Enhancement of Photoelectrochemical Activity of SnS Photoelectrodes using TiO_2, Nb_2O_5, and Ta_2O_5 Metal Oxide Layers

Junie Jhon M. Vequizo[1], Masanori Yokoyama[1], Masaya Ichimura[2], and Akira Yamakata[1,3*]

[1]Quantum Interface Laboratory, Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan

[2]Department of Engineering Physics, Electronics, and Mechanics, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

[3]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

Abstract

SnS fine photoelectrode fabricated by 3-step pulsed electrodeposition was active for H_2 evolution. The incident-photon-conversion-efficiency (IPCE) increases from 900 nm and is in good fit with the absorption spectrum. The activity was enhanced 3.4, 3.0, and 1.8 times higher than bare SnS by loading Nb_2O_5, TiO_2, and Ta_2O_5, respectively. Nb_2O_5 was most efficient because its conduction band is low enough for the effective electron transfer from SnS, but also has enough high-potential for H_2 evolution. The overall activity is determined by the competitive interfacial electron transfer between SnS/metal-oxide and metal-oxide/water. Therefore, construction of appropriate heterojunction is necessary for the further improvement of photoelectrochemical systems.

*Corresponding Author: yamakata@toyota-ti.ac.jp

Water splitting reaction has gained great attention due to its clean and environmentally friendly approach to generate hydrogen gas by utilizing solar energy. Photoelectrochemical (PEC) system involving semiconductor electrodes is one of the feasible methods to produce hydrogen gas. For the development of PEC system, a suitable choice of semiconducting electrodes is necessary. The conduction band and valence band of the semiconductor should be located at more negative and positive than the reduction potential of H_2O (0 V vs SHE) and oxidation potential of H_2O (1.23 V vs SHE), respectively.[1]

Metal sulfides with p-type conductivity such as copper indium gallium sulfide (CIGS), copper indium sulfide (CIS), and tin sulfide (SnS) are expected to be promising candidates for H_2 gas generation. These sulfides are studied for solar cells and photoelectrochemical cells. Among these sulfides, SnS is relatively easy to fabricate. Moreover, it has high absorption coefficient, $\alpha > 10^4$ cm^{-1},[2] and strongly absorbs visible and near IR light up to 900 nm. Furthermore, the conduction band of SnS is located at -1.22 V vs SHE at pH = 0, which is more negative than the potential of water reduction.[3] SnS has been utilized as an absorber layer in solar cells, but its application in photoelectrochemistry has not been reported to the best of our knowledge.

Loading of metal oxide is often used to protect the photoelectrodes from photocorrosion. Especially, photoanodes made of metal sulfides and nitrides are readily oxidized in anodic conditions. The metal oxides are stable and they can therefore protect the electrodes from photocorrosion. Furthermore, for photoelectrodes fabricated from the powder particles by thermal sintering, metal oxides provide effective contacts between particles, hence promoting inter-particle charge transfer by the so called “necking effects”. Therefore, metal oxides such as TiO_2, Ta_2O_5, ZnO, and Al_2O_3 are used to cover the n-type semiconductors such as ZnO[4], GaAs[5], $LaTiO_2N$ [6], TaON, and Ta_3N_5.[7,8] Metal oxides are also useful to protect photocathodes, although the photocathodes are relatively stable in the cathodic condition. TiO_2 has been used as protective layers of photocathodes such as p-Si, p-GaAs[9], p-Cu_2O[10,11], p-InP[12], and p-Cu_2ZnSnS_4,[13] and several authors proposed that TiO_2 would enhance the charge separation at the electrode/TiO_2 interface. As the position of the CB of the loaded metal oxides becomes lower, the electron transfer from electrode to the metal oxides is enhanced. However, the reactivity of electrons in the metal oxides becomes lower. In the case of TiO_2, the height of the CB is not sufficiently high compared to the potential for water reduction; therefore TiO_2 would not be always the best material for the effective H_2 evolution reaction. We therefore expect that a more suitable material other than TiO_2 should be highly considered to enhance the H_2 evolution; however the

application of other metal oxides such as Nb_2O_5 and Ta_2O_5 to p-type semiconductors has not been systematically studied as far as we know.

In this work, we fabricated p-type SnS thin film electrodes and examined the effects of metal-oxide loading on the photoelectrochemical activity. TiO_2, Nb_2O_5, and Ta_2O_5 were loaded on SnS, and we found that all of them enhanced the PEC activity of SnS photocathode for H_2 evolution. Among these metal oxides, Nb_2O_5 was most effective to enhance the activity. The favorable position of the conduction band of the metal oxide with respect to SnS is responsible for the enhancement.

SnS thin film photoelectrodes were fabricated by electrodeposition technique onto the ITO-coated glass following the procedure developed by Prof. Ichimura and co-workers.[14-16] Electrodeposition method has been considered as one of the attractive methods to produce smooth, flat, and high quality oxides[17-23] and sulfides[14,24,25] thin films owing to its simplicity, feasibility at room temperature operation, and easy scalability. It has also been utilized for the fabrication of heterojunction structures for solar cells.[26,27] Especially, pulse electrodeposition method produces denser and smoother SnS compared to DC (one-step potential) electrodepositon.[16] As evidenced in the PEC experiment, the pulse electrodeposited SnS exhibited 3-fold increase of photocurrent compared to DC electrodeposited SnS (Figure S1). Therefore, a 3-step pulsed potential (V_1 = -1.0, V_2 = -0.6, and V_3 = 0 V vs Ag/AgCl) was employed to deposit SnS thin films onto the ITO substrate (1 x 1 cm^2 area). The pulse duration for each potential was fixed at 10 s and the total deposition time was maintained at 10 min. The mixture of $SnSO_4$ (30 mM) and $Na_2S_2O_3$ (100 mM) aqueous solution was used as precursor solution. The detailed reaction of these Sn and S precursors to produce SnS was reported elsewhere.[14,15] The chemical composition was characterized by Auger electron spectroscopy (JEOL JAMP-9500F) and X-ray photoelectron spectroscopy (XPS PHI-5000, ULVAC-PHI), and the optical absorption of the as-prepared SnS film were measured by UV-VIS absorption spectrometer (JASCO V-670), respectively.

For the SnS electrodes loaded with TiO_2, Nb_2O_5, and Ta_2O_5: $TiCl_4$, $NbCl_5$, and $TaCl_5$ ethanol solution (10 mM) was dropped on the SnS film, respectively. The deposited metal ions react with water vapor in air to produce the metal oxide thin layer on SnS. For photoelectrochemical (PEC) measurement, the electrodes were irradiated from the substrate side by using 660 nm-LED lamp (Thorlabs, M660L3) with a power density of 200 mW cm^{-2}. The resulting photocurrent response under intermittent irradiation was measured in 0.1 M $NaSO_4$ aqueous solution, which was deaerated with Ar gas bubbling prior to each measurement. The potential was linearly scanned from +0.2 to -1.0 V vs Ag/AgCl at a rate of 10 mV s^{-1}.

The composition of the SnS photoelectrode deposited by 3-step pulsed electrodeposition was characterized by Auger electron spectroscopy. The Auger differential spectrum (Figure S2) clearly shows that the Sn and S peaks are nearly stoichiometric Sn/S ratio. The composition of the film was further analyzed by X-ray photoelectron spectroscopy (Figure S3). The binding energies of Sn 3d and S 2p peaks indicate that the film is mainly SnS. The band gap was estimated to be 1.4 eV from the absorption edge at 880 nm (Figure S4). The SnS film consists of aggregated particles (Figure S5a), and the thickness was estimated to be around 2.2 mm in our previous experiments.[15] The photocurrent response of bare SnS electrode was measured under 660 nm intermittent irradiation from +0.2 to -1.0 V (Figure 1a). The photocurrent of the SnS electrode was clearly observed upon irradiation, i.e. the cathodic current was observed below -0.2 V. At more negative potentials, the photocurrent was further increased. This cathodic current is ascribed to water reduction producing H_2 gas. This result also confirms us that SnS has p-type conductivity.

Figure 1b shows the incident-photon-energy-conversion (IPCE) curve of SnS photoelectrode measured at an applied potential of -0.6 V. As seen in the figure, the IPCE gradually increases from 900 nm towards shorter wavelength, and it is in good agreement with the absorption spectrum. The conversion efficiency at 400 nm is estimated to be 10.8 %. These results, therefore, indicate that the observed cathodic current is due to the band gap photoexcitation of SnS, i.e. SnS converts photons into current for H_2 gas generation.

We then examined the effect of metal oxides (TiO_2, Nb_2O_5, and Ta_2O_5) loadings on the activity of SnS electrode. These metal oxides are chemically stable and optically transparent to visible and near-IR light. The morphologies of TiO_2, Nb_2O_5, and Ta_2O_5 loaded SnS look very similar to that of bare SnS (Figure S5). To confirm whether the loaded metal oxide covers the SnS surface, we further performed elemental mapping by EDX. For brevity, the elemental mapping of Nb_2O_5 loaded SnS was only presented (Figure S6). As seen in the figure, it looks like the Nb_2O_5 fully covered the SnS film, but we could not exclude the possibility that pinholes are formed in the SnS particles.

By TiO_2 loading (Fig. 2b), the photocurrents increased by 3 times (547 mA/cm^2) compared to that obtained for bare SnS (183 mA/cm^2) at -0.76 V. In the case of Nb_2O_5 loading (Fig. 2c), the cathodic current further increased by nearly 3.4 times (620 mA/cm^2) at the same applied potential. However, in the case of Ta_2O_5 loading (Fig. 2c), the cathodic current only increases by 1.8 times (320 mA/cm^2) compared to that of bare SnS at -0.76 V. The efficiency of charge separation and the reactivity of

electrons in the metal oxides are responsible for the difference in the degree of photocurrent enhancement as will be discussed later. Nevertheless, these results suggest that loading of metal oxides such as TiO_2, Nb_2O_5, and Ta_2O_5 improve the activity of SnS photocathodes, but the degree of enhancement depends on the metal oxides used for coatings. The dependence of the photocurrent enhancement on the thickness of metal oxide layer was also examined. The thickness of the metal oxides loaded on SnS was estimated and listed in Table S1 (Supporting Information). As shown in Figure S7, the increased of photocurrent is almost constant at ~50 μL loading, indicating that the enhancement is less sensitive to the amount of metal oxides loaded on SnS.

The properties of metal oxide layers fabricated by hydrolysis of metal chlorides are further examined by XRD. No characteristic peaks associated to crystalline TiO_2, Nb_2O_5, and Ta_2O_5 were observed in the XRD patterns for all the samples, suggesting that these oxide layers are in amorphous phase (Figure S8). However, their band gap energies are different. From the absorption edges of the UV-Vis absorption spectra in Fig. 3, the band gaps are estimated to be 3.2 (385 nm), 3.4 (360 nm), and 4.1 eV (300 nm) for TiO_2, Nb_2O_5, and Ta_2O_5, respectively. The positions of CB and VB of metal oxides are identified in referenced to the reported band structures of TiO_2, Nb_2O_5, and Ta_2O_5.[3,28-30] In the case of TiO_2, the VBM and CBM are located at +3.0 and -0.2 eV from the hydrogen evolution potential. In the case of Nb_2O_5, the VBM is also located near to +3.0 eV. Since the band gap of Nb_2O_5 is higher than TiO_2 by 0.2 eV, then the CBM is positioned at -0.4 eV above the hydrogen evolution potential. In the case of Ta_2O_5, the VBM is located at +3.0 - 3.5 eV in referenced to the hydrogen evolution potential. The slight difference depends on the method of measurement as reported in the literatures. Since the CB of these oxides are lower than that of SnS, the photoexcited electrons in SnS will migrate to these oxides layers, leaving the holes in SnS. This effective charge separation would be the primary reason why the activity is enhanced by metal-oxide loading on SnS. We found that Nb_2O_5 is most effective for H_2 evolution. This mechanism can be explained as follows. The efficiency of the charge separation between SnS and oxides becomes higher as the CB of oxides becomes lower. Therefore, the efficiency of the charge separation becomes higher in the order of TiO_2, Nb_2O_5, and Ta_2O_5. However, this order is opposite for the reactivity of electrons in CB: it is higher in the order of Ta_2O_5, Nb_2O_5, and TiO_2. In the case of TiO_2, CB is lowest; therefore the efficiency of the charge separation is highest. However, the conduction band of TiO_2 is almost comparable with that of redox potential for H_2 evolution; hence the activity for the H_2 evolution is lowest. In the case of Nb_2O_5, the height of the CB is adequate for the effective charge separation and the electrons have enough potential

for H_2 evolution. These are the reasons why Nb_2O_5 shows higher activity for H_2 evolution than TiO_2. On the contrary, in the case of Ta_2O_5, CB is highest therefore the reactivity of electrons is highest, but the efficiency of charge separation is lowest. These findings suggest that the overall activity is determined by the competition between the efficiency of charge separation and the reactivity of electrons.

In this work, we have fabricated fine SnS thin film electrodes by 3-step pulsed electrodeposition, and examined the photoelectrochemical activity. It is found that SnS is active for H_2 evolution under illumination of visible and NIR light shorter than 900 nm. The photoelectrochemical activity of SnS was much improved by loading metal oxides such as TiO_2, Nb_2O_5, and Ta_2O_5. TiO_2 has been often used as protective layers to suppress photocorrosion of unstable electrodes,[31-33] and several authors proposed that TiO_2 also enhances the charge separation at the heterojunction. In the present case, the enhancement of the charge separation would be also responsible for the improved activity. However, we found that Nb_2O_5 exhibited the highest activity among the metal oxides examined here. This activity enhancement depends on the height of the CB of metal oxides, which determines the efficiency of charge separation at the SnS/metal-oxide heterojunction as well as the reactivity of electrons for H_2 evolution on the metal oxides. The overall activity is determined by the competitive interfacial electron transfer between SnS/metal-oxide and metal-oxide/water. These findings suggest that the construction of appropriate band structures between SnS and metal oxide layers can further improve the activity for H_2 evolution reaction.

This work was supported by the PRESTO/JST program, the Grant-in-Aid for Specially Promoted Research (No. 23000009) and Basic Research (B) (No. 23360360), and the Strategic Research Infrastructure Project of MEXT. The authors would like to thank Mr. Yukihisa Moriguchi of Nagoya Institute of Technology for his technical assistance in XPS measurement and Dr. Sampath Ranasinghe of Toyota Technological Institute for his assistance in EDX measurement.

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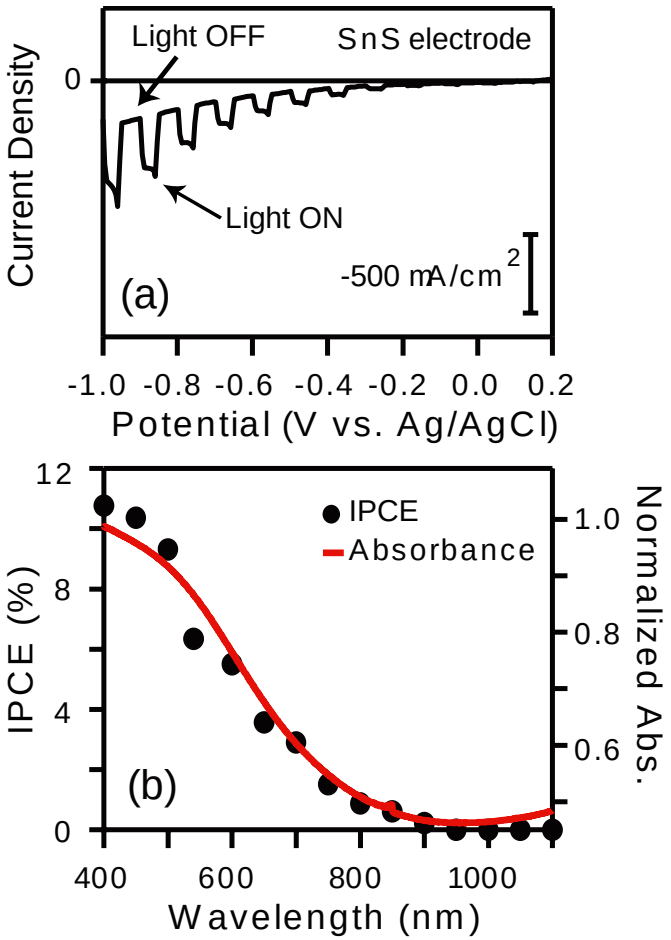

Figure 1. (a) Photocurrent response of SnS photocathode upon 660 nm intermittent illumination. (b) IPCE curve of SnS photocathode deposited by 3-step pulsed electrodeposition for 10 min. Electrolyte: 0.1 M Na_2SO_4 aqueous solution.

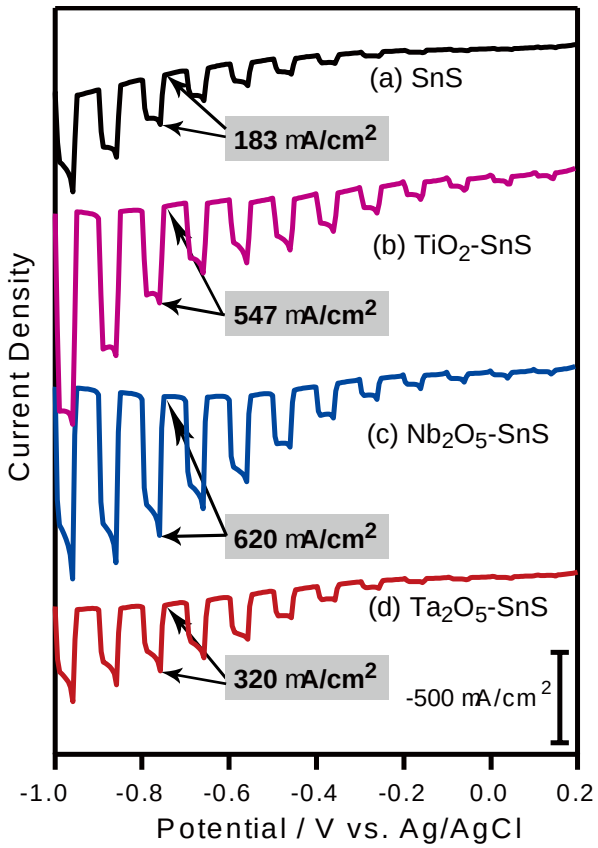

Figure 2. Photoactivity of (a) bare SnS photoelectrode, and SnS coated with different metal oxides: (b) TiO_2-SnS, (c) Nb_2O_5-SnS, and (d) Ta_2O_5-SnS. Electrolyte: 0.1 M Na_2SO_4 aqueous solution.

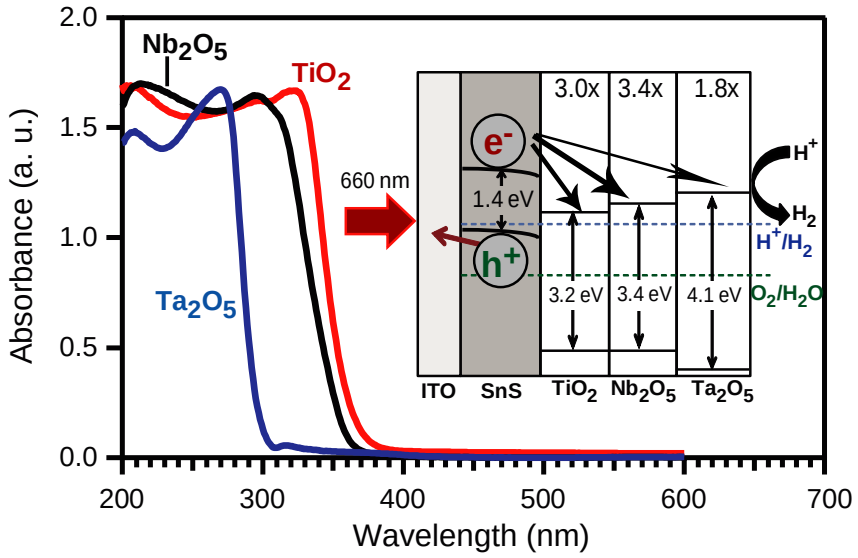

Figure 3. UV-Vis diffuse reflectance spectra of TiO_2, Nb_2O_5, and Ta_2O_5 films synthesized from the hydrolysis of metal chlorides. Inset shows the proposed mechanism of electron migration from SnS to metal oxide coatings that results to the enhancement of photocathodic currents.