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**Study of Early Transition Metal-Oxysulfides and (Oxy)nitrides
as Visible Light-Driven Photocatalysts**

Akio Ishikawa

2004

Doctoral thesis of science at Tokyo Institute of Technology

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Chapter 1

General introduction

1-1. Introduction

We depend on the energy system utilizing fossil fuels such as petroleum, coal, and natural gas. This energy system consuming fossil fuels brings us high level of modern civilization, while two serious global problems have arisen. One is the energy problem with the limited reserves of fossil fuels. Another is global warming owing to emission of CO₂ which is one of the greenhouse-effect gases. We are, therefore, under the necessity to develop a new alternative energy resource to the fossil fuels. The development of new resource is indispensable for sustainment of high level of modern civilization and clean environment.

Almost all energy of the earth is derived from sunlight. Although the large amount of the light energy from the sun reaches the earth, only a little part of it is practically availed by green plants and so on. We should utilize sunlight instead of fossil fuels as energy resource. Photon energy needs to be converted to electric or chemical energy, which are useful forms of energy media.

Solar batteries which convert photon energy to electric one are going to be made practicable. However, present solar batteries consisting of crystal Si can not supply all the energy consumed by the human until now. Main reason for this is attributed to the high cost of crystal Si. The researchers in this filed are going to tackling the problem and developing interesting examples of solar batteries such as so-called Grätzel cell^{1,2}. Since Grätzel et al. reported an impressive energy conversion efficiency of 7.9% in 1991¹, tremendous amount of trace experiments have been carried out.

On the other hand, photocatalysts which convert photon energy to chemical one are also attracted considerable interest and intensively studied up to now. The concrete reaction is the overall water-splitting reaction to produce H₂ and O₂ with photocatalysts and photon energy. Thus, photocatalytic water splitting by the solar light energy mimicking the photosynthesis (artificial photosynthesis) is one of the ways to develop a desirable energy-producing system. The overall water-splitting reaction has already been well established in many wide-gap oxide semiconductors³⁻⁶ in the early 1980s. These oxides

absorb only the UV region photons. The response to visible light is, however, desired for photocatalytic water splitting from the view point of efficient solar energy conversion. Any systems to photocatalytically generate H_2 and O_2 under visible light ($\lambda \geq 400$ nm) irradiation have not been accomplished yet.

To utilize sunlight as the alternative energy resource to fossil fuels, solar batteries, and photocatalysts are promising candidates.

1-2. Basic Principles

One of the first essential steps of all photoelectrochemical and photocatalytic reactions is the absorption of photons by electrodes or catalysts materials. Photoelectrochemical and photocatalytic reactions are based on the same principle from the view point of generating separated charges. Here, the explanation of basic principle is limited to the photocatalytic reactions. In most heterogeneous photocatalytic reactions, semiconductor powders are used. The band mode of a semiconductor photocatalyst, in this case for an

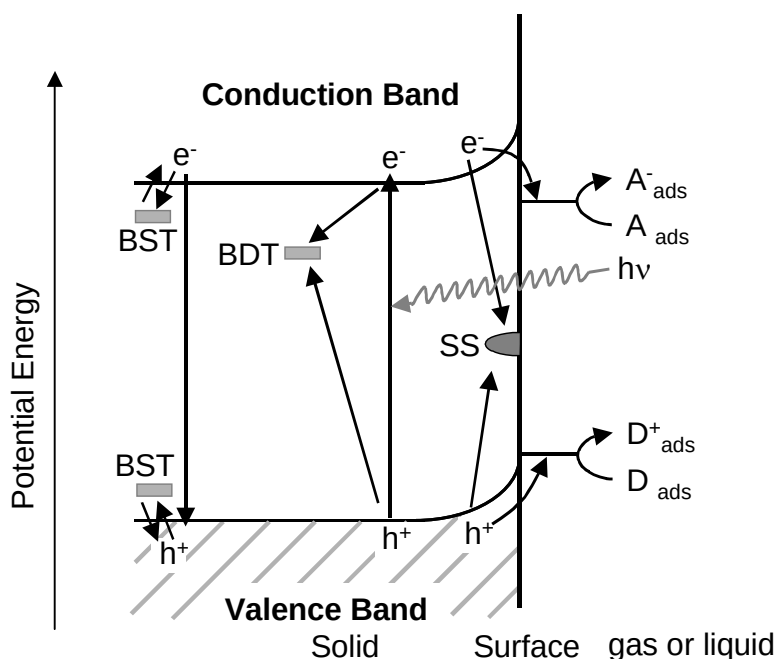


Figure 1-1. Band model of electronic structure of n-type semiconductor in contact with gas or liquid phase. A, electron acceptor; D, electron donor; SS, surface state; BST, bulk shallow trap; BDT, bulk deep trap.

n-type semiconductor, are schematically depicted in Figure 1-1. For a semiconductor, there is the so-called band structure consisting of the valence band filled with electrons and the conduction band that is almost empty of electrons. In between these bands, there exists a void region of electronic energy levels, which is called the forbidden band. The width of the forbidden band is called the band gap (E_{BG}). A semiconductor absorbs photons with energy ($h\nu$) larger than the band gap, and electrons are excited to the conduction band from the filled valence band, where positive holes are thus formally generated (Figure 1-1). The excess energy, *i.e.* $h\nu - E_{BG}$, given to electrons and holes is transformed to lattice vibration (phonon) or thermal energy typically in less than a picosecond and the electrons and holes relax to the energy levels of each band edge. These electrons and holes are often in equilibrium with those in shallow traps via thermal energy as shown in Figure 1-1. Owing to the existence of the band gap, these electron-hole pairs have a sufficiently long lifetime, typically in the nanosecond regime or longer, unlike in metals that have a continuum of electronic states. The electron-hole pairs in a semiconductor can recombine either directly or indirectly (*e.g.* via bulk or surface defects) by radiative and nonradiative processes. If the excited electrons and holes are transferred, directly or via surface states, to the adsorbed species on the photocatalyst and thus generated intermediate species subsequently turn to stable products before back-electron-transfer to the semiconductor, a photocatalytic redox reaction proceeds.

One of the typical examples of photo-induced up-hill reactions is photocatalytic decomposition of water into H_2 and O_2 , which is in a sense included in “photosynthesis”. The first overall water-splitting reaction,



was reported in 1972, in which a photoelectrochemical cell with a rutile TiO_2 photoanode and a Pt counter electrode was used.⁷ The energetics of such a macrophotoelectrosynthetic cell for driving a reaction are illustrated in Figure 1-2. In a photoelectrochemical cell with an n-type semiconductor electrode, the Schottky barrier at

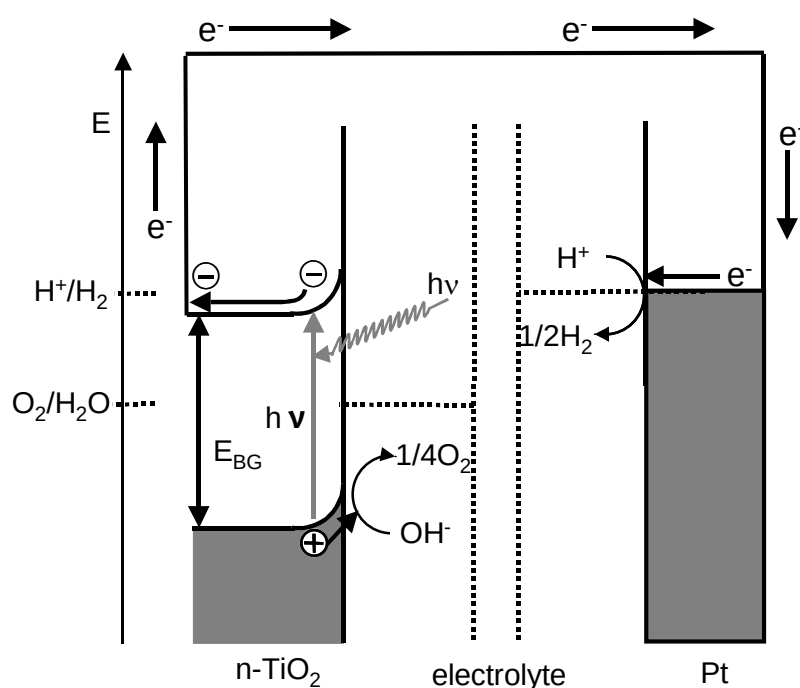
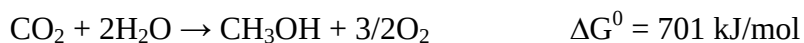


Figure 1-2. Energetics of a photosynthetic cell for water splitting.

the interface between a semiconductor electrode and an aqueous solution is formed resulting in the formation of band bending. The band bending promotes the charge separation of photogenerated electron from holes as shown in Figure 1-2. The electrons transfer to a Pt counter electrode through an external circuit and thus H_2 is produced at Pt cathode. Water is oxidized to O_2 by the holes transferring to TiO_2 surface. It is noted that the first report of TiO_2 (rutile)/ H_2O /Pt photoelectrochemical cell requires a degree of chemical or electrical bias to make it work, because $E_{CB}(TiO_2; \text{rutile})$ is approximately 0.2 V more positive than $E(H^+/H_2)$. From this work, many studies for overall water-splitting reaction have been triggered in both photoelectrochemical and photocatalytic systems.

Simultaneously, from the viewpoint of artificial photosynthetic reaction, CO_2 or N_2 fixation using H_2O as a reducing reagent has been carried out. In the cases of methanol or ammonia formation from CO_2 or N_2 , respectively, the overall reaction is expressed as follows:





There are many reports concerning the CO_2 and N_2 reduction.^{8,9} However, in almost all works the amounts of the products were very small compared to the amount of the catalysts used. Recently, various photocatalyses such as decomposition of organic compounds¹⁰ and hydrogenation of unsaturated hydrocarbons¹¹ have been studied actively.

1-3. Photocatalytic Water Splitting over Semiconductor Photocatalysts

1-3-1. Mechanism.

The mechanism of the decomposition of water by a semiconductor photocatalyst is interpreted as shown in Figure 1-3. When a semiconductor adsorbs photons with energy ($h\nu$) larger than E_{BG} , excited electrons and holes are produced in conduction and valence bands, respectively. Water is reduced to H_2 by excited electrons in conduction band and oxidized to O_2 by holes in valence band as shown in Figure 1-3. In this reaction, it is noted that the relationship between the band positions of a photocatalyst and the redox potentials (H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$) of reactants is important. The bottom of the conduction band E_{CB} should be more negative than the H^+/H_2 redox potential, that is, 0 V vs NHE at $\text{pH} = 0$. The top of the valence band E_{VB} should be more positive than the $\text{O}_2/\text{H}_2\text{O}$

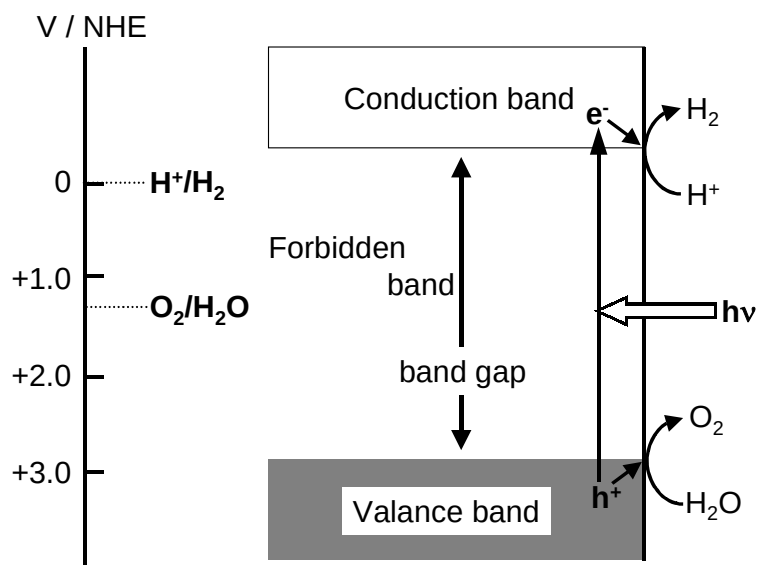


Figure 1-3. Scheme for photocatalytic water splitting.

redox potential, that is, +1.23 V vs. NHE at pH = 0. Unless these two requirements are satisfied, H₂ and O₂ evolutions are thermodynamically restricted. Therefore, the band position of a photocatalyst is an important factor. The band-edge positions of several semiconductors are presented in Figure 1-4.¹²⁻¹⁵ The internal energy scale given on the left for comparison to the vacuum level and on the right for comparison to normal hydrogen electrode (NHE). The E_{CB} of WO₃ and TiO₂ (rutile) are positive than H⁺/H₂ redox potential as shown in Figure 1-4. Therefore, if one uses these materials for water splitting, any reactions do not almost occur. On the other hand, some metal chalcogenides such as CdS and CdSe appear to be suitable photocatalysts, since they have energy gaps small enough to absorb visible light and their conduction and valence bands are in sufficient potentials for many redox reactions as shown in Figure 1-4. These chalcogenides, however, are not stable for oxidizing water to form O₂ because the surface S²⁻ and Se²⁻ anions are more susceptible to oxidation than water,^{16,17} thus CdS and CdSe themselves are oxidized as follows:

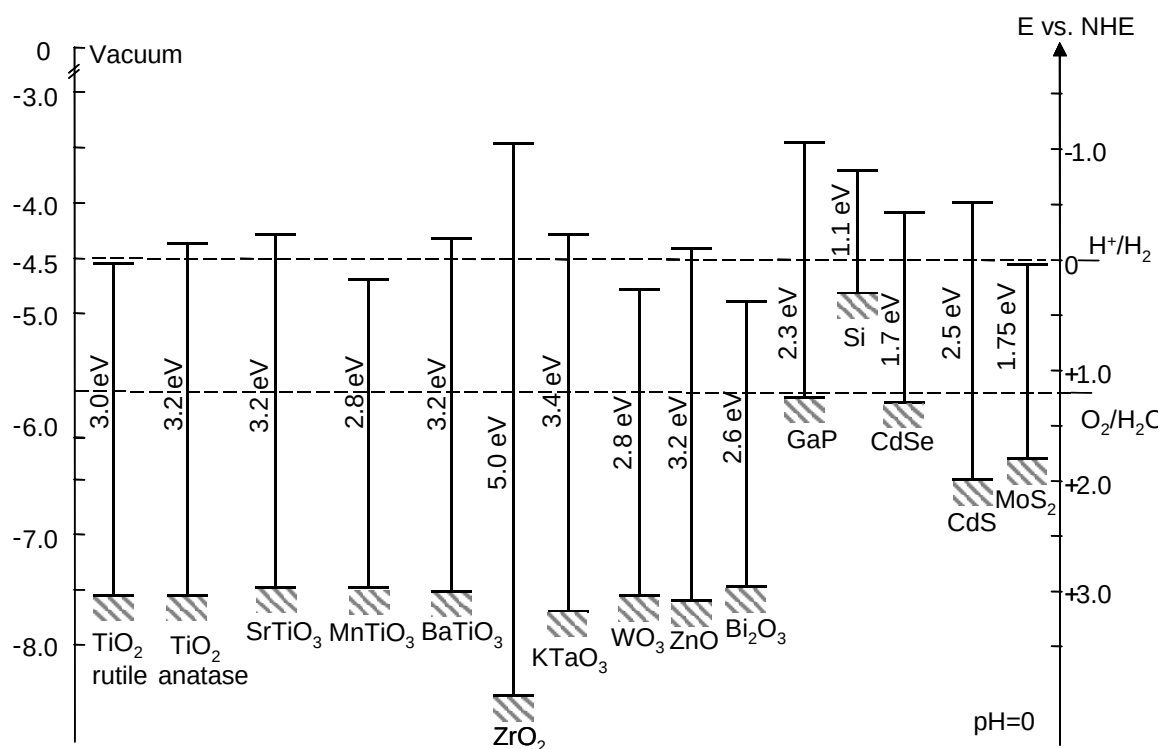


Figure 1-4. Band-edge positions of several semiconductors at pH = 0.



This means that a band position is just one of necessary conditions concerned with thermodynamics. There are several important factors required for photocatalytic water splitting reaction. The apparent requirements for heterogeneous photocatalysts suitable for overall water splitting are as follows.

(1) **Band positions of the photocatalysts:** The importance of the band position has been described above.

(2) **Stability of the photocatalysts:** If one uses a photocatalyst for some photocatalysis, the photocatalyst itself should not subject to any dissociation.

(3) **Crystallinity of the photocatalysts:** Photocatalytic reactions compete with the recombination between photogenerated electrons and holes as shown in Figure 1-5. If the crystallinity of a photocatalyst is enhanced, the number of defects that work as recombination center for photogenerated electrons and holes decreases. This results in less probability of recombination, leading to higher photocatalytic activity.

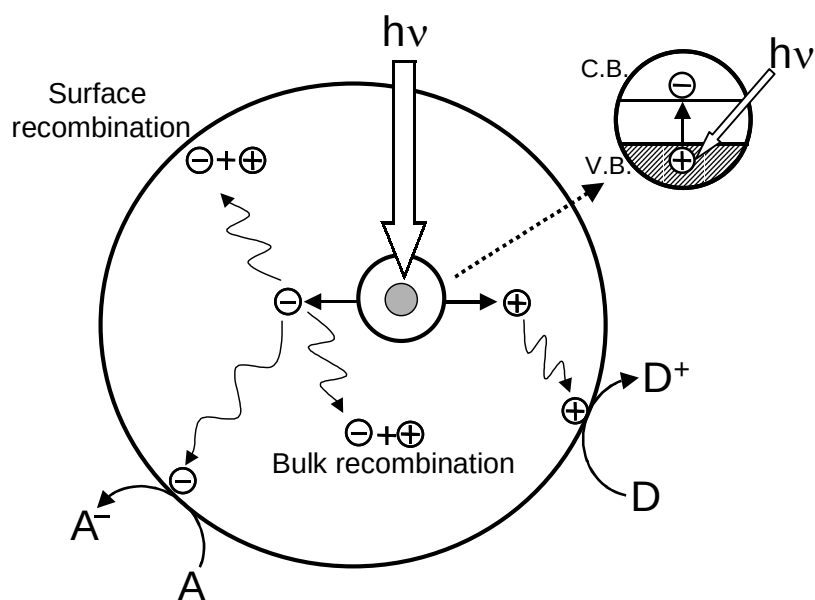


Figure 1-5. Schematic photoexcitation in a semiconductor particle followed by de-excitation and electron-transfer events.

(4) **Active site for the formation of H₂ and O₂:** Many photocatalysts^{18–22} are often combined with co-catalysts such as NiO_x and Pt to promote H₂ evolution. This means that the introduction of active site by loading of co-catalysts is often necessary to obtain high photocatalytic activities. If one develops a new photocatalyst, various co-catalysts as well as their loading methods suitable for the photocatalyst should be deliberately examined.

To evaluate capability of a photocatalyst for overall water decomposition to H₂ and O₂, H₂ and O₂ evolution is separately done tentatively in the presence of so-called sacrificial reagents as shown in Figures 1-6a and b. Unless at least one of the above mentioned requirements are satisfied well, the following reactions (H₂ or O₂ evolution) do not proceed.

H₂ evolution (Figure 1-6a): Excited electrons in conduction band reduce H⁺ to H₂, while holes in valence band oxidize electron donors via band gap excitation as follow:

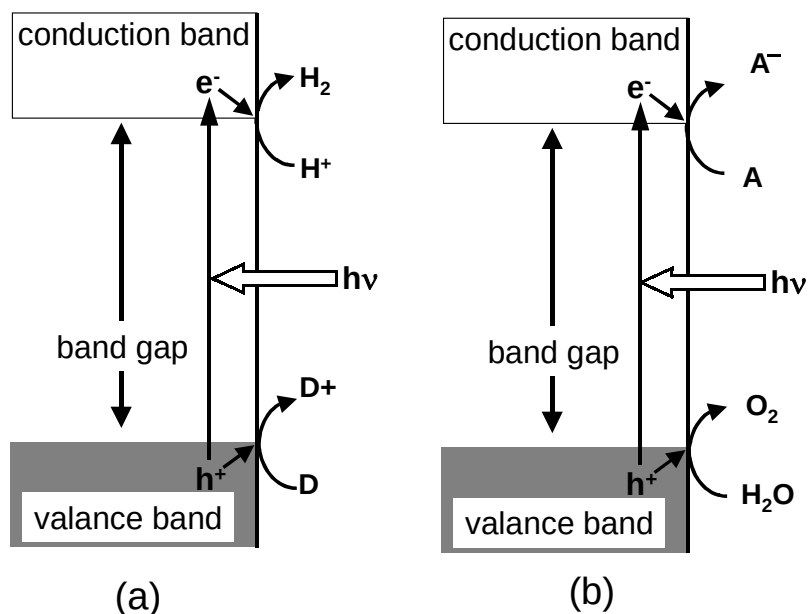
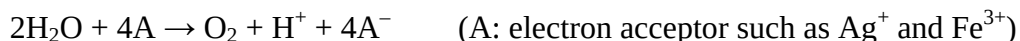


Figure 1-6. Schemes for (a) H₂ and (b) O₂ formation from water containing sacrificial reagents on semiconductor photocatalysts. D, electron donor; A, electron acceptor.

O₂ evolution (Figure 1-6b): Excited electrons in conduction band reduce electron acceptors, while valence band holes oxidize H₂O to O₂ as follow:



Electron transfer to/from sacrificial reagent is irreversible process, thus H₂ and O₂ formation is promoted. A photocatalyst which evolves both H₂ and O₂ in these tentative reactions is recognized to have a potential to decompose H₂O to H₂ and O₂. However, it does not always lead to the success in overall water splitting, because photocatalysis in sacrificial reagents just proves the requirements for (a) H₂ and (b) O₂ evolution.

1-3-2. Photocatalyst Materials for Water Splitting under UV–Light Irradiation.

Photocatalysts successfully applied to overall water splitting include several transition–metal oxides, *e.g.* TiO₂,^{23–25} SrTiO₃,¹⁸ ZrO₂,²⁶ BaTi₄O₉,²⁷ NaTaO₃,²⁸ K₄Nb₆O₁₇,²⁹ and K₂La₂Ti₃O₁₀.³⁰ Some UV light–driven photocatalysts for overall water splitting are summarized in Table 1-1. All of these catalysts are wide–gap semiconductors (band gap energy = 3–5 eV) and include metal cations with d⁰ or d¹⁰ electronic configuration.

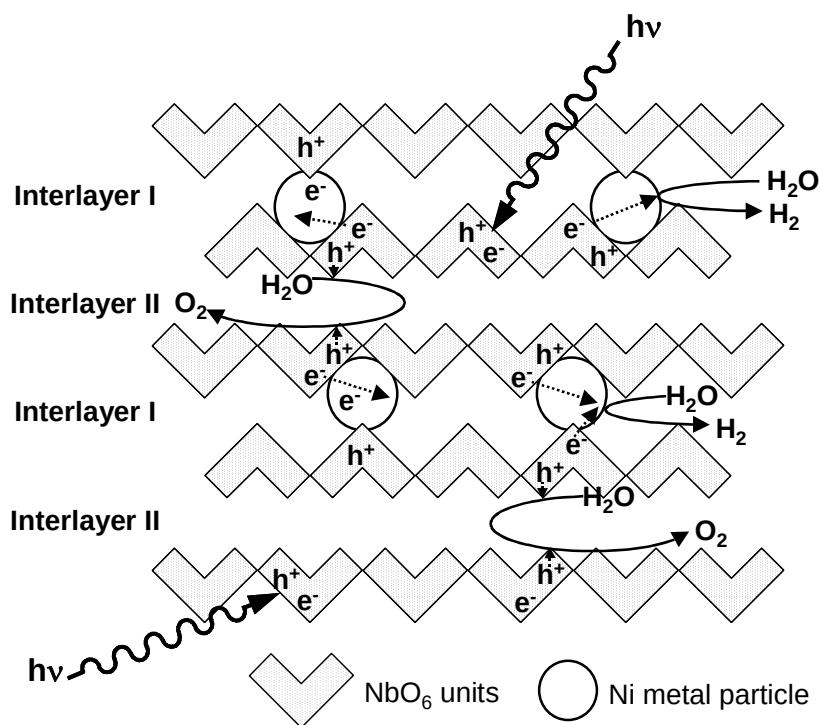
One of the controversial systems is anatase TiO₂ loaded with a Pt co-catalyst. If one uses Pt/TiO₂ for water splitting, it is usually not possible to observe the accumulation of produced H₂ and O₂ production because of the rapid reverse reaction on Pt. However, if the reaction is carried out in a concentrated Na₂CO₃ solution, evolution of H₂ and O₂ is observed.^{24,31} In this reaction system, carbonate species (CO₃^{2–}) cover the surface of Pt, resulting in the suppression of the reverse reaction. Moreover, the carbonate species adsorbed on the TiO₂ surface also play an important role for O₂ formation.

To use NiO_x co-catalysts is one of the ways to effectively suppress the reverse reaction. NiO_x co-catalysts work as active sites for H₂ formation in which the reverse reaction to form water from H₂ and O₂ is suppressed. Therefore, NiO_x has been widely used as an effective co-catalyst for photocatalytic water splitting.^{18,32,33}

One of the ways to effectively suppress the reverse reaction is to separate the reduction and oxidation sites in a photocatalytic system. An example of the system applied to the

Table 1-1. Photocatalyst materials for water splitting under UV light irradiation.

photocatalyst	co-catalyst	reaction condition	light source	activity ($\text{H}_2 / \mu\text{molh}^{-1}$)
TiO_2	Pt	$\text{H}_2\text{SO}_4\text{aq}$	—	12
	RuO_2	H_2O vapor	500 W Hg	0.6
	Pt/ RuO_2	HClaq	450 W Xe	120
	Pt	NaOH coating and H_2O vapor	500 W Hg	280
	Pt	$\text{Na}_2\text{CO}_3\text{aq}$	400 W Hg	1100
	NiO_x	$\text{Na}_2\text{CO}_3\text{aq}$	—	100
	Pt	distilled water (illumination from the top-side of a cell)	—	110
SrTiO_3	NiO_x	H_2O vapor	450 W Hg	0.2
	RhO_x	NaOH coating	1 kW Hg-Xe	55
ZrO_2	—	NaHCO_3aq	400 W Hg	600
$\text{Na}_2\text{Ti}_6\text{O}_{13}$	RuO_2	distilled water	400 W Xe	7.3
BaTi_4O_9	RuO_2	distilled water	400 W Xe	25
CaIn_2O_4	RuO_2	distilled water	400 W Xe	20
SrIn_2O_4	RuO_2	distilled water	400 W Xe	7.2
NaTaO_3	NiO	distilled water	400 W Hg	2200
$\text{K}_3\text{Ta}_3\text{Si}_2\text{O}_{13}$	NiO	distilled water	400 W Hg	370
$\text{K}_4\text{Nb}_6\text{O}_{17}$	NiO_x	distilled water	450 W Hg	1800
$\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$	NiO_x	KOHaq	450 W Hg	2200

**Figure 1-7.** Schematic view of $\text{Ni-K}_4\text{Nb}_6\text{O}_{17}$ and reaction mechanism of H_2O decomposition.

separation of the reduction and oxidation sites is shown in Figure 1-7.^{34,35} In this system ion-exchangeable layered niobate, $K_4Nb_6O_{17}$, is used with ultrafine Ni metal particles as H_2 formation sites. $K_4Nb_6O_{17}$ possesses two different kinds of interlayers alternately, and the interlayer space is hydrated. According to the proposed reaction model, photoexcited electrons in niobate sheets move to the ultrafine Ni metal particles in interlayer I and reduce H^+ to H_2 , and holes oxidize H_2O into O_2 at the interlayer II. This results in the overall water splitting.

The acceleration of the charge separation by the dipole moments in photocatalysts, such as $BaTi_4O_9$ ²⁷ and MIn_2O_4 ($M = Ca, Sr$)³⁶, have been reported by Inoue and co-workers. In these cases, the distortions of TiO_6 and InO_6 octahedra play an important role. These distortions cause the formation of the local dipole moments, resulting in the efficient charge separation. Inoue et al. have also reported the finding of new group of photocatalysts including metal cations (*e.g.* In^{3+}) with d^{10} electronic configuration.³⁷ The valence band of MIn_2O_4 consists of the $O2p$ orbitals, whereas the conduction band is made up of the hybridized $In5s5p$ orbitals with large dispersion. These metal oxides including metal cations with d^{10} electronic configuration were evidently different in the characteristic of conduction bands from transition metal oxides such as TiO_2 including metal cations with d^0 configuration. The conduction bands of these transition metal oxides with d^0 electronic configuration usually consist of the empty transition metal's d orbitals such as $Ti3d$ with less delocalization dispersion compared to the hybridized sp orbitals. The delocalized hybridized sp orbitals in the conduction band with large dispersion are helpful for conduction of photogenerated electron in the bulk to the surface of catalyst.

The above-mentioned photocatalysts used for the photodecomposition of water absorb only the UV region photons, and do not function as visible light-driven photocatalysts.

1-3-3. Development of Visible Light–Driven Photocatalysts.

The response to visible light is desired for photocatalytic water splitting from the view point of the solar light energy conversion. It have been reported that $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ ³⁸ and Pt/CdS/RuO_2 ³⁹ function as visible light–driven photocatalysts for overall water splitting. However, those data were not clear and were not reproducible. Satisfactory photocatalysts working under visible light irradiation have never been devised to date. Here, the various approaches to development of visible light–driven photocatalysts are described. Table 1-2 summarizes visible light–driven photocatalysts for the H_2 formation. Pt/CdS is a well–known visible light–driven photocatalyst for H_2 evolution from water containing sacrificial electron donor such as Na_2S and Na_2SO_3 .^{40,41} When CdS is used for water splitting, CdS itself is oxidized instead of the oxidation of water. Mechanism of photocorrosion was mentioned above. Kaneko and co-workers have reported that the sensitization of platinized TiO_2 particles by $\text{Ru}(\text{bpy})_3^{2+}$, tris(bipiridine) $\text{Ru}(\text{II})$ ($\text{Ru}(\text{bpym})_3$), and porphyrins allows H_2 evolution by visible light

Table 1-2. Photocatalyst materials for H_2 formation under visible light irradiation.

Photocatalyst	Band gap / eV	Sacrificial reagent	activity (H_2 / μmolh^{-1})
Pt/CdS	2.4	Na_2S - Na_2SO_3	850
$\text{Ru}(\text{bpy})_3^{2+}/\text{Pt/TiO}_2$	2.8	EDTA	15
SrTiO_3 doped with Cr and Sb	2.4	CH_3OH	78
SrTiO_3 doped with Cr and Ta	2.3	CH_3OH	70
ZnS doped with Cu	2.5	Na_2SO_3	450
ZnS doped with Ni	2.3	Na_2SO_3	280
$\text{Pt/HPb}_2\text{Nb}_3\text{O}_{10}$	2.5	CH_3OH	3.2
Ru/TaON	2.4	CH_3OH	120
$\text{Pt/Ta}_3\text{N}_5$	2.1	CH_3OH	10
$\text{Pt/LaTiO}_2\text{N}$	2.1	CH_3OH	20

EDTA: Ethylenediaminetetraacetic acid

in the presence of sacrificial electron donor.⁴² However, this system is inactive for the O₂ evolution from water due to poor reaction sites for oxidation of water based on 4-electrons process.

There are many reports that the doped photocatalysts, such as TiO₂, SrTiO₃, and ZnS with transition metal dopants, function as visible light-driven photocatalysts for the H₂ evolution from water containing sacrificial electron donors.^{43–45} It appears to be difficult to decompose water by these doped photocatalysts because of the small mobility of excited electrons or holes generated in the dopant level.

HPb₂Nb₃O₁₀ with a layered perovskite structure also shows the photocatalytic activities for H₂ formation from an aqueous methanol solution under visible light irradiation.⁴⁶ However, HPb₂Nb₃O₁₀ is not active for the O₂ evolution from an aqueous silver nitrate solution. It is due to acidic property of the interlayer which should be oxidation sites.

(Oxy)nitrides containing Ta⁵⁺ or Ti⁴⁺, such as TaON, Ta₃N₅, and LaTiO₂N, are potential visible light-driven photocatalysts.^{47–51} Under visible light irradiation, these (oxy)nitrides reduce H⁺ to H₂ or oxidize H₂O to O₂ in the presence of a sacrificial electron donor or acceptor without significant degradation of the materials. The photocatalytic activities of these (oxy)nitrides are relatively low for H₂ evolution from aqueous methanol solutions, but relatively high for O₂ evolution from aqueous AgNO₃ solutions. TaON exhibits particularly high photocatalytic activity for the oxidation of water, with quantum efficiency for O₂ evolution at 420–500 nm of *ca.* 30%.⁴⁷ This value is one of the highest values reported so far. To accomplish overall water splitting under visible light irradiation using these (oxy)nitrides, it is necessary to improve the H₂ evolution efficiency.

Development of a photocatalyst which evolves H₂ and O₂ simultaneously under visible light irradiation is still desired.

1-4. Objects of the Present Thesis

The overall water-splitting reaction has already been well established in many wide-gap oxide semiconductors. Many photocatalysts with high activities have been reported. In particular, the apparent quantum yield of NiO (0.05 wt%)/NaTaO₃ doped with La (1 mol%) was estimated to be *ca.* 50% at 270 nm, which is the highest value reported so far.⁵² However, all the photocatalysts used for the photodecomposition of water absorb only the UV region photons. The development of the highly efficient photocatalyst for water splitting under visible light irradiation is important. In the present thesis, the author has studied heterogeneous photoelectrochemical and photocatalytic system consisting of various novel materials to (i) develop new visible light-driven photoelectrode and photocatalyst materials, and (ii) obtain a guiding principle for the design of active photocatalysts.

Chapter 1: The first chapter describes trends and principles of photocatalytic and photoelectrochemical reactions. The progress of visible light-driven photocatalysts up to the present was also introduced.

Chapter 2: Grätzel cell which is a photoelectrochemical cell composes of the dye-sensitizer, TiO₂ thin film and redox species. TiO₂ thin film plays roles of (i) the medium of the electron transfer and (ii) substrate adsorbing dye-sensitizer. Recently, the preparation of a thin film composed of an ion-exchangeable layered titanate has been reported.^{53,54} The application of the layered thin film as an electrode of photoelectrochemical cell has been expected because the thin film functions as a photocatalyst (the good mobility of electron) and has ion-exchange properties (the fix of metal complexes). Therefore, in Chapter 2, the electrochemical and photoelectrochemical properties of a thin film composed of an ion-exchangeable layered oxide $\text{HxTi}_{(2-x/4)}\square_{x/4}\text{O}_4$ (HTiO) were investigated to expand the utility of this thin film.

Chapter 3: A nitride, Ta₃N₅, is potential photocatalyst for overall water splitting with good visible light absorption.⁴⁸ Ta₃N₅ performs as a stable photocatalyst for O₂ evolution from aqueous solution containing a sacrificial electron acceptor under visible

light. Ta_3N_5 , therefore, expected to be interesting as an electrode material for a photoelectrochemical cell. In Chapter 3, the photoelectrochemical properties of a thin film composed of a nitride, Ta_3N_5 , were investigated to develop a new photoelectrode. The application and stability of Ta_3N_5 electrode were discussed.

Chapter 4: The photocatalytic activities of TaON and Ta_3N_5 for O_2 evolution are relatively high but relatively low for H_2 evolution.^{47,48} It is considered that the low activity for H_2 evolution might be related to the band positions of TaON and Ta_3N_5 . This is a significant and controversial point to be examined. In Chapter 4, the band positions of Ta_2O_5 , TaON , and Ta_3N_5 were, therefore, investigated by ultraviolet photoelectron spectroscopy (UPS) and electrochemical analyses to evaluate the adequacy of these materials as visible light-responsive photocatalysts for water oxidation and reduction. Moreover, the fourth chapter demonstrates that the proposed UPS technique is reliable and alternative mean to determine the band positions of a wide range of photocatalyst materials.

Chapter 5: The photocatalytic activity of a Ti-based oxysulfide, $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, was investigated to develop a new visible light-driven photocatalyst. The band position of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was also investigated by electrochemical analysis to evaluate the adequacy of this material as visible light-driven photocatalyst. The characteristics of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, such as the electronic structure and the stability, were examined.

Chapter 6: $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ performs as a stable photocatalyst for H_2 or O_2 evolution from aqueous solution containing a sacrificial electron donor or acceptor under visible light. The synthesis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was studied to enhance the photocatalytic activities. In Chapter 6, the novel synthesis and photocatalytic activities of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ are presented. The factors affecting the photocatalytic activities were discussed.

Chapter 7: The photocatalytic activities of the series $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$) were investigated to obtain a highly active photocatalyst. Moreover, the electronic band structure and bulk material structure were examined. The relationship between those structures and the photocatalytic activity was discussed.

Chapter 8: The results described in the Chapters 2–7 were summarized.

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Chapter 2

Layered Titanate Thin Film as an Electrode Material

2-1. Introduction

Thin films of inorganic materials are generally prepared by techniques such as chemical vapor deposition (CVD), sputtering, or molecular beam epitaxy (MBE). These methods, however, require high technologies and severe conditions such as high temperature or ultrahigh vacuum. Methods that do not require such extreme conditions have also been investigated. Soft chemical techniques such as hydrothermal–electrochemical processes are attractive for the formation of complex oxide thin films, and polycrystalline thin films of cubic BaTiO_3 on Ti substrates have been successfully prepared by this method,¹ as have other titanates such as SrTiO_3 .² The exfoliation of layered compounds has also been investigated as a means of producing thin films, and layered materials such as layered titanates and niobates have been reportedly exfoliated in aqueous solutions containing amine surfactants.^{3–6} Ultrathin films based on exfoliated layers originating from $\alpha\text{-Zr}(\text{HPO}_4)_2$ and $\text{K}_4\text{Nb}_6\text{O}_{17}$ have also been successfully synthesized.^{5,6}

Recently, a method for the preparation of thin films by a soft chemical route has been developed.^{7–11} $\text{K}_4\text{Nb}_6\text{O}_{17}$ and $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ($\square$; vacancy), are ion–exchangeable oxides,^{12,13} are representative photocatalytic materials with layered structures. The two–dimensional sheets forming the layered structure of these compounds can be exfoliated by a soft chemical method, and the thin films reconstructed from the exfoliated sheets maintain the layered structure and ion–exchange properties. Grätzel cell which is a photoelectrochemical cell composes of the dye–sensitizer, TiO_2 thin film and redox species. TiO_2 thin film plays roles of (i) the medium of the electron transfer and (ii) substrate adsorbing dye–sensitizer. The application of the layered thin film as an electrode of photoelectrochemical cell has been expected because the thin film functions as a photocatalyst (the good mobility of electron) and has ion–exchange properties (the fix of metal complexes). In this chapter, $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films are prepared on indium tin oxide (ITO) substrates and the electrochemical properties of the films are investigated with respect to application as an electrode material.

2-2. Experimental Section

2-2-1. Synthesis of $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ Thin Films.

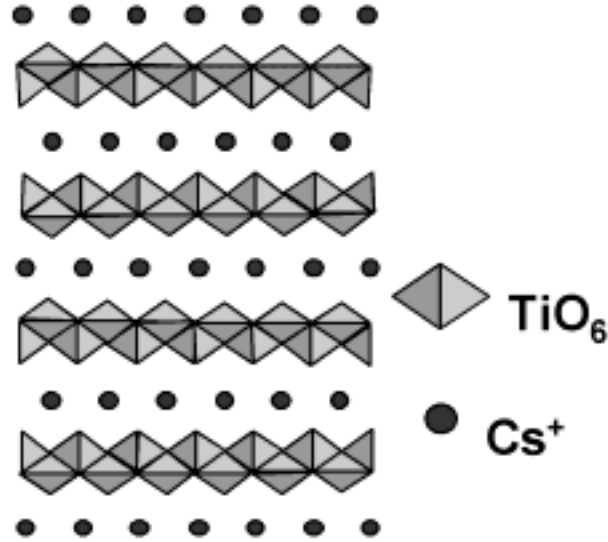


Figure 2-1. Schematic structure of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$.

Figure 2-1 shows the schematic structure of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ($x = 0.67$). This oxide is isostructural to FeOOH and belongs to the lepidocrocite structural group. Layered titanate was synthesized from a stoichiometric mixture of Cs_2CO_3 (Kanto Chemical Co., Inc.) and TiO_2 (Kanto Chemical Co., Inc.) by calcination at 1073 K for 20 h. Interlayer Cs^+ ions were proton-exchanged in an aqueous HCl (1.0 M) solution by stirring for 1 day at room temperature. The H^+/Cs^+ ratio was estimated to be 0.95 by measuring Cs and Ti contents of the sample before and after proton-exchange by using energy-dispersive X-ray spectroscopy (EDX).^{9,14} The product $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ was then exfoliated into several titanate layers by stirring in an aqueous ethylamine solution for 1 day at room temperature. The resultant aqueous suspension was centrifuged at 2000 rpm for 30 min and the supernatant was used as a mother suspension to obtain thin exfoliated layers (referred to as HTiO).

2-2-2. Preparation and Characterization of HTiO/ITO Electrode.

An HTiO-modified electrode was prepared according to the following procedure. An ITO substrate was fixed on a spin coater, and *ca.* 0.1 ml of aqueous suspension was dropped onto the substrate. The substrate was rotated at about 3000 rpm to spread the suspension uniformly. Repeating this procedure 3 times lead to the formation of a thin titanate film on the ITO substrate. A Cu wire was then attached to the bare ITO surface using silver paste, and the surface was sealed with epoxy resin to prevent electrical leakage. The HTiO electrode had dimensions of $1 \times 1 \text{ cm}^2$.

$\text{Ru}(\text{bpy})_3^{2+}$ ions cannot be intercalated directly into the interlayer space of HTiO due to the large ionic radius of $\text{Ru}(\text{bpy})_3^{2+}$. However, $\text{Ru}(\text{bpy})_3^{2+}$ ion-exchange can be achieved by a two step process.⁷ First, the HTiO/ITO electrode was soaked in aqueous solution containing 1.0 M *n*-octylammonium chloride at 353 K for 4 days. $\text{Ru}(\text{bpy})_3^{2+}$ ion-exchange was then performed by soaking the HTiO/ITO in 1 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution at 353 K for 7 days. The calculated $\text{Ru}(\text{bpy})_3^{2+}$ exchange was approximately 500 nmol according to the weakening of the 453 nm absorption peak of the aqueous solution by UV-vis transmittance spectroscopy. The amount of $\text{Ru}(\text{bpy})_3^{2+}$ in the interlayers also was estimated by UV-vis transmittance spectroscopy before and after the present reactions. The thin films were characterized by atomic force microscopy (AFM; TMX-2100, TopoMetrix), X-ray diffractometry (XRD; Geigerflex Rad-B, Rigaku; Cu $K\alpha$, 15 mA) and field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi).

2-2-3. Electrochemical Measurement and Photochemical Analysis.

A quartz cell with a flat window was used for photoelectrochemical measurements, with Pt counter and Ag/AgCl reference electrodes. An aqueous solution containing 0.1 M KNO_3 as an electrolyte and 0.1 M triethanolamine (TEOA) as a sacrificial electron donor was employed. Action spectra were measured under the application of an external potential (+0.35 V vs Ag/AgCl) and irradiation with monochromatic light via various band-pass filters using a 300 W Xe lamp. The photon count at each wavelength

reaching the electrode surface was measured using an Si photodiode. The incident monochromatic photon-to-current conversion efficiency (IPCE) was defined as follows.¹⁵

$$\text{IPCE} = \frac{1250 \times \text{photocurrent density } (\mu\text{A}/\text{cm}^2)}{\text{wavelength (nm)} \times \text{photo flux } (\text{W}/\text{cm}^2)}$$

The photocurrent density was obtained at short circuit with an electrode potential set to +0.35 V vs Ag/AgCl.

2-3. Results and Discussion

2-3-1. AFM, SEM image, and XRD Pattern of HTiO/ITO.

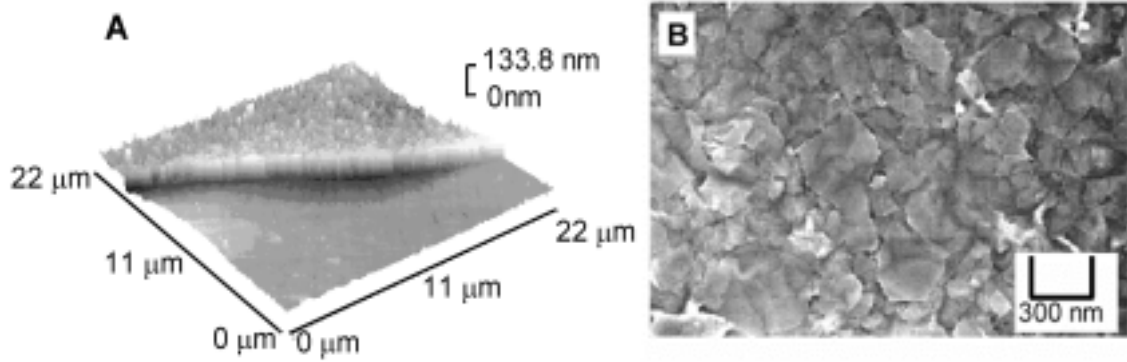


Figure 2-2. (A) AFM image of HTiO thin film on ITO substrate, and (B) SEM image of the surface of HTiO thin film.

Figure 2-2 shows an AFM image of HTiO/ITO electrode. The foreground region is bare ITO. From the difference in height between the HTiO-coated and bare-ITO areas, the thickness of the HTiO film was estimated to be about 100 nm. An SEM image of the HTiO film is also shown in Figure 2-2. Even and tabular HTiO crystals of several-hundred nm in size were observed, apparently orientated parallel to the substrate.

Figure 2-3 shows the XRD patterns of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$, $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$, HTiO film and HTiO film with intercalated n-octylammonium ions. A strong (020) diffraction peak was observed for all samples. The (020) interlayer distances for $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ and $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ were 8.6 and 9.2 Å, respectively. The appearance of diffraction peaks attributed to (0n0) planes is indicative of the well-ordered re-stacking of titanate sheets

along the *b*-axis parallel to the substrate. The interlayer distance of the HTiO[n-octylamine] film was remarkably higher than the other films, with an increment of 13.9 Å from the original powder. This is attributable to expansion due to the intercalation of n-octylammonium ions into the titanate sheets, allowing subsequent ion-exchange with Ru(bpy)₃²⁺.

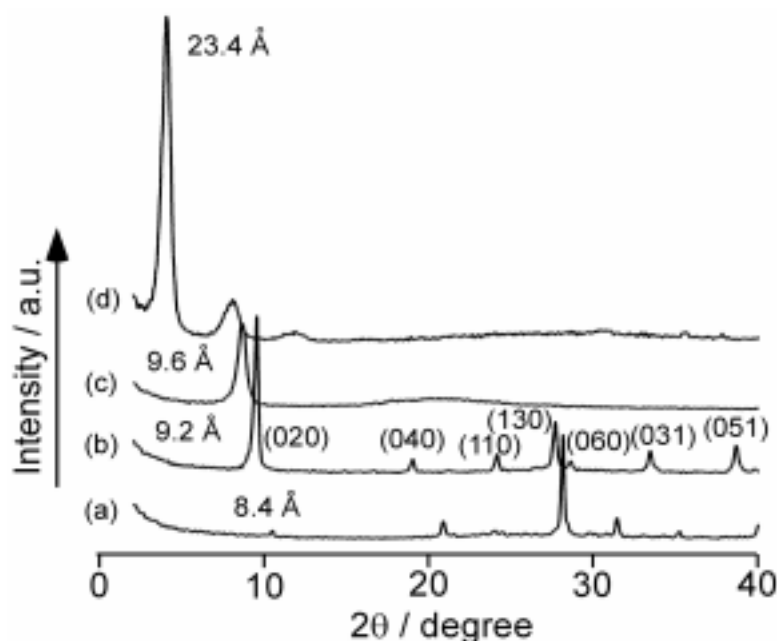


Figure 2-3. XRD patterns of (a) $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$, (b) $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$, (c) HTiO thin film and (d) HTiO film with intercalated n-octylammonium ions.

2-3-2. Cyclic Voltammograms of HTiO/ITO and HTiO[n-octylamine]/ITO Electrodes.

Cyclic voltammograms of (A-a) HTiO/ITO and (B-a) HTiO[n-octylamine]/ITO electrodes in aqueous KNO₃ (0.1 M) solution are shown in Figure 2-4. The two cyclic voltammograms are very similar, and almost constant in the range -0.5 to +1.5 V vs Ag/AgCl. Moreover, no noticeable difference was observed in the XRD patterns and SEM images before and after the measurements. The HTiO film did not detach from the substrate, indicating stable electrochemical properties.

The electrochemical properties of the HTiO/ITO and HTiO[n-octylamine]/ITO electrodes

were examined in the presence of various redox species. Cyclic voltammograms of bare ITO and HTiO/ITO in aqueous $\text{Ru}(\text{bpy})_3^{2+}$ (1 mM) solution are shown in Figure 2-4A(b). The redox peak attributed to $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}$ was observed for the bare ITO electrode but not for the HTiO/ITO electrode under repeated potential scanning. Cyclic voltammograms of HTiO[n-octylamine]/ITO in aqueous $\text{Ru}(\text{bpy})_3^{2+}$ solution are shown in Figure 2-4B(b). The redox peaks due to $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}$ were observed for the HTiO[n-octylamine]/ITO electrode with the long interlayer distance (23.4 Å). Those peaks were, however, not observed for the HTiO/ITO electrode with the short interlayer distance (9.6 Å). It was, therefore, suggested that the long interlayer distance enables HTiO[n-octylamine]/ITO to oxidize and reduce Ru complex ions. XRD results also indicated that HTiO[n-octylamine]/ITO can intercalate $\text{Ru}(\text{bpy})_3^{2+}$ while HTiO/ITO can

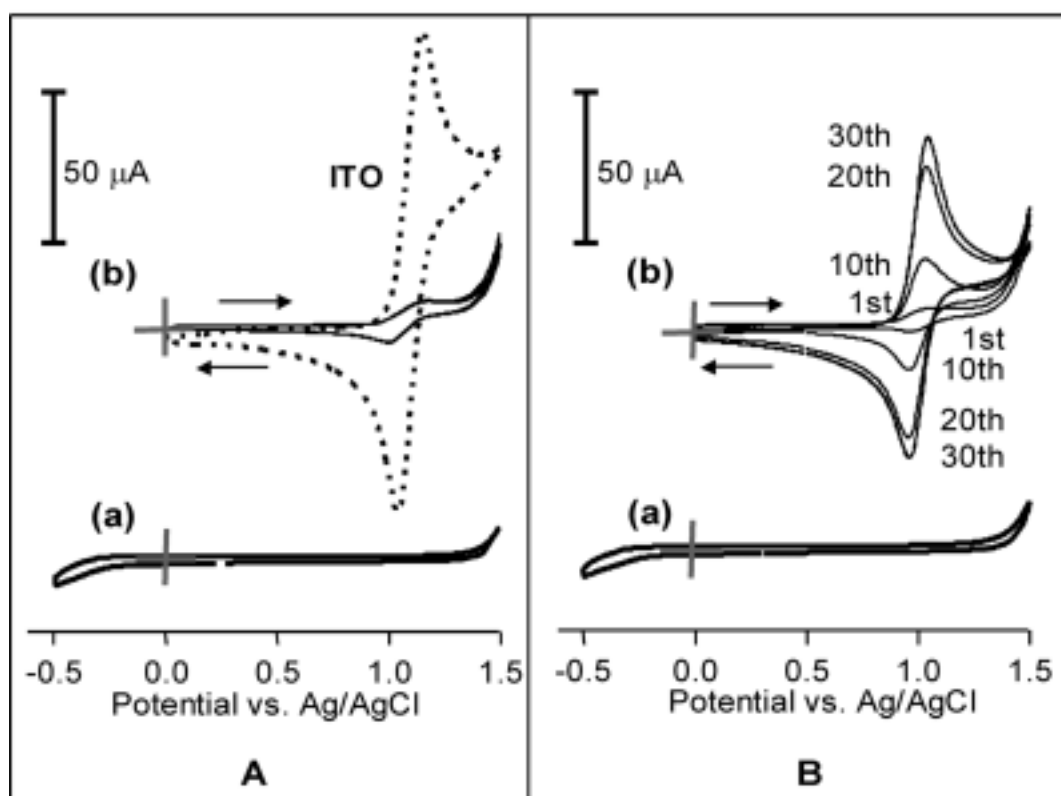


Figure 2-4. Cyclic voltammograms of (A) HTiO film and (B) HTiO[n-octylamine] electrode in (a) 0.1 M KNO_3 and (b) 0.1 M KNO_3 containing 1mM $\text{Ru}(\text{bpy})_3^{2+}$. Scan rate: 20 mV/s.

not. The electrochemical results, therefore, appear to be related to the XRD results.

The intensity of the redox current peaks increased with repeated potential scanning, and both the anodic and cathodic peaks shifted gradually. This can be attributed to (i) the slow exchange reactions between n-octylammonium ions and the Ru complexes and (ii) the slow diffusion of Ru complexes. It has been reported that the diffusion of such Ru complexes is slow in some clay films¹⁶. The shift in redox potentials was also reported by Ege and Bard upon incorporation of cationic complexes in a clay-modified electrode.¹⁷ The redox reaction on the HTiO[n-octylamine]/ITO electrode may in fact proceed not on the external surface but in the interlayer spaces.

Figure 2-5 shows cyclic voltammograms of HTiO[n-octylamine]/ITO and ITO in aqueous $\text{Fe}(\text{CN})_6^{4-}$ (1 mM) solution. The redox peak attributed to $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ was observed for the ITO electrode but not for the HTiO[n-octylamine]/ITO electrode. Although potential scanning was repeated several times, the redox reaction of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ did not take place on the HTiO[n-octylamine]/ITO electrode. As $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ is a cation exchanger, intercalation of $\text{Fe}(\text{CN})_6^{4-}$ would have been

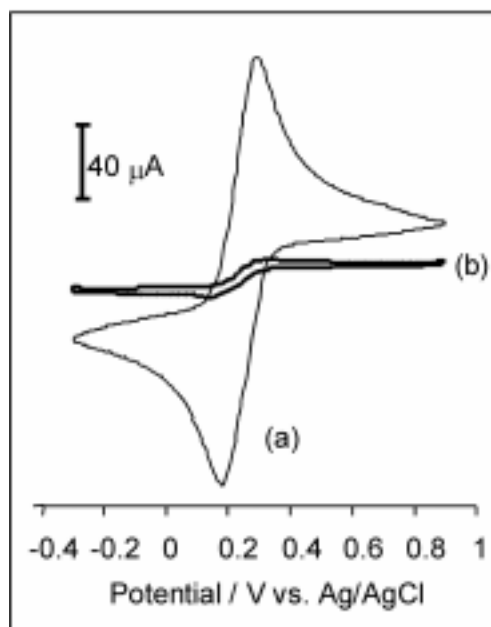


Figure 2-5. Cyclic voltammograms of (a) ITO and (b) HTiO[n-octylamine]/ITO electrodes in 1 mM $\text{Fe}(\text{CN})_6^{4-}$ and 0.1 M KNO_3 solution (scan rate 20 mV/s).

inhibited by electrostatic repulsion. Based on these results, it is considered that ITO/HTiO thin film functions as an electrode material that is active in the interlayer spaces, allowing selective reactions with cationic species.

2-3-3. Characterization of $\text{Ru}(\text{bpy})_3^{2+}$ -intercalated HTiO/ITO.

The calculated $\text{Ru}(\text{bpy})_3^{2+}$ exchange after soaking HTiO[n-octylamine]/ITO in 1 mM of aqueous $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution at 353 K for 7 days was 500 nmol. $\text{Ru}(\text{bpy})_3^{2+}$ ions in the interlayer spaces did not elute into aqueous solution when the electrode was soaked in pure water without any cations. Most of $\text{Ru}(\text{bpy})_3^{2+}$ ions in the interlayer spaces were, however, easily exchanged with K^+ ions when the electrode was soaked in 0.1 M KNO_3 solution. The calculated amount of $\text{Ru}(\text{bpy})_3^{2+}$ elution into the 0.1 M KNO_3 aqueous solution was approximately 400 nmol.

Figure 2-6 shows the XRD patterns of HTiO[$\text{Ru}(\text{bpy})_3^{2+}$] thin film and HTiO[$\text{Ru}(\text{bpy})_3^{2+}$] soaked in 0.1 M KNO_3 solution. The interlayer distance was 15.4 Å for 500 nmol of

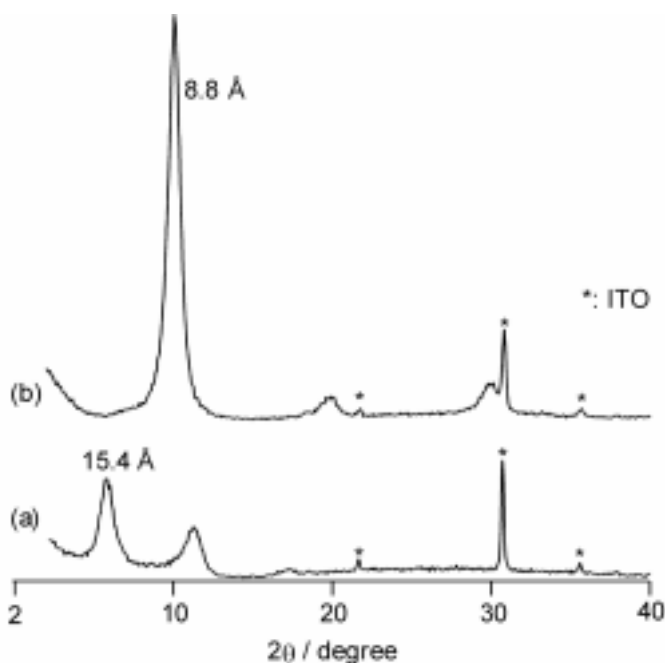


Figure 2-6. XRD patterns of HTiO[$\text{Ru}(\text{bpy})_3^{2+}$] thin film (a) before and (b) after being soaked in 0.1 M KNO_3 solution.

intercalated $\text{Ru}(\text{bpy})_3^{2+}$. After soaking, the interlayer distance of $\text{HTiO}[\text{Ru}(\text{bpy})_3^{2+}]$ decreased to 8.8 Å, similar to the original HTiO thin film. Because *ca.* 80% of intercalated Ru was eluted in 0.1 M KNO_3 solution due to exchange of K^+ for intercalated $\text{Ru}(\text{bpy})_3^{2+}$, the subsequent experiments were performed by using the electrode that was washed with distilled water after soaking the KNO_3 solution. It was confirmed that intercalated $\text{Ru}(\text{bpy})_3^{2+}$ was not eluted during experiment.

The electrochemical reactivity of interlayer $\text{Ru}(\text{bpy})_3^{2+}$ was examined based on the absorption spectrum. $\text{Ru}(\text{bpy})_3^{2+}$ produces an absorption maximum at 453 nm due to metal-to-ligand charge transfer (MLCT).¹⁹ $\text{Ru}(\text{bpy})_3^{3+}$, an oxidized form of $\text{Ru}(\text{bpy})_3^{2+}$, also has an absorption maximum at 450 nm, but the molar absorptivity of $\text{Ru}(\text{bpy})_3^{3+}$ is 0.04 times that of $\text{Ru}(\text{bpy})_3^{2+}$.^{18–20} Although the absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ in the interlayer space is similar to that of $\text{Ru}(\text{bpy})_3^{2+}$ in solution, the absorption maximum is shifted to 463 nm. The red-shift can be attributed to a somewhat strained configuration of the complex ions in the interlayers.^{10,21–23}

Figure 2-7 shows the in-situ UV-vis transmittance spectra of $\text{HTiO}[\text{Ru}(\text{bpy})_3^{2+}]/\text{ITO}$ at the external potentials (A) from 0 to 1.3 V and (B) from 1.3 to 0 V. The absorption band in the visible region began to weaken above +0.7 V, as shown in Figure 2-7A. Figure 2-7C shows the cyclic voltammogram of $\text{HTiO}[\text{Ru}(\text{bpy})_3^{2+}]/\text{ITO}$ measured simultaneously with the above UV-vis measurements. A redox potential of interlayer $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}$ appeared at 1.0 V. Anodic current was not observed at potentials lower than +0.6 V, while anodic current due to oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ was observed at potentials higher than +0.6 V. The peak anodic current occurred at 1.05 V. As shown in Figure 2-7A, the absorption band of $\text{Ru}(\text{bpy})_3^{2+}$ weakens significantly at around +1.0 to +1.1 V, corresponding closely with the change in current. Therefore, the weakening of absorption represents the oxidation or decomposition of $\text{Ru}(\text{bpy})_3^{2+}$ by electrochemical reaction. However, as no noticeable change in the cyclic voltammogram was observed over 10 potential scans (0–1.3 V vs Ag/AgCl) as shown in Figure 2-7C, indicating that the redox reaction of the Ru complex in the interlayer space can be regarded as reversible, the

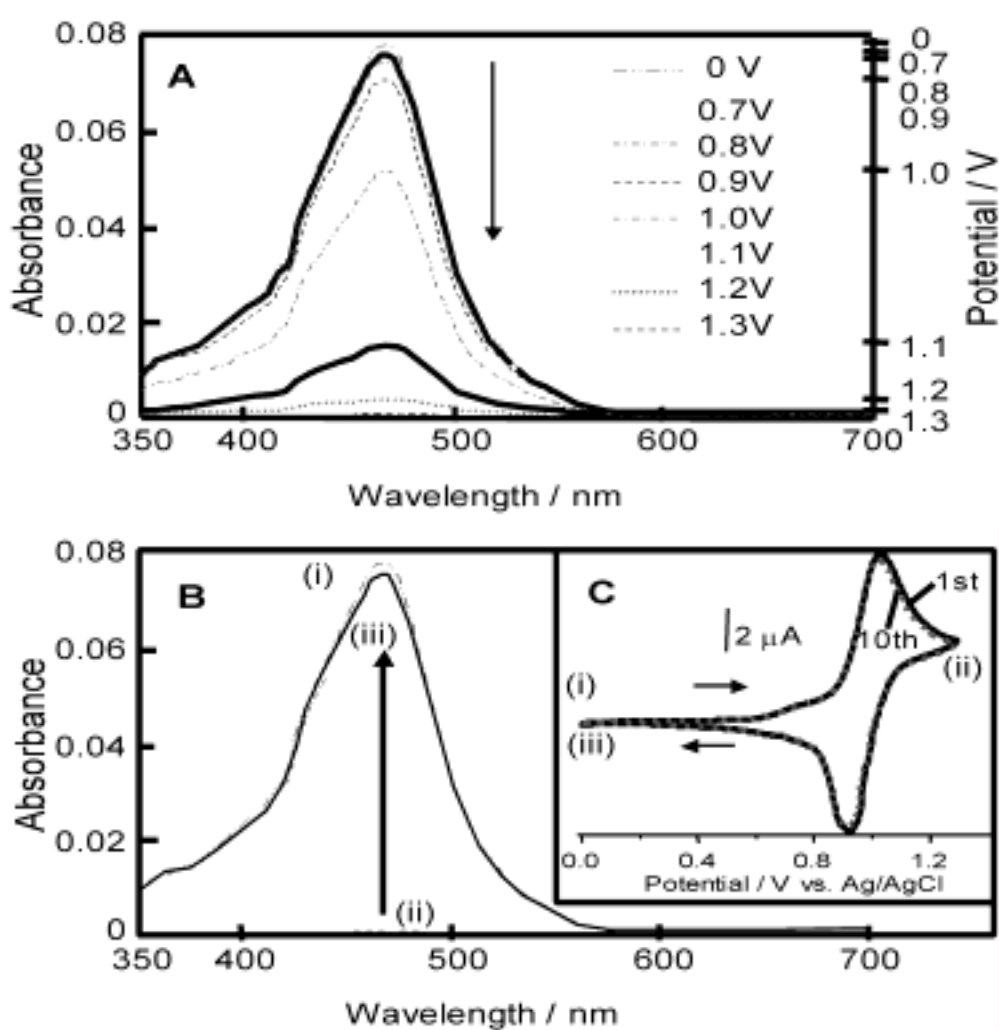


Figure 2-7. UV-vis transmittance spectra of HTiO[Ru(bpy)₃²⁺]/ITO electrode at the externally applied potentials (A) from 0 to 1.3 V, (B) from 1.3 to 0 V and (C) Cyclic voltammogram of HTiO[Ru(bpy)₃²⁺]/ITO electrode (scan rate 2 mV/s, electrolyte 0.1 M KNO₃, N₂ atmosphere). (i): 0 V, (ii): 1.3 V and (iii): 0 V.

weakening of the absorption band must be due to oxidation of Ru(bpy)₃²⁺, not decomposition. It was also found that the absorption spectrum at 0 V almost recovered reversibly when voltages were reduced from 1.3 to 0 V as shown in Figure 2-7B. These results imply that the redox reaction of the Ru complex occurred in the interlayer space of the HTiO film, and that Ru(bpy)₃²⁺ fixed in the interlayer space was electrochemically active and stable. As such, HTiO thin film on ITO appears to be a stable composite suitable as an electrode material.

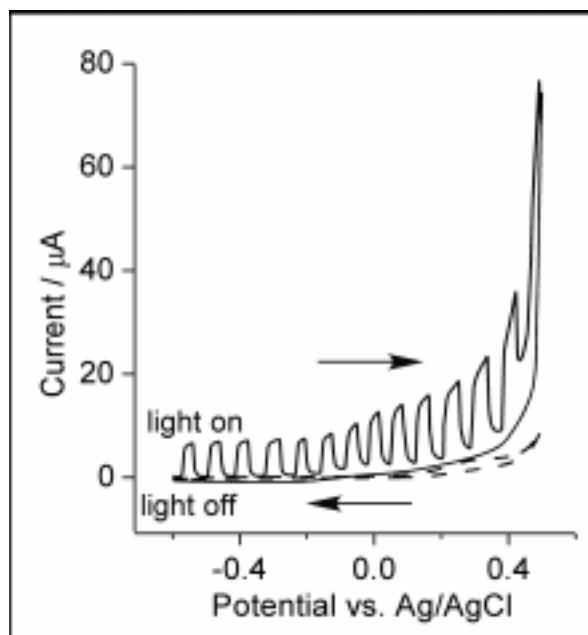


Figure 2-8. Cyclic voltammograms of HTiO[Ru(bpy)₃²⁺]/ITO (solid line) and HTiO/ITO (broken line) under intermittent visible–light irradiation ($\lambda \geq 420$ nm). Scan rate 5 mV/s, N₂ atmosphere, electrolyte 0.1 M KNO₃, sacrificial electron donor 0.1 M TEOA.

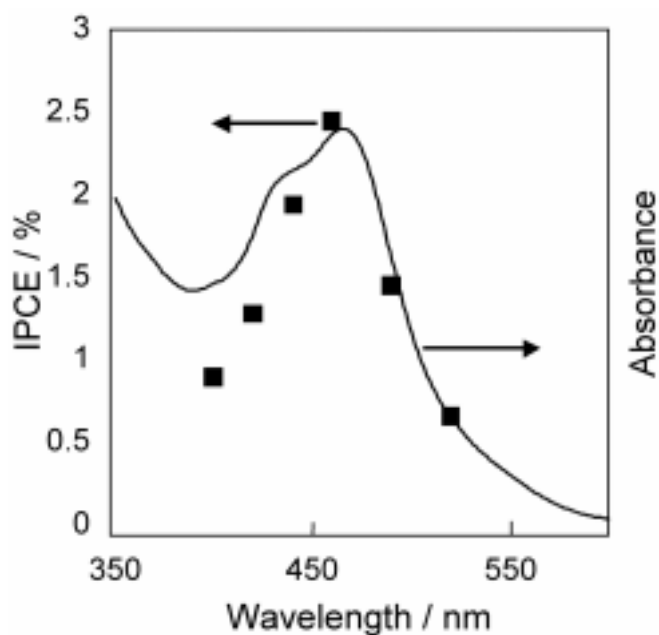


Figure 2-9. Action spectrum of photocurrent generated at the HTiO[Ru(bpy)₃²⁺]/ITO electrode at +0.35 V vs. Ag/AgCl under illumination with a 300 W Xe lamp through various band–pass filters, and absorption spectrum (solid line) of HTiO[Ru(bpy)₃²⁺] (electrolyte 0.1 M KNO₃, sacrificial electron donor 0.1 M TEOA).

Cyclic voltammograms were also measured under intermittent visible-light irradiation ($\lambda \geq 420$ nm) in the presence of TEOA as a sacrificial electro donor at pH = 7. Figure 2-8 shows typical voltammograms of HTiO[Ru(bpy)₃²⁺]/ITO and HTiO/ITO electrodes. HTiO[Ru(bpy)₃²⁺]/ITO exhibited anodic photocurrent, whereas HTiO/ITO did not. This result suggests that the intercalated Ru(bpy)₃²⁺ functions as a visible light-driven sensitizer.

The dark anodic current due to oxidation of TEOA was observed at potentials higher than +0.4 V. The anodic current increased with increasing the potential because of the oxidation of TEOA. The action spectrum of the HTiO[Ru(bpy)₃²⁺]/ITO electrode measured at +0.35 V vs Ag/AgCl) under illumination with a 300 W Xe lamp through a band-pass filter at various wavelengths is shown in Figure 2-9. The plots of photocurrent vs wavelength are in good accordance with the absorption spectrum of the Ru(bpy)₃²⁺ complex. The observed photocurrent is attributed to the sensitization by Ru(bpy)₃²⁺ in the interlayer spaces, and indicates that this electrode has potential application as a wet-type solar cell.

2-4. Conclusion

A thin film composed of an ion-exchangeable layered oxide, Cs_xTi_(2-x/4)□_{x/4}O₄, functioned effectively as an electrode without noticeable degradation in the potential range -0.5 to +1.5 V vs Ag/AgCl. Redox reaction of Ru(bpy)₃²⁺/Ru(bpy)₃³⁺ occurred on an n-octylammonium-modified electrode HTiO[n-octylamine]/ITO, but not on the as-prepared HTiO/ITO thin film. Neither of the electrodes reacted with Fe(CN)₆⁴⁻, attributed to interlayer charge. Based on these results, the modified HTiO/ITO thin film is considered to function as an electrode material with activity in the interlayer spaces rather than on the surface.

Ru(bpy)₃²⁺ was successfully incorporated and fixed into the interlayer spaces of the HTiO[n-octylamine]/ITO electrode. The fixed Ru(bpy)₃²⁺ was electrochemically active and stable, and the electrode exhibited photocurrent generation under visible-light

irradiation. HTiO is therefore a potentially useful electrode material for wet-type solar cells.

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Chapter 3

Electrochemical Behavior of Thin Ta₃N₅ Semiconductor Film

3-1. Introduction

A number of semiconductors have attracted considerable interest for the conversion of photon energy.¹⁻³ Photon energy can be converted by semiconductors such as TiO_2 , SrTiO_3 , CdS or Si , into electrical or chemical energy. Many researchers reported the photoelectrochemical cells with chalcogenide photoanodes such as CdS and CdSe from the view point of efficient solar energy conversion.⁴⁻⁶ The energy conversion efficiencies of those systems are relatively high, whereas the systems have some problems such as the stability of electrode and harmful system which composes of electrode materials such as CdS and CdSe . Therefore, it is also important to develop more stable and less harmful visible light-response photoelectrode than Chalcogenides. In Chapter 2, I described the application of the layered thin film, HTiO , as an electrode of photoelectrochemical cell. A $\text{Ru}(\text{bpy})_3^{2+}$ -intercalated form of the electrode generated photocurrent under visible-light irradiation. However, the incident monochromatic photon-to-current conversion efficiency (IPCE) was low. Recently, a number of (oxy)nitrides of early transition metals such as Ti and Ta have been found to function as photocatalysts with a visible-light response.⁷⁻¹⁰ Through band gap excitations under visible-light irradiation, Ta_3N_5 powder with a band gap of ca. 2 eV evolves H_2 or O_2 from aqueous solutions containing a sacrificial electron donor (methanol) or acceptor (Ag^+) without noticeable degradation.⁷

I have developed a method for the preparation of thin films of Ta_3N_5 .¹¹ Considering the stability of Ta_3N_5 as a visible light-driven photocatalyst,⁷ the $\text{Ta}_3\text{N}_5/\text{Ta}$ system is expected to be applicable as a visible light-driven photoelectrode. It is expected that the IPCE for $\text{Ta}_3\text{N}_5/\text{Ta}$ is higher than that for HTiO . However, the electrochemical and photoelectrochemical properties of this thin film have not yet been examined in detail. In this chapter, the electrochemical property of Ta_3N_5 thin film under dark and visible-light irradiation was investigated to develop a new photoelectrode.

3-2. Experimental Section

3-2-1. Sample Preparation.

Ta₃N₅ thin film (Ta₃N₅/Ta) was prepared by the nitridation of a Ta₂O₅ layer formed on Ta foil (Ta₂O₅/Ta). Ta₃N₅ could not be formed by nitridation of metallic Ta. The Ta₂O₅/Ta precursor was obtained by oxidizing Ta foil (10 × 10 × 0.2 mm³, 99%, Nilaco Co.) in air at 823 K for 30 min. The nitridation of Ta₂O₅/Ta was performed in a quartz reaction cell according to the method in the literature¹¹. Ta₃N₅/Ta was obtained by exposing a Ta₂O₅/Ta foil to NH₃ at a flow rate of 20 mL/min and a temperature of 1123 K for 4 h. One side of the Ta₃N₅/Ta specimen was polished to expose the Ta metal. A Cu wire was then attached to the polished side of the foil using silver paste. All samples were waterproofed (except for the front surface) using an epoxy resin in order to prevent current leakage. The samples were characterized by X-ray powder diffraction (XRD; Geigerflex Rad-B, Rigaku; Cu K α), field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi), ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS; V-560, JASCO) and X-ray photoelectron spectroscopy (XPS; ESCA 3200, Shimadzu).

3-2-2. Electrochemical Measurement.

Cyclic voltammetry was carried out using a conventional electrochemical cell with a Pt counter electrode and an Ag/AgCl reference electrode. A Pyrex cell was used as the electrolytic cell and was filled with 20 mL of electrolyte. The electrolyte was saturated with Ar prior to electrochemical measurements. The photochemical properties were measured under irradiation with visible light ($\lambda \geq 420$ nm) from an Xe lamp (300 W) via a cutoff filter. The gases evolved were analyzed by a thermal conductivity detector (TCD) gas chromatograph. Action spectra were measured under irradiation with a monochromatic lamp. A quartz cell with a flat window was used for action spectra measurement, in which working, counter and reference electrodes were set. The number of photons of monochromatic light reaching the electrode surface was measured at each

wavelength using a Si photodiode. The incident monochromatic photon-to-current conversion efficiency (IPCE)¹² is defined as follows.

$$\text{IPCE} = \frac{1250 \times \text{photocurrent density } (\mu\text{A}/\text{cm}^2)}{\text{wavelength (nm)} \times \text{photo flux } (\text{W}/\text{cm}^2)}$$

3-3. Results and Discussion

3-3-1. Characterization of Ta₃N₅ Thin Film.

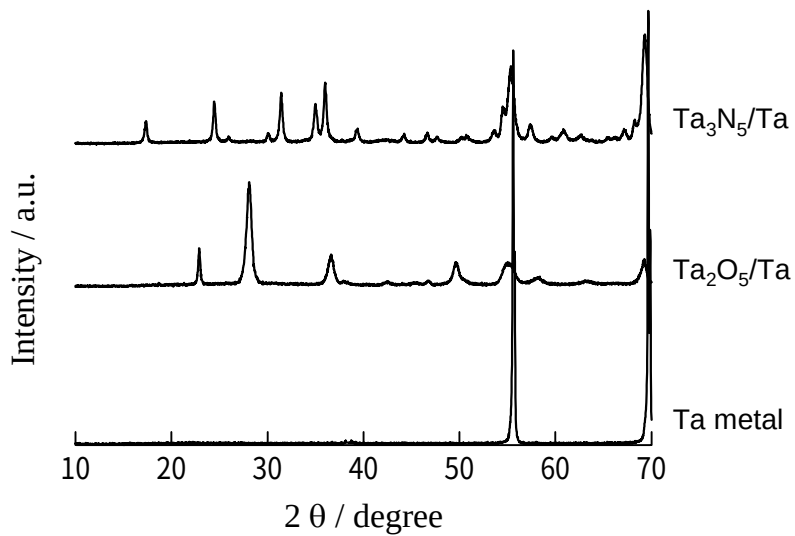


Figure 3-1. XRD patterns of Ta metal, Ta₂O₅/Ta, and Ta₃N₅/Ta.

Figure 3-1 shows the XRD patterns of Ta₂O₅/Ta, and Ta₃N₅/Ta. For comparison, the XRD patterns of Ta foil and Ta₃N₅ powder are also shown. All diffraction peaks of Ta₂O₅/Ta and Ta₃N₅/Ta were assigned to those of Ta₂O₅ and Ta₃N₅, respectively, in addition to the substrate material.

Figure 3-2 shows SEM images of the Ta foil, Ta₂O₅/Ta, and Ta₃N₅/Ta, with corresponding cross-sections also shown. The surfaces of Ta₂O₅/Ta and Ta₃N₅/Ta were rougher than that of the original Ta foil, and exhibited several cracks. Oxidation or nitridation of the Ta foil resulted in a rough surface morphology. The rough part (*ca.* 2 μm) of Ta₂O₅/Ta and Ta₃N₅/Ta in the cross-sectional images appears to correspond to Ta₂O₅ and Ta₃N₅ layers. The thickness of the Ta₃N₅ layer was almost the same as that of the Ta₂O₅ layer,

indicating that only the oxidized part of the Ta foil was nitrided and that the thickness of the Ta_3N_5 is determined by the thickness of the Ta_2O_5 layer.

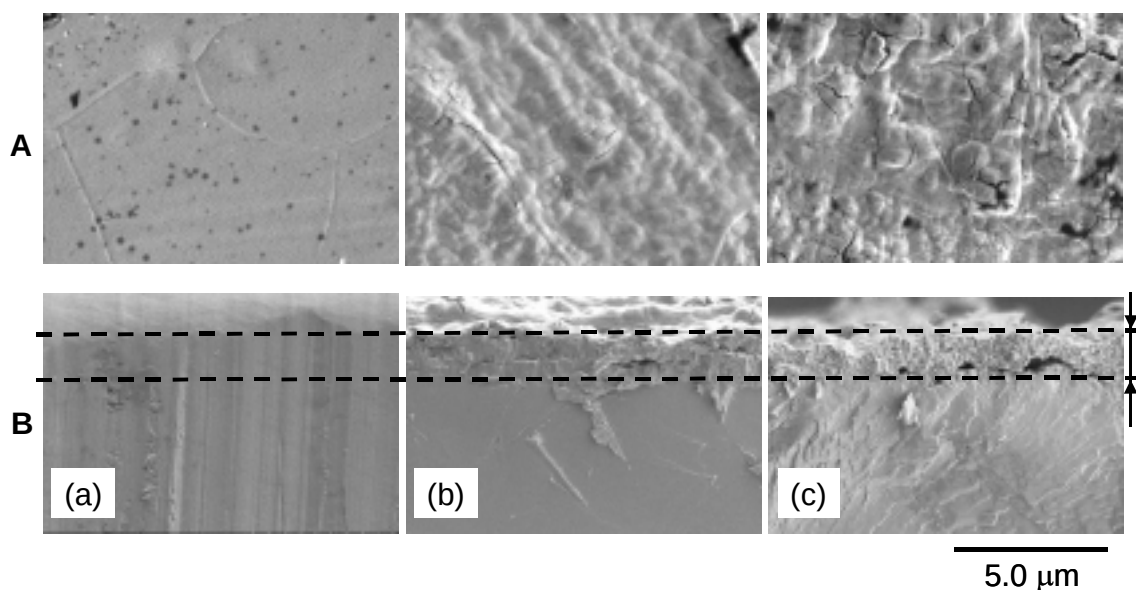


Figure 3-2. SEM images of (a) Ta foil, (b) $\text{Ta}_2\text{O}_5/\text{Ta}$, and (c) $\text{Ta}_3\text{N}_5/\text{Ta}$.

A: surface, B: cross-section.

3-3-2. Cyclic voltammetry of Ta_2O_5 and Ta_3N_5 electrodes.

Cyclic voltammograms of $\text{Ta}_2\text{O}_5/\text{Ta}$ (a) and $\text{Ta}_3\text{N}_5/\text{Ta}$ (b) in 0.1 M H_3PO_4 solution at pH 4 as the supporting electrolyte solution are shown in Figure 3-3. The pH of the solution was adjusted with KOH. A cathodic current was detected, accompanied by copious bubbling, attributable to hydrogen evolution due to negative polarization of $\text{Ta}_3\text{N}_5/\text{Ta}$. In the cyclic voltammograms of $\text{Ta}_2\text{O}_5/\text{Ta}$, the cathodic current, again due to negative polarization, was smaller than for $\text{Ta}_3\text{N}_5/\text{Ta}$. The small cathodic current for Ta_2O_5 appears to be attributable to the low electric conductivity of $\text{Ta}_2\text{O}_5/\text{Ta}$. The anodic current for both $\text{Ta}_3\text{N}_5/\text{Ta}$ and $\text{Ta}_2\text{O}_5/\text{Ta}$ was very small, even at 2.0 V vs Ag/AgCl ($J_D < 50 \mu\text{A cm}^{-2}$), as shown in Figure 3-3(B). The two cyclic voltammograms are essentially identical, with constant values in the potential range of -1.5 to $+2.0$ V vs Ag/AgCl. Therefore, these results indicate that $\text{Ta}_3\text{N}_5/\text{Ta}$ and $\text{Ta}_2\text{O}_5/\text{Ta}$ act as n-type semiconductor electrodes, and that the electrochemical properties of $\text{Ta}_3\text{N}_5/\text{Ta}$ and

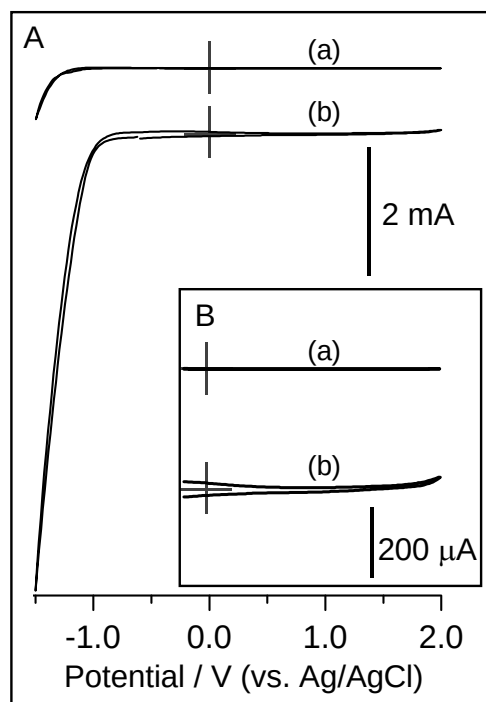


Figure 3-3. Cyclic voltammograms of (a) $\text{Ta}_2\text{O}_5/\text{Ta}$ and (b) $\text{Ta}_3\text{N}_5/\text{Ta}$ in 0.1 M H_3PO_3 solution at pH = 4. Scan rate: 40 mV/s.

$\text{Ta}_2\text{O}_5/\text{Ta}$ are very similar. The XRD patterns and SEM images of $\text{Ta}_3\text{N}_5/\text{Ta}$ did not reveal any noticeable change due to voltammetry measurements, suggesting that the Ta_3N_5 film does not tend to detach from the substrate during voltage cycling and thus has stable electrochemical properties.

3-3-3. Electrochemical Properties of Ta_3N_5 Electrode under Visible-Light Irradiation.

3-3-3-1. Photoelectrolytic Oxidation of Water on Ta_3N_5 Electrode.

The electrochemical properties of $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode under visible-light irradiation were examined in an aqueous solutions of 0.1 M H_3PO_4 (pH = 4) and 0.1 M K_2SO_4 (pH = 11). The pH of the solutions was adjusted with KOH. Figure 3-4(a) shows the current density-potential curve for Ta_3N_5 in H_3PO_4 solution as the supporting electrolyte under chopped visible-light irradiation ($\lambda \geq 420$ nm). Anodic photocurrent based on water oxidation was observed at scanning potentials of -0.6 to +1.9 V vs Ag/AgCl. However, a small amount of nitrogen evolution based on anodic dissolution of Ta_3N_5 itself was also

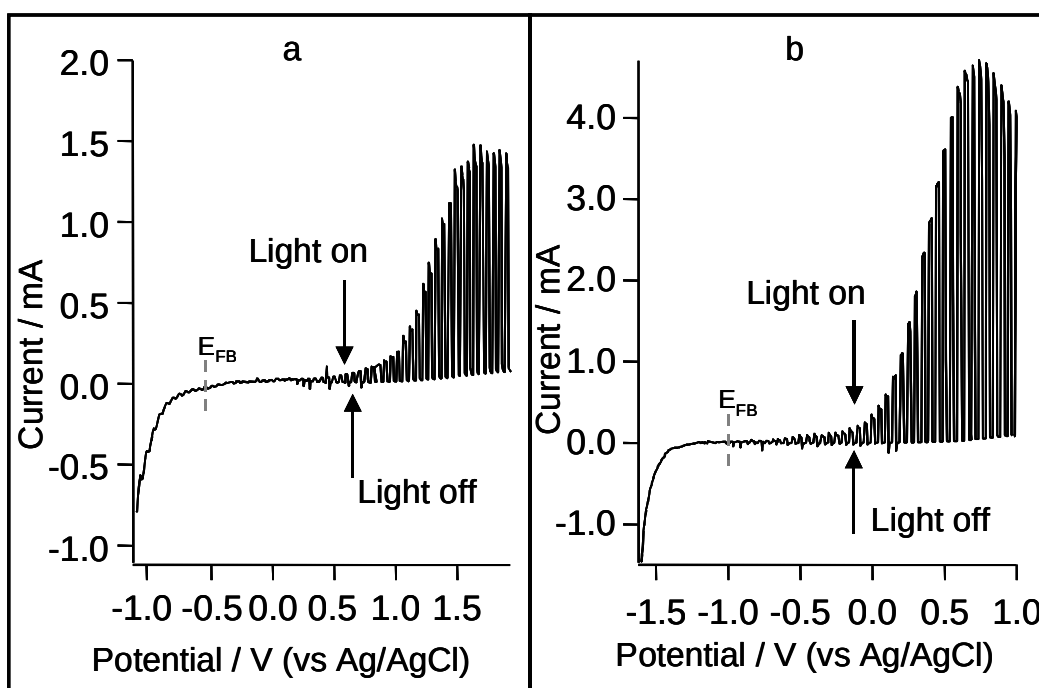


Figure 3-4. Cyclic voltammograms of Ta₃N₅/Ta electrode in (a) 0.1 M H₃PO₃ (pH = 4) and (b) 0.1 M K₂SO₄ (pH = 11) under intermittent visible-light irradiation ($\lambda \geq 420$ nm). Scan rate: 5 mV/s.

observed. Figure 3-4(b) shows a cyclic voltammogram of the Ta₃N₅/Ta electrode in 0.1 M K₂SO₄ solution under chopped visible-light irradiation ($\lambda \geq 420$ nm). Anodic photocurrent at the Ta₃N₅/Ta electrode appeared in the range -1.0 to $+1.0$ V vs Ag/AgCl. The onset potential of photocurrent at pH = 11 was ca. -1.0 V vs Ag/AgCl, which is more negative than that obtained at pH = 4 (see Figure 3-4(a)). The onset potential of photocurrent corresponds to the flat band potential (E_{FB}) of the semiconductor, and the E_{FB} of Ta₃N₅ shifts almost linearly depending on the pH of the electrolyte solution, with a slope of ca. -60 mV/ Δ pH. The intensity of the photocurrent at pH = 11 is also higher compared with that obtained at pH = 4. This result is consistent with that for photocatalysis in the powder suspension system,⁷ where high activity for O₂ evolution was obtained in alkaline solutions.

3-3-3-2. Ta₃N₅ Band Positions.

Figure 3-5 shows the action spectra of Ta₃N₅ electrode measured at a natural bias of -0.1 V vs Ag/AgCl while irradiated with monochromatic light. The UV-vis diffuse reflectance spectrum of Ta₃N₅ powder is also shown for reference. Photocurrent was observed at up to 620 nm, and the plots of photocurrent vs wavelength are in good agreement with the diffuse reflectance spectrum of Ta₃N₅. The observed photocurrent was therefore confirmed to occur as a result of band gap transition. E_{BG} is estimated to be 2.1 eV, and E_{FB} of the Ta₃N₅ thin film is estimated to be *ca.* -1.0 V vs Ag/AgCl at pH = 11 (see Figure 3-4). This E_{FB} is equal to the Fermi level (E_F) of Ta₃N₅. The energy difference between the bottom of the conduction band (E_{CB}) and E_F is assumed to be about 0.3 eV considering that Ta₃N₅ is an insulating n-type semiconductor.¹³ The E_{CB} of Ta₃N₅ is estimated to be *ca.* -1.3 V vs Ag/AgCl at pH = 11 (*ca.* -1.1 V vs NHE), and the E_{VB} of Ta₃N₅ is estimated from the following relationship.

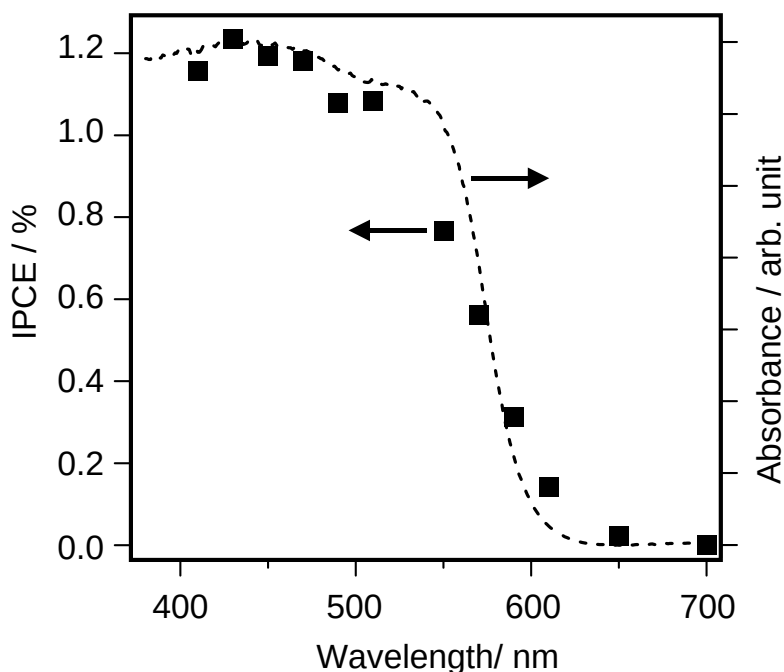


Figure 3-5. Action spectra of photocurrent generated on Ta₃N₅/Ta electrode in 0.1 M K₂SO₄ solution at pH = 11 and -0.1 V under monochromatic visible-light irradiation ($\lambda \geq 420$ nm), and UV-vis diffuse reflectance spectrum of Ta₃N₅ powder (broken line).

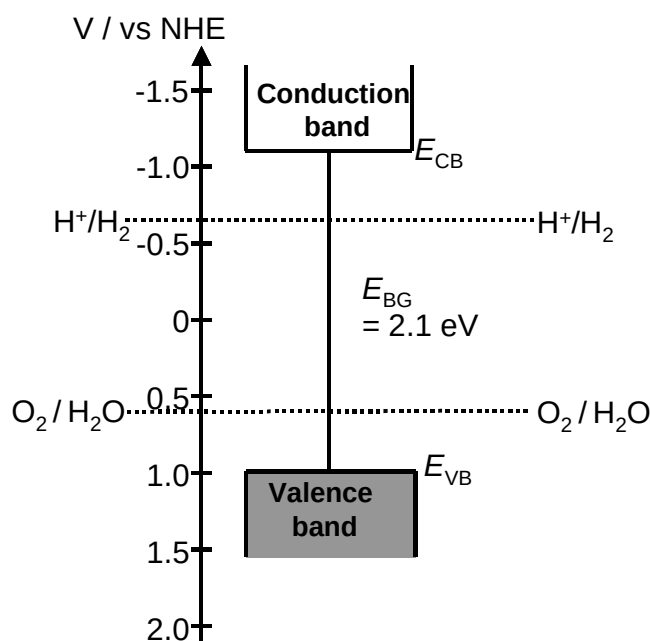
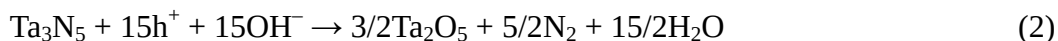


Figure 3-6. Estimated band positions of Ta_3N_5 in 0.1 M K_2SO_4 solution at pH = 11.

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{BG}} \quad (1)$$

where E_{BG} represents the band gap energy of Ta_3N_5 . Based on this relationship, E_{VB} is estimated to be *ca.* +0.8 V vs Ag/AgCl at pH = 11 (*ca.* +1.0 V vs NHE). The estimated band structure of Ta_3N_5 at pH = 11 is illustrated in Figure 3-6. E_{CB} and E_{VB} are sufficient for the reduction of H^+ to H_2 (−0.6 V vs NHE at pH = 11) and the oxidation of water to O_2 (+0.6 V vs NHE at pH = 11) via band gap irradiation. However, photoelectrolysis of water carried out at pH = 11 and −0.1 V vs Ag/AgCl under visible–light irradiation ($\lambda \geq 420$ nm) gave only low photocurrent densities (*ca.* $5 \mu\text{Acm}^{-2}$) and O_2 evolution was not correctly detectable because of the small amount of evolved O_2 . Photoelectrolysis of water at +0.5 V vs Ag/AgCl yielded a lower quantum efficiency (0.03%) of water oxidation on the Ta_3N_5 electrode in the early stage of photoelectrolysis (1 h) compared to that (10%) achieved by the Ta_3N_5 powder suspension system.⁷ In addition, the efficiency of photoelectrolysis decreased with increasing irradiation time. This may be due to degradation of the electrode according to the following decomposition reaction of Ta_3N_5 .



The surface of the Ta_3N_5 thin film was almost entirely oxidized after photoelectrolysis at +0.5 V vs Ag/AgCl for 24 h. These results therefore differ from the stable photocatalysis obtained for the previous powder system.⁷ After photoelectrolysis at -0.1 V vs Ag/AgCl, only approximately one-third of the Ta_3N_5 surface was oxidized. Therefore, the instability of $\text{Ta}_3\text{N}_5/\text{Ta}$ is probably due to excessive positive polarization.

3-3-3-3. Photoelectrochemical Properties of Ta_3N_5 in $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ Solution.

As Ta_3N_5 acts as an n-type semiconductor electrode, the application of the Ta_3N_5 electrode to photoelectrochemical cells was examined in an aqueous solution containing 0.1 M $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ complexes.^{14,15} Figure 3-7 show the current density–potential curve for the $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode under copped visible–light irradiation ($\lambda \geq 420$ nm) in a solution of 0.1 M $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. Anodic photocurrents were detected on the $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode from -0.7 V. Although the photocurrent density for the photoelectrolysis of water at pH = 11 remained between 0.02 and 0.3 mAcm^{-2} below

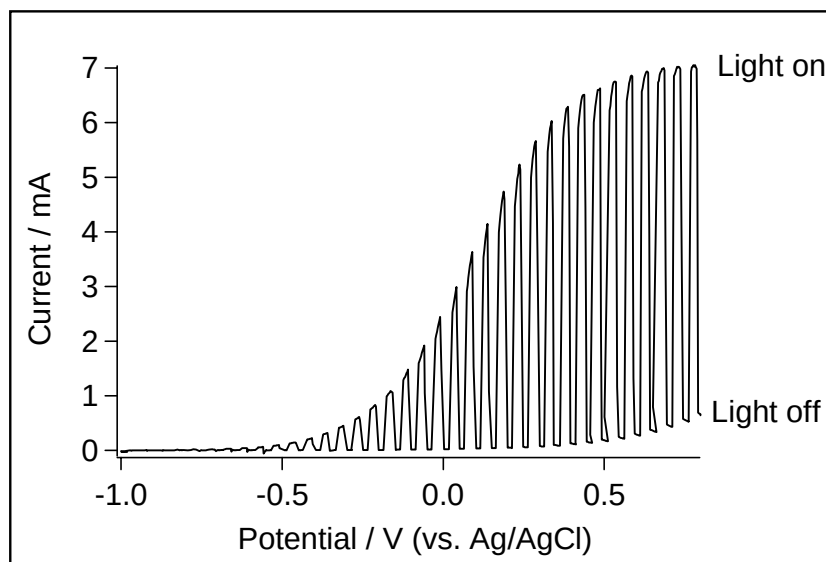


Figure 3-7. Cyclic voltammogram of $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode in a solution of 0.1 M $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ under copped visible–light irradiation ($\lambda \geq 420$ nm) at pH = 8. Scan rate: 5 mV/s.

0 V vs Ag/AgCl, anodic photocurrent increased remarkably as the electrode was positively polarized from -0.7 V in the presence of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox media. The maximum photocurrent was obtained in $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution at 0.6 V. These results are probably attributable to a greater activity for the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ compared to the oxidation of water. Figure 3-8 shows the current–time curve for the Ta_3N_5 electrode at 0 V vs Pt under visible–light irradiation. The current–time curve was obtained in an electrochemical cell with $\text{Ta}_3\text{N}_5/\text{Ta}$ and Pt electrodes. The current density slowly decreased from 4.5 to 4.0 mA cm^{-2} throughout the experimental period (27 h), attributable to surface oxidation of the Ta_3N_5 film and/or the decomposition of Fe complexes.

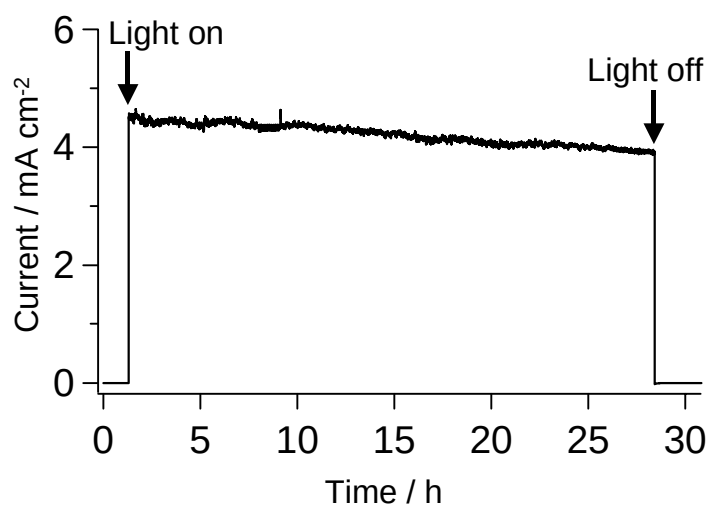


Figure 3-8. Current–time curve for $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode in a solution of 0.1 M $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ at 0 V vs Pt under visible–light irradiation at pH = 8.

3-3-3-4. Stability of Ta₃N₅ in Aqueous Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ Solution under Visible-Light Irradiation.

The stability of the Ta₃N₅ electrode under visible-light irradiation was evaluated based on surface observations of the Ta₃N₅/Ta electrode by XPS. Figure 3-9 shows the XPS

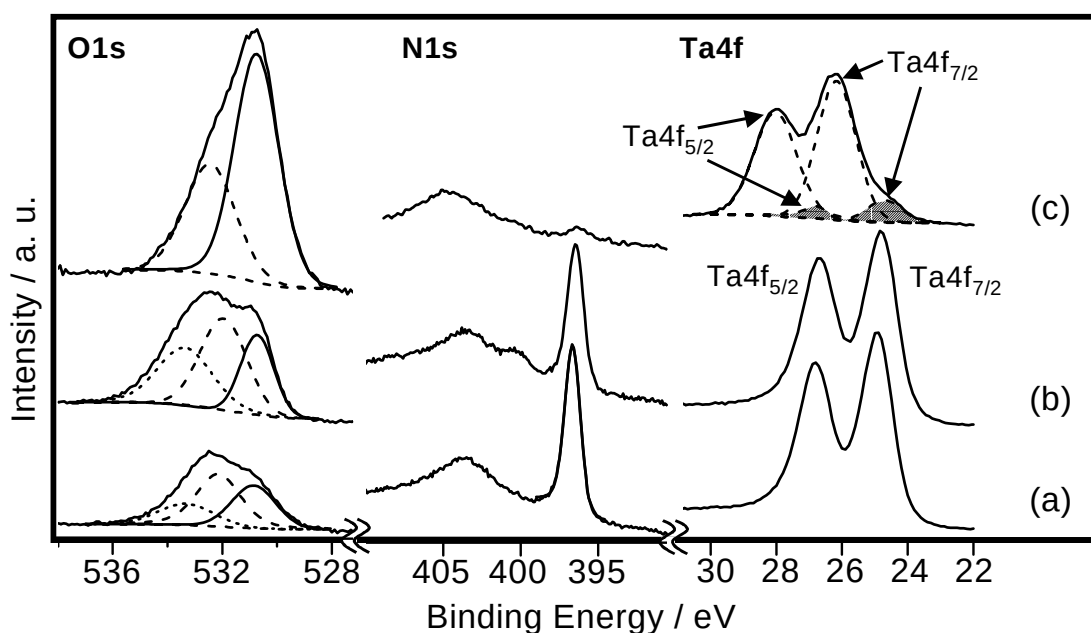


Figure 3-9. XPS spectra of Ta₃N₅/Ta (a) before and (b,c) after photoelectrolysis, (b) in 0.1 M Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ solution at pH = 8 under 0 V vs Pt, and (c) in 0.1 M K₂SO₄ solution at pH = 11 under 0.5 V vs Ag/AgCl.

Table 3-1. Surface Atomic Ratios of O/Ta and N/Ta of Ta₃N₅ Before and After the Photoelectrolysis.

	Oxidized species	O/Ta	N/Ta
Ta ₃ N ₅ thin film	—	0.3	1.4
^a after photoelectrolysis for 27 h	Fe(CN) ₆ ⁴⁻	0.5	1.2
^b after photoelectrolysis for 24 h	H ₂ O	2.6	0.1

^a 0.1 M Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ solution at pH = 8.

^b 0.1 M K₂SO₄ solution at pH = 11.

spectra for Ta₃N₅/Ta samples before and after visible–light irradiation for 27 h, and Table 3-1 summarizes the surface atomic ratios of N/Ta and O/Ta for these samples. For comparison, the XPS spectra for Ta₃N₅/Ta after photoelectrolysis without Fe complexes for 24 h at +0.5 V vs Ag/AgCl are also shown. The surface atomic ratio of O/Ta was estimated from the O1s peak at 531.0 eV assigned to lattice oxygen.¹⁶ After photoelectrolysis for 24 h in aqueous solution without Fe complexes, the N1s peak disappeared and Ta4f_{7/2} and Ta4f_{5/2} peaks appeared at 26.6 and 28.5 eV. These energy values correspond to Ta⁵⁺ in Ta₂O₅, as reported in the literature.¹⁶ The surface atomic ratio of O/Ta (2.6) was close to the stoichiometry of Ta₂O₅ (2.5). No significant difference in the binding energies of the Ta4f and N1s peaks was observed after photoelectrolysis for 27 h in an aqueous solution with Fe complexes. Irradiating the Ta₃N₅ electrode in an aqueous solution with Fe complexes resulted in a small increase in the O1s peak (531.0 eV). The authors have reported that hydrolysis of the surface of Ta₃N₅ thin film in water occurs slowly, and almost ceases after 10 days.¹⁷ A total of approximately one–third of the top surface of the Ta₃N₅ is hydrolyzed by immersion in distilled water for any length of time (< 20 days). The surface N/Ta atomic ratio as shown in Table 3-1 is smaller than that of the sample hydrolyzed by immersion in water. It is considered from the XPS data that the observed chemical stability led to the stable electrochemical function of the Ta₃N₅ electrode.

Although Ta₃N₅/Ta was unstable for water oxidation at +0.5 V vs Ag/AgCl, it was stable for the oxidation of Fe(CN)₆⁴⁻ complexes. The stability of the Ta₃N₅ electrode in an aqueous solution containing Fe complexes appears to be attributable to high activity for Fe(CN)₆⁴⁻ oxidation compared to water oxidation.

3-4. Conclusion

A thin film of Ta_3N_5 acted as an n-type semiconductor electrode. An anodic photo-induced ($\lambda \geq 420$ nm) current associated with the oxidation of water appeared under the application of a potential bias. Action spectra suggested that the observed photocurrent occurred via a band gap transition. Although an anodic photocurrent due to the oxidation of water appeared under visible-light irradiation, the $\text{Ta}_3\text{N}_5/\text{Ta}$ electrode itself underwent oxidation simultaneously. In a solution of $0.1 \text{ M Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$, the photocurrent density was steady at ca. 4 mA cm^{-2} for 27 h, without bias application. No noticeable oxidation of the Ta_3N_5 surface was observed in the aqueous $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ system according to XPS. Thus, $\text{Ta}_3\text{N}_5/\text{Ta}$ has been demonstrated to be a suitable electrode material for visible light-driven photochemical cells.

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Chapter 4

Conduction and valence Band Position of Ta_2O_5 , TaON , and Ta_3N_5
by UPS and Electrochemical Methods

4-1. Introduction

For most photoelectronic applications of semiconductors and insulators, the knowledge of absolute band gap positions is essential. Domen and co-workers have been investigating the utilization of various oxides and non-oxide materials as photocatalysts for overall water splitting in an effort to achieve efficient photochemical energy conversion.¹⁻⁶ The thermodynamic requirements for solid-state photocatalysts suitable for overall water splitting are as follows.

The bottom of the conduction band E_{CB} should be more negative than the H^+/H_2 redox potential, that is, 0 V vs NHE at pH = 0 (or the electron potential should be more positive than -4.44 eV vs the vacuum level).

The top of the valence band E_{VB} should be more positive than the O_2/OH^- redox potential, that is, +1.23 V vs NHE at pH = 0 (or more negative than -5.6 eV vs the vacuum level).

At present, many researchers are concentrating on developing promising materials for overall water splitting under visible light irradiation ($400\text{ nm} < \lambda < 800\text{ nm}$). A number of (oxy)nitrides of early transition metals such as Ti^4 and $Ta^{5,6}$ have been found to be potential candidates for this application. The photocatalytic activities of (oxy)nitride, such as TaON and Ta_3N_5 , are relatively high for O_2 evolution, but relatively low for H_2 evolution. The low activity for H_2 evolution might be related to the band positions of (oxy)nitrides because the band gap positions of these materials were unknown. This is a significant and controversial point. Chapter 3 revealed that the band position of Ta_3N_5 has satisfactory potentials for the reduction of H^+ to H_2 and the oxidation of H_2O to O_2 . It was, therefore, found that the low activity for H_2 evolution was attributed to other factors such as the presence of surface state trapping photogenerated electrons and the poor electronic contact of co-catalysts with Ta_3N_5 . However, in most cases the fabrication of suitable electrodes has been unsuccessful due to difficulties in processing the powder samples. It was also difficult to prepare TaON electrode for electrochemical measurements. Therefore, the author has begun to use photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy (UPS) in particular, to determine the band gap

positions of these materials. This method is a useful technique for this situation because the correlation between the photoelectrode potential and the absolute potential of electrons has already been established.⁷ The sole difficulty in performing UPS measurements for such wide band gap and low-conductivity materials is undesirable charging of the samples during measurement.

In this chapter, Ta₂O₅, TaON and Ta₃N₅ samples prepared by several methods are analyzed by electrochemical methods and UPS to determine the band positions and to confirm the validity of UPS analysis for this purpose.

4-2. Experimental Section

4-2-1. Sample Preparation.

Two different series of samples were prepared. One series was prepared from Ta foil for analysis by electrochemical methods and UPS. The Ta foil ($10 \times 10 \times 0.2 \text{ mm}^3$, 99%, Nilaco Co.) was oxidized at 823 K in air for 30 min to give a Ta₂O₅/Ta sample, and a Ta₃N₅/Ta sample was obtained by exposing a Ta₂O₅/Ta foil sample to NH₃ at 1123 K and a flow rate of 20 mL/min for 4 h. I also attempted to prepare TaON/Ta; however, the surface layer peeled off easily for all samples and a suitable preparation condition was not found. The second series was prepared from powder samples. TaON and Ta₃N₅ powders were synthesized by the following procedures according to the literature.⁸ Bright yellow TaON was obtained by exposing Ta₂O₅ (99%, Rare Metallic Co., Ltd.) to NH₃ (99.999%, Mitsui Chemicals Co. Ltd.) at 1023 K and a flow rate of 20 mL/min for 20 h. Pure wine-red Ta₃N₅ was prepared by a similar method at 1123 K and a flow rate of 1000 mL/min for 10–15 h. Initially, powder samples pressed into disks were employed for UPS measurement; however, reliable and reproducible data could not be obtained due mainly to sample charging. Therefore, samples were prepared by electrophoretic deposition on Pt foils.^{9,10} TaON or Ta₃N₅ powder (50 mg) was suspended in 50 mL of acetone containing 10 mg of I₂ by ultrasonication. The electrophoretic deposition of TaON or Ta₃N₅ was performed using a thin Pt foil

($25 \times 10 \times 0.1 \text{ mm}^3$) as an anode. Deposition was carried out for 1 min at 20 V. The prepared sample was then washed thoroughly with acetone prior to UPS measurement.

4-2-2. Characterization.

Samples were characterized by atomic force microscopy (AFM; TMX-2100, TopoMetrix), X-ray diffractometry (XRD; Geigerflex Rad-B system Cu $K\alpha$ 15 mA, Rigaku), field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi) and UV-visible diffuse reflectance spectroscopy (UV-vis DR; V-560, JASCO). X-ray photoelectron spectroscopy (XPS) was performed using a VG-ADES 400 instrument (Vacuum Generators Co.) with Mg $K\alpha$ X-ray source at a residual gas pressure of below 10^{-8} Pa. The binding energy was calibrated against Au $4f_{7/2}$ (83.9 eV).

4-2-3. Electrochemical Measurement.

A Cu wire was attached to the $\text{Ta}_2\text{O}_5/\text{Ta}$ or $\text{Ta}_3\text{N}_5/\text{Ta}$ foil with silver paste, and all samples were waterproofed, except for the front surface, with epoxy resin to prevent current leakage. A Pyrex electrolytic cell was employed, filled with 20 mL of Ar-purged 0.5 M K_2SO_4 . The pH of the solution was adjusted with 0.1 M NaOH and 0.1 M H_2SO_4 . A Pt wire and Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. Impedance measurements were recorded using a frequency response analyzer (HZ-3000, Hokuto, Ltd.).

4-2-4. UPS Measurement.

UPS spectra were measured using He I excitation (21.2 eV) and recorded with a constant pass energy of 5 eV in the ultrahigh vacuum (UHV) chamber of the XPS instrument. UPS binding energies were referenced to the Fermi edge of Au, which was sputtered onto the sample in the UPS chamber. Figure 4-1 shows an illustration of a foil coated with Au. The spot diameters of the deposited Au and UV light were 2 mm. None of the samples were damaged in these measurements. Prior to XPS and UPS measurements,

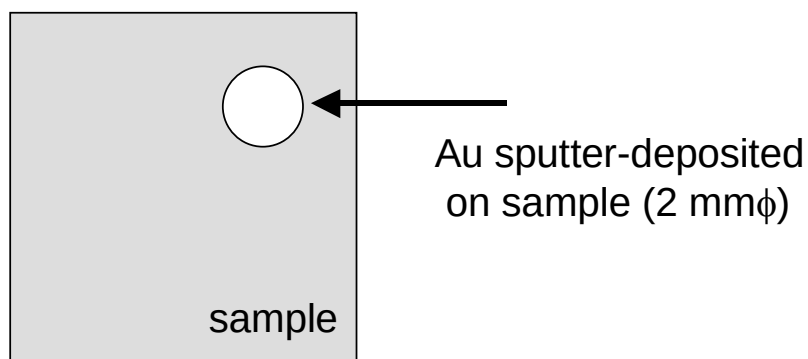


Figure 4-1. Schematic illustration of sample coated with Au.

the Ta₂O₅/Ta sample was oxidized at 823 K for 30 min in the UHV chamber in an O₂ (99.999% purity) atmosphere at 5×10^{-3} Pa to remove surface impurities. To maintain the purity of O₂ in the UHV chamber, the chamber was evacuated to 10^{-5} Pa and charged with fresh O₂ every 5 min. The TaON/Pt, Ta₃N₅/Ta, and Ta₃N₅/Pt samples were subjected to low-temperature H₂ treatment to remove surface contamination. The samples were heated for 1 h at 523 K in the UHV chamber in an H₂ (99.999% purity) atmosphere at 5×10^{-3} Pa. Fresh H₂ was introduced every 10 min.

4-2-5. Measurement of ζ Potential.

The ζ potential was measured on a DELSA 440SX (Coulter). The suspension fluid was 0.01 M aqueous solution of KCl with pH adjusted by the addition of 0.01 M HCl and 0.01 M KOH solutions.

4-3. Results

4-3-1. XRD, SEM, AFM and UV-vis DRS.

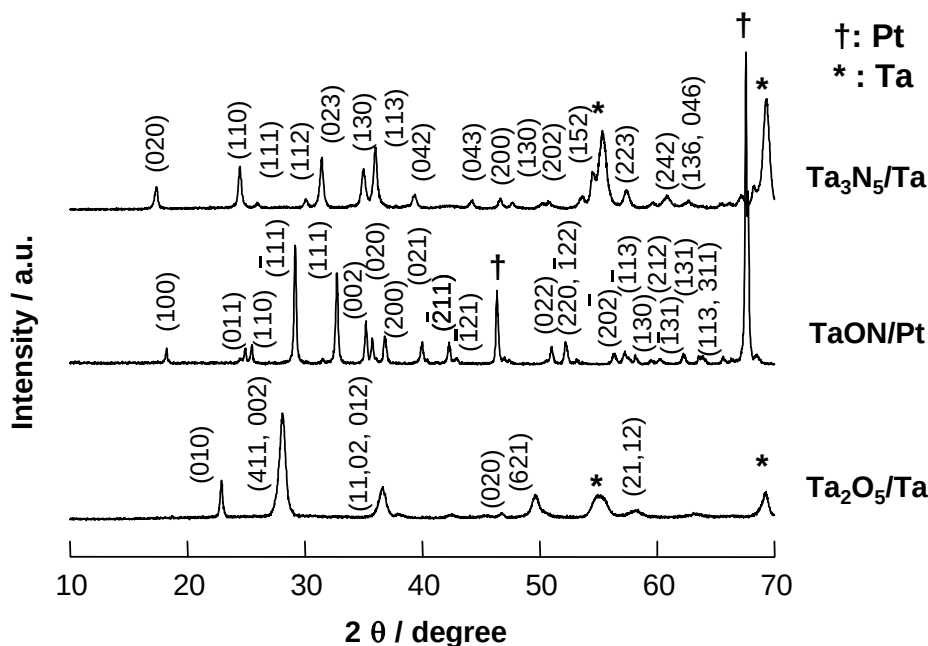


Figure 4-2. X-ray diffraction patterns of $\text{Ta}_2\text{O}_5/\text{Ta}$, TaON/Pt , and $\text{Ta}_3\text{N}_5/\text{Ta}$.

XRD patterns of $\text{Ta}_2\text{O}_5/\text{Ta}$, TaON/Pt , and $\text{Ta}_3\text{N}_5/\text{Ta}$ are shown in Figure 4-2. All diffraction peaks were assigned to Ta_2O_5 , TaON, and Ta_3N_5 , respectively, in addition to the substrate materials.^{11,12} No impurity phases were observed.

Figure 4-3 shows SEM images of $\text{Ta}_2\text{O}_5/\text{Ta}$, $\text{Ta}_3\text{N}_5/\text{Ta}$, and TaON/Pt . The surfaces of $\text{Ta}_2\text{O}_5/\text{Ta}$ (a) and $\text{Ta}_3\text{N}_5/\text{Ta}$ (b) were essentially flat, with several cracks. TaON particles electrophoretically deposited on Pt were estimated to be 0.5–1.0 μm in diameter, and the Pt substrate surface could not be observed, as shown in Figure 4-3c,d.

Figure 4-4 shows the AFM image of the TaON/Pt sample. The dark (lower) part of the image is a bare Pt area where TaON deposition was prevented. From the difference in height between the bare and coated Pt areas, the thickness of the TaON film was estimated to be about 2 μm .

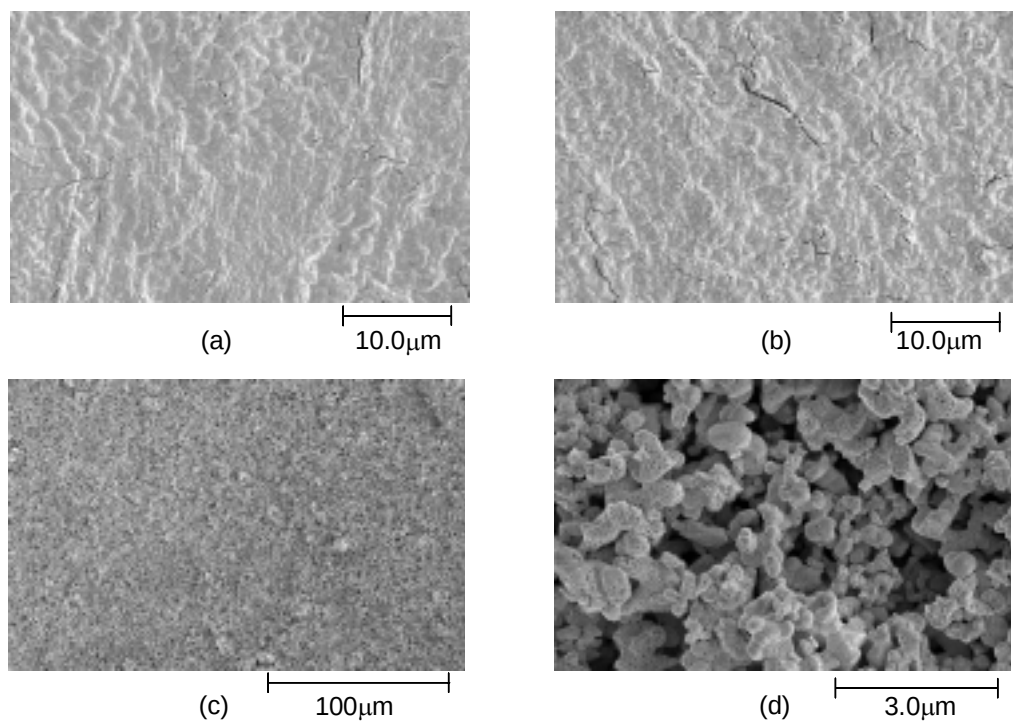


Figure 4-3. SEM images of (a) $\text{Ta}_2\text{O}_5/\text{Ta}$, (b) $\text{Ta}_3\text{N}_5/\text{Ta}$, and (c,d) TaON/Pt .

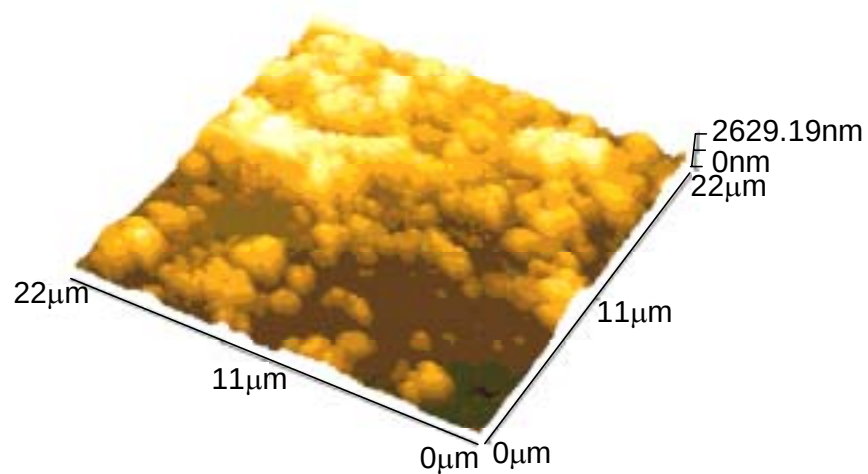
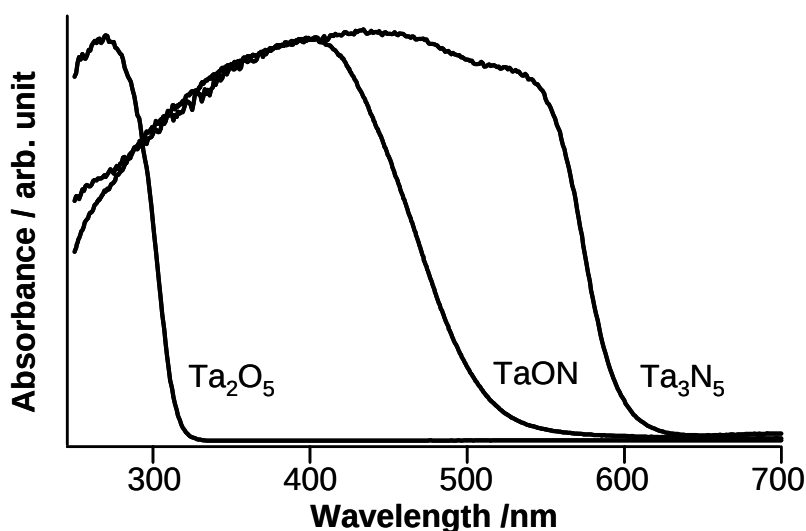


Figure 4-4. AFM image of TaON/Pt .

Figure 4-5 shows the UV-vis DR spectra for powder samples of Ta_2O_5 , TaON, and Ta_3N_5 . TaON/Pt was prepared from TaON powder by electrophoretic deposition. The Ta_3N_5 /Pt sample was also prepared by electrophoretic deposition with Ta_3N_5 powder. The spectra of TaON/Pt and Ta_3N_5 /Pt should be the same with the powder samples. The values of E_{BG} were, therefore, determined by UV-vis DR spectra for powder samples in this paper. In the UV-vis spectra, the absorption band-edges of TaON and Ta_3N_5 occur at 520 and 600 nm, respectively, and are shifted by about 200 and 280 nm from that of Ta_2O_5 . The band gap energies (E_{BG}) of Ta_2O_5 , TaON and Ta_3N_5 were estimated to be 3.9, 2.4, and 2.1 eV, respectively.



4-3-2. XPS Analysis.

XPS was used to examine the surface composition of Ta, N, and O and the oxidation state of Ta in the samples. Figure 4-6 shows the O1s, N1s, and Ta4f spectra of $\text{Ta}_2\text{O}_5/\text{Ta}$, TaON/Pt and $\text{Ta}_3\text{N}_5/\text{Ta}$, respectively. Peak positions are summarized in Table 4-1. Sample charging was often observed for the oxide powders, but was not observed for the thin-film samples including TaON/Pt. The peak positions of the O1s spectra were very similar in all samples. The observed O1s spectrum of $\text{Ta}_3\text{N}_5/\text{Ta}$ most likely contains

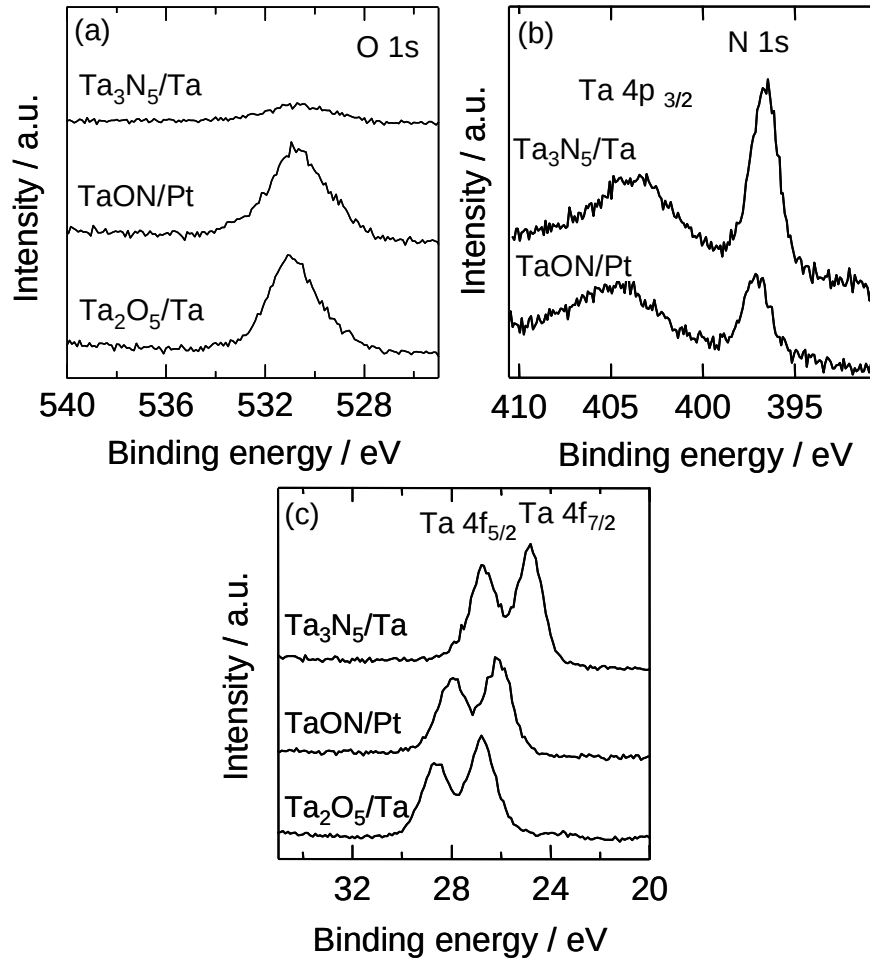


Figure 4-6. X-ray photoelectron spectra of Ta₂O₅/Ta, TaON/Pt, and Ta₃N₅/Ta: (a) O1s, (b) N1s, and (c) Ta4f regions.

Table 4-1. Binding Energies of O1s, N1s, Ta4f_{5/2}, and Ta4f_{7/2} Peaks for Ta₂O₅/Ta, TaON/Pt, and Ta₃N₅/Ta.

electrodes	O1S /eV	N1S /eV	Ta4f _{5/2} / eV	Ta4f _{7/2} / eV
Ta metal	N/A	N/A	23.7	21.8
Ta ₂ O ₅ /Ta	530.9	N/A	28.5	26.6
TaON/Pt	530.8	397.1	27.7	25.8
Ta ₃ N ₅ /Ta	530.7	396.5	26.7	24.8

information from the area out side the sample. The spot size of the irradiated X-ray is much larger than the He I used for the UPS measurement, which is 2 mm in diameter.

Judging from actual intensity, the contribution of the surface oxygen on Ta₃N₅/Ta should be negligibly small for UPS measurement.

No Ta⁰ or Pt⁰ metal peak was observed in any of the samples, indicating that the substrate was completely obscured. In Ta₂O₅/Ta, Ta4f_{7/2}, and Ta4f_{5/2} peaks appeared at 26.6 and 28.5 eV, respectively. These energy values correspond to Ta⁵⁺ in Ta₂O₅ as reported in the literature.¹³ Ta4f peaks for TaON/Pt and Ta₃N₅/Ta are shifted to lower binding energies by *ca.* 0.8 and 1.8 eV compared to those of Ta₂O₅. Considering the difference in electronegativity between O and N, it is considered that the electron density around Ta atom increases with the N/O ratio. In other words, the covalency between Ta and N is greater than between Ta and O. This kind of difference could affect the band gap positions of these materials.

4-3-3. Electrochemical Measurements.

To estimate flat band potentials (E_{FB}), plots of (differential capacitance)⁻² against electrode potential (Mott–Schottky plots) under different pH conditions for both electrodes were constructed, as shown in Figure 4-7. It was found that the flat band potential of Ta₂O₅ depends almost linearly on the pH of the electrolyte solution with a slope of

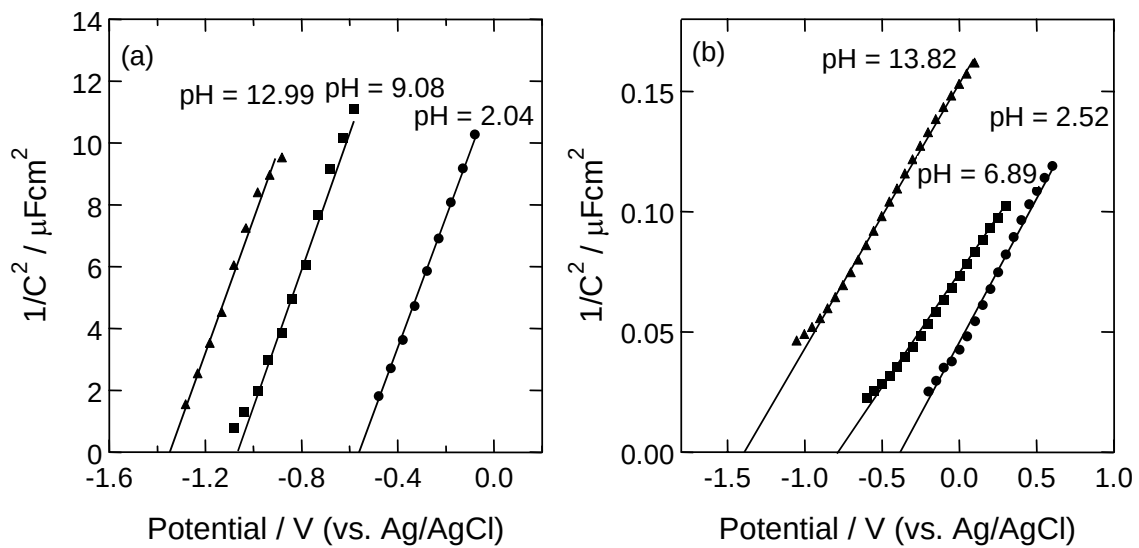


Figure 4-7. Mott–Schottky plots of (a) Ta₂O₅ and (b) Ta₃N₅ under various pH conditions.

ca. $-60 \text{ mV}/\Delta\text{pH}$ as seen in Figure 4-7(a). It is known that oxide semiconductors in general react with H^+ or OH^- ions in solution, and the band edges at the interface consequently shift with the pH of the solution by 60 mV per pH unit change in the solution. Interestingly, it was also found that the E_{FB} of Ta_3N_5 varies linearly with pH, as seen in Figure 4-7b. Huygens reported that the E_{FB} of GaN is also a linear function of pH.¹⁴ The E_{FB} of Ta_2O_5 is approximately -1.3 V vs Ag/AgCl (-1.1 V vs NHE) at $\text{pH} = 13$ and -0.5 V vs Ag/AgCl at $\text{pH} = 0$ (-0.3 V vs NHE), and the E_{FB} of Ta_3N_5 is approximately -1.0 V vs Ag/AgCl (-0.8 V vs NHE) at $\text{pH} = 13$ and -0.3 V vs Ag/AgCl at $\text{pH} = 0$ (0.0 V vs NHE). The band position of Ta_3N_5 is the same as that obtained by photocurrent voltage response as describe in Chapter 3. Impedance measurements could not be completed for the TaON/Pt electrode because the electrolyte penetrated down to the Pt substrate.

4-3-4. UPS Measurement.

As an example, UPS spectra of TaON/Pt measured at various sample biases (0, -10 , and -15 V) are shown in Figure 4-8. The cutoff of the UPS spectrum (or low kinetic energy

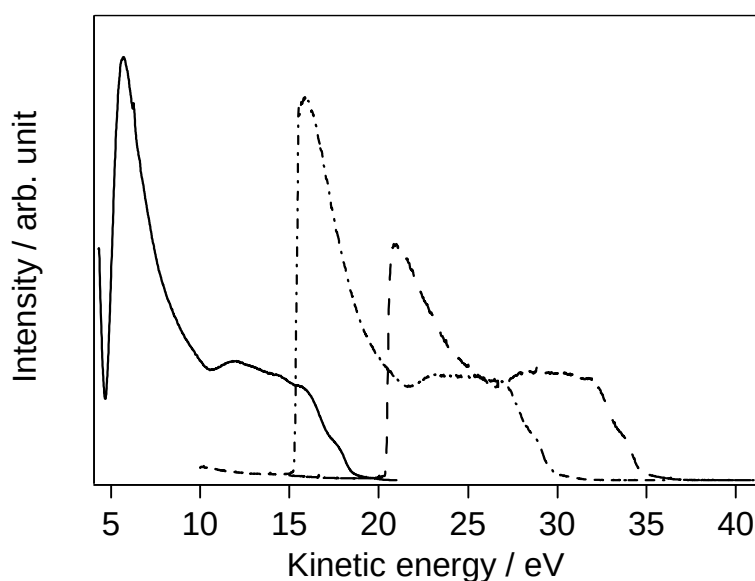


Figure 4-8. UPS spectra of TaON/Pt measured at various sample biases. Solid line: 5 V, Dash-dotted line: 10 V and Dashed line: 15 V.

region) with the sample bias of 0 V cannot be observed clearly. The cutoff position ($E_K = 0$ eV) needs to be identified to estimate the vacuum level, and sample biases higher than the work function allow this to be achieved. At -10 and -15 V, clear cutoffs could be observed in the UPS spectra, as shown in Figure 4-8. The following equation should then hold:

$$E_B + E_K + \phi_{\text{analyzer}} = 21.2 \text{ eV} \quad (1)$$

where E_B , E_K and ϕ_{analyzer} are the binding energy measured from the Fermi level, the kinetic energy of the electron, and the work function of the analyzer. Therefore, ϕ_{analyzer} was found to be smaller than 10 eV, and an applied potential of 10 eV was sufficient to capture the entire spectrum.

Features in the valence band and the entire spectrum remained unchanged with respect to the different biases, although the background attributed to secondary electron emission was reduced. It should be noted that none of the samples charged up during UPS measurement as in the case for XPS measurement. Figure 4-9 shows the UPS spectra of TaON/Pt and Au on TaON/Pt. The Fermi level of Au on TaON/Pt was estimated to be at $E_K = 31.8$ eV in the spectrum. The Fermi level of TaON/Pt is at the same position as

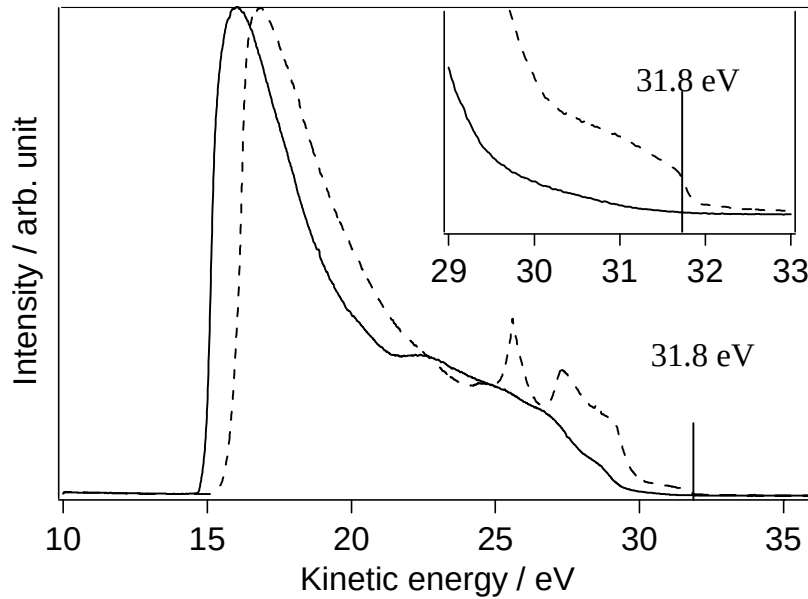


Figure 4-9. UPS spectra of TaON/Pt (solid line) and Au on TaON/Pt (dashed line).

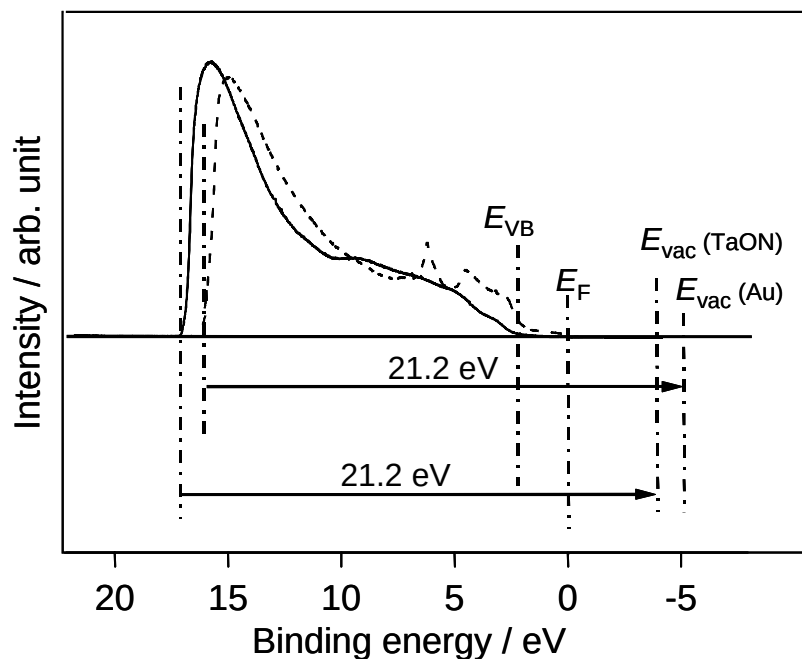


Figure 4-10. Comparison and relationship of E_{VB} , E_F , and E_{vac} of UPS spectra.
Solid line: TaON/Pt and Dashed line: Au on TaON/Pt.

that of Au deposited on TaON/Pt, which allows the Fermi level to be determined experimentally.

The relationship between several energy levels (E_{VB} , E_F and E_{vac}) and the UPS spectrum of TaON/Pt and Au is shown in Figure 4-10. The figure shows the scale of binding energy with the Fermi level of Au set at 0 V. The vacuum level (E_{vac}) should be located 21.2 eV above the cutoff energy of the spectrum. The work functions of TaON and Au based on this definition are estimated to be 4.4 and 5.1 eV, respectively. The work function of Au is in good agreement with the literature,¹⁵ and the estimated work functions of Au on Ta₂O₅/Ta and Ta₃N₅/Ta are the same as that of Au alone. Figure 4-11 shows a series of UPS spectra for Ta₂O₅/Ta, Ta₃N₅/Ta, and TaON/Pt in the valence band region. Ta₃N₅/Pt sample was prepared by electrophoretic deposition with Ta₃N₅ powder and the UPS result was coincided with the result of Ta₃N₅/Ta. (UPS spectrum of Ta₃N₅/Pt is not shown.) In this figure, the three spectra were compared with E_{vac} at the same position. The position of the top of the valence band (E_{VB}) for each sample is indicated on the spectrum. The E_{VB} positions in all measurements based on linear extrapolation are

shown in Figure 4-11. E_{VB} shifts to lower binding energies with increasing nitrogen content in the sample. The E_{VB} and Fermi level for each sample are summarized in Table 4-2.

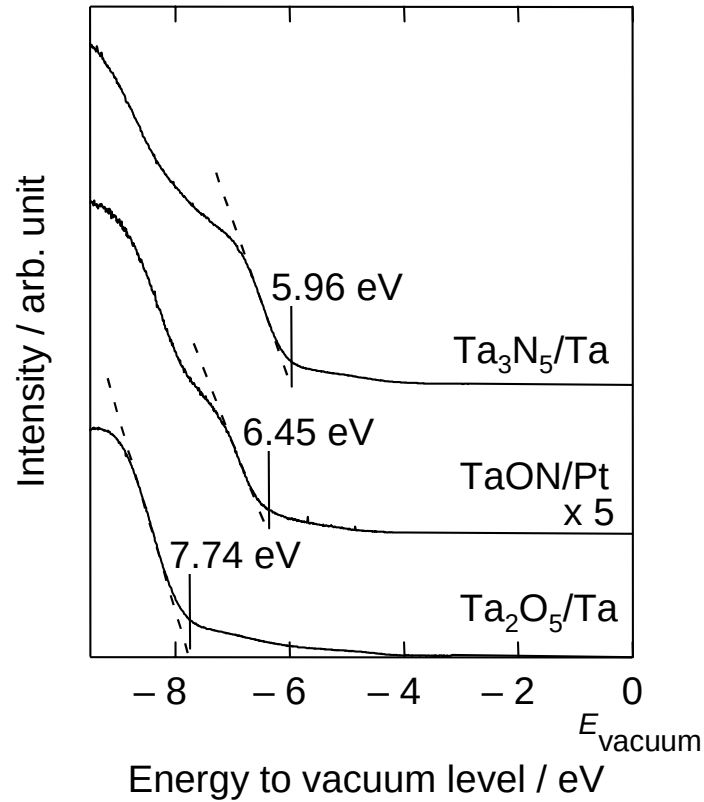


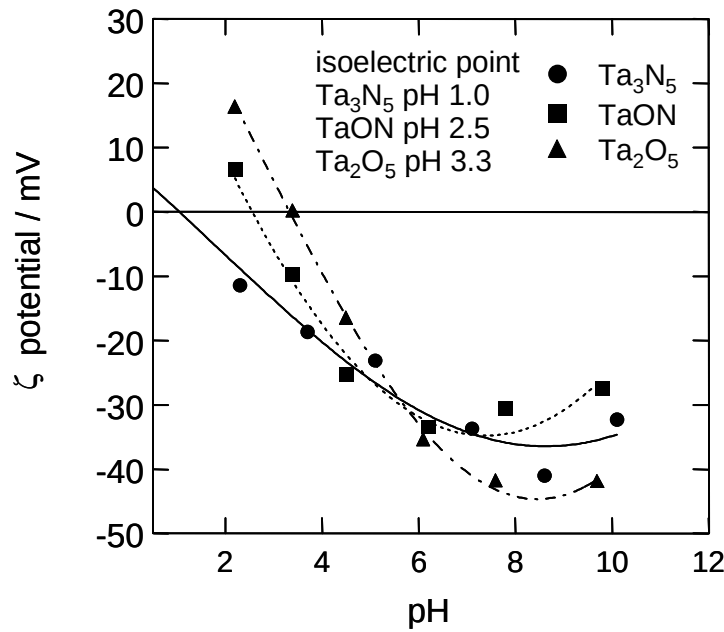
Figure 4-11. UPS spectra of Ta_2O_5/Ta , $TaON/Pt$, and Ta_3N_5/Ta in the valence band region.

Table 4-2. Band Energies of Ta_2O_5/Ta , $TaON/Pt$, and Ta_3N_5/Ta by UPS.

Electrodes	Fermi level / eV	E_{VB} / eV
Ta_2O_5/Ta	-4.25	-7.74
$TaON/Pt$	-4.26	-6.45
Ta_3N_5/Ta	-4.15	-5.96

4-3-5. Measurement of ζ Potential.

To correlate the data obtained by the two methods, the ζ potential was measured to determine the isoelectric point of each sample. The ζ potential curves against pH are shown in Figure 4-12. The isoelectric points of Ta_2O_5 and TaON thus determined occur at pH values of 3.3 and 2.5, respectively. For Ta_3N_5 , the isoelectric point was estimated to occur at a pH of about 1.0 by extrapolation of the ζ potential curve.



4-4. Discussion

The relationship between the absolute electron potential of an electrode (E_{abs}) and the standard electrode potential (E^0) is expressed as follows.

$$E_{\text{abs}} = -E^0 - 4.44 \text{ (at 298 K)} \quad (2)$$

where the electron energy is 0 eV in a vacuum. This equation appears to allow correlation of the data obtained by the two methods. However, there is still uncertainty in terms of the pH to which the data obtained by UPS should be correlated. Generally, in an aqueous solution, the potential energies such as E_{CB} , E_{VB} and E_{F} , vary depending on the pH, particularly for oxide semiconductors. This is due to surface ionization driven by adsorbed species (e.g., H^+ and OH^-). It is considered that the net charge of the

sample in UHV is zero. Therefore, the energy levels determined by UPS are assumed to correspond to those obtained in an electrolyte at the pH at which the surface charge of the sample is zero. The pH of the isoelectric points of the samples in aqueous solution was determined by measurement of the ζ potential. From Mott–Schottky plots, the E_{FB} of Ta_2O_5 and Ta_3N_5 was found to shift with pH of the solution by -60 mV per pH unit change. The E_{FB} of TaON is also expected to be a linear function of pH because the surface of TaON should behave similarly to the surfaces of Ta_2O_5 and Ta_3N_5 .

On the basis of the relationship discussed above, Figure 4-13 illustrates the comparison of band positions determined by UPS and electrochemical measurements at pH = 0. Table 4-3 lists the values of E_{BG} , E_{F} , E_{VB} and E_{CB} determined by UV–vis diffuse reflectance spectra, electrochemical analysis and UPS measurements. The UPS result of $\text{Ta}_3\text{N}_5/\text{Ta}$ was coincided with the result of $\text{Ta}_3\text{N}_5/\text{Pt}$ sample. Ta_3N_5 prepared on Ta and Ta_3N_5 powder should have the same UV–vis DR spectra. The value of E_{BG} was, therefore, determined by UV–vis DR spectra for Ta_3N_5 powder. It is generally known that the E_{CB}

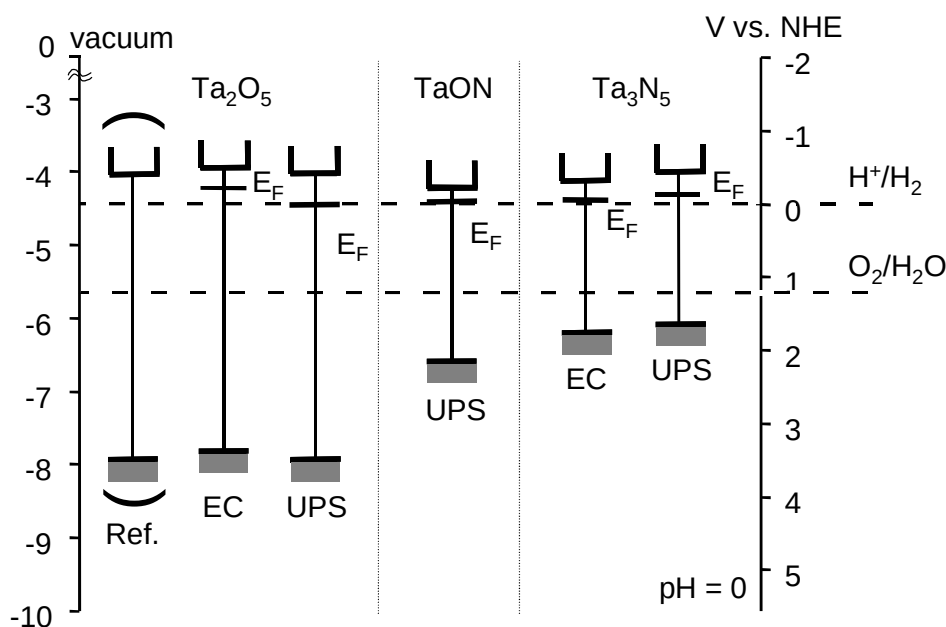


Figure 4-13. Band positions of Ta_2O_5 , TaON and Ta_3N_5 determined by electrochemical analysis and UPS measurements.

Table 4-3. Band Energies of Ta₂O₅, TaON, and Ta₃N₅ by Electrochemical Measurement and UPS.

method	material	E_{BG}	E_F	E_{VB}	E_{CB}	ΔE^a
electrochem.	Ta ₂ O ₅ /Ta	3.9	-4.23	-7.83	-3.93	
measmt (EC)	TaON/Pt	2.4	N/A	N/A	N/A	0.3 (assumed)
at pH = 0	Ta ₃ N ₅ /Ta	2.1	-4.44	-6.02	-4.14	
UPS	Ta ₂ O ₅ /Ta	3.9	-4.45	-7.93	-4.03	0.42
	TaON/Pt	2.4	-4.41	-6.6	-4.2	0.21
	Ta ₃ N ₅ /Ta	2.1	-4.21	-6.02	-3.92	0.29

^a Difference between E_{CB} and E_F

of many n-type semiconductors is 0.1–0.3 eV more negative than E_F .^{16,17} On the basis of this, the difference is assumed to be –0.3 eV for the determination of the band positions of Ta₂O₅ and Ta₃N₅ by electrochemical measurements. The band positions determined by the two methods for Ta₂O₅ and Ta₃N₅ are in good agreement. In addition, the band position of Ta₂O₅ determined here is consistent with electrochemical potential measurement in the literature.¹⁸

The difference between E_F and E_{CB} can be determined experimentally by UPS. E_F is assumed to occur at the same position as for Au deposited on the samples. Thus, the difference between E_F and E_{CB} can be determined directly. The results indicate that the assumption made for electrochemical analysis, the difference being –0.3 V, is reasonable.

Although the E_{CB} values for Ta₂O₅, TaON, and Ta₃N₅ are similar, the E_{VB} values vary significantly between these materials as shown in Figure 4-13. The E_{VB} values of TaON and Ta₃N₅ are at higher potential energies than that of Ta₂O₅.

The change in band positions obtained in this work is reasonably explained by density function theory (DFT) calculations.¹⁹ DFT calculations revealed that a structure at –9 eV in UPS spectrum was attributed to O2p orbitals for TaON and Ta₂O₅. But it was suggested that some structures at around –8 eV were attributable to N2p orbitals for Ta₃N₅. The calculations of electronic band structures indicated that the valence bands of Ta₂O₅,

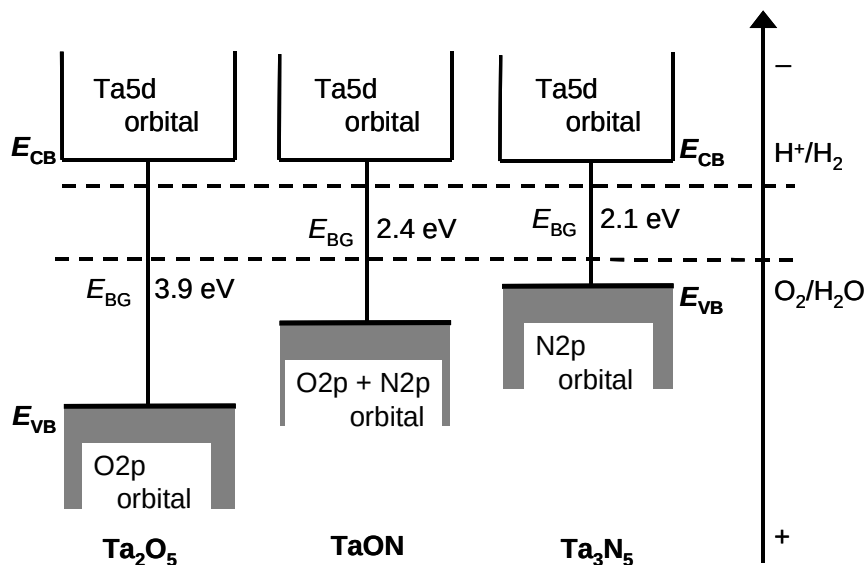


Figure 4-14. Schematic band structures of Ta_2O_5 , TaON , and Ta_3N_5 .

TaON , and Ta_3N_5 consist mainly of $\text{O}2\text{p}$, $\text{O}2\text{p} + \text{N}2\text{p}$ and $\text{N}2\text{p}$ orbitals, respectively. The conduction bands consist of $\text{Ta}5\text{d}$ orbitals for all three materials.¹⁹ The E_{CB} values, however, vary slightly among three samples, as shown in Figure 4-13. It might occur due to the difference of the crystal structures. But it is difficult to examine the detail of the difference at the present stage because the errors of UPS and electrochemical methods in our experiments are estimated to be 0.1–0.2 eV. Thus, the band gaps of an oxynitride or nitride are smaller than the corresponding oxide. These band structures are shown schematically in Figure 4-14.

It should be noted that all the materials studied in this work have the potential for overall water splitting. Of particular interest are TaON ($\lambda \leq 520 \text{ nm}$) and Ta_3N_5 ($\lambda \leq 600 \text{ nm}$), which have good absorption in the visible regime. Moreover, previous investigations of photocatalytic reactions by us^{5,6} demonstrated that TaON and Ta_3N_5 are essentially stable during photooxidation and photoreduction of water. These results indicate that this oxynitride and nitride are potential photocatalysts for overall water splitting with good visible light absorption.

4-5. Conclusion

The band gap positions of Ta_2O_5 , TaON , and Ta_3N_5 were determined by electrochemical analysis and UPS. The conduction band positions of Ta_2O_5 , TaON , and Ta_3N_5 were found to be largely similar, whereas the valence band positions vary significantly ($\text{Ta}_2\text{O}_5 < \text{TaON} < \text{Ta}_3\text{N}_5$). The change in the band positions is reasonably consistent with the results of DFT calculations. The results indicate that TaON and Ta_3N_5 are potential photocatalysts for overall water splitting utilizing solar radiation. Moreover, the results of UPS analysis are in good agreement with the electrochemical analysis, demonstrating that the proposed UPS technique is a reliable alternative means of determining the band positions of a wide range of photocatalytic materials.

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Chapter 5

Oxysulfide $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ as a Stable Photocatalyst for Water
Oxidation and Reduction under Visible–Light Irradiation

5-1. Introduction

Some Ti^{4+} , Nb^{5+} , and Ta^{5+} -based mixed metal oxides, such as SrTiO_3 ¹, $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ ², $\text{K}_4\text{Nb}_6\text{O}_{17}$ ³, and NaTaO_3 ⁴, have been successfully applied for overall water splitting. These oxides, however, are not effective in the visible-light region ($\lambda \geq 400$ nm) because the band gap energies of these materials exceed 3 eV. In these metal oxide photocatalysts, the bottoms of the conduction bands, which consist mainly of the empty transition metal d orbitals, are located at a potential slightly more negative than 0 V vs NHE at pH = 0, and the tops of the valence bands, consisting of O2p orbitals, are at a potential more positive than *ca.* 3 V as shown in Figure 5-1a. This situation causes large band gap energies. It has been found that several (oxy)nitrides are potential photocatalysts for overall water splitting with good visible-light absorption.^{5,6} In the case of these (oxy)nitrides, the bottoms of the conduction bands are based on empty transition metal d orbitals, whereas the top of the valence bands consist of N2p, a

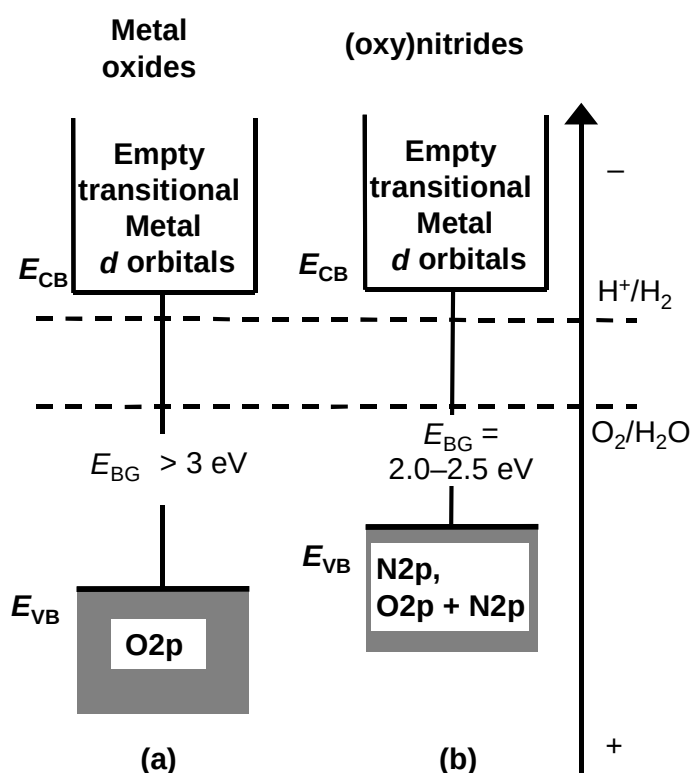


Figure 5-1. Schematic band structures of metal oxides and (oxy)nitride photocatalysts.

hybridization of N2p and O2p orbitals as shown in Figure 5-1b. The potential energies of the hybridized orbitals are higher than that of an O2p orbital in an oxide, resulting in smaller band gap energies sufficient to absorb visible–light as described in Chapter 2 and 3. This suggests that the introduction of other anions with high potential energies also reduce the band gap energies of metal oxide as well as “N”. Therefore, the non–oxide materials appear to be potential candidates for overall water splitting under visible–light irradiation.

The author is interested in oxysulfide material which is one of non–oxide materials. It is expected that the top of the valence band consists of a hybridization of S3p and O2p orbitals and the bottom of the conduction band is made up of empty transition metal d orbitals, resulting in small band gap energy sufficient to absorb visible–light as well as (oxy)nitrides.

In this chapter, I describe the photocatalytic reactions and photoelectrochemical properties of the oxysulfide, $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. Figure 5-2 shows the projection of the

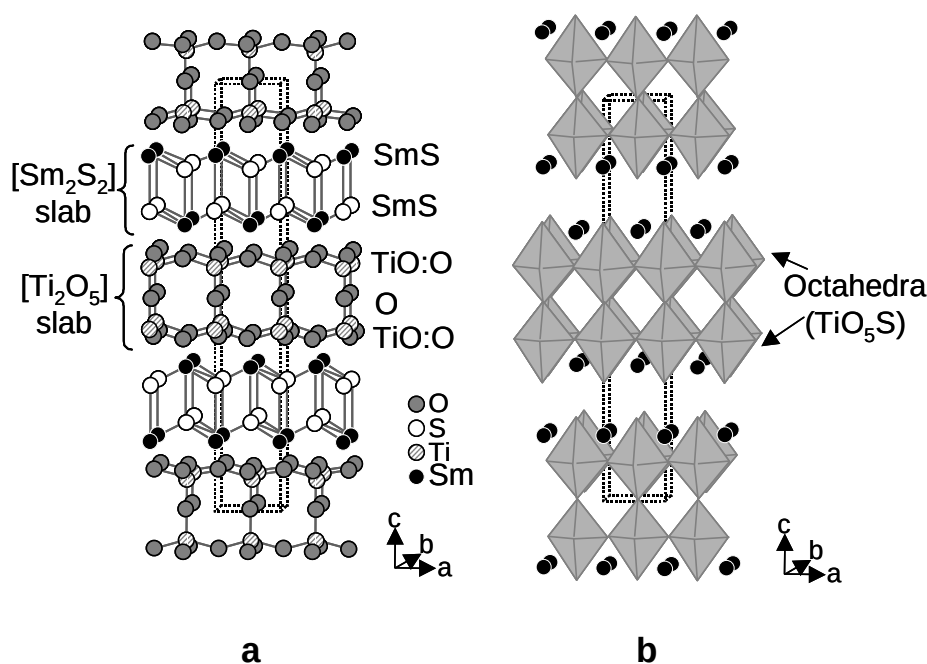


Figure 5-2. Schematic structures of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. (a) Staking of the two kinds of layers along the c axis; $[\text{Sm}_2\text{S}_2]$ and $[\text{Ti}_2\text{O}_5]$ slabs. (b) View down the b axis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ showing the double layer of Ti octahedra.

structure of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ compounds that crystallize in the tetragonal symmetry, space group $I4/mmm$.^{7,8} The schematic structural description in terms of "separated 2D building blocks" hides in fact strong interlayer connections. Indeed, the Ti atoms are involved in the oxide layer built from a 2D development of double corner-sharing octahedral (Figure 5-2a). However, one of the two apical atoms of the Ti octahedra is a sulfur atom, which is also engaged in the sulfide layer. Sm atoms are coordinated by five sulfur atoms in a square pyramidal arrangement. However, these Sm atoms are also coordinated by four oxygen atoms. Therefore, Sm atoms are coordinated by nine anions (five sulfur and four oxygen atoms), corresponding to a tricapped trigonal prismatic coordination (Figure 5-2b). In this chapter, I describe that $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ functions as a photocatalyst for the oxidation of water to O_2 or reduction of H^+ to H_2 in the presence of a sacrificial electron acceptor (Ag^+) or donor (Na_2S , Na_2SO_3 , or methanol), without any noticeable degradation.

5-2. Experimental Section

5-2-1. Synthesis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ samples were obtained by heating a mixture of Sm_2S_3 (99.999%, Soekawa Chemical Co., Ltd.), Sm_2O_3 , and TiO_2 (99.95%, 98.5%, Kanto Chemical Co., Inc.), (molar ratio, $\text{Sm}_2\text{S}_3:\text{Sm}_2\text{O}_3:\text{TiO}_2 = 2:1:6$)^{7,9} in a sealed quartz tube under vacuum at 1273 K. After 4 to 7 days, the sintered samples were ground up and again heated in the vacuum-sealed tube for 7 days. The obtained orange samples were ground into a powder.

5-2-2. Characterization of Catalysts.

Characterization of the prepared samples was carried out using X-ray powder diffraction (XRD; Geigerflex Rad-B system Cu $K\alpha$ 15 mA, Rigaku), scanning electron microscopy (FE-SEM; S-4700, Hitachi), energy-dispersive X-ray spectroscopy (EDX; EMAX-7000, Horiba), UV-visible diffuse reflectance spectroscopy (UV-vis DR; V-560, JASCO), and

X-ray photoelectron spectroscopy (XPS; ESCA 3200, Shimadzu).

5-2-3. Preparation and Deposition of IrO₂ Colloid.

IrO₂ colloid was used as a catalyst for the oxidation of water. The colloid solution was prepared by hydrolysis of Na₂IrCl₆.¹⁰ The diameters of the IrO₂ particles were estimated to be 1–5 nm by transmission electron microscopy (TEM) images of the colloid. While Sm₂Ti₂S₂O₅, as prepared, did not adsorb the IrO₂ colloid, the following treatment resulted in the adsorption of the IrO₂ colloid on Sm₂Ti₂S₂O₅. The procedure for deposition of IrO₂ is shown in Figure 5-3. A 1.0-g amount of Sm₂Ti₂S₂O₅, 1.4×10^{-2} g of Ca(OH)₂ and 2 mL of methanol solution were mixed in an agate mortar and ground until dry. The

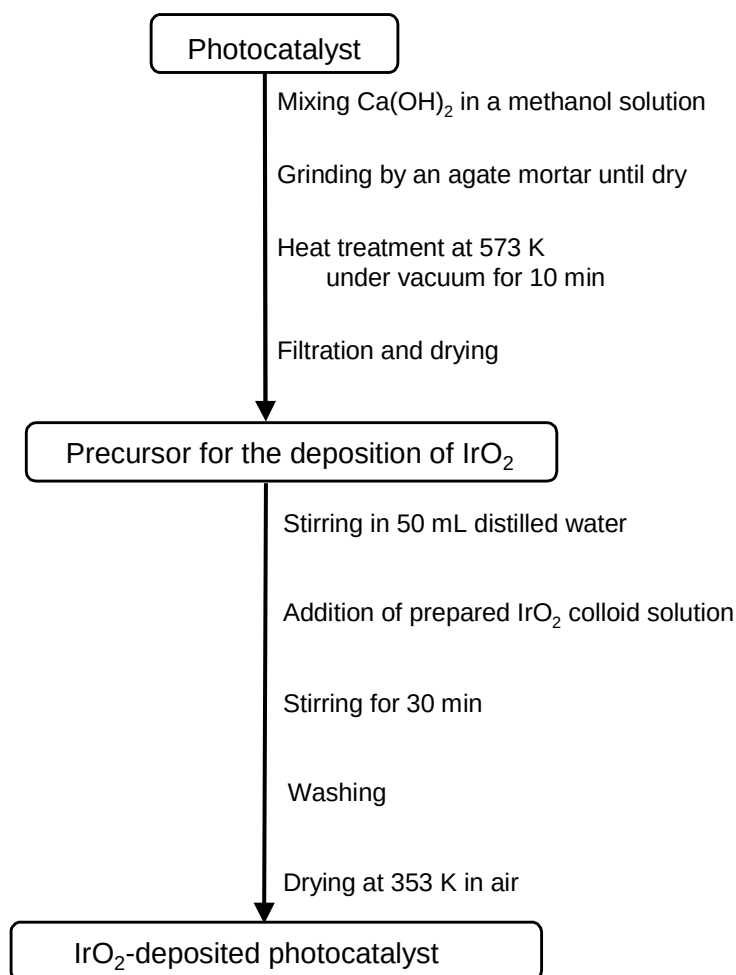


Figure 5-3. Procedure for deposition of IrO₂ colloids on photocatalyst.

mixture was heated at 573 K under vacuum for 10 min, and then washed with distilled water several times to remove excess Ca(OH)_2 . A 0.3-g amount of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ sample loaded with Ca(OH)_2 ($\text{Ca(OH)}_2/\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$) and *ca.* 0.1–12.8 mL of the colloid solution ($\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ *ca.* 0.3–6.0 mg) was added to vigorously stirred distilled water (50 mL). After stirring for 30 min, the transparent supernatant was decanted and the sample with adsorbed $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$ ($\text{IrO}_2\text{--Ca(OH)}_2/\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$) was rinsed 3 times in distilled water. The sample was dried at 353 K in air. The amount of colloidal IrO_2 adsorbed onto the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was estimated in each case by measuring the absorbance over 500–700 nm of the supernatant rinse solutions. As colloidal IrO_2 has a broad absorption band in the range 500–700 nm,¹¹ these measurements revealed that 0.3 g of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ can adsorb 6 mg of colloidal IrO_2 as the maximum loading.

5-2-4. Photocatalytic Reactions.

The reaction was carried out in a Pyrex reaction vessel connected to a closed gas circulation and evacuation system as shown in Figure 5-4. The photocatalyst powder was dispersed in aqueous solutions by a magnetic stirrer in a Pyrex reaction vessel. Photoreduction of H^+ to H_2 and photooxidation of H_2O to O_2 in the presence of a sacrificial electron donor and acceptor were examined as test photoreactions. H_2 evolution was typically examined in 200 mL aqueous solution containing 0.20 g of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, 1.0 μmol of H_2PtCl_6 and sacrificial electron donors (0.01 M Na_2S –0.01 M Na_2SO_3). The photooxidation of water to O_2 was performed in 200 mL of 0.01 M AgNO_3 solution (Ag^+ : sacrificial electron acceptor) containing 0.20 g of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ and 0.20 g of La_2O_3 powder. Photooxidation of water decreases the pH of the solution because H^+ is produced with O_2 evolution. In the presence of La_2O_3 , the pH of the solution during the photoreaction is buffered at pH = 8–9 by the dissolution of La_2O_3 or La(OH)_3 , a basic metal oxide. To remove air from the reactor, the solution was evacuated several times and then irradiated with a 300 W Xe lamp equipped with cut-off filters. The number of photons reaching the solution was measured with a Si photo-diode, and the rate of total incident photons at

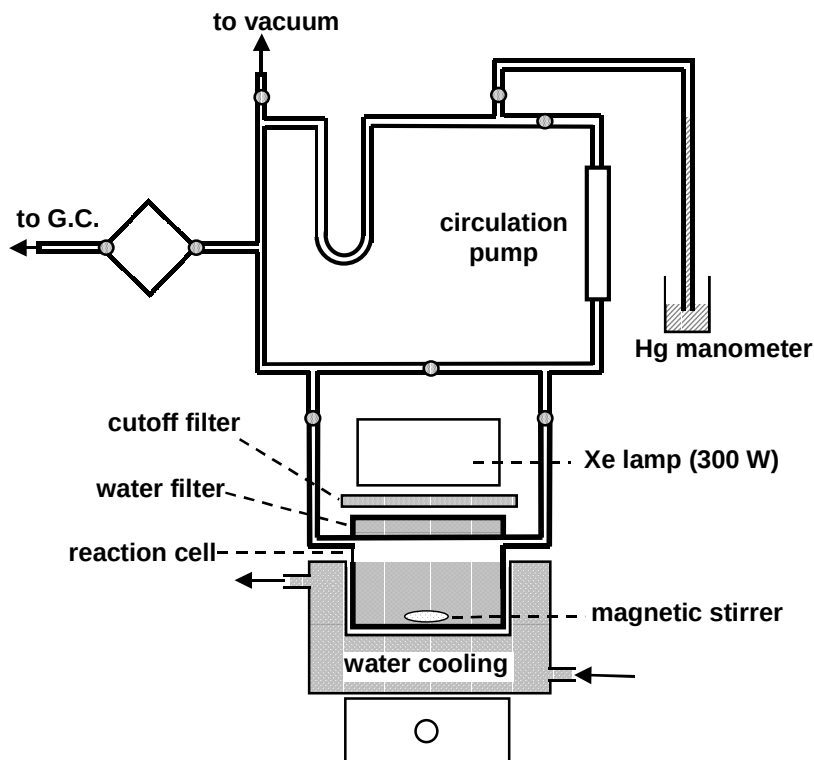


Figure 5-4. Schematic view of the photocatalytic reaction system for visible-light irradiation.

$440 \text{ nm} \leq \lambda \leq 650 \text{ nm}$ was typically $8.6 \times 10^{21} \text{ photons h}^{-1}$. Quantum efficiencies (Φ) were calculated using the following equation:

$$\Phi (\%) = (AR/I) \times 100$$

A , R , and I represent the coefficients based on the reactions (H_2 evolution: 2, O_2 evolution: 4), the H_2 or O_2 evolution rate (molecules h^{-1}) and the rate of absorption of incident photons, respectively. Here, Φ is the apparent quantum efficiency because we assume that all incident photons are absorbed by the suspension.

The oxidation of ^{18}O labeled water (H_2^{18}O) by $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ under visible-light irradiation was carried out in a small Pyrex cell. O_2 evolution was examined in 3 mL of a mixture of H_2^{16}O and H_2^{18}O ($\text{H}_2^{16}\text{O} / \text{H}_2^{18}\text{O} = 4.2$) containing 0.06 g of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, 570 μmol of AgNO_3 and 0.06 g of La_2O_3 . The time course of gas evolution under visible-light irradiation ($\lambda \geq 440 \text{ nm}$) was analyzed by both of a gas chromatograph and quadrupole mass spectrometer.

5-2-5. Electrochemical Analysis.

The electrochemical properties of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ were examined using electrodes fabricated as follows. $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ powder was pressed into a disk (10 mm diameter, 1 mm thickness). The disk was heated in a vacuum-sealed quartz tube at 1273 K for one week. The disk was cut into a square electrode ($1 \times 5 \times 1 \text{ mm}^3$) after calcination. Metallic indium was sputter-deposited on one side of the electrode, and a Cu wire was attached on the deposited indium film using silver paste. The Cu wire side of the electrode was sealed with epoxy resin to prevent current leakage. The electrode was examined in an electrochemical cell made of Pyrex. A Pt wire and Ag/AgCl electrode were employed as the counter and reference electrodes, and 20 mL of 0.1 M K_2SO_4 was used as the electrolyte. The impedance of the electrochemical cell was measured using a frequency response analyzer (HZ-3000, Hokuto, Ltd.). For photoelectrochemical analysis, the cell was irradiated by a 300 W Xe lamp equipped with a monochromator.

5-3. Results and Discussion

5-3-1. XRD pattern, SEM Image and UV-vis Spectrum of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

Figure 5-5 shows X-ray diffraction (XRD) patterns for the prepared samples. Sample A was synthesized by heating the mixture of the starting materials for 4 days. In the case of Sample B, a sintered sample obtained by heating for one week was ground and again heated for one week. Diffraction peaks corresponding to those of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ ⁷ appear even in the XRD pattern of Sample A obtained with the short heating time. The intensities of the diffraction peaks increase with increasing heating time, accompanied by decrease in the impurity phase, as shown in the XRD pattern of Sample B. Energy-dispersive X-ray spectroscopy (EDX) revealed the composition of Sample B to be Sm:Ti:S = 1.0:1.0:0.9 (atomic), an S content slightly lower than the stoichiometric amount. From the scanning electron microscopy (SEM) image of Sample B, shown in Figure 5-6, the diameter of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ particles was estimated to be 2–4 μm . The large size of the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ particles is ascribed to the long-duration high-temperature sintering.

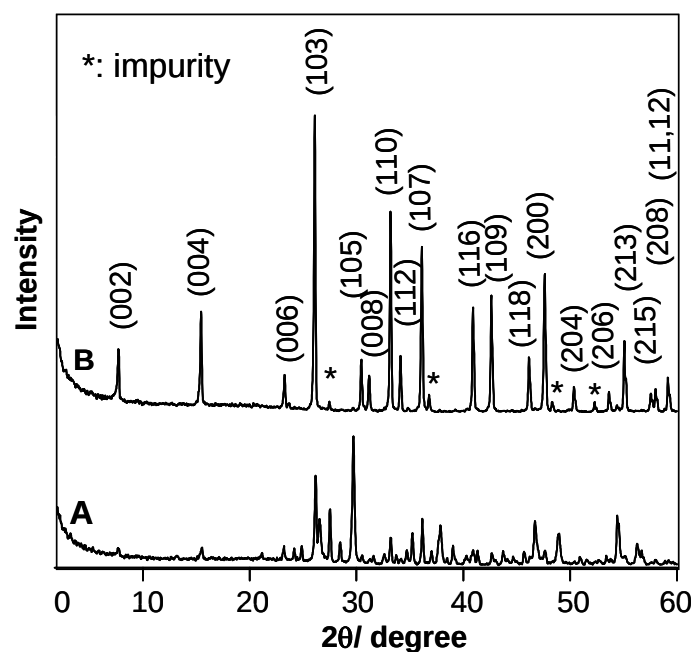


Figure 5-5. XRD patterns for the samples prepared at 1273 K. Sample A was synthesized by heating the mixture of the starting materials for 4 days. In the case of Sample B, a sintered sample obtained by heating for one week was ground and again heated for a further week.

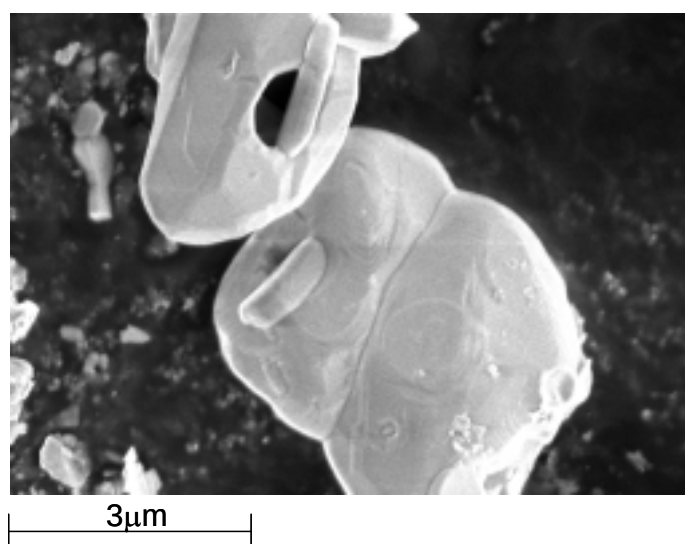


Figure 5-6. Scanning electron microscopy (SEM) image of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Sample B).

Figure 5-7 shows UV-vis diffuse reflectance (UV-vis DR) spectra for $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Sample B). In the UV-vis spectra, the absorption band-edge of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is at 600 nm with a shoulder up to 650 nm, being shifted about 250 nm from that of $\text{Sm}_2\text{Ti}_2\text{O}_7$, and the band gap energy is estimated to be 1.9 or 2.1 eV.

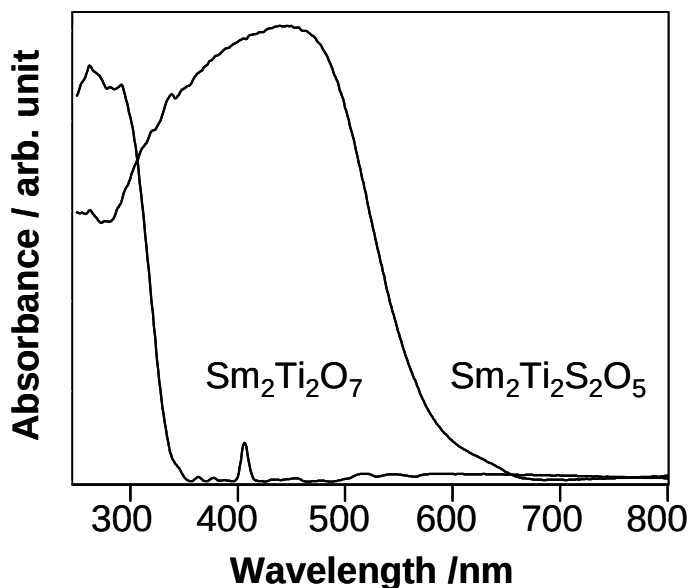


Figure 5-7. UV-vis diffuse reflectance (UV-vis DR) spectra for $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Sample B).

5-3-2. Electronic Structure Calculation.

In contrast to the large energy gap of $\text{Sm}_2\text{Ti}_2\text{O}_7$ (ca. 3.6 eV), the small band gap energy of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is attributable to the incorporation of S^{2-} . Because S3p orbitals have higher potential energies than O2p orbitals, the top of the valence band of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ may consist predominantly of S3p orbitals, resulting in the small energy gap. To verify this explanation, the electronic band structure of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was calculated using the plane wave based density functional theory (DFT) program, CASTEP.¹² The core orbitals were replaced by the ultrasoft core potentials,¹³ and the O:2s²2p⁴, S:3s²3p⁴, Ti:3s²3p⁶3d²4s², and Sm:5s²5p⁶4f⁶6s² electrons were treated explicitly. The kinetic energy cutoff was set to 280 eV. The atomic coordinates of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ measured by Boyer-Candalen *et al.* were used in the DFT calculation.⁷ The unit cell includes $(\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5)_2$ structure, and

the total number of valence electrons is 196. Because the Sm4f orbitals have smaller overlap and lower ionization potential, the SCF convergence is not good. I employed the fractional occupation technique, which allows withdrawing and accumulation of small amount of electron density, respectively, in the top of valence band and the bottom of conduction band.

Calculated band dispersion relation and density of states are shown in Figure 5-8. In Figure 5-8, the top of valence band corresponds to the orbital #98, and the bottom of conduction band to the orbital #99. The contents of each band are shown in the figure. For example, orbitals from #47 to #88 are composed of O2p and S3p orbitals. The band gap, which is apparently very small, lies between the orbitals #88 and #89. Figure 5-9 also shows the electron density contour maps for orbitals (a) #117, (b) #116, (c) #89, and

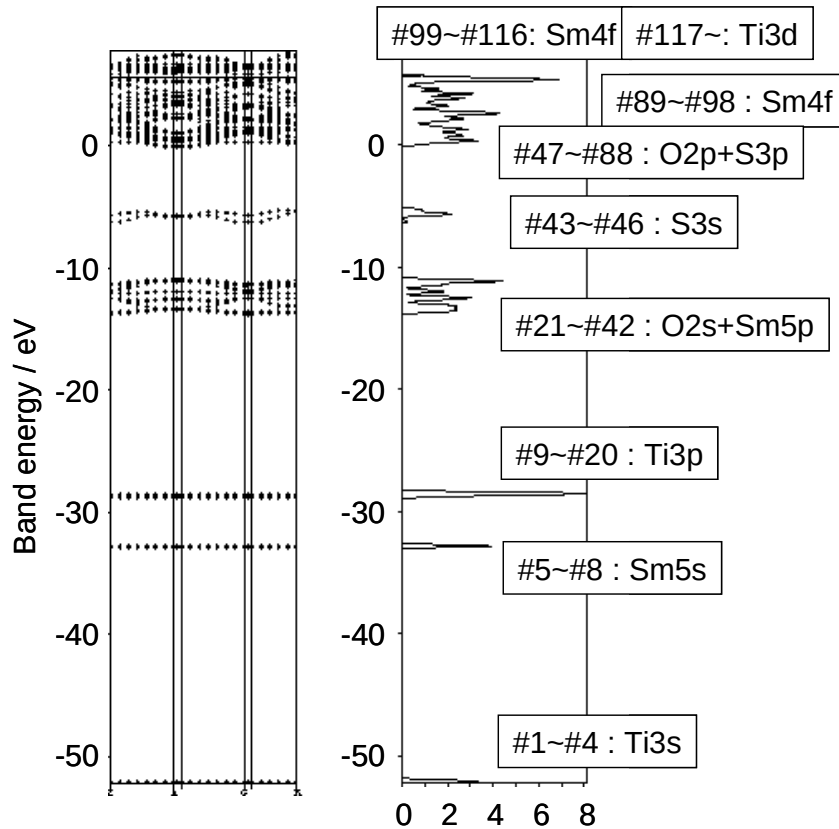


Figure 5-8. Band dispersion and density of states for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

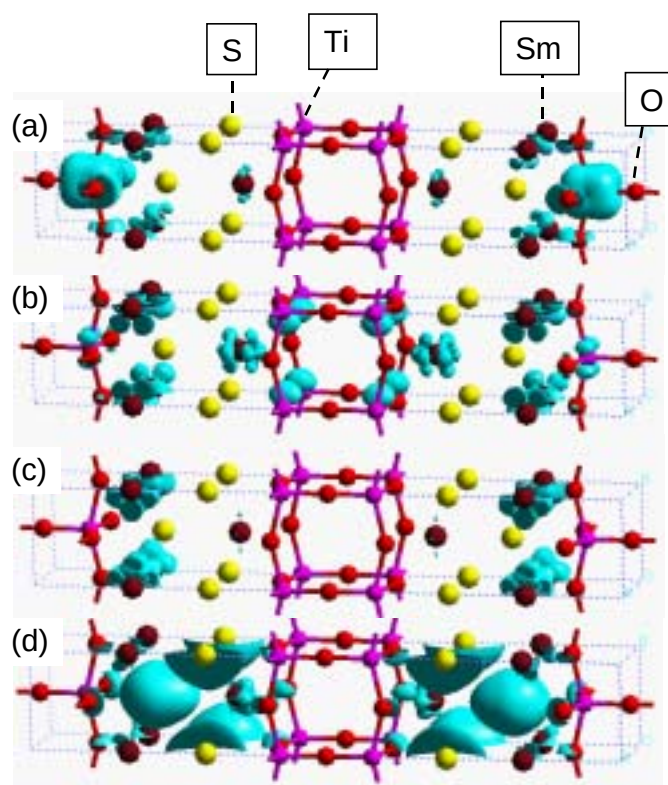


Figure 5-9. Density contour maps for four typical orbitals. (a) #117: bottom of unoccupied Ti3d band, (b) #116: top of unoccupied Sm4f band, (c) #89: bottom of occupied Sm4f band, and (d) #88: top of O2p+S3p hybrid band. Greater density is seen on S atoms.

(d) #88. Orbital #88 is located at the top of O2p+S3p hybrid band, and most electron density is localized on the S atoms rather than the O atoms. This means that the S3p orbitals constitute the upper part of the band and these orbitals make an essential contribution to the small band gap energy. Orbitals #89 and #116 are the Sm4f orbitals, and show the beginning and end of the Sm4f orbital manifold. Orbital #117 is composed of the Ti3d orbitals with small fraction of O2p and Sm4f orbitals, and substantially forms the bottom of the conduction band. The O2p orbitals mix into the Ti3d orbitals with *out of phase*. This mixing is a counterpart of that occurring in the bottom of O2p+S3p band (*e.g.* #47), where the Ti3d orbitals mix into the O2p orbitals with *in phase*. The occupied energy bands obtained in DFT calculation, in increasing order of energy, are Ti3s, Sm5s, Ti3p, O2s+Sm5p, S3s, O2p+S3p, and Sm4f(part). The unoccupied bands are Sm4f(part) and Ti3d. The valence band is made up of the O2p

and S3p hybridized orbitals and the localized Sm4f orbitals. The conduction band consists of the Ti3d and localized Sm4f orbitals. Although the partially filled Sm4f orbitals appear both at the top of valence band and at the bottom of conduction band, their highly localized nature makes them less effective in photoconductivity or photocatalysis and their contribution should, therefore, be ignored when considering photocatalytic and photoelectrochemical phenomena. The apparent electronic structure is like a metal, as shown in Figure 5-8. However, this is caused by the isolated atom-like Sm4f orbitals, and these orbitals do not contribute to the band gap property. Thus the band gap is reasonably estimated to be 1.4 eV as the energy difference between the top of O2p+S3p band and the bottom of Ti3d band. This value is just two thirds of our experimental value (1.9 or 2.1 eV). The major reason for this discrepancy is ascribed to underestimation of the character of the band gap in current DFT.

The DFT calculation indicates that the energy gap of f–f transition of Sm^{3+} is smaller than the band gap. In contrast, the DRS indicates that the band gap is much smaller than the f–f transition energy, which is mainly observed at *ca.* 400 nm for $\text{Sm}_2\text{Ti}_2\text{O}_7$. The f–f transition energy is evaluated not only from the difference of occupied and vacant 4f orbital energies but also from the electron repulsion term related to the occupied and vacant orbitals. The transition energy for band calculations of solids is usually approximated by only the orbital energy difference if the orbitals are widely extending (*i.e.*, band picture). However, the extension of Sm4f orbitals is rather core like, and the band picture shown in Figure 5-8 does not correctly represent the f–f transition energy. The aim of our study is not to evaluate the f–f transition energy, but to estimate the contents of realistic photoexcitation. This is not due to the f–f transition, but the transition from the O2p+S3p orbitals to the Ti3d orbitals.

5-3-3. Photocatalytic Reactions of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

5-3-3-1. O_2 Evolution in AgNO_3 Solution.

Time courses of O_2 evolution on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ samples as well as on CdS in AgNO_3 solution under visible-light irradiation ($\lambda \geq 440$ nm) are shown in Figure 5-10. For the as-prepared $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ sample, O_2 was evolved with irradiation (curves A and B) after a short induction period (ca. 1 h). No reaction took place in dark. The XRD patterns of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ samples before and after the reaction were essentially identical except for the emergence, after the reaction, of a diffraction pattern attributable to metallic Ag. Oxidation of ^{18}O labeled water (H_2^{18}O) by $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ under visible-light irradiation was performed in an aqueous AgNO_3 solution ($\text{H}_2^{16}\text{O} / \text{H}_2^{18}\text{O} = 4.2$, AgNO_3 : 0.19 M), and it was confirmed that the ratio of $^{16}\text{O}/^{18}\text{O}$ in evolved O_2 ($^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$) was always

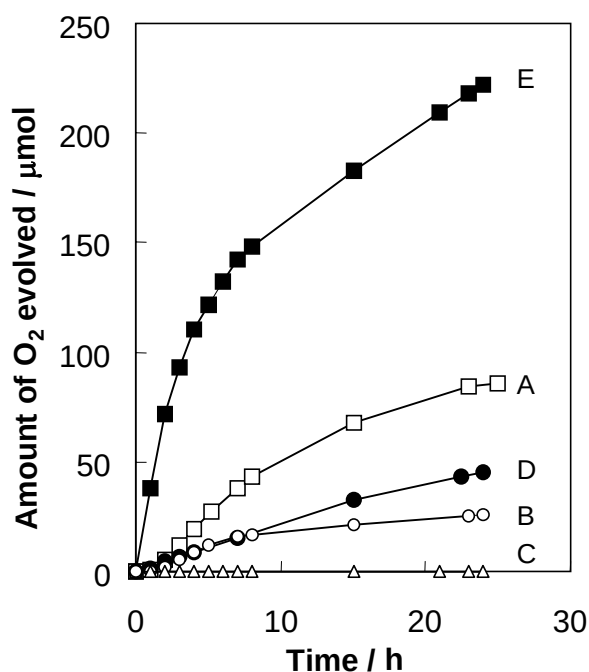


Figure 5-10. Time courses of O_2 evolution from $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ and CdS under visible-light irradiation ($\lambda \geq 440$ nm). (A) $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Sample B). (B) $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Sample A). (C) CdS. (D) $\text{Ca}(\text{OH})_2/\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. (E) IrO_2 (0.25 wt%)- $\text{Ca}(\text{OH})_2/\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, catalyst(0.2 g), 0.01 M AgNO_3 solution(200 mL), La_2O_3 (0.2 g).

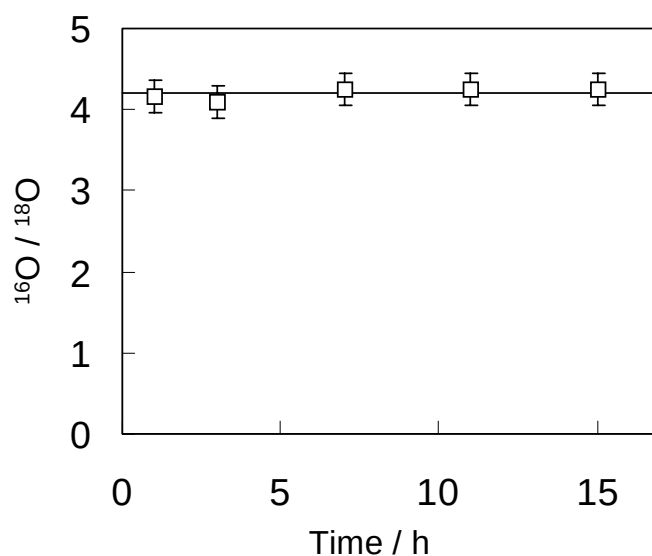


Figure 5-11. Ratio of $^{16}\text{O}/^{18}\text{O}$ in O_2 evolved ($^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$).
Catalyst (0.06 g), 0.19 M AgNO_3 solution (3 mL), La_2O_3 (0.06 g).

c

a. 4.2 during reaction (10 h) as shown in Figure 5-11. Apparently, evolved O_2 is derived from water. It was confirmed that O_2 evolution on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ depends largely on pH. O_2 evolution was examined in a basic solution (*ca.* pH = 8) buffered by La_2O_3 , as described above. However, when the reaction was carried out in acidic conditions (pH < *ca.* 6), O_2 did not evolve with irradiation. This implies that alkaline conditions are favorable for O_2 evolution on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. It is suggested, from the electrochemical analysis shown below, that the valence band of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ does not have satisfactory potential for oxidation of water to O_2 in acidic conditions with the band gap irradiation. Sample A, which was not completely crystallized in comparison with the case of Sample B, had a slower rate of O_2 evolution than that of Sample B, indicating that the impurity phase lowers the activity of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. Sample B was, therefore, used in all subsequent experiments. Despite the impurity phase, the rate of O_2 evolution on Sample A reaches approximately one-half of that of Sample B. This suggests that there still remains a considerable amount of defects although sample B shows relatively high peak intensities in XRD. The quantum efficiency for O_2 evolution in Sample B was estimated to be 0.2%.

For comparison, the time course with CdS under the same experimental conditions is also shown in Figure 5-10 (curve C). CdS in the AgNO₃ solution turned black immediately due to decomposition of CdS with the formation of Ag₂S, and no O₂ evolution was observed.

It is noteworthy that the O₂ evolution rate increased when I modified the catalyst by adsorption of IrO₂ colloid, *i.e.* IrO₂–Ca(OH)₂/Sm₂Ti₂S₂O₅. Figure 5-10 also shows time courses of O₂ evolution from Ca(OH)₂/Sm₂Ti₂S₂O₅ and IrO₂ (0.25 wt%)-Ca(OH)₂/Sm₂Ti₂S₂O₅. While Ca(OH)₂/Sm₂Ti₂S₂O₅ had a lower activity for O₂ evolution than Sm₂Ti₂S₂O₅, the rate of O₂ evolution increased with increasing the amount of adsorbed IrO₂ colloid, reaching a maximum at 0.25 wt%. Further adsorption beyond 0.25 wt% decreased the rate of O₂ evolution. The quantum efficiency at 0.25 wt% adsorption was 1.1%, more than 5 times of that of the as-prepared Sm₂Ti₂S₂O₅. These results indicate that the IrO₂ colloid functions as an effective O₂ evolution promoter for Sm₂Ti₂S₂O₅.

5-3-3-2. Sm₂Ti₂S₂O₅ Surface before and after O₂ Evolution under Visible-Light ($\lambda \geq 440$ nm) Irradiation.

To evaluate the stability of Sm₂Ti₂S₂O₅ during photooxidation of water in visible-light, the surface of the Sm₂Ti₂S₂O₅ was examined by XPS. Figure 5-12 shows the XPS spectra. After reaction for 20 h, the filtrated mixture of Sm₂Ti₂S₂O₅ and La₂O₃ was stirred in 100 mL of 1 M HCl solution for 30 min to dissolve the La₂O₃, and the Sm₂Ti₂S₂O₅ was filtered out for XPS analysis. The total turnover number based on the number of O atoms in Sm₂Ti₂S₂O₅ for O₂ evolution (20 h) was 0.1. While the amount of O atoms in Sm₂Ti₂S₂O₅ (0.2 g) was 1.9 mmol, that of evolved O₂ in 20 h was 0.10 mmol. Note that the amount of surface O atoms estimated from BET surface area of 0.59 m²/g and (100) face structure of Sm₂Ti₂S₂O₅ is 3.8 nmol. Therefore, the turnover number based on the number of surface O atoms was estimated to be *ca.* 1.3×10^4 . Even if S²⁻ is oxidized to S⁰ species during the reaction, it is known that S⁰ species are stable in the

HCl solution. There was no significant difference in the binding energies of the $\text{Sm}3d_{5/2}$, $\text{Ti}2p$, $\text{S}2p$, and $\text{O}1s$ peaks before and after the reaction. In Figure 5-12A, the intensity of $\text{Sm}3d_{5/2}$ peak after reaction was smaller than that before the reaction, and the $\text{O}1s$ peak (Figure 5-12B) assigned to OH (532.4 eV) became slightly larger after the reaction. The surface atomic ratios of Sm/Ti , S/Ti , and O/Ti are summarized in Table 5-1. The surface atomic ratios of O/Ti were estimated from $\text{O}1s$ peaks at 530 eV. Table 5-1 shows that the proportions of surface Ti, S, and O did not change during reaction, whereas a considerable amount of Sm disappeared from the surface of the sample after the reaction and HCl treatment. The decrease in surface Sm is not attributed to photooxidation of water but to dissolution of Sm^{3+} into the conc. HCl solution during HCl treatment. As

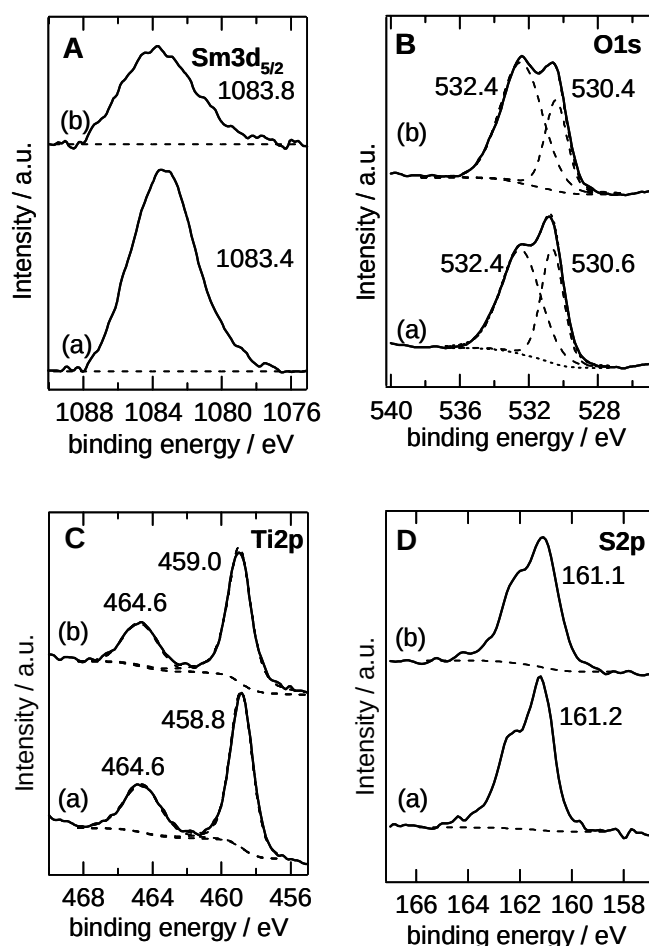


Figure 5-12. XPS spectra for (A) $\text{Sm}3d_{5/2}$, (B) $\text{O}1s$, (C) $\text{Ti}2p$ and (D) $\text{S}2p$ of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ before and after O_2 evolution under visible light ($\lambda \geq 440$ nm). (a) represents before the reaction, and (b) after the reaction.

Table 5-1. Surface Atomic Ratios of Sm/Ti, S/Ti and O/Ti of Sm₂Ti₂S₂O₅ (a) Before and (b) After O₂ Evolution in Visible Light ($\lambda \geq 440$ nm).

sample	Sm/Ti	S/Ti	O/Ti
a	0.7	1.2	3
b ¹⁾	0.23	1.2	2.9
c ²⁾	0.31	1.2	2.6

1) After the reaction for 20 h, the filtrated mixture of Sm₂Ti₂S₂O₅ and La₂O₃ was stirred in 100 mL of 1 M HCl solution for 30 min in order to dissolve La₂O₃, and Sm₂Ti₂S₂O₅ was filtered out for XPS analysis.

2) Sample c was obtained by treating the mixture of Sm₂Ti₂S₂O₅ and La₂O₃ powders without photoreaction by HCl solution in a similar manner as above.

can be seen in Table 5-1, after similar HCl treatment, surface Sm also decreased in a sample mixture of Sm₂Ti₂S₂O₅ and La₂O₃ powders that did not undergo photoreaction. These XPS and XRD results indicate that the surface and bulk of Sm₂Ti₂S₂O₅ is essentially unchanged during the reaction, and that Sm₂Ti₂S₂O₅ functions as a stable photocatalyst for the oxidation of H₂O to O₂ in AgNO₃ solution.

XPS spectra for CdS before and after reaction were shown in Figure 5-13A, 13B, and 13C. 0.20 g of CdS was irradiated with visible-light ($\lambda \geq 440$ nm) for 6 h in an aqueous AgNO₃ solution containing La₂O₃ powder as in the case of Sm₂Ti₂S₂O₅. After the reaction, intense peaks of Ag3d appeared and simultaneously Cd3d decreased. Formation of Ag₂S was also confirmed by XRD after the reaction. There was no noticeable difference in XPS spectra and XRD patterns for CdS in dark and under visible-light irradiation for 6 h. These results indicate that in the presence of Ag⁺, CdS surface is transformed to Ag₂S with dissolution of Cd²⁺ cations. This confirms that CdS is not stable against oxidation by Ag⁺ even in dark condition. In contrast to CdS, Sm₂Ti₂S₂O₅ is stable in dark and under visible-light irradiation although the valence band partially consists of S3p. Sm₂Ti₂S₂O₅ has a layered perovskite structure that may be more stable than that of CdS.

The formation of TiSO_5 octahedra results in hybridization of S3p and O2p orbitals forming the valence band. It is presumably more than that of pure S3p orbitals.

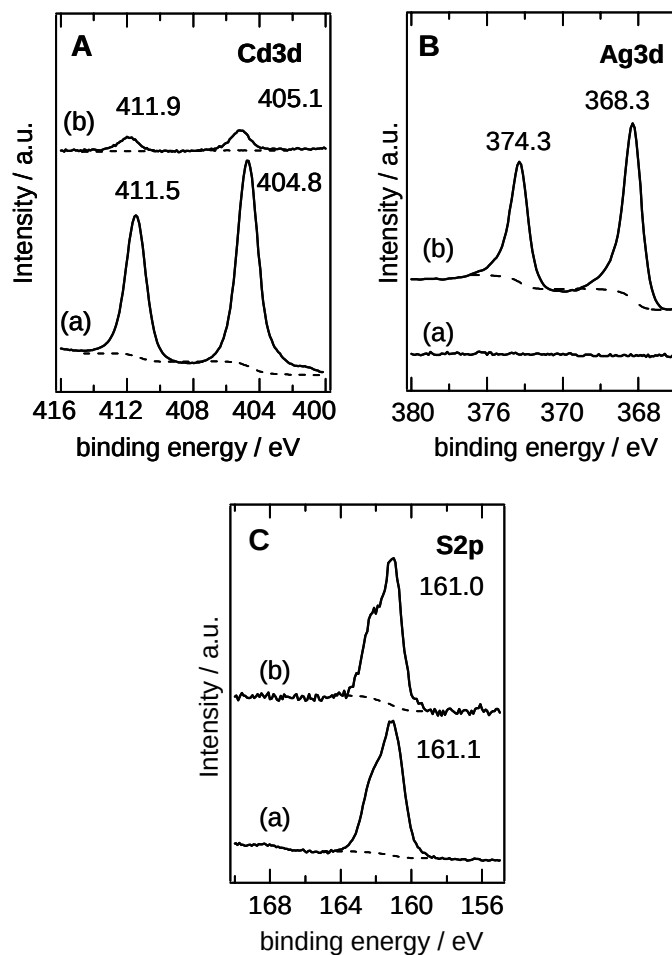


Figure 5-13. XPS spectra for (A) Cd3d, (B) Ag3d and (C) S2p of CdS before and after O_2 evolution under visible light ($\lambda \geq 440$ nm). (a) represents before the reaction, and (b) after the reaction.

5-3-4. H_2 Evolution in the Presence of Sacrificial Electron Donors.

Figure 5-14 shows the time courses of H_2 evolution on 1.0 wt% Pt- $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ in the presence of Na_2S - Na_2SO_3 and methanol under visible-light irradiation ($\lambda \geq 440$ nm). The pHs of the aqueous Na_2S - Na_2SO_3 and methanol solutions for H_2 evolution were 13.0 and 5.6, respectively. In the case of the Na_2S - Na_2SO_3 solution, the fastest rate of H_2 evolution was obtained by a Pt loading of 1.0 wt%. In the early stage of the reaction

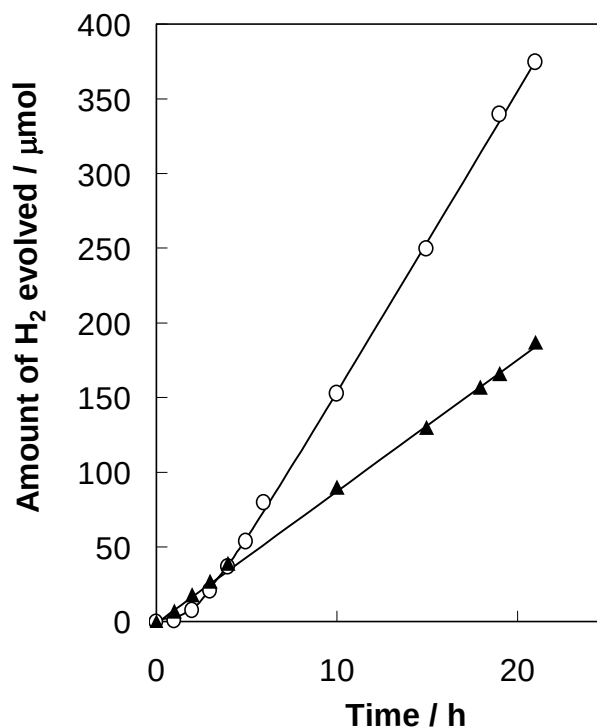


Figure 5-14. Time courses of H₂ evolution from 1.0 wt% Pt–Sm₂Ti₂S₂O₅ under visible–light irradiation ($\lambda \geq 440$ nm). (O) Pt–Sm₂Ti₂S₂O₅ (0.2 g), 0.01 M Na₂S and 0.01 M Na₂SO₃ solution (200 mL); (▲) Pt–deposited Sm₂Ti₂S₂O₅ (0.2 g), 200 mL methanol solution (distilled water 180 mL, methanol 20 mL).

(~3 h), H₂PtCl₆ added is reduced to Pt⁰ as an H₂ evolution promoter on the Sm₂Ti₂S₂O₅ surface. After the induction period, H₂ evolves steadily, indicating that excited electrons in the oxysulfide can reduce H⁺ to H₂. The quantum efficiency for H₂ evolution at a steady state was 0.3%. XRD and XPS analyses confirmed that H₂ evolution proceeded without any degradation of Sm₂Ti₂S₂O₅. This indicates that Sm₂Ti₂S₂O₅ also functions as a stable photocatalyst for the reduction of H⁺ to H₂ under visible–light irradiation ($\lambda \geq 440$ nm).

Figure 5-14 also displays H₂ evolution in the presence of methanol. The reaction was performed in an aqueous solution (200 mL) containing 0.20 g of the sample loaded with 1.0 wt% Pt and 20 mL of methanol. Pt was loaded by the impregnation method from [Pt(NH₃)₄]Cl₂, followed by reduction in H₂ at 573 K. Again H₂ was evolved steadily,

indicating that methanol also works as a sacrificial electron donor on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

Although $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ and Pt-deposited $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ were irradiated with visible-light in distilled water, no gas evolution was observed. There was no difference in XPS and XRD for the samples before and after the light irradiation. Therefore, it is obvious for photocatalytic overall water splitting under visible-light irradiation to modify the oxysulfide surface appropriately.

5-3-5. Wavelength Dependence.

Figure 5-15 shows the dependence of the steady rate of H_2 evolution and the initial rate of O_2 evolution on the cut-off wavelength of incident light. The filters were used in order to cut-off the light with shorter wavelengths than the indicated numbers. The UV-vis DR spectrum of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is also shown in the figure to indicate the absorption edge of the oxysulfide. The rates of O_2 evolution were measured using $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ without

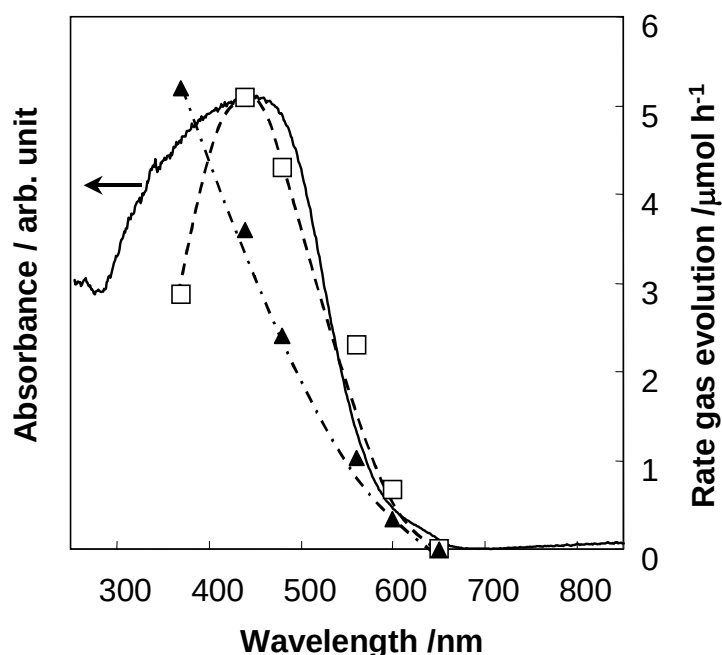


Figure 5-15. Dependence of the rates of H_2 or O_2 evolution on cut-off wavelength of incident light and UV-vis diffuse DR spectrum of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. (▲) H_2 evolution from Pt(1.0 wt%)- $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (0.2 g)-0.01 M Na_2S and 0.01M Na_2SO_3 solution system. (□) O_2 evolution from $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (0.2 g)- La_2O_3 (0.2 g)-0.01 M AgNO_3 solution system.

IrO₂-colloid. Although both rates decrease with increasing cut-off wavelength due to the reduction in the number of absorbed photons, evolution of H₂ and O₂ was observed up to 600–650 nm, corresponding to the band gap transition of Sm₂Ti₂S₂O₅. These photoreactions are, therefore, confirmed to proceed via band gap transition.

5-3-6. Electrochemical Analysis.

To study the electrochemical properties of Sm₂Ti₂S₂O₅, the electrode was examined under various electrochemical conditions. Figure 5-16 correlates the current and potential of the Sm₂Ti₂S₂O₅ electrode under anodic polarization (pH = 12.7), measured in dark and under intermittent visible-light irradiation ($\lambda \geq 440$ nm). A photocurrent with oxidation of water is established at $> ca. -1.2$ V vs Ag/AgCl, indicating that Sm₂Ti₂S₂O₅ has an n-type semiconductor character, and that the flat band potential is $ca. -1.2$ V. Figure 5-17 shows Mott–Schottky (M–S) plots, $1/C^2$ vs. E , for the Sm₂Ti₂S₂O₅ electrode at pH = 13.2 and 4.1. The M–S plots were obtained at the frequency of 1 kHz. The

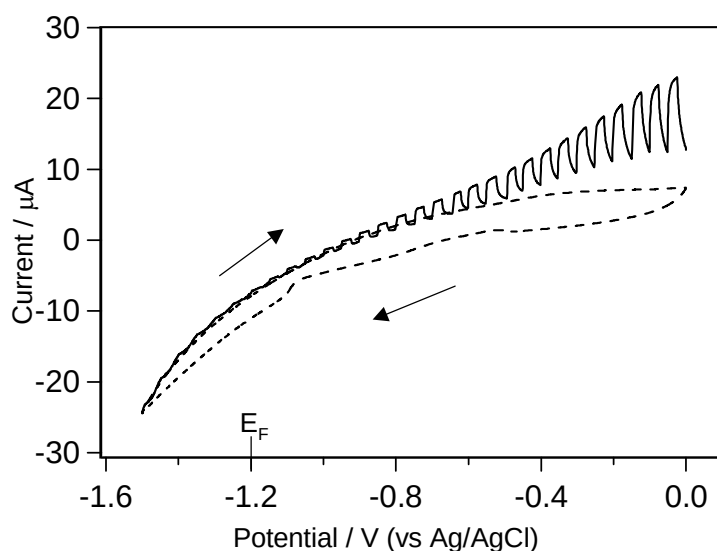


Figure 5-16. Photocurrent vs potential curve for Sm₂Ti₂S₂O₅ electrode ($\lambda \geq 440$ nm). Counter electrode: Pt. Reference electrode: Ag/AgCl. Electrolyte: 0.1 M K₂SO₄ (20 mL) pH = 12.7. The solid line is the photoanodic current, and the dashed line is the dark current.

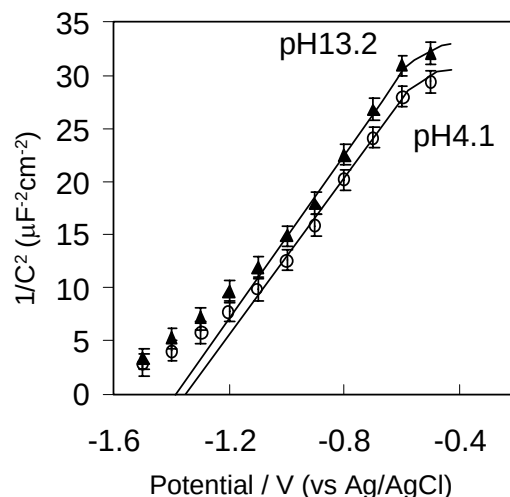


Figure 5-17. Mott–Schottky plots for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ electrode. (▲) pH = 13.2; (○) pH = 4.1. Counter electrode: Pt. Reference electrode: Ag/AgCl. Electrolyte: 0.1 M K_2SO_4 (20 mL). Frequency: 1 kHz.

intersection point of the potential and linear $1/C^2$ –potential curves gives a flat band potential, which in this case is approximately -1.4 V vs Ag/AgCl (-1.2 V vs NHE) and almost independent of pH. When M–S analysis was performed at 1, 2, 5, and 10 kHz, the slope of the plots increased with increasing frequency. However, no dependence of the intersection points on frequency was observed. The flat band potential of the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ electrode was therefore estimated to be *ca.* -1.4 V vs Ag/AgCl (-1.2 V vs NHE) that is independent of pH. This is consistent with the photocurrent–potential curve in Figure 5-16: the photocurrent is observed at *ca.* -1.2 V vs Ag/AgCl. Dependence of the slope of linear M–S plots on used frequency can be attributed to polycrystalline $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ electrode. In the case of polycrystalline electrodes, the slope of linear M–S plots depends on frequency in M–S analysis because of various surface states. Judging from the measurement of the relative permittivity of the oxysulfide, the difference between the bottom of conduction band and the Fermi level was estimated to be 0–0.1 eV. It is generally known that the bottom of the conduction bands in many n-type semiconductors is more negative by *ca.* -0.1 V than the flat band potential.^{14,15} The estimated band structure of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is illustrated in Figure 5-18.

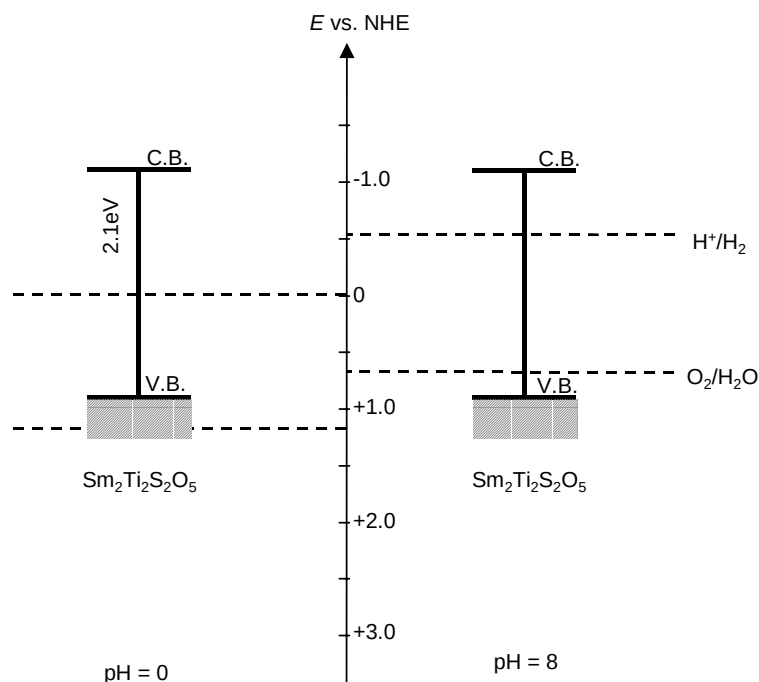


Figure 5-18. Estimated band positions of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ at $\text{pH} = 0$ and 8.

The conduction and valence bands have enough potentials for the reduction of H^+ to H_2 and oxidation of water to O_2 at $\text{pH} = 8$ with the band gap irradiation, and this is consistent with the results of the photocatalytic reactions. Interestingly, the flat band potential of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is almost independent of pH . In metal oxide photocatalysts such as TiO_2 , the flat band potential shifts to more negative potentials with increasing pH because of the dissociation of surface hydroxyl groups. As shown in the XPS spectra, $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ has surface hydroxyl groups, while the flat band potential is unchanged for pH . A possible explanation for that is the small acid dissociation constant of hydroxyl groups on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. S in $\text{S}-(\text{TiO}_2)-\text{O}-(\text{TiO}_2)-\text{S}$ or Sm might give rise to this feature of the hydroxyl groups. In the case of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, the difference between the oxidation potential of water and the valence band level is small, so that oxidation of water is not efficient. Such an appropriate surface modification as deposition of O_2 evolution catalyst or synthesis of oxysulfides with valence band levels suitable for oxidation of water might result in efficient oxidation of water under visible-light irradiation. These possibilities are currently under investigation.

5-4. Conclusion

$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, a Ti^{4+} -based oxysulfide, was confirmed to be a stable visible light-driven photocatalyst for the oxidation of water to O_2 or reduction of H^+ to H_2 without oxidation of S^{2-} or decomposition of the structure. The bottom of the conduction band and the top of the valence band are sufficient for the reduction of H^+ and the oxidation of water, respectively. As such, this oxysulfide performs as a stable photocatalyst for H_2 or O_2 evolution from aqueous solution containing a sacrificial electron donor or acceptor under visible-light ($\lambda \leq 650 \text{ nm}$).

The deposition of an IrO_2 colloid on $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ as an O_2 evolution promoter enhanced the photooxidation activity 5-fold, demonstrating that such surface modification can improve the photocatalytic activity of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

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Chapter 6

Novel Synthesis and Photocatalytic Activity of Oxysulfide $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$

6-1. Introduction

Oxysulfides have recently attracted considerable attention due to the interesting physical properties these materials exhibit, including superconductivity¹ and charge density wave character.² I was interested in utilizing various oxides and other materials as photocatalysts for overall water splitting to accomplish conversion of photon energy into chemical energy.³⁻⁵ Chapter 5 has revealed that $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ with a band gap of *ca.* 2 eV evolves H_2 or O_2 from aqueous solutions containing a sacrificial electron donor (Na_2S – Na_2SO_3 or methanol) or acceptor (Ag^+) without noticeable degradation under visible–light ($440 \text{ nm} \leq \lambda \leq 650 \text{ nm}$) irradiation.⁶ $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was obtained by calcining a mixture of Sm_2S_3 , Sm_2O_3 , and TiO_2 powders at 1273 K in an evacuated sealed quartz tube,⁶ according to a previously reported solid–state reaction method.¹ This solid–state method requires calcination for 2 weeks at 1273 K because of the slow reaction rate at the solid–solid boundary. However, the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ material prepared at such high temperature over a long period has large particle size, which is undesirable for use as a catalyst. Physically, smaller particles result in a shortened diffusion length for photogenerated electron–hole pairs, leading to less recombination of electron–hole pairs and enhanced photocatalytic activity. Therefore, the use of fine particles with good crystallinity is favorable for photocatalysis. As it is difficult to synthesize fine particles of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ by the solid–state method, I developed a new synthetic route to $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ using H_2S . The method is presented here, along with a comparison of the photocatalytic activity of the new material with that of the material prepared by the solid–state method.

6-2. Experimental section

The procedure for synthesis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is shown in Figure 6-1. Samarium titanate $\text{Sm}_2\text{Ti}_2\text{O}_7$ was prepared by the polymerized complex method⁷ using $\text{Ti}(\text{OiPr})_4$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as starting materials. Ethylene glycol and methanol were employed as solvents, and anhydrous citric acid was employed as a complexing agent to immobilize Ti and Sm ions. After polymerization of a mixture containing stoichiometric amounts of

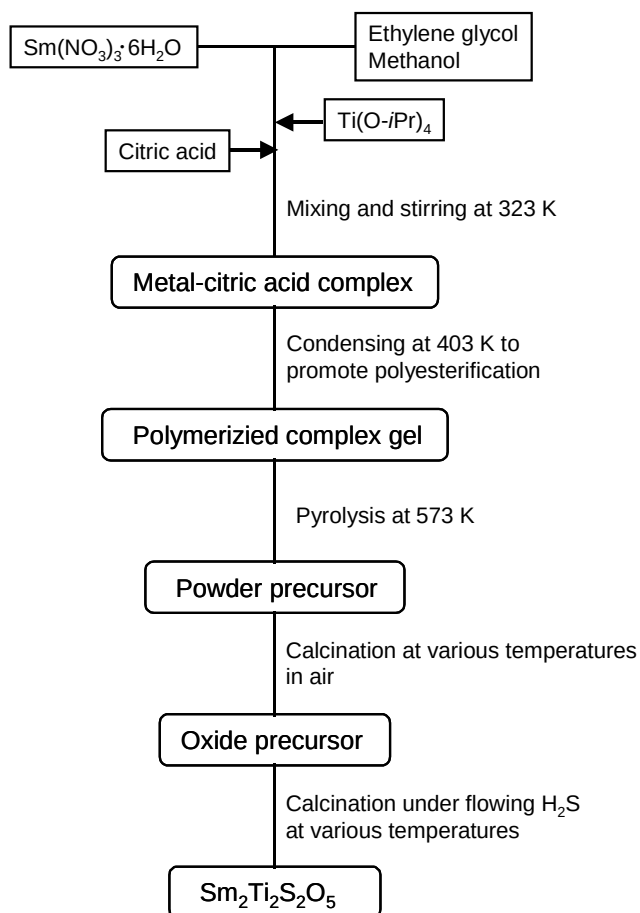


Figure 6-1. Flowchart for preparing oxysulfide $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ via a new synthetic route.

Sm and Ti ($\text{Sm}/\text{Ti} = 1:1$) according to the method in the literature,⁸ samarium titanates were obtained by calcination at various temperatures in air. This samarium titanate $\text{Sm}_2\text{Ti}_2\text{O}_7$ is referred to as the oxide precursor. $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was prepared from the oxide precursor (0.5 g) by calcination under flowing H_2S (flow rate: 10 mL min^{-1}) at various temperatures. This synthesis method is abbreviated as the HGS (H_2S gas sulfurization) method, and the solid-state reaction of Boyer-Candalen et al.¹ is abbreviated as the SSR (solid-state reaction) method. The prepared samples were characterized by X-ray powder diffraction (XRD; Geigerflex Rad-B system $\text{Cu K}\alpha$ 15 mA, Rigaku).

Photocatalytic reactions were carried out as described in Chapter 5. For H_2 evolution, Pt was loaded by impregnation from H_2PtCl_6 followed by reduction in H_2 at 473 K. The Pyrex vessel was employed (Figure 5-4). The light source was a 300 W Xe lamp equipped with cut-off filters.

UV–vis diffuse reflectance spectra were obtained using an UV–vis spectrometer (UV–vis DR; V–560, JASCO) and were converted from reflection to absorbance by the Kubelka–Munk method. The SEM and TEM images were obtained by field–emission scanning electron microscopy (FE–SEM; S–4700, Hitachi) and field–emission transmission electron microscopy (FE–TEM; JEM–2010F, JEOL). XPS spectra were obtained by X-ray photoelectron spectroscopy (XPS; ESCA 3200, Shimadzu).

6-3. Results and Discussion

6-3-1. Preparation of Oxide Precursor for Sulfurization.

Figure 6-2 shows the schematic structures of $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. The crystal system of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is tetragonal with space group $I4/mmm$, whereas $\text{Sm}_2\text{Ti}_2\text{O}_7$ has cubic symmetry with space group $Fd3m$. The effect of calcination temperature of the oxide precursor was investigated to produce a sample appropriate for sulfurization. The polymers obtained by the polymerized complex method were calcined in air, and oxide precursors were obtained at temperatures above 773 K. Figure 6-3 shows the XRD patterns of the oxide precursors prepared by calcination at various temperatures between 773 and 1473 K. Crystallization occurred for $\text{Sm}_2\text{Ti}_2\text{O}_7$ at 1073 K and above, and the intensities of the diffraction peaks produced by $\text{Sm}_2\text{Ti}_2\text{O}_7$ increased with calcination

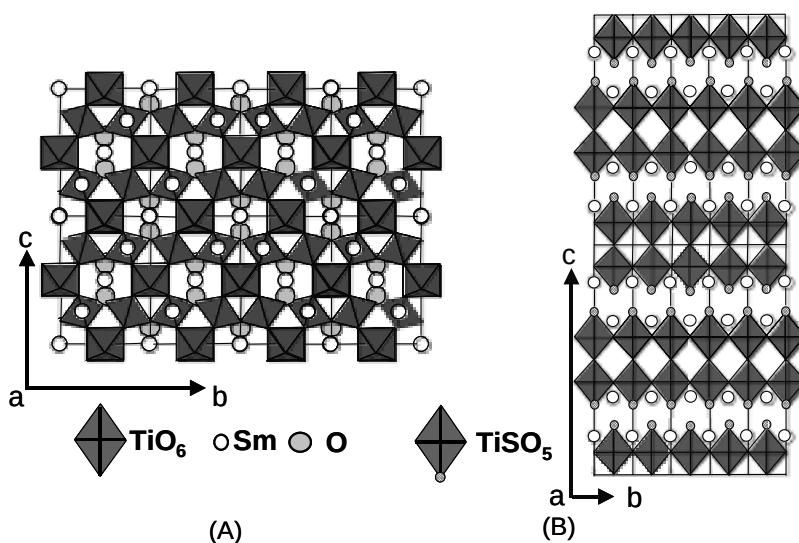


Figure 6-2. Schematic structures of (A) $\text{Sm}_2\text{Ti}_2\text{O}_7$ and (B) $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

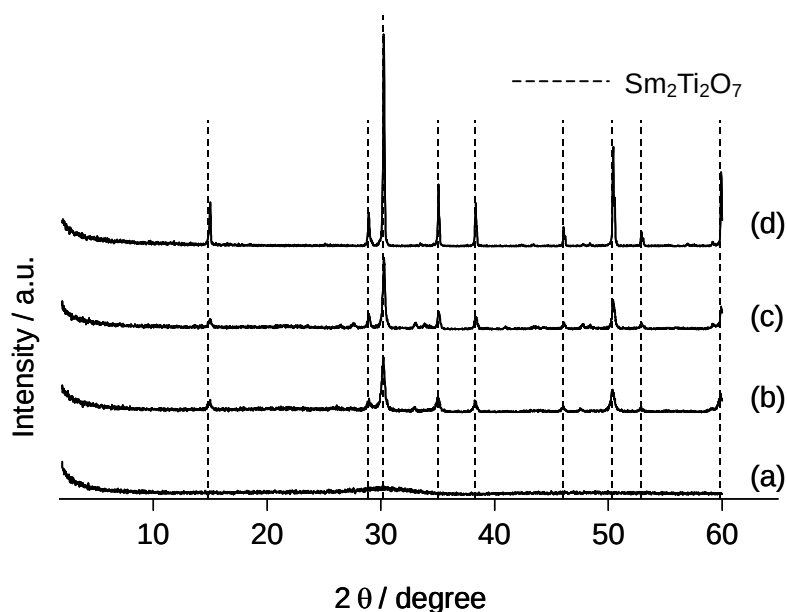


Figure 6-3. XRD patterns of oxide precursors prepared at (a) 773 K for 12 h, (b) 1073 K for 5 h, (c) 1273 K for 5 h, and (d) 1473 K for 5 h.

temperature without the appearance of impurity phases. The series of oxide precursors calcined at above 773 K and below 1023 K for 12 h were amorphous. The BET surface area measured by N₂ adsorption at 77 K was 60 m² g⁻¹ for the amorphous precursor prepared at 773 K. The surface area decreased with increasing calcination temperature, such that the crystalline Sm₂Ti₂O₇ prepared at 1473 K had a surface area of only 0.4 m² g⁻¹.

6-3-2. Sulfurization of Oxide Precursor.

Figure 6-4 shows the XRD patterns of various oxide precursors after sulfurization at 1273 K for 5 h. The sulfurized samples A, B, C and D correspond to the oxide precursors a, b, c, and d in Figure 6-3. Sample A included a single phase of Sm₂Ti₂S₂O₅, whereas sample B, C, and D exhibited two distinct phases of Sm₂Ti₂S₂O₅ and Sm₂Ti₂O₇. Sample A, calcined at 773 K, exhibits only a single phase of Sm₂Ti₂S₂O₅ upon sulfurization, and is therefore the most suitable sample for sulfurization and synthesis of Sm₂Ti₂S₂O₅. In all samples prepared hereafter, the oxide precursor was calcined at 773 K.

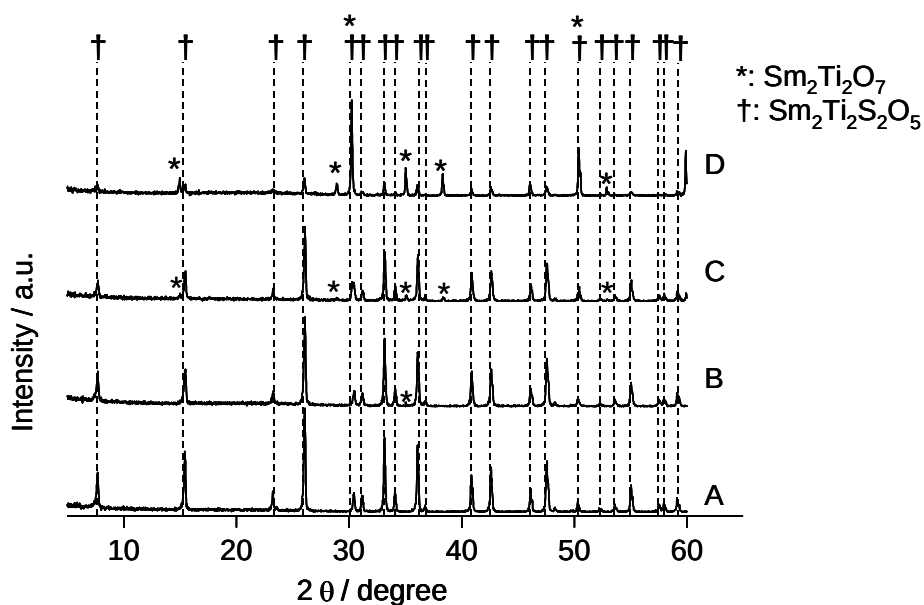


Figure 6-4. XRD patterns of oxide precursors sulfurized under H₂S flow at 1273 K for 5 h. Precursors were prepared by calcination at (A) 773 K for 12 h, (B) 1073 K for 5 h, (C) 1273 K for 5 h, and (D) 1473 K for 5 h.

Figure 6-5 shows the XRD patterns of Sm₂Ti₂S₂O₅ obtained at various temperatures by the proposed method. Diffraction peaks corresponding to Sm₂Ti₂S₂O₅ appeared for the sample sulfurized at 1073 K even after 1 h. After 10 h sulfurization at 1073 K, the diffraction peaks of Sm₂Ti₂O₇ disappeared. At sulfurization temperature of 1123 K or above, a single phase of Sm₂Ti₂S₂O₅ was obtained even after a short period of sulfurization (1 h). Thus, the proposed method allows for very quick synthesis of Sm₂Ti₂S₂O₅ compared to the solid-state method, which took up to 2 weeks. Figure 6-6 shows the variation in crystallite size of Sm₂Ti₂S₂O₅ with sulfurization temperature. Each sample was sulfurized for 1 h at the stated temperature. The crystallite sizes of Sm₂Ti₂S₂O₅ powders were determined by the Scherrer's equation, using the (013) reflection of Sm₂Ti₂S₂O₅ for calculation. The crystallite size of Sm₂Ti₂S₂O₅ increased gradually with sulfurization temperature from 1073 to 1123 K. The crystallite size of Sm₂Ti₂S₂O₅ prepared at 1073 K for 1 h was estimated to be *ca.* 65 nm, and continued to grow with sulfurization time.

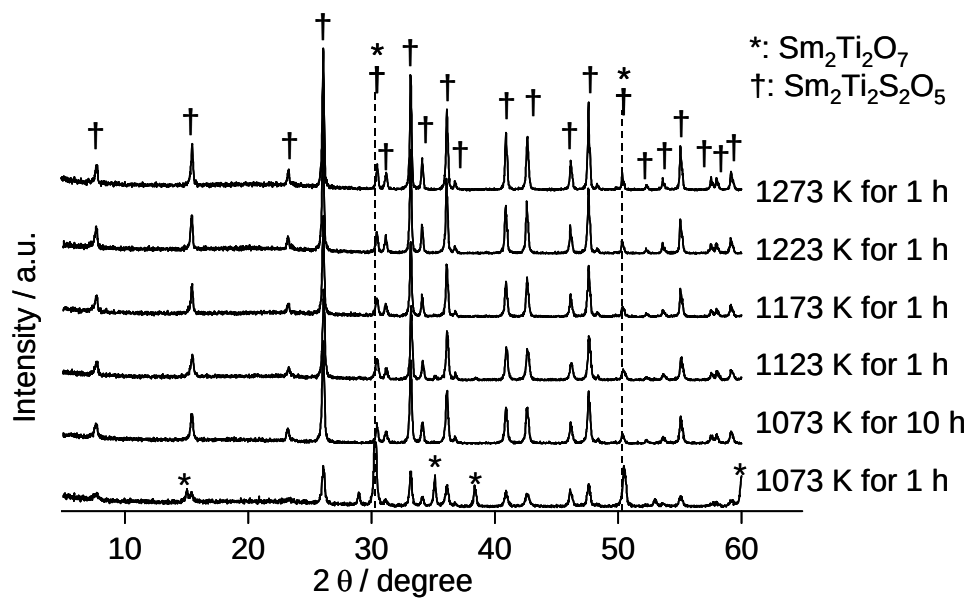


Figure 6-5. XRD patterns of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) obtained at various temperatures.

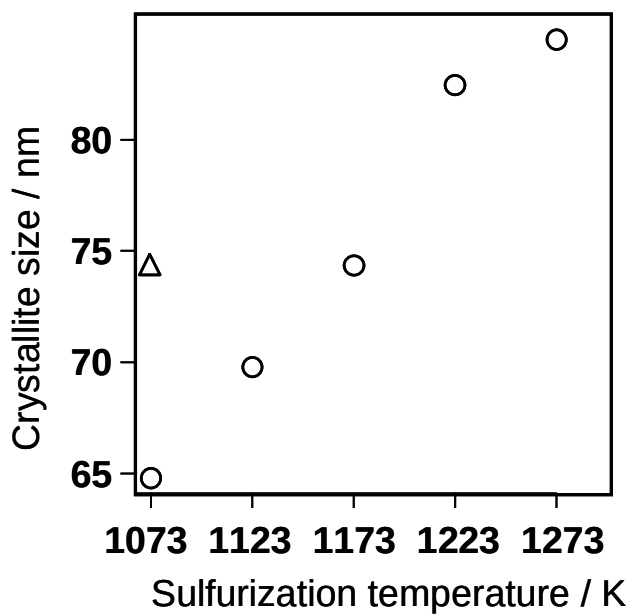


Figure 6-6. Variation in crystallite size of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ with sulfurization temperature. (Δ) after 10 h sulfurization. (O) after 1 h sulfurization.

6-3-3. Characterization of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

The UV–vis DR spectra of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS, 1173 K, 1 h) and $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (SSR) are shown in Figure 6-7. The absorption edge at 600 nm was observed for both samples, whereas an absorption in the near–infrared region beyond 600 nm was also observed only for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS). This near–infrared absorption is attributed to the existence of a small amount of Ti^{3+} species in the sample, reduced from Ti^{4+} by exposure of the oxide precursor to H_2S . The spectra of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) after heat treatment in air at 473 K for 2 h and in a vacuum at 1273 K for 4 d are shown in Figures 6-7c and d. Heat treatment in a vacuum was carried out by calcining a mixture of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS, 1.0 g) and sulfur (0.2 g) in a sealed quartz tube. Heating the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) in air or vacuum resulted in a weakening of the absorption band above 600 nm. Heat treatment did not change the crystal structure or bulk composition, but appeared to cause Ti^{3+} to oxidize to Ti^{4+} , as indicated by XRD and energy–dispersive X-ray spectroscopy (EDX).

Figure 6-8 shows SEM images of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ prepared by the SSR and HGS methods. In

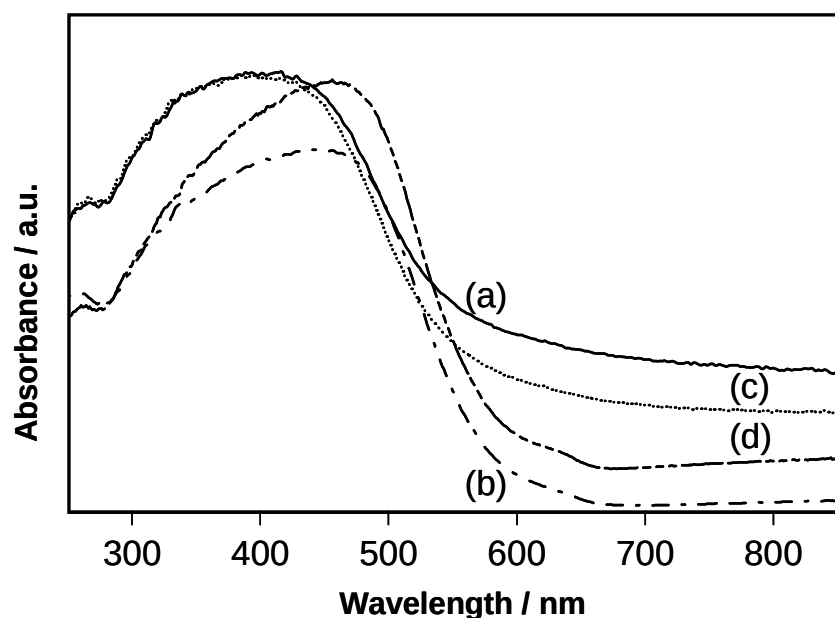


Figure 6-7. UV–vis DR spectra of (a) $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS, at 1173 K for 1 h), and (b) $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (SSR), and after heating sample (a) in air at 473 K for 2 h (c), and in a sealed quartz tube with S at 1273 K for 4 days (d).

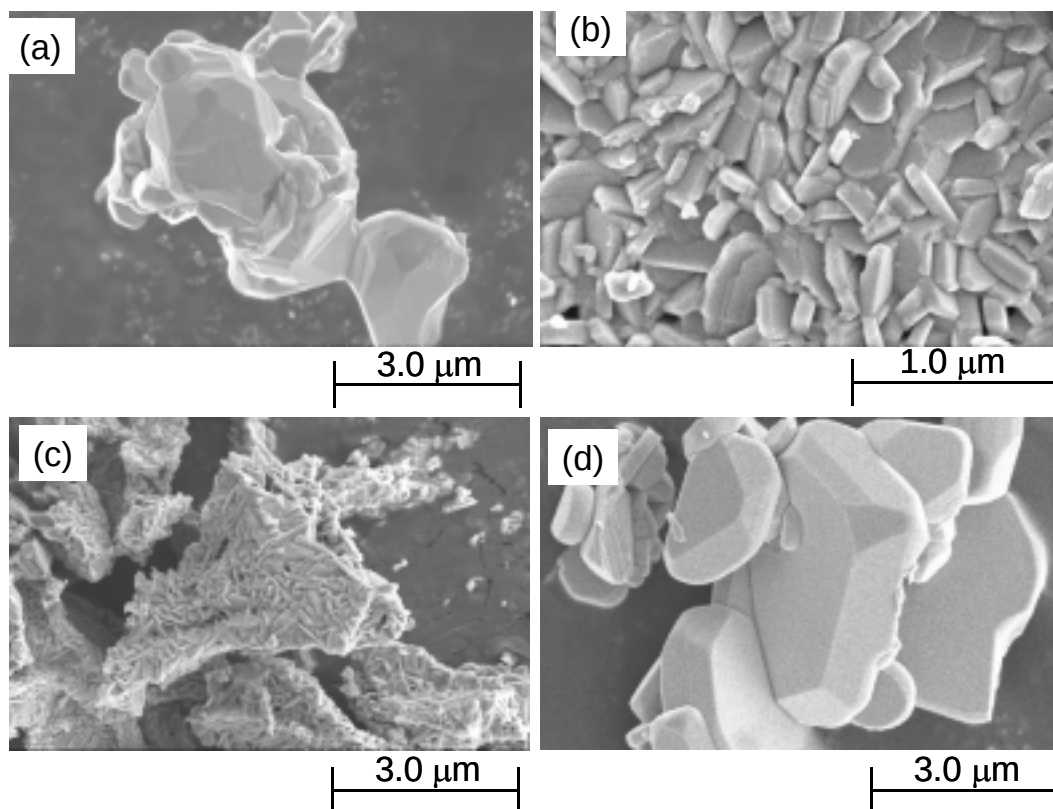


Figure 6-8. SEM images of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ produced by (a) the SSR method, (b and c) the HGS method, and (d) the HGS method followed by heating in a vacuum at 1273 K for 4 days.

the case of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (SSR), round particles (2–4 μm) were observed, and the BET surface area as measured by N_2 adsorption at 77 K was $0.6 \text{ m}^2 \text{ g}^{-1}$. In the case of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS), platelike particles with smooth surfaces were obtained. This morphology was relatively constant, and independent of sulfurization temperature. SEM observation of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) revealed that primary particles of about 0.1–0.5 μm diameter aggregate to form large secondary particles of 0.5–5.0 μm . The difference in the particle size between those calculated by the Scherrer's equation and those observed by SEM suggests that the particles observed by SEM are the polycrystalline particles. The BET surface area of the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) sample was $6.0 \text{ m}^2 \text{ g}^{-1}$. Therefore, the HGS method provides a 10-fold increase in surface area compared to that of the SSR method. An SEM image of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ after heating in a vacuum at 1273 K for 4 days is shown in Figure 6-8(d). Heating resulted in an increase in $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ particle size, and the

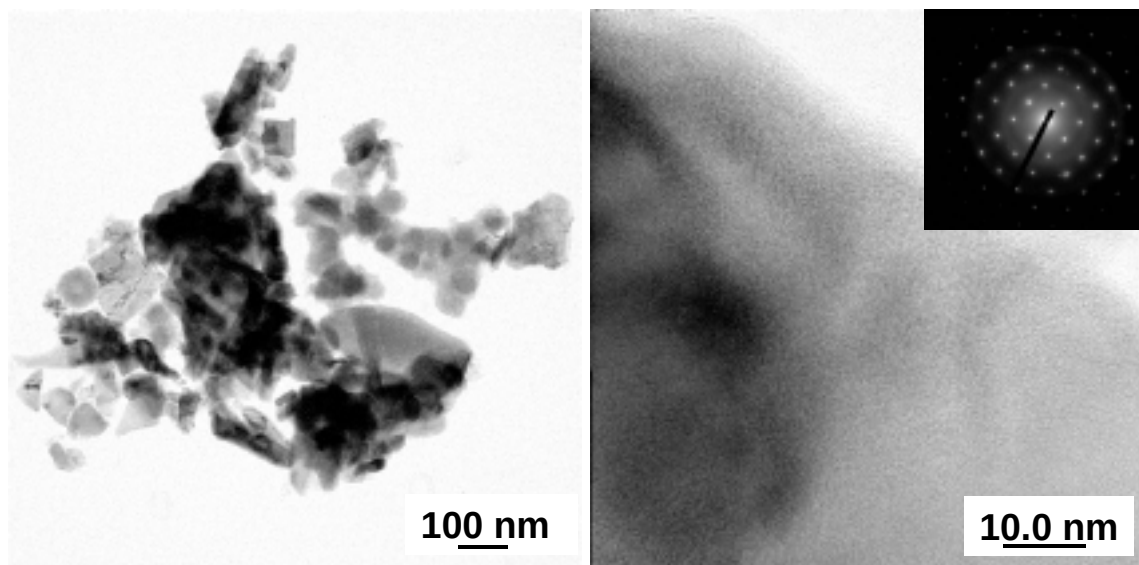


Figure 6-9. TEM images and electron diffraction pattern of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS, 1173 K).

morphology became essentially the same as that of the $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (SSR) sample. A TEM image of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) prepared at 1173 K for 1 h is shown in Figure 6-9. The TEM image and electron diffraction pattern indicate that well-crystallized $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is formed by sulfurizing for 1 h. The particle size calculated by the Scherrer's equation is almost coincident with that observed by TEM.

Figure 6-10 shows the XPS spectra of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) before and after heat treatment in air at 473 K for 2 h. The surface atomic ratios of Sm/Ti, O/Ti and S/Ti are summarized in Table 6-1. The surface atomic ratio of O/Ti was estimated from the O1s peak at 530 eV.⁶ Two S species were observed for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ before heat treatment (Figure 6-10D(a)); one assigned to S^{2-} species (S2p3/2, 160.8; 2p1/2, 162.0 eV) and the other to S^0 (S2p3/2, 163.3 eV; 2p1/2, 164.8 eV) deposited on the surface of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$. The features of the XPS spectra remained unchanged after heat treatment except for the S2p peaks. The surface atomic ratios of Sm/Ti, O/Ti, and S/Ti (S^{2-}) also remained unchanged. After heat treatment, the intensity of the S^0 peaks (163.3 and 164.8 eV) decreased and new peaks appeared at 168.2 (S2p3/2) and 169.4 eV (2p1/2), assigned to S^{4+} species (Figure 6-10D(b)). This indicates that the adsorbed sulfur S^0 species was oxidized by heat treatment. The S^{4+} species disappeared after the sample was suspended

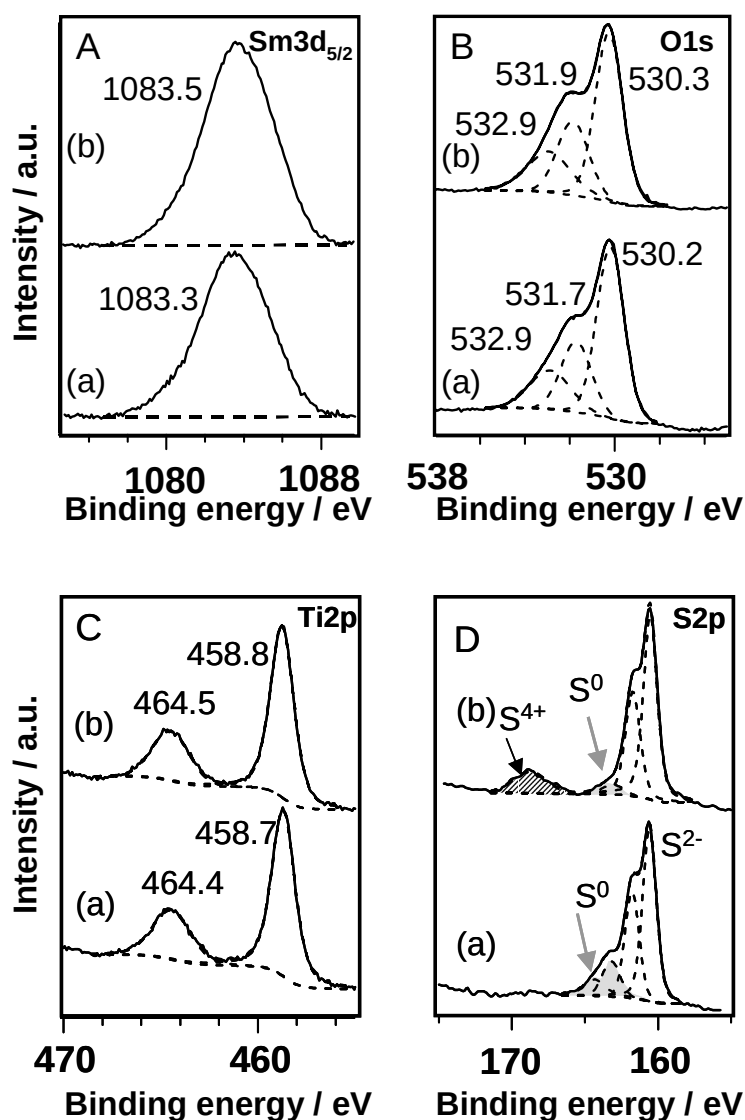


Figure 6-10. XPS spectra for (A) $\text{Sm}3d_{5/2}$, (B) $\text{O}1s$, (C) $\text{Ti}2p$, and (D) $\text{S}2p$ of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ before and after heat treatment in air at 473 K for 2 h.

Table 6-1. Surface Atomic Ratios of Sm/Ti , S/Ti , and O/Ti of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ Before and After Heat Treatment.

sample	Sm/Ti	S/Ti			O/Ti
		S^{2-} (160.8 + 162.0 eV)	S^0 (163.3 + 164.8 eV)	S^{4+} (168.2 + 169.4 eV)	
before HT	0.9	1.2	0.2	0.0	3.0
after HT	0.9	1.2	0.1	0.2	3.0

in water (data not shown). It is therefore considered that sulfur species other than S^{2-} can be removed by heat treatment. The XPS results indicate that heat treatment in air oxidizes S^0 species on the surface of $Sm_2Ti_2S_2O_5$ to S^{4+} , whereas the surface S^{2-} species of $Sm_2Ti_2S_2O_5$ remain essentially unchanged.

6-3-4. Photocatalytic activity of $Sm_2Ti_2S_2O_5$.

Table 6-2 shows the dependence of the photocatalytic activity of $Sm_2Ti_2S_2O_5$ (HGS) upon sulfurization temperature. O_2 evolution was examined in a basic solution (*ca.* pH 8) buffered by La_2O_3 .^{8,9} The pH of the aqueous Na_2S – Na_2SO_3 solution for H_2 evolution was 13. Pt as an H_2 evolution promoter was loaded by impregnation from H_2PtCl_6 , followed by reduction in H_2 at 473 K. The highest activity of H_2 or O_2 evolution was obtained for the sample prepared at 1123 K for 1 h. The photocatalytic activity of $Sm_2Ti_2S_2O_5$ prepared at 1073 K for 10 h was lower than that of the sample prepared at 1123 K for 1 h due to lower crystallinity. The photocatalytic activity decreased with increasing sulfurization temperature from 1123 to 1273 K due to particle growth and the generation of Ti^{3+} species. The steady-state quantum efficiency for H_2 evolution was

Table 6-2. Dependence of Photocatalytic Activity of $Sm_2Ti_2S_2O_5$ on Calcination Temperature.

sulfurization temp (K) ^a	rate of gas evolution ($\mu\text{mol/h}$)			
	O_2		H_2	
	before HT	after HT (473 K, 2 h)	before HT	after HT (473 K, 2 h)
1073 ^b	6	10	0.3	6
1123	15	17	6.6	22
1173	12	20 [10] ^c	0.9	22 [8] ^c
1223	9	12	0.2	8
1273	5	8	1.5	5

^a Sulfurization for 1 h. ^b Sulfurization for 10 h.

^c After heat treatment at 1273 K for 4 days in a vacuum.

0.03%, and that for O₂ evolution was estimated to be 0.4% for the Sm₂Ti₂S₂O₅ sample prepared at 1123 K for 1 h. In contrast, the quantum efficiencies of H₂ and O₂ evolutions for Sm₂Ti₂S₂O₅ (SSR) were estimated to be 0.3% and 0.2%, respectively. The proposed synthesis route therefore provides catalysts with enhanced photocatalytic activity for O₂ evolution, yet with decreased activity for H₂ evolution. The low activity for H₂ evolution is expected to be due to the presence of Ti³⁺ species in the bulk and S⁰ species on the Sm₂Ti₂S₂O₅ surface. The presence of Ti³⁺ species in the sample means the existence of the vacancies. The vacancies would work as recombination centers for photoexcited electrons and holes to reduce the efficiency. It is also considered that S⁰ species interfere with the deposition of Pt on Sm₂Ti₂S₂O₅ surface. Pt was indispensable for H₂ evolution reaction. In the case of O₂ evolution reaction, no co-catalyst is needed for Sm₂Ti₂S₂O₅ and S⁰ species is oxidized during O₂ evolution reaction. Therefore, the activity for O₂ evolution was little affected by the presence of S⁰ species. Table 6-2 also shows the photocatalytic activities of Sm₂Ti₂S₂O₅ (HGS) after heat treatment in air or a vacuum. Heating in air at 473 K for 2 h enhanced photocatalytic activities for both H₂ and O₂ evolution. After this heat treatment, the Sm₂Ti₂S₂O₅ sample prepared at 1173 K for 1 h exhibited a quantum efficiency for H₂ and O₂ evolution of 0.3% and 0.6%, respectively. It is considered that the decrease of S⁰ species on the surface and the vacancies in the bulk by heating in air brought about the enhancement of the photocatalytic activities. The H₂ evolution activity (22 μmol/h) of Sm₂Ti₂S₂O₅ (HGS) was equivalent to that (18 μmol/h) of Sm₂Ti₂S₂O₅ (SSR) because the removal of the vacancies and S⁰ species was not complete, as shown in Figures 6-7 and 6-10. Heating Sm₂Ti₂S₂O₅ in a vacuum at 1273 K for 4 d with sulfur resulted in a decrease in the photocatalytic activities. Although the concentration of Ti³⁺ species in the bulk decreased by heat treatment in a vacuum, the abundance of S⁰ species on the surface increased and the surface area decreased. This increased prevalence of S⁰ species on the surface and the lower surface area are considered to be responsible for the reduced photocatalytic activities.

The proposed method can produce Sm₂Ti₂S₂O₅ with equivalent H₂ and superior O₂

evolution activity compared to that of the solid–state method, with a far shorter preparation time and at lower temperature. It is expected that the complete removal of the vacancies and S^0 species enhance photocatalytic activities.

6-4. Conclusion

A new method for the synthesis of oxysulfide $Sm_2Ti_2S_2O_5$ using H_2S was presented. The photocatalytic activities of the catalyst produced by this method were improved by heating in air at 473 K for 2 h. This new method allows $Sm_2Ti_2S_2O_5$ to be synthesized with a much shorter heating period (1 h) and at much lower temperature than those used for the previous solid–state method. Synthesis under H_2S flow is expected to be applicable to the preparation of other oxysulfide catalysts with high activities.

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Chapter 7

Oxysulfides $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ as Stable Photocatalysts for Water
Oxidation and Redaction under Visible–Light Irradiation

7-1. Introduction

Photocatalysts for overall water splitting have great potential for solar energy applications. A range of oxide semiconductors with ultraviolet–light response function as stable photocatalysts for overall water splitting to generate stoichiometric H_2 and O_2 .^{1–3} These materials are, however, not active under visible light. The development of photocatalysts with visible–light response would therefore be valuable for application to H_2 production using solar energy. Chapter 5 has revealed that the oxysulfide $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ functions as a stable photocatalyst for the reduction of H^+ to H_2 and oxidation of H_2O to O_2 in the presence of a sacrificial electron donor and acceptor under visible–light irradiation.⁴ In Chapter 6, a new synthetic route to $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ using H_2S was also described.⁵ Recently, the series $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$) has been synthesized by Boyer-Candalen et al.,⁶ and it is expected that the members of this $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ series will also function as visible light–responsive photocatalysts. This chapter reports a new synthetic route to $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ using H_2S , and discusses the photocatalytic activities of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ on the basis of electronic band structure calculations and crystal structures determined by X-ray diffraction (XRD) analysis.

7-2. Experimental Section

$\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ was synthesized by two methods. The first method involved a solid–state reaction as can be found in the literature.^{6,7} By this method, $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ samples were obtained by heating a mixture of Ln_2S_3 (99.999%, Soekawa Chemical Co., Ltd.), Ln_2O_3 , and TiO_2 (99.95%, 98.5%, Kanto Chemical Co., Inc.) at a molar ratio of 2:1:6 ($\text{Ln}_2\text{S}_3\text{:Ln}_2\text{O}_3\text{:TiO}_2$) in a sealed quartz tube under vacuum at 1273 K. After 1 week, the sintered samples were ground and heated in the vacuum–sealed tube for an additional week. The obtained samples were finally ground into powders. This synthesis method is abbreviated as the solid–state reaction (“SSR”) method. The obtained samples were used for structure refinement. The other method involved the sulfurization reaction of lanthanide titanate under H_2S flow. Precursors, that is, the lanthanide titanates, to be

sulfurized under flowing H_2S were prepared by the polymerized complex method⁸ using $\text{Ti}(\text{OiPr})_4$ and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as starting materials. Ethylene glycol and methanol were used as solvents, and anhydrous citric acid was employed as a complexing agent to stabilize Ti and Ln ions. After polymerization of the mixture containing Ti and Ln ions according to the method in the literature,⁷ lanthanide titanates were obtained by calcination at 773 K in air. The obtained samples are labeled as “oxide precursor” samples. $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ was prepared from the oxide precursor (0.5 g) by calcination under flowing H_2S (flow rate: 10 mL/min) at various temperatures and for sulfurization times. This synthesis method is abbreviated as the H_2S –gas sulfurization (“HGS”) method. The obtained samples were used for photocatalytic reactions because the HGS method could produce $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ with superior photocatalytic activity compared to the solid–state method.

Photocatalytic reactions were carried out as described in Chapter 5.

7-3. Results and Discussion

7-3-1. Structure Refinement.

Figure 7-1 shows the schematic structures of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$. The crystal system of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ is tetragonal with space group $I4/mmm$. The atomic coordinates of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ were refined by Rietveld analysis using the computer program RIETAN–2000.⁹ The diffraction data were collected for 3°s at each 0.03° step over a 2θ range of 10–120°. These refinements gave agreement factors of $R_p = 6.67\text{--}9.70\%$, $R_{wp} = 9.65\text{--}15.8\%$, and $S = R_{wp}/R_e = 1.3\text{--}1.9$. The estimated atomic coordinates of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ were in good agreement with those in the literature.^{6, 10}

Figure 7-2 shows the relationship between the ionic radii of 9–coordinated Ln^{3+} ions¹¹ and O(1)–Ti, O(2)–Ti, S–Ln(1), S–Ln(2), and S–Ti distances taken from the X-ray Rietveld refinement results for $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$. All binding distances except for O(1)–Ti increased with increasing ionic radii of the Ln^{3+} ions, indicating that a change in the O(1)–Ti distance gives rise to distortion of the TiSO_5 octahedra. The rate of S–Ln(1) lengthening also

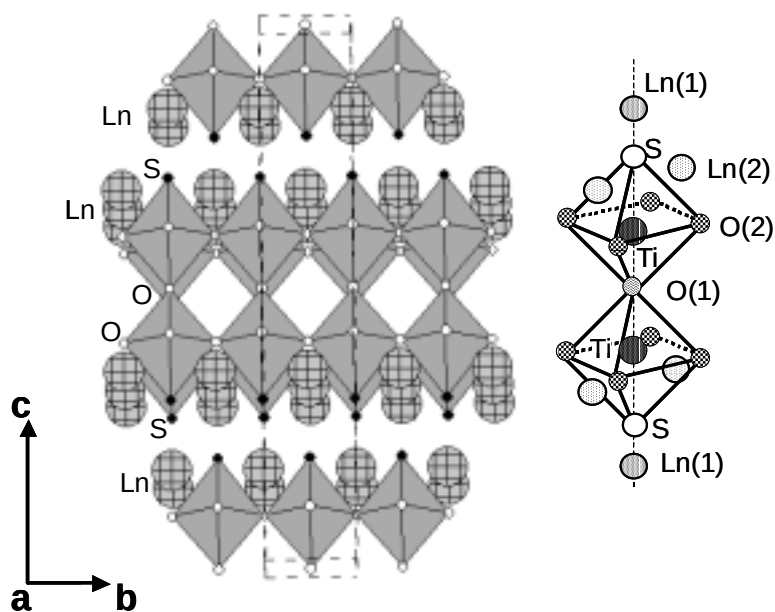


Figure 7-1. Schematic structure of the $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ structure.

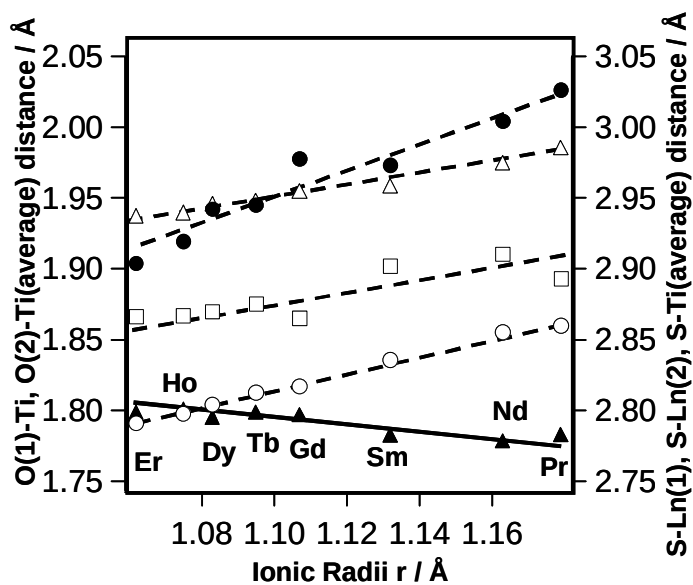


Figure 7-2. Relationships between ionic radii and O-Ti, S-Ln and S-Ti bond distances: (▲) O(1)-Ti; (Δ) O(2)-Ti; (●) S-Ln(1); (○) S-Ln(2); (□) S-Ti.

differed from that for S–Ln(1), S–Ti, or O(2)–Ti. The change in the S–Ln(1) distance appears to be related to the change in O(1)–Ti.

Figure 7-3 shows the relationship between the lattice constants of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ and the ionic radii of Ln^{3+} ions. In $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Ln = Er, Ho, Dy, Tb, Gd, Sm, Nd, and Pr), the a and b axis distances of the lattice constants increased linearly with increasing ionic radii of the lanthanide ions, from Er to Pr. Although the c -axis distance increased with the ionic radius, the increase was not linear. It is considered that this change in the c axis distance is caused by an increase or decrease in the O(1)–Ti and S–Ln(1) distances. The X-ray Rietveld refinement results therefore imply that the structure of $[\text{Pr,Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ is distorted from the ideal perovskite structure.

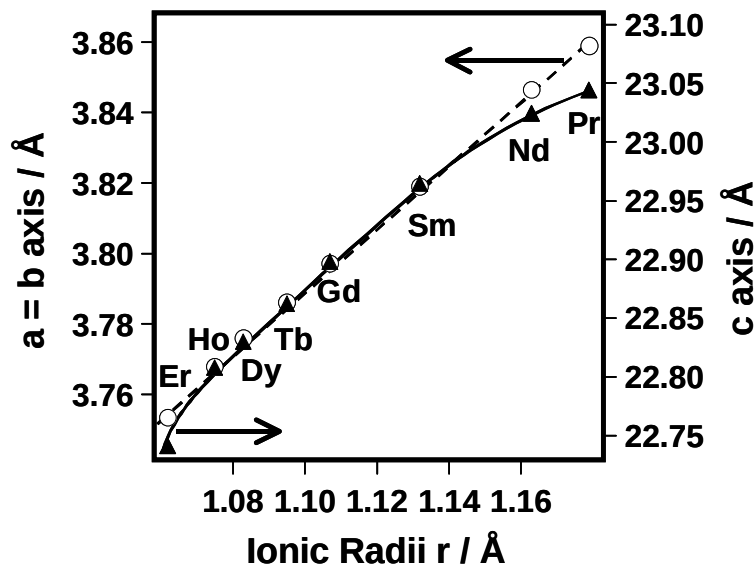


Figure 7-3. Relationships between ionic radii and lattice parameters of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$: (○) $a = b$ axis; (▲) c axis.

7-3-2. Electronic Structure Calculations.

The series $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ was further investigated by calculating the electronic band structure on the basis of plane-wave density functional theory (DFT) using CASTEP.¹² The atomic coordinates of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ refined by the Rietveld analysis were used in the DFT calculations. The core orbitals were replaced by the ultrasoft core potentials,¹³ and

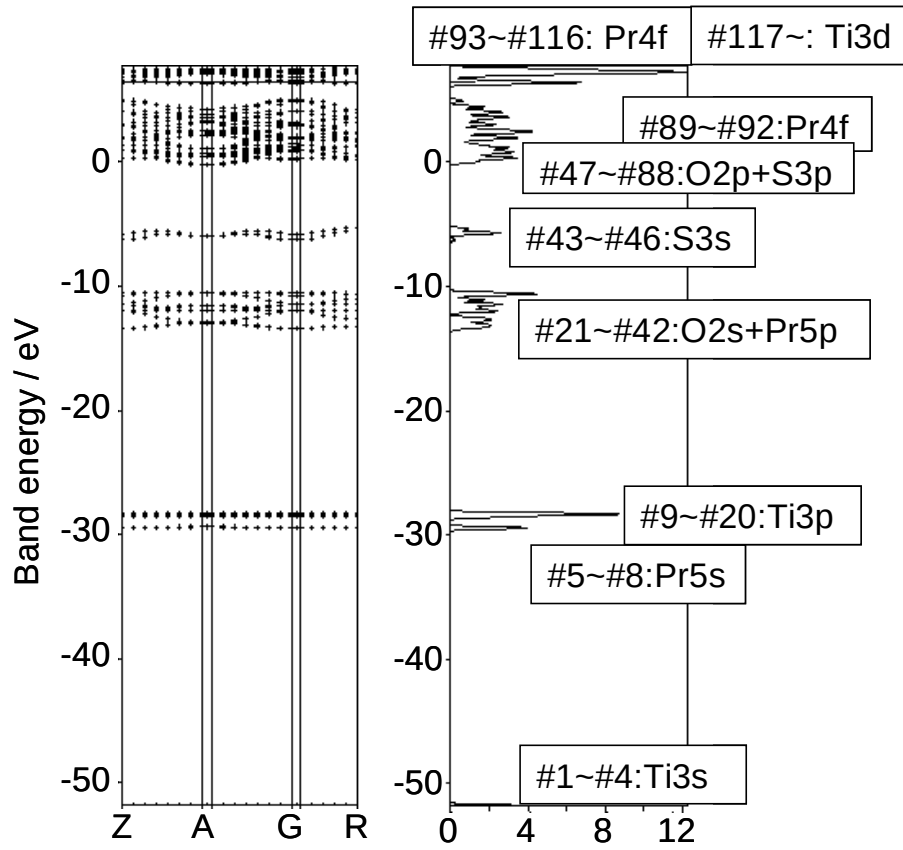


Figure 7-4. Band dispersion and density of states for $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$.

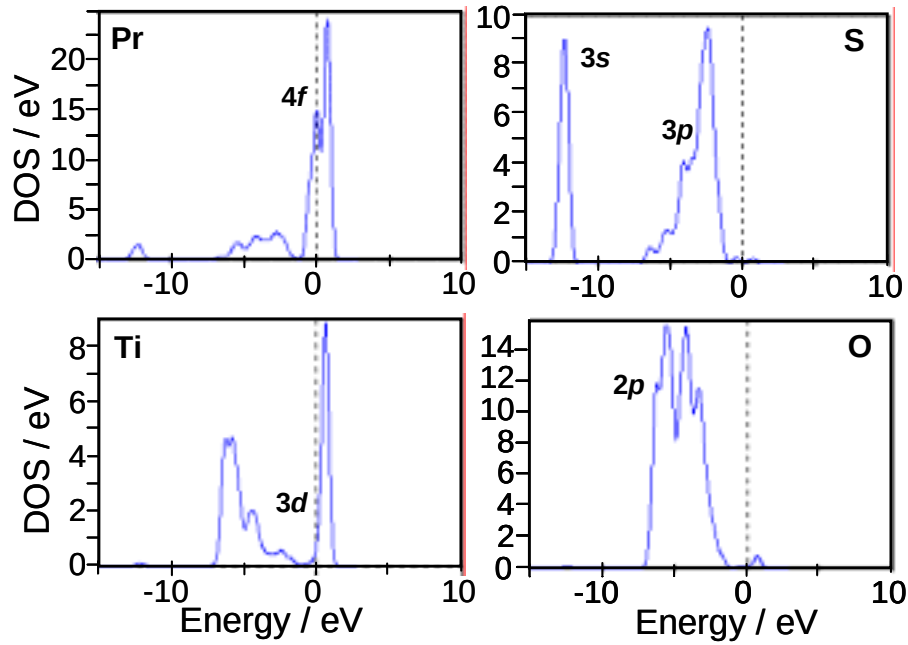


Figure 7-5. Partial DOS for $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$.

the $\text{O}2s^22p^4$, $\text{S}3s^23p^4$, $\text{Ti}3s^23p^63d^24s^2$, and Ln ($\text{Pr}5s^25p^64f^36s^2$, $\text{Nd}5s^25p^64f^46s^2$, $\text{Sm}5s^25p^64f^66s^2$, $\text{Gd}4f^75d^16s^2$, $\text{Tb}4f^96s^2$, $\text{Dy}4f^{10}6s^2$, $\text{Ho}4f^{11}6s^2$, and $\text{Er}4f^{12}6s^2$) electrons were

treated explicitly. The kinetic energy cutoff was set at 280 eV. As the Ln4f orbitals (Ln = Pr ~ Er) have smaller overlap and lower ionization potential, the self-consistent field (SCF) convergence was not good. Therefore, a fractional occupation technique was employed, which allows for the withdrawal and accumulation of a small amount of electron density in the top of the valence band and bottom of the conduction band. The calculated band dispersions and densities of states for $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$ are shown in Figure 7-4. The top of the valence band corresponds to orbital #92, and the bottom of the conduction band corresponds to orbital #93. The contents of each band are shown in the Figure 7-4. For example, orbitals #47 to #88 are composed of O2p and S3p orbitals. The band gap, which is apparently very small, lies between orbitals #92 and #93. The partial DOS for $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$ are also shown in Figure 7-5 in the energy region from -15 to +10 eV, where the Fermi level is set to zero on the abscissa. The valence band is made up of hybridized O2p and S3p orbitals and then localized Pr4f orbitals, whereas the conduction band starts with localized Pr4f orbitals and then Ti3d orbitals. The valence band also contains small contributions from Ti3d orbitals by the overlap with O2p and S3p orbitals. Except for just the top of the valence band, the higher energy region is occupied by S3p orbitals and the lower energy region is occupied by O2p orbitals. Although the Pr4f orbitals appear both at the top of the valence band and at the bottom of the conduction band, the 4f orbitals are relatively localized and the overlap between 4f orbitals is small. In our understanding, even if the 4f orbitals accept electrons by visible-light irradiation, it is less effective to transfer those electrons to the catalyst surface and the materials reduced. The 4f orbitals can contribute to the photocatalytic activities by hybridization with the S3p and O2p orbitals, that is, rather indirect fashion. Thus, the band gap is reasonably estimated to be 2.46 eV, taken as the energy difference between the top of the O2p+S3p band and the bottom of the Ti3d band.

The calculated band dispersions and densities of states for $\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$ are shown in Figure 7-6. The top of the valence band corresponds to orbital #94, and the bottom of the conduction band corresponds to orbital #95. Figure 7-7 shows the partial DOS for

$\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$ for the width of 25 eV in the band gap region. The valence band is made up of O2p+S3p, O2p+S3p+Er4f, and Er4f (partial), in increasing order of energy. The valence band also contains small contributions from Ti3d orbitals by the overlap with O2p and S3p orbitals. The band electronic structure of $\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$ differs on two points from that of $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$; hybridization of the O2p, S3p, and Er4f orbitals, as shown in Figure 7-7, and the contents of the conduction band or the relative location of 4f orbitals. Although it is difficult to recognize the small fraction of Er4f in the conduction band in Figure 7-7 because of the stronger peak of Er4f in the valence band, the unoccupied bands consist of Er4f (partial), S3p+Er4f, and Ti3d, as shown in Figure 7-6. The band gap is reasonably estimated to be 0.87 eV, taken as the energy difference between the top of the O2p+S3p+Er4f band and the bottom of the S3p+Er4f band.

The electronic band structure changes gradually over the lanthanide series. The two largest changes are lowering of the Ln4f band energy and increasing hybridization along with the increase of 4f electron number. In the papers by Machida et al., LnTaO_4 (Ln = La, Ce, Pr, Nd, and Sm)¹⁴ and $\text{RbLnTa}_2\text{O}_7$ (Ln = La, Pr, Nd, and Sm)¹⁵ are treated. The lowering of the Ln4f band energy over the lanthanide series was also reported. In this point, our result is consistent with them. Just the top of the valence band and just the bottom of the conduction band consist of solely 4f orbitals for all the $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ compounds. However, for the earlier lanthanide elements such as Pr, Pr4f orbitals do not mix with O2p and S3p orbitals in the valence band and conduction band. For the late lanthanide elements such as Er, Er4f orbitals mix with O2p and S3p orbitals in the valence band and mix with S3p orbitals in the conduction band. The latter is caused by a lowering of 4f orbital energy.

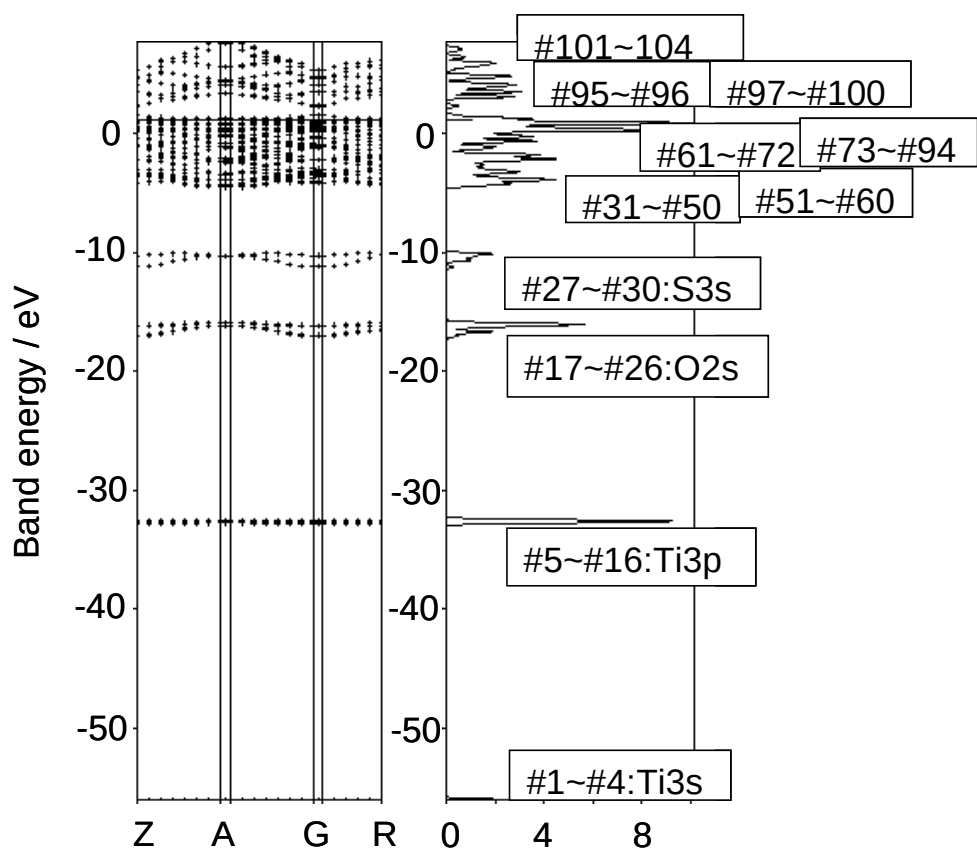


Figure 7-6. Band dispersion and density of states for $\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$: #31~#50, O2p; #51~#60, O2p+S3p; #61~#72, O2p+S3p+Er4f; #73~#94, Er4f; #95~#96, Er4f; #97~#100, S3p+Er4f; #101~#104, Ti3d.

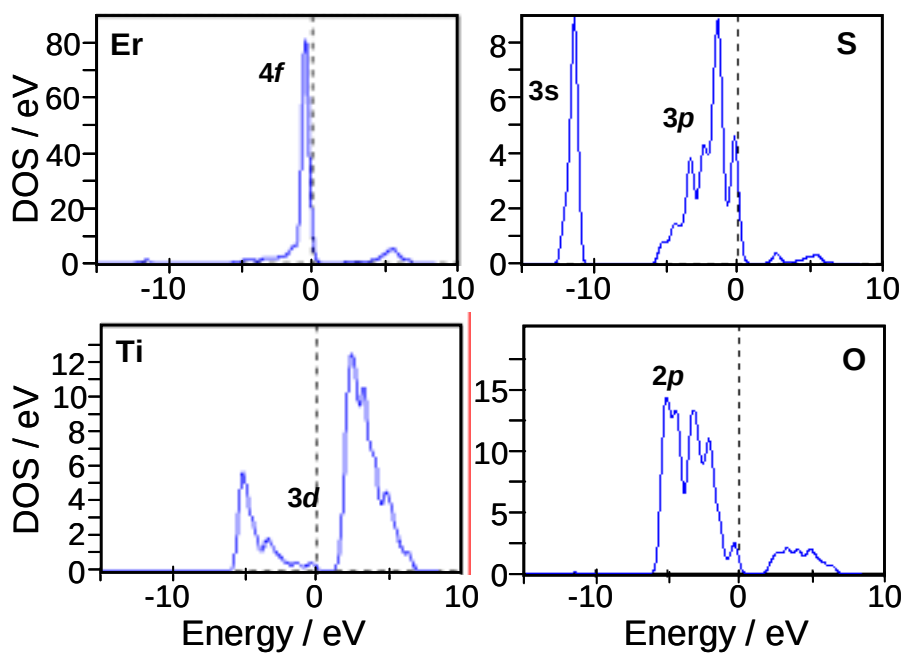


Figure 7-7. Partial DOS for $\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$.

The DFT calculations revealed that the series $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ can be separated into two groups according to the electronic band structure. $\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$ and $\text{SmTi}_2\text{S}_2\text{O}_5$ have the same electronic band structures as $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$, whereas the Gd, Tb, Dy, Ho, and Er forms represent a different structurally similar group. In the case of the Pr, Nd, and Sm forms, the valence band is made up of hybridized O2p and S3p orbitals and separated Ln4f orbitals to the higher energy region, and the conduction band consists of separated Ln4f orbitals to lower energy region and Ti3d orbitals. On the other hand, the top of the valence band for the Gd~Er group is made up of hybridized O2p, S3p, and Ln4f orbitals and the conduction band consists of S3p+Ln4f and Ti3d orbitals.

The diffuse reflectance spectra of $[\text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ are shown in Figure 7-8. The Tb, Dy, Ho, and Er forms exhibit a weak absorption band at 600–700 nm due to an f–f transition. The band gap energies calculated from the absorption band–edge positions, excepting the f–f transition, are summarized in Table 7-1. The band gap energies of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ decrease with increasing atomic number of the lanthanide ions from Sm^{3+} to Er^{3+} . It is considered that the O2p+S3p+Ln4f, and S3p+Ln4f hybridized orbitals in the valence and conduction bands for the Gd, Tb, Dy, Ho, and Er forms gives rise to this decrease in band gap energy.

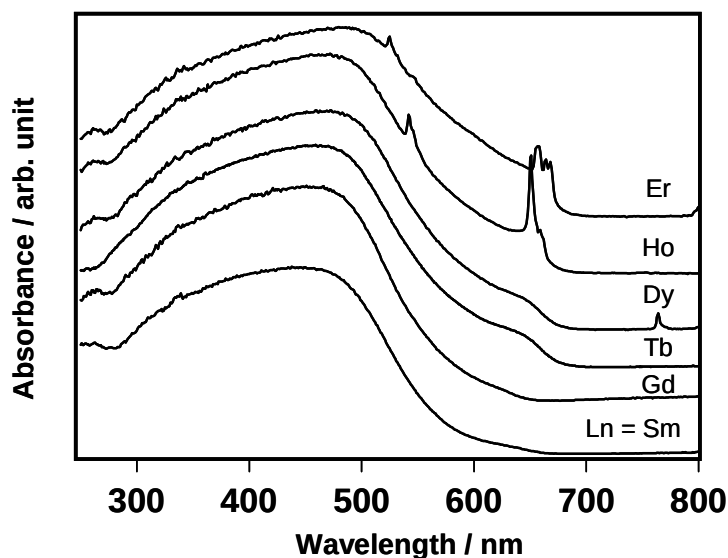


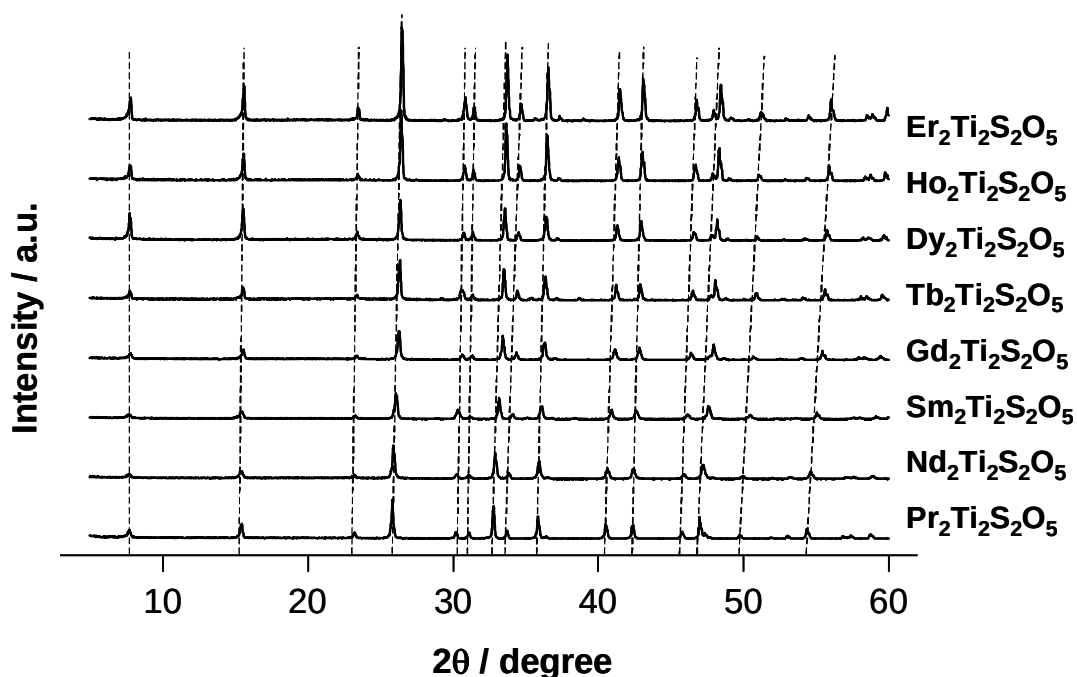
Figure 7-8. UV–vis diffuse reflectance spectra of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Ln = Sm, Gd, Tb, Dy, Ho, and Er).

Table 7-1. Optical Band Gap of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$.

Compound	Band gap (eV)
$\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$	1.94
$\text{Ho}_2\text{Ti}_2\text{S}_2\text{O}_5$	1.98
$\text{Dy}_2\text{Ti}_2\text{S}_2\text{O}_5$	2.00
$\text{Tb}_2\text{Ti}_2\text{S}_2\text{O}_5$	2.04
$\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$	2.09
$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$	2.13

7-3-3. Crystal Forms of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ Prepared by H_2S –Gas Sulfurization.

The advantages of the new synthetic route to $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ using H_2S with respect to preparation of active photocatalysts were described in Chapter 6. For the HGS synthesis reported here, the optimal conditions for sulfurization of $\text{Ln}_2\text{Ti}_2\text{O}_7$ are determined on the basis of the photocatalytic activity for O_2 evolution. Figure 7-9 shows the XRD patterns of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ obtained by sulfurization of the various amorphous oxide precursors at 1173–1273 K for 1–4 h. The products obtained consisted of a single $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ phase.

**Figure 7-9.** XRD patterns for $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS).

The sulfur content in the Er, Nd, and Pr forms of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ were, however, slightly lower than in the other $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ forms, as determined by EDX analysis.

Figure 7-10 shows SEM images of amorphous $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS). $\text{Gd}_2\text{Ti}_2\text{O}_7$ was granular with an uneven surface, and individual particles are clearly distinguishable. The BET surface area of the amorphous $\text{Gd}_2\text{Ti}_2\text{O}_7$ was $50 \text{ m}^2\text{g}^{-1}$. Similar morphologies were observed for the other oxide precursors. $\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) was observed to consist of platelike particles and have a flat surface. This morphology was also common to all other HGS samples. The BET surface area of the $\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) sample was $6 \text{ m}^2\text{g}^{-1}$, and although this surface area is significantly lower than for the precursor, the value is 10 times that of samples prepared by the SSR method ($0.6 \text{ m}^2\text{g}^{-1}$).

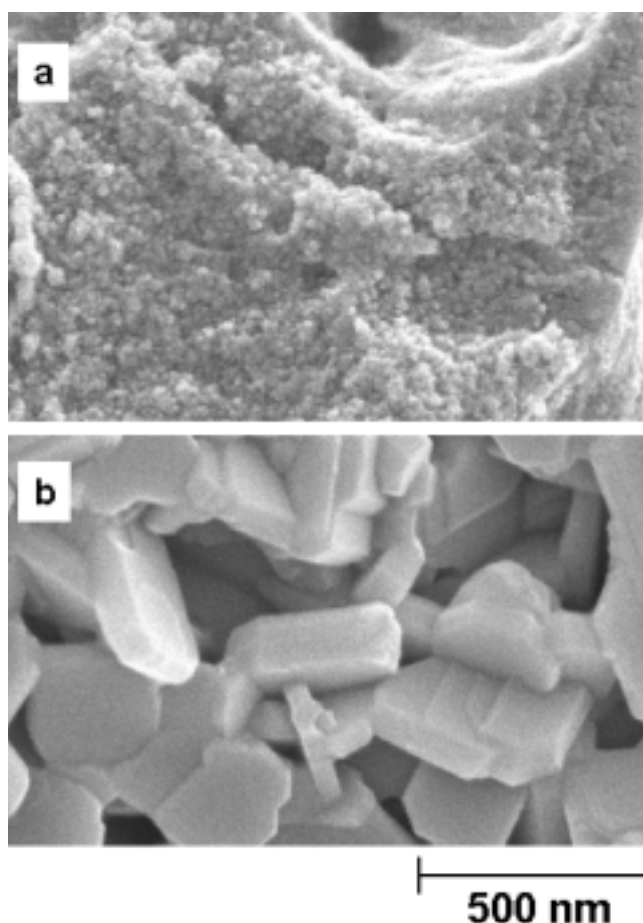


Figure 7-10. SEM images of amorphous $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS).

7-3-4. Photocatalytic Activity of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ under Visible-Light Irradiation.

Heating $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ in air at 473 K for 2 h has been found to enhance the photocatalytic activity of this catalyst for both H_2 and O_2 evolution through the oxidation of surface S^0 species.⁵ In the case of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$, heat treatment again enhanced the photocatalytic activities. Table 7-2 lists the photocatalytic activities of heat-treated $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (HGS) for the reduction of H^+ to H_2 and oxidation of H_2O to O_2 in the presence of a sacrificial electron donor or acceptor. O_2 evolution was examined in a basic solution (*ca.* pH = 8) buffered with La_2O_3 . In this reaction, the rate of O_2 evolution decreased with reaction time due to deposition of metallic silver on the surface of the catalyst, effectively shielding the catalyst from incident light. Therefore, the initial rate of O_2 evolution was regarded as the activity. The highest activity for O_2 evolution was obtained for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, with an estimated quantum efficiency of 0.7%. The pH of the aqueous Na_2S – Na_2SO_3 solution for H_2 evolution was 13. Platinum as an H_2 evolution promoter was loaded by the impregnation method from H_2PtCl_6 , followed by reduction under H_2 at 473 K. The rate of H_2 evolution was stable, and the steady H_2 evolution rates are summarized in Table 7-2. The highest activity for H_2 evolution was obtained for $\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$, with a steady-state quantum efficiency of 0.1%.

Table 7-2. Photocatalytic Activity of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$.

Compound	Rate of O_2 evol., $\mu\text{mol/h}$	Rate of H_2 evol., $\mu\text{mol/h}$
$\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$	0	0
$\text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5$	3	4
$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$	22	22
$\text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5$	21	24
$\text{Tb}_2\text{Ti}_2\text{S}_2\text{O}_5$	20	19
$\text{Dy}_2\text{Ti}_2\text{S}_2\text{O}_5$	9	10
$\text{Ho}_2\text{Ti}_2\text{S}_2\text{O}_5$	5	22
$\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$	1	21

7-3-5. Relationship between Photocatalytic Activity and Band Structure.

The optimal conditions for sulfurization of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ in the HGS method were determined on the basis of the photocatalytic activity of O_2 evolution, and may not be optimal for H_2 evolution. Therefore, the photocatalytic activities of O_2 evolution are discussed here. The photocatalytic activity for the oxidation of water in the presence of a sacrificial acceptor can be summarized by the order $\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5 < \text{Nd}_2\text{Ti}_2\text{S}_2\text{O}_5 \ll \text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5 > \text{Gd}_2\text{Ti}_2\text{S}_2\text{O}_5 > \text{Tb}_2\text{Ti}_2\text{S}_2\text{O}_5 > \text{Dy}_2\text{Ti}_2\text{S}_2\text{O}_5 > \text{Ho}_2\text{Ti}_2\text{S}_2\text{O}_5 \gg \text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$. The highest activity for O_2 evolution was obtained for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$.

The structural refinements implied that the frameworks of $[\text{Pr,Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ are distorted from the ideal perovskite structure. The colors of these materials were black ($\text{Pr}_2\text{Ti}_2\text{S}_2\text{O}_5$) and dark brown ($[\text{Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$), whereas the other $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ forms were orange. Furthermore, EDX analysis revealed the S content in the Pr, Nd, and Er forms to be slightly lower than that in the other $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ forms. Apparently, $[\text{Pr,Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ contains larger amounts of sulfur defects than other oxysulfides, resulting in the distortion. Many sulfur defects in $[\text{Pr,Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ probably arise from difference in ionic radius: the ionic radii¹¹ of Pr^{3+} and Nd^{3+} (Pr^{3+} , 1.179 nm; Nd^{3+} , 1.163 nm) are larger than that of Sm^{3+} – Ho^{3+} (1.132–1.072 nm), whereas Er^{3+} (1.062 nm) has a smaller radius than Sm^{3+} . Because distorted structures in metal oxide photocatalyst often stimulate efficient charge separation,^{16–19} the low photocatalytic activities of $[\text{Pr,Nd,Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ can be attributed to the sulfur defects, rather than distortion.

Figure 7-11 shows the schematic band structure of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$. DFT calculations indicated that the top of the valence band of $[\text{Gd~Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ is made up of hybridized $\text{O}2p$, $\text{S}3p$, and $\text{Ln}4f$ orbitals, whereas $\text{Ln}4f$ orbitals are localized in other $[\text{Pr~Sm}]_2\text{Ti}_2\text{S}_2\text{O}_5$. In addition, the conduction band of $[\text{Gd~Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ consists of $\text{S}3p+\text{Er}4f$ and $\text{Ti}3d$ orbitals. The band gap energies of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ decrease with increasing atomic number of the lanthanide ions from Sm^{3+} to Er^{3+} due to the occurrence of these hybridized orbitals. The difference between the oxidation potential of water and the valence band level of

$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ is small at $\text{pH} = 8$.⁴ The valence band of $[\text{Gd}\sim\text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ appears to shift to higher potential energies because of the smaller band gap energy of the $\text{Gd}\sim\text{Er}$ forms, and the difference between the oxidation potential of water and the valence band decreases with decreasing band gap energy. It is, therefore, considered that the decrease in photocatalytic activities of $[\text{Gd}\sim\text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ for the oxidation of H_2O to O_2 is attributed to the thermodynamically less favorable valence band position for water oxidation. On the other hand, the conduction band position seems not to affect the rate of H_2 evolution. According to DFT calculation, the conduction band positions of $\text{Ho}_2\text{Ti}_2\text{S}_2\text{O}_5$ and $\text{Er}_2\text{Ti}_2\text{S}_2\text{O}_5$ are expected to be more positive than that of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, but there is no significant difference in H_2 evolution among these oxysulfides. This means that H_2 evolution cannot be simply attributed to conduction band position in oxysulfides. Such a phenomenon is also observed in oxynitride photocatalysts.^{20–22}

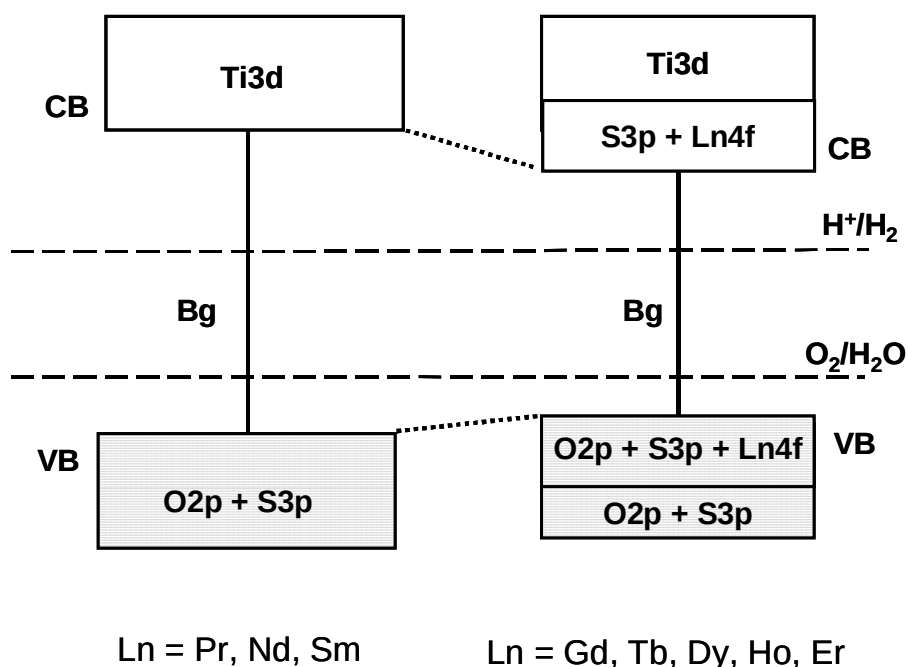


Figure 7-11. Schematic band structure of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$.

7-4. Conclusion

The results of this study imply that the photocatalytic activity of lanthanides is governed by electronic band structure. The series of isotopic compounds with the $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ composition were confirmed to be stable visible light-driven photocatalysts for the oxidation of water to O_2 or reduction of H^+ to H_2 . The photocatalytic activity of $[\text{Pr},\text{Nd},\text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$, containing sulfur defects and Ti as Ti^{3+} , was lower than that of the other $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ forms. The band gap energies of $[\text{Gd}\sim\text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ decreased with increasing atomic number of the lanthanide ions from Gd^{3+} to Er^{3+} due to the occurrence of the hybridized orbitals. The difference between the oxidation potential of water and the valence band level appears to decrease with decreasing band gap energy. It is considered that the photocatalytic activities of $[\text{Gd}\sim\text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ for the oxidation of H_2O to O_2 are lower because of thermodynamically less favorable valence band position for water oxidation. The highest activity for O_2 evolution ($\Phi = 0.7\%$) was obtained for $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ prepared by the HGS method.

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Chapter 8

Conclusion

In the present study, heterogeneous photoelectrochemical and photocatalytic system consisting of various novel materials were studied to develop new visible light-driven photoelectrode and photocatalyst materials, and to obtain a guiding principle for the design of active photocatalysts.

In Chapter 1, trends and principles of photocatalytic and photoelectrochemical reactions were described. The progress of visible light-driven photocatalysts up to the present was also introduced.

In Chapter 2, the electrochemical and photoelectrochemical properties of a thin film composed of an ion-exchangeable layered oxide $H_xTi_{(2-x/4)}□_{x/4}O_4$ (HTiO) was investigated to expand the utility of this thin film. The thin film prepared on an ITO substrate functions as an electrode for the redox reaction of $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$ without noticeable degradation. The fact that no reaction took place in aqueous $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ solution proved that reaction on this electrode occurs in the interlayers between titanate sheets. These results suggest that HTiO functions as an electrode material in which interlayer spaces function as active sites rather than on the surface. Moreover, a $Ru(bpy)_3^{2+}$ -intercalated form of the electrode generates photocurrent under visible-light irradiation. It was, therefore, revealed that HTiO is a potentially useful electrode material for wet-type solar cells.

In Chapter 3, a thin film composed of a nitride, Ta_3N_5 , was studied as an photoelectrode material. Anodic photocurrent based on oxidation of water appeared on Ta_3N_5/Ta electrode under visible-light irradiation. However, current density gradually decayed owing to anodic oxidation of Ta_3N_5 surface. Sustained photo-induced redox cycling was performed in aqueous $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ solution. The XPS analysis revealed that the surface of Ta_3N_5 thin film remained unchanged after long duration of photoelectrolysis. Thus, Ta_3N_5 was demonstrated to be a new potential electrode material in photochemical cells.

In Chapter 4, the conduction and valence band edges for electronic band gaps and Fermi levels were investigated for Ta_2O_5 , $TaON$, and Ta_3N_5 by ultraviolet photoelectron

spectroscopy (UPS) and electrochemical analyses to evaluate the adequacy of these materials as visible light-responsive photocatalysts for water oxidation and reduction. The tops of the valence bands were found to shift toward higher potential energies in the order $\text{Ta}_2\text{O}_5 < \text{TaON} < \text{Ta}_3\text{N}_5$, whereas the bottoms of the conduction bands are very similar in the range -0.3 to -0.5 V (vs NHE at pH = 0). From the results, it is concluded that TaON and Ta_3N_5 are promising catalysts for the reduction and oxidation of water using visible light in the ranges $\lambda \leq 520$ nm and $\lambda \leq 600$ nm, respectively. Moreover, the results of UPS analysis are in good agreement with the electrochemical analysis, demonstrating that the proposed UPS technique is a reliable alternative means of determining the band positions of a wide range of photocatalytic materials.

In Chapter 5, A Ti-based oxysulfide, $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$, was examined as a new visible light-driven photocatalyst. Under visible light ($440 \text{ nm} \leq \lambda \leq 650 \text{ nm}$) irradiation, $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ with a band gap of *ca.* 2 eV evolved H_2 or O_2 from aqueous solutions containing a sacrificial electron donor (Na_2S – Na_2SO_3 or methanol) or acceptor (Ag^+) without any noticeable degradation. The electronic band structure of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ was calculated using the plane wave based density functional theory (DFT) program. It was elucidated that the S3p orbitals constitute the upper part of the valence band and these orbitals make an essential contribution to the small band gap energy. The conduction and valence bands' positions of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ were also determined by electrochemical measurements. As a result, conduction and valence bands were found to have satisfactory potentials for the reduction of H^+ to H_2 and oxidation of H_2O to O_2 . As such, this oxysulfide performs as a stable photocatalyst for H_2 or O_2 evolution from aqueous solution containing a sacrificial electron donor or acceptor under visible light ($\lambda \leq 650$ nm).

In Chapter 6, a new method for the synthesis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ using H_2S was studied to enhance the photocatalytic activities. Amorphous $\text{Sm}_2\text{Ti}_2\text{O}_7$ was found to be an appropriate precursor for the synthesis of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ at the temperature above 1073 K. The relationship between the preparation conditions and the photocatalytic activities for H^+

reduction to H_2 and H_2O oxidation to O_2 was investigated. The highest activities for both H_2 and O_2 evolution were obtained at a sulfurization temperature of 1123 K. Subsequent heating of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ in air enhanced the activities further. Sulfurization by H_2S allowed the formation of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ structure at lower temperatures with a significantly shorter heating period (1 h) than that of conventional solid-state reaction. The synthesis method of sulfurization under H_2S flow is expected to be applicable to the preparation of various oxysulfide catalysts with high activities.

In Chapter 7, $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ ($\text{Ln} = \text{Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er}$) were synthesized by sulfurization of amorphous corresponding oxides under H_2S flow, and the photocatalytic activities of the series of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ were examined. The series $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ was demonstrated to evolve H_2 or O_2 from aqueous solutions under visible-light ($440 \text{ nm} \leq \lambda \leq 650 \text{ nm}$) irradiation in the presence of a sacrificial electron donor (Na_2S – Na_2SO_3) or acceptor (Ag^+) without noticeable degradation. $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ form was found to have the highest activity for O_2 evolution. The photocatalytic activities of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ (Pr, Nd, Er) were lower than those of the other $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ forms because of the existence of many sulfur defects. The band gap energies of $[\text{Gd} \sim \text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ decreased with increasing atomic number of the lanthanide ions from Gd^{3+} to Er^{3+} due to the occurrence of the hybridized orbitals. The energy gap between the $\text{H}_2\text{O}/\text{O}_2$ level and top of valence band levels appears to decrease with decreasing band gap energy. It is considered that the photocatalytic activities of $[\text{Gd} \sim \text{Er}]_2\text{Ti}_2\text{S}_2\text{O}_5$ for the oxidation of H_2O to O_2 are lower because of thermodynamically less favorable valence band position for water oxidation. These results imply that the photocatalytic activity of $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ is governed by electronic band structure.

List of publications

1. For Chapter 2; “Layered Titanate Thin Film as an Electrode Material”

A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, Y. Matsumoto and K. Domen, *J. Mater. Res.*, **19**, 661 (2004).

2. For Chapter 3; “Conduction and Valence Band Positions of Ta₂O₅, TaON, and Ta₃N₅ by UPS and Electrochemical Methods”

W.-J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, M. Hara, M. Kawai, Y. Matsumoto and K. Domen, *J. Phys. Chem. B*, **107**, 1798 (2003).

3. For Chapter 4; “Electrochemical Behavior of Thin Ta₃N₅ Semiconductor Film”

A. Ishikawa, T. Takata, J. N. Kondo, M. Hara and K. Domen., *in preparation*.

4. For Chapter 5; “Oxysulfide Sm₂Ti₂S₂O₅ as a Stable Photocatalyst for Water Oxidation and Reduction under Visible Light Irradiation ($\lambda < 650$ nm)”

A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, **124**, 13547 (2002).

5. For Chapter 6; “Novel Synthesis and Photocatalytic Activity of Oxysulfide Sm₂Ti₂S₂O₅”

A. Ishikawa, Y. Yamada, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *Chem. Mater.*, **15**, 4442 (2003).

6. For Chapter 7; “Oxysulfides Ln₂Ti₂S₂O₅ as Stable Photocatalysts for Water Oxidation and Reduction under Visible-Light Irradiation”

A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *J. Phys. Chem. B*, **108**, 2637 (2004).

Others

1. "Sensitization of TiO₂ Particles by Dyes to Achieve H₂ Evolution by Visible Light"
K. Hirano, E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi and M. Kaneko, *J. Photochem. Photobiol. A*, **136**, 157 (2000).
2. "Femtosecond Transient Absorption Spectroscopy on Photocatalysts: K₄Nb₆O₁₇ and Ru(bpy)₃²⁺-Intercalated K₄Nb₆O₁₇ Thin Films"
A. Furube, T. Shiozawa, A. Ishikawa, A. Wada, K. Domen and C. Hirose, *J. Phys. Chem. B*, **106**, 3065 (2002).
3. "Primary Process of Photogenerated Carriers in Ion-Exchanged K₄Nb₆O₁₇ Thin Films Investigated by Femtosecond Transient Absorption Spectroscopy"
A. Furube, T. Shiozawa, A. Ishikawa, A. Wada, C. Hirose and K. Domen, *Chem. Phys.*, **285**, 31 (2002).
4. "Ta₃N₅ as a Novel Visible Light-Driven Photocatalyst ($\lambda < 600$ nm)"
G. Hitoki, A. Ishikawa, T. Takata, J. N. Kondo, M. Hara and K. Domen, *Chem. Lett.*, 736 (2002).
5. "Ta₃N₅ and TaON Thin Films on Ta Foil Surface Composition and Stability"
M. Hara, E. Chiba, A. Ishikawa, T. Takata, J. N. Kondo and K. Domen, *J. Phys. Chem. B*, **107**, 13441 (2003).