論文の内容の要旨

Photocatalytic and Photoelectrochemical Water Splitting on Particulate $SrTiO_3$

（チタン酸ストロンチウム微粒子上での光触媒的及び光電気化学的水分解反応）

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1. Introduction

Photocatalytic water splitting under solar irradiation potentially leads to a construction of clean and sustainable energy cycle. There are mainly two different types of systems for utilizing photocatalysts. One is as photocatalyst powder suspended in aqueous solution, and other is as a photoelectrode dipped in aqueous electrolyte solution. The particulate photocatalyst system has its strength in its simplicity. However, it is difficult to obtain high quantum efficiency with this system probably because it is difficult to control the movement of excited carrier inside particles. On the other hand, it is possible to control the movement of excited carriers in photoelectrode systems to some extent, because an elecric field could be applied across this system. The downside of photoelectrode systems comes from its complexity. The preparation methods are limited compared to powder synthesis, and the cost of photoelectrodes are usually much higher than that of photocatalyst powders. In this thesis, the $SrTiO_3$ photocatalyst was employed to test the limitations of each systems.

2. Experimental

As-purchased $SrTiO_3$ (99.9%), was employed as a raw material without any post-treatment (hereafter STO(pristine)). For the synthesis of flux-treated $SrTiO_3$, $SrTiO_3$ (99.9%), Al_2O_3, and $SrCl_2$ (98.0%, anhydrous) were used as raw materials. $SrTiO_3$ and $SrCl_2$ were thoroughly mixed in an agate mortar. The mixture was heated either in an yttria or an alumina crucible at 1100 °C for 10 h. The $SrTiO_3$ samples treated in yttria and alumina crucibles will hereafter be referred to as STO(flux-Y) and STO(flux-Al), respectively, where -Y and -Al are used to highlight the material of the crucible used for the flux treatment. For the synthesis of STO(flux-Y) with Al dopant, Al_2O_3 was mixed together with $SrTiO_3$ and $SrCl_2$ and the same procedure was followed subsequently, and these samples will hereafter be referred to as *x*%Al-STO(flux-Y). For the synthesis of Al-doped $SrTiO_3$, $SrTiO_3$ (99.9%) and Al_2O_3 were thoroughly mixed in an agate mortar and heated in an yttria crucible at 1100 °C for 10 h. These samples will hereafter be referred to as *x*%Al-STO(ssr-Y). As a cocatalyst $Rh_{2-y}Cr_yO_3$ was loaded by an impregnation method. Detailed procedures are explained in other report.[3]

The activities of the photocatalyst samples were tested in a closed gas circulation system with a top-irradiation-type reactor. The evolved gases were analyzed by a gas chromatograph (Shimadzu, GC-8A) equipped with a thermal conductivity detector, using Ar as a carrier gas.

To prepare electrode of 1%Al-STO(flux-Y) powder, the particle transfer method was used.[2] The contact layer was deposited either by vacuum evaporation method or radio-frequency magnetron sputtering method. Ti was used as a conductor layer and formed using radio-frequency magnetron sputtering on top of the contact layer.

Electrodes prepared from 1%Al-STO(flux-Y) by particle transfer method will hereafter be referred to as Al-STO(flux)/M, where M represents the type of metal used as a contact layer. Single crystalline wafer of 0.01 wt% Nb doped $SrTiO_3$ was purchased and used without any post-treatment. The contact layer was deposited on unpolished side of the crystal by vacuum evaporation method or radio-frequency magnetron sputtering method. The electrodes prepared this way will hereafter be referred to as STO:Nb(SC)/M where M represents the type of metal used as a contact layer.

PEC properties were measured by a typical 3-electrode setup. The prepared electrode, an Ag/AgCl electrode in 3 M NaCl aqueous solution, and a Pt wire were connected to a potentiostat as working, reference, and counter electrodes, respectively. A 300 W xenon lamp (λ >300 nm) was used as a light source. All PEC measurements were performed under an Ar atmosphere.

3. Results and Discussion

3.1. Photocatalytic Overall Water Splitting on Flux-treated $SrTiO_3$ Particles

$SrTiO_3$ particles were treated with $SrCl_2$ flux and its physical and photocatalytic properties were investigated. As-purchased $SrTiO_3$ (STO(pristine)) was treated with $SrCl_2$ flux ($SrCl_2/SrTiO_3$ = 10 in molar ratio) at 1100 °C for 10 h in alumina crucible (STO(flux-Al), and its water splitting activity dramatically enhanced. To investigate the effect of flux treatment conditions on the photocatalytic activity of $SrTiO_3$, treatment temperatures, soak times, cooling rates, and the ratios of $SrCl_2$ flux to the $SrTiO_3$ precursor were varied. As is discussed in Chapter 2 of the thesis, the treatment temperatures and the ratio of $SrCl_2$ flux to $SrTiO_3$ precursors had significant effect on the physical properties and the photocatalytic overall water splitting activities of the $SrTiO_3$ samples while the soak times and cooling rates did not. The water splitting activity of STO(flux-Al) increased with increasing the treatment temperature. When the amount of flux was examined from $SrCl_2/SrTiO_3$ = 0.0 to 10 in molar ratio, their crystallinity and their photocatalytic activity showed no linear relationship with each other (Table 1). Therefore, the enhancement in photocatalytic activity of flux treated $SrTiO_3$ is not solely due to the improvement in crystallinity.

Table 1: Water splitting activity of STO(flux-Al) treated with different amount of $SrCl_2$.

Molar ratio of $SrCl_2/SrTiO_3$	FWHM of (110) peak in XRD pattern / °	Evolution rate / μmol h^{-1}	
		H_2	O_2
pristine	0.107	< 1	< 1
0.01	0.083	1	1
0.1	0.058	6	6
1.0	0.061	40	21
5.0	0.064	470	240
10	0.066	450	240

Reaction conditions: Photocatalyst, 0.1 g; Cocatalyst, $Rh_{2-y}Cr_yO_3$ (Rh 0.3 wt%, Cr 0.3 wt%); Reaction solution, 100 mL H_2O; Light source, 300 W Xe lamp (λ >300 nm).

3.2. Effect of Impurity Doping on $SrTiO_3$ Particles during Flux Treatment

It was postulated that impurity existing in $SrCl_2$ flux was doped into $SrTiO_3$ during the treatment and this impurity doping affected the water splitting activity of $SrTiO_3$. Inductively-coupled optical emission spectroscopy (ICP-OES) analysis revealed that a very small amount of Al (< 1%) was indeed incorporated into STO(STO-Al). To examine the effect of impurity doping, yttria crucibles were used instead of alumina crucibles and the same flux treatment was applied to STO(pristine) to obtain STO(flux-Y). Although this sample showed improved

crystallinity, its water splitting activity was much lower than the series of the STO(flux-Al) samples. Also, in an attempt to control Al doping in the presence of the $SrCl_2$ flux, $SrTiO_3$ and Al_2O_3 were mixed at molar ratios of Al/Ti = 1% and heated together with the $SrCl_2$ flux in yttria crucibles. A high activity for the overall water splitting reaction, comparable to that for STO(flux-Al), was obtained using yttria crucibles when 1% of Al was added. These results supports that Al doping is the controlling factor for the enhancement of photocatalytic activity of $SrTiO_3$. It should be noted that Al doping of $SrTiO_3$ was more effective when $SrCl_2$ was present during the heating. The doping amount of Al in the STO(flux-Al) sample from an alumina crucible may vary depending on the treatment conditions. Nevertheless, this sample showed a higher photocatalytic activity than the samples which Al was doped by solid state reaction (Al-STO(ssr-Y)) containing various and controlled amounts of Al. The difference in photocatalytic overall water splitting activities of $SrTiO_3$ is summarized in Figure 1, along with the use of flux and the existence of Al for dopant for each samples. It is thought that Al was not effectively doped into $SrTiO_3$ during the solid state reaction because Al had to diffuse from the outer surface of the particles. In contrast, a significant portion of the $SrTiO_3$ particles was once dissolved and recrystallized in the presence of $SrCl_2$ flux, together with alumina derived from the crucibles. During this process, some of the Al ions may be doped into the middle part of the $SrTiO_3$ particles and occupy the most stable state thermodynamically. As a result, Al doping can show stronger enhancement of photocatalytic activity when the $SrCl_2$ flux is used.

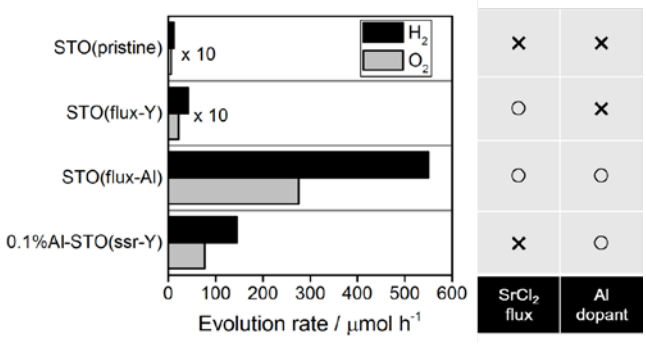

Figure 1. Water splitting activity of $SrTiO_3$ photocatalysts. Reaction conditions: Catalyst, 0.1 g; Cocatalyst, $Rh_{2-y}Cr_yO_3$ (Rh 0.1 wt%, Cr 0.1 wt%); Reaction solution, 100 mL H_2O; Light source, 300 W Xe lamp (λ >300 nm).

3.3. Photoelectrochemical Water Splitting on Particulate $SrTiO_3$ Electrodes

The $SrTiO_3$ powders prepared by different methods as in Chpater 2 were fabricated into electrodes by particle transfer method, and their properties as photoanodes were examined. The performance of these phoanode depended on the morphology of $SrTiO_3$ particles while they were not much affected by the properties of $SrTiO_3$ particles, unlike their photocatalytic activity for overall water splitting. The electrodes prepared from 1%Al-STO(flux-Y) showed the best performance among the prepared electrodes, probably due to its relatively uniform particle size. It should be noted that the uniform size distribution is beneficial to obtain metal foil – photocatalyst assembly with less cracks and pinholes.

To examine the effect of the contact layer, the electrodes of 1%Al-STO(flux-Y) powder were prepared by particle transfer method using Ta, Ti, Au, and Ni as contact layers (Figure 2). The electrodes prepared with Ta and Ti as contact layer showed similar behavior. Both had negative onset potential at around - 0.15 V_{RHE} and high current density of 6.7 and 5.0 mA cm^{-2} for Ta and Ti at 1.23 V_{RHE}, respectively. The current density of the electrodes prepared with Au and Ni as contact layer showed much lower current density and their onset potential was much more positive. This result could be well explained with the work function of the metal used as contact layer. The work function of $SrTiO_3$ is about 4.2 eV. [4] When it made contact with metals having work function larger than that of $SrTiO_3$ such as Au and Ni, obvious Schottky barrier was formed and it prevented the transfer of

photo-excited electrons in $SrTiO_3$ to the metal layer. For metals such as Ta and Ti, the difference between their work function and that of $SrTiO_3$ was not significant. Therefore, the Schottky barrier formed at the interfaces did not hinder electrons moving from $SrTiO_3$ to metal contact layer. To conclude, the metal used as contact layer should be chosen considering the work function of the semiconductor in addition to the stability of the metal in the electrolyte.

The electrode prepared by the particle transfer method was compared with the electrode prepared with single crystalline wafer of Nb doped $SrTiO_3$. STO:Nb(SC)/Ta worked as a photoanode and showed low onset potential of - 0.25 V_{RHE} and relatively high photocurrent of about 5.3 mA cm^{-2} at 1.23 V_{RHE}. The onset potential of Al-STO(flux)/Ta was slightly more positive than that of STO:Nb(SC)/Ta, and the current density of Al-STO(flux)/Ta at 1.23 V_{RHE} was higher than STO:Nb(SC)/Ta. This result demonstrates that particle transfer method is one of the promising methods to obtain highly efficient photoelectrodes from semiconductor particles.

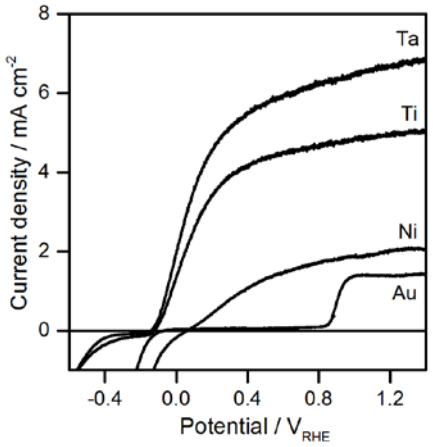

Figure 2. *I-E* curves of Al-STO(flux)/M electrodes with different metal as contact layer. Measurement conditions: 3-electrode system with Ag/AgCl reference and Pt counter; Reaction solution, 0.1 M Na_2SO_4 aqueous solution + NaOH (pH = 13); Light source, 300 W Xe lamp (λ >300 nm).

4. Conclusion

In my thesis, particulate $SrTiO_3$ was investigated as photocatalyst powder and photoelectrode. The photocatalytic activity of $SrTiO_3$ in the overall water splitting reaction was dramatically improved by $SrCl_2$ flux treatment at 1100 °C in an alumina crucible, reaching apparent quantum efficiency of 30% at 360 nm. It was confirmed that $SrTiO_3$ doped with Al under a $SrCl_2$ flux showed even higher water splitting activity than $SrTiO_3$ doped with Al by a solid state reaction. $SrTiO_3$ photoelectrodes prepared by particle transfer method and their photoelectrochemical properties were examined. The $SrTiO_3$ electrode prepared by using flux treated and Al-doped $SrTiO_3$ and Ta as contact layer showed current density of 6.7 mA cm^{-2} at 1.23 V_{RHE}. This electrode comparable performance with $SrTiO_3$ photoelectrode fabricated from single crystalline wafer of Nb doped $SrTiO_3$. This result demonstrates the possibility of efficient photoelectrodes prepared from photocatalyst particles which is advantageous in large scale application.

References

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