4$  is attributed to the narrow band gap compared to  $ZrO_2$  as well as the high photoreduction ability. The rate of



Figure 3. (a) UV-vis absorption spectra and (b) band structures of  $ZrSnO_4$ ,  $ZrO_2$ , and  $SnO_2$ .

hydrogen production exhibited 1909  $\mu$ mol·h<sup>-1</sup>, which was remarkably higher than that of  $ZrO_2$  (396 µmol·h<sup>-1</sup>). The turnover number was estimated from the amount of evolved hydrogen and the amount of ZrSnO<sub>4</sub>, and the result for  $ZrSnO_4$  after the reaction for 2.5 h reached up to ca. 17; i.e., the hydrogen production occurred catalytically. In addition, the collapse of the ZrSnO<sub>4</sub> structure was not observed after the reaction (Figure S4). Under dark condition, the hydrogen evolution was not observed (Figure S5), indicating that hydrogen was produced during photoirradiation. In order to investigate the water oxidation ability of ZrSnO<sub>4</sub>, the photocatalytic oxygen evolution was carried out by using AgNO<sub>3</sub> (0.01 M) as a sacrificial reagent and La<sub>2</sub>O<sub>3</sub> (0.2 g) as a pH buffer. As shown in Figure 5, the oxygen production was clearly observed, and the initial evolution was ca. 116 µmol for 1 h. Here, the oxygen evolution rate decreased with irradiation time, due to the deposition of metallic silver on the photocatalyst. From these results, the ZrSnO<sub>4</sub> solid exhibited the photocatalytic activity to produce hydrogen and oxygen gases from water.

In conclusion, we developed a novel photocatalyst of  $ZrSnO_4$  by the control of the bandgap and the bottom of the conduction band. The single-phase with the metastable  $\alpha$ -PbO<sub>2</sub>-type structure was successfully obtained by a coprecipitation method. The  $ZrSnO_4$  solid exhibited the



**Figure 4**. Hydrogen production from the aqueous methanol solution over  $ZrSnO_4$ ,  $ZrO_2$ , and  $SnO_2$  with 0.7 wt% platinum loading under UV irradiation.



Figure 5. Oxygen evolution from aqueous  $AgNO_3$  solution over  $ZrSnO_4$  under UV irradiation.

photocatalytic activity for hydrogen evolution from water under the UV irradiation, and the ability was higher than the  $ZrO_2$  and  $SnO_2$  cases. Since the evolution of oxygen was also confirmed for  $ZrSnO_4$  under the photoirradiation, the  $ZrSnO_4$ solid is the novel photocatalyst for hydrogen and oxygen productions from water.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.\*\*\*\*\*.

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