論文の内容の要旨

論文題目　Development of $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ Photocatalysts for Hydrogen Production under Visible Light

(可視光を用いた水素生成のための$La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$光触媒の開発)

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Photocatalytic solar water splitting to generate H_2 and O_2 has attracted much attention recently because this reaction does not depend onto fossil fuels such as coal, natural gas, and etc. Several metal oxides are well known as photocatalysts for water splitting with exceptionally high quantum efficiencies, although only being capable of absorbing UV radiation in most cases because of their wide band gap energy(>3eV). It is indispensable to extend the absorption edge of photocatalysts to the visible region in order to use solar light more efficiently. Several (oxy)sulfide (*e.g.*, $La_5In_3S_9O_3$, La_3GaS_5O, and etc.) materials function as photocatalysts for H_2 evolution under visible light irradiation. For these (oxy)sulfide materials, N2p and S3p orbital mainly form the top of the valence band at a more negative potential than O2p orbital while the conduction band minimum remains unaltered largely. Therefore, band gap becomes narrower than the corresponding oxide materials. This phenomenon describes the significance of using (oxy)sulfide materials for solar hydrogen production over metal oxides. Kudo's group recently developed several metal sulfide solid solution photocatalysts namely $ZnS-CuInS_2-AgInS_2$.

$La_5Ti_2CuS_5O_7$ (LTCSO), an oxysulfide semiconductor, absorbs visible light of up to 650 nm and can generate hydrogen or oxygen from aqueous solutions containing sacrificial electron donors or acceptors, respectively.[3] Moreover, substitution of Se^{2-} for S^{2-} generally reduces the bandgap of chalcogenide semiconductors. In this study, $La_5Ti_2Cu(S_{1-x}Se_x)_5O_7$ ($LTCS_{1-x}Se_xO$) solid solutions were prepared in an attempt to extend the absorption edge toward longer wavelengths by substituting selenide ions (Se^{2-}) for sulfide ions (S^{2-}) and their physical and photocatalytic properties for hydrogen evolution were investigated.

In chapter 2, substitution of selenide for sulfide ions in $La_5Ti_2CuS_5O_7$ (LTCSO) were studied, aiming to develop visible light driven photocatalysts with longer absorption edge wavelengths. $LTCS_{1-x}Se_xO$ solid solutions were synthesized over the whole composition range of $0 \leq x \leq 1$ by a solid state reaction. Structural refinements revealed that the lattice constants and cell volumes of the $LTCS_{1-x}Se_xO$ series followed Vegards' law. With increases in the Se^{2-} content, absorption edge of $LTCS_{1-x}Se_xO$ solid solutions shifted monotonically toward longer wavelengths, to a maximum of 820 nm for LTCSeO (x= 1). Those materials for which $x \leq 0.8$ generated H_2 from aqueous solutions containing Na_2S and Na_2SO_3 as electron donors under visible light irradiation ($\lambda > 420$ nm) after surface modification with in situ precipitated NiS. Comparatively higher H_2 evolution was observed for $LTCS_{1-x}Se_xO$ with lower Se^{2-} levels, though the sample for which $x = 0.2$ generated H_2 under visible light irradiation at wavelengths longer than 640 nm, whereas the LTCSO did not. This study offers that newly developed oxysulfoselenide materials are sufficiently active toward photocatalytic water splitting reaction to produce H_2 under visible light irradiation while the active wavelength region has been also extended to longer wavelength by partial substitution of selenide for sulfide.

In chapter 3, $LTCS_{1-x}Se_xO$ ($0 \leq x \leq 0.6$) solid solution photocatalysts were synthesized by solid state reactions at varying temperatures to control their morphologies, and the photocatalytic H_2 evolution activity of the resultant samples were discussed in terms of the particle size. The $LTCS_{1-x}Se_xO$ phases with the similar absorption edges were obtained by calcination over two days at 1223-1323 K for LTCSO ($x = 0$), at 1173-1273 K for $LTCS_{0.8}Se_{0.2}O$ ($x = 0.2$), at 1123-1273 K for $LTCS_{0.6}Se_{0.4}O$ ($x = 0.4$), and at 1123-1273 K for $LTCS_{0.4}Se_{0.6}O$ ($x = 0.6$). The particle size of $LTCS_{1-x}Se_xO$ became greater with the increase in the Se content when they were prepared at the same temperatures. However, the particle size became significantly smaller by lowering the calcination temperature. The calcination temperature realizing the highest photocatalytic H_2 evolution rates for NiS-loaded $LTCS_{1-x}Se_xO$ became lower with increasing the Se content. Specifically, $LTCS_{0.8}Se_{0.2}O$,

$LTCS_{0.6}Se_{0.4}O$, and $LTCS_{0.4}Se_{0.6}O$ calcined at 1223, 1173, and 1123 K showed approximately 3, 5, and 3 times higher H_2 evolution rates than that synthesized the conventional temperature of 1273 K, along with the increment in the apparent quantum yields. The photocatalytic activity can be further improved by coloading the Pt and NiS cocatalysts. This finding offers an opportunity to harvest long wavelength light more effectively by controlling particle size for the synthesis of narrow bandgap photocatalysts such as oxysulfoselenide materials.

In chapter 4, $LTCS_{1-x}Se_xO$ ($0 \leq x \leq 0.6$) solid solution photocatalysts coloaded with Pt and NiS cocatalysts were found to exhibit higher activity than those loaded with Pt or NiS alone during the H_2 evolution reaction from aqueous solutions containing Na_2S and Na_2SO_3. The apparent quantum efficiency of LTCSO ($x = 0$) loaded with Pt and NiS. was 1.8 % at 420 ± 10 nm, a value that is three times higher than that for LTCSO loaded with NiS alone. The roles of thecocatalysts in the H_2 evolution reaction were studied by assessing photocathodes and photoanodes composed of LTCSOloaded with Pt and/or NiS. It is suggested that Pt effectively facilitates the water reduction reaction while NiS enhances both H_2 evolution and the oxidation of the sacrificial reagents. The ability of the coloaded cocatalysts to promote both the reduction and oxidation processes is considered to be of particular importance for the activation of narrow-bandgap photocatalysts with relatively low reactivities.

In chapter 5, post-annealing of LTCSO with Se powder was performed under different conditions and the final products were characterized in detail. It was found thermal diffusion of Se into LTCSO by post-annealing extended the absorption edge wavelength similarly to $LTCS_{1-x}Se_xO$ solid solutions but showed better photocatalytic activity. The absorption edge of $Sm_2Ti_2S_2O_5$ was also found to extend in a similar fashion by annealing with Se. Compositions of all the materials were measured by SEM-EDX analysis which revealed that extent of Se incorporation can be well controlled by tuning annealing temperature and the number of treatment has been performed. Aforementioned outcomes indicates that successful development of oxysulfoselenide materials solve shortage of absorption edge wavelength of LTCSO by incorporation of selenide ions and AQY values was improved significantly by coloading of cocatalysts with different functionality. Synthesis of oxysulfosleenides by post-annealing treatment causes minimal decrement photocatalytic activity while synthesized from parent oxysulfide materials. Therefore, I conclude that $LTCS_{1-x}Se_xO$ oxysulfoselenide materials was activated almost similar to LTCSO oxysulfide by post-annealing treatment for sacrificial H_2 evolution reaction, even though they have much narrower bandgap energy than oxysulfides.

In Chapter 6, overall water splitting is considered as a dream reaction in Chemistry to produce clean and renewable hydrogen. Domen *et al.* suggests that a solar-to-hydrogen (STH) energy conversion efficiency of 10% is needed for a photocatalytic system for practical use. In order to achieve such high STH, it is urgent to develop new photocatalysts which absorb visible light much longer than 600 nm with reasonable quantum efficiency as reserve fossil fuels will no longer last beyond few several decades. There are many reported photocatalysts absorbing visible light upto 600 nm. However, it has been observed that the AQY value decreases significantly that with increasing the absorption edge wavelength as the driving force for surface chemical reaction decreases. Moreover, photocatalysts operating upto 600 nm is not enough to achieve the desired STH. Newly developed oxysulfoselenides are considered potential candidates utilize longer wavelength photons. Development and activation of narrow bandgap photocatalysts are extremely challenging for efficient overall water splitting. The Author thinks that Se diffusion into various parent oxysulfides photocatalysts (for e.g. $La_2Ta_2TiS_2O_8$, and $La_2Nb_2TiS_2O_8$) can be applied for the development of several other oxysulfoselenide materials having much narrower bandgap energy with minimum decrement in H_2 evolution activity and should be combined with a suitable oxygen evolution photocatalyst (OEP) likely $BaTaO_2N$ has an absorption edge 650 nm for Z-scheme overall water splitting which will give potentially higher STH.