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学 位 論 文 要 旨
(Summary of the Doctoral Dissertation)

学位論文題目 (Dissertation Title)	Development of Highly Functional $SrTiO_3$ Photocatalyst for Overall H_2O Splitting (H_2O 分解反応のための高機能性 $SrTiO_3$ 光触媒の開発)
氏　名(Name)	姜 君哲 (JIANG JUNZHE)

The energy crisis and environmental pollution are primary problems with the development of human society and civilization. Photocatalytic technology as a low-cost, efficient, and environment-friendly path is considered to be one of the best solutions to the severe energy crisis and environmental pollution problems. So far, various photocatalytic materials with activity in the water-splitting reaction have been developed. Strontium Titanate ($SrTiO_3$) as one of the typical photocatalysts has been investigated for more than thirty years. However, the efficiency of this photocatalyst for the H_2O splitting reaction is low, and a significant improvement in the efficiency is required.

In this thesis, to significantly improve the efficiency of the $SrTiO_3$ photocatalyst for overall H_2O splitting, the bulk, surface, and morphology of the $SrTiO_3$ photocatalyst were controlled, and their effects on the activity and photoconversion efficiency (AQY) of the photocatalyst were investigated. From the obtained research results, the factors for improving the efficiency of the photocatalyst for the H_2O decomposition reaction were discussed.

The major aspects of the investigations in the thesis are presented as follows:

Chapter 1: General introduction.

This chapter presents the general research background of this paper, the development and progress of photocatalysts, especially the historical background of photo energy conversion and research on H_2O decomposition reactions, and methods for improving photocatalytic efficiency.

The outline, the structure of this paper, and the purpose of the research are described.

Chapter 2: Investigation on the highly active $SrTiO_3$ photocatalyst toward overall H_2O splitting by doping Na ion

To prepare Na ion-doped $SrTiO_3$ (Na^+-$SrTiO_3$) with high photocatalytic activity for overall H_2O splitting, the polymerizable complex (PC), and solid-state reaction (SSR) methods were applied to elucidate the factors on the improvement of the activity by doping Na ions and mechanisms. Here, $Rh_{0.7}Cr_{1.3}O_3$ was used as the co-catalyst. The photocatalytic activity of the photocatalyst prepared using the high-purity raw material was significantly improved, and it was noticed that the purity of the photocatalyst is a factor for improving the photocatalytic activity of Na^+-$SrTiO_3$. Co-loading $Rh_{0.7}Cr_{1.3}O_3$ for H_2 evolution reaction (HER) co-catalyst and CoOOH for O_2 evolution reaction (OER) co-catalyst further improved the photocatalytic activity and significantly extended lifetime. From the structural analysis of the photocatalyst and the measurement of the transient absorption spectrum, the improvement of the photocatalytic activity by Na ion doping was attributed to the oxygen vacancies in the $SrTiO_3$ crystal, which formed trapped sites of electrons generated by light irradiation, and separated electrons and holes.

Chapter 3: Controllable modification of metal ion-doped $SrTiO_3$ photocatalysts for photocatalytic overall H_2O splitting to almost the ultimate quantum yield

For Al ion-doped $SrTiO_3$ (Al-$SrTiO_3$ (flux)), using the flux method can prepare fine particles with a single crystal, the HER cocatalyst Rh-Cr_2O_3, and the OER cocatalyst CoOOH is loaded on the surface by the photocatalytic deposition method. As a result, we found that the apparent quantum yield (AQY, $\lambda = 360$ nm) for the H_2O splitting reaction was 96%. The crystal facet where electrons and holes generated by light irradiation appear is different due to the difference in surface energy of the photocatalyst particles whose specific crystal

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plane is exposed by the flux method with Al-doping. This is since the co-catalyst could be efficiently loaded on the surface. Furthermore, Mg-$SrTiO_3$ was prepared and examined using the PC method, SSR method, and flux method. When the photocatalytic activity was examined using $Rh_{0.7}Cr_{1.3}O_3$ as a co-catalyst, Mg-$SrTiO_3$ (flux) showed the highest photocatalytic activity compared to Mg-SrTiO3 prepared by other methods, and its AQY (λ = 365 nm) was 55%. Therefore, the effect of the co-catalyst was examined using Mg-$SrTiO_3$ (flux). As a result, by co-loading OER co-catalyst CoOOH, AQY (= 365 nm) reached 68% at 365 nm. The HER co-catalyst Rh-Cr_2O_3 and the OER co-catalyst CoOOH are coloaded on the surface by the photocatalytic method as that of Al-$SrTiO_3$ (flux). The AQY of 94% nearly the ultimate quantum yield was achieved at 350 nm and 360 nm.

Chapter 4: Fabrication of $SrTiO_3$ doped metal ions utilizing the $SrCl_2$ flux as a medium for photocatalytic water splitting under visible light

Finally, to prepare a visible light-responsive $SrTiO_3$ photocatalyst that can be applied to the H_2O splitting reaction, a metal ion-doped $SrTiO_3$ was synthesized using the flux method and its photocatalytic properties under visible light irradiation were examined. The prepared metal ion-doped $SrTiO_3$ showed a cubic morphology and light absorption in visible light. The photocatalytic performances were examined under visible light irradiation (λ > 420 nm) with HER using Pt as a cocatalyst and methanol as a sacrifice, and OER using IrO_2 as a cocatalyst and Ag^+ as sacrificing agents.

Chapter 5: Summary and outlook

In this chapter, the results presented in Chapter 2-4 were summarized, and the application and prospects of photocatalytic technology for overall H_2O splitting to produce H_2 under sunlight irradiation using a photocatalyst are discussed.

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学位論文審査の結果及び最終試験の結果報告書

山口大学大学院創成科学研究科

氏　　名	JIANG JUNZHE（姜　君哲）
審査委員	主　　査：　酒多喜久
	副　　査：　小松隆一
	副　　査：　中山雅晴
	副　　査：　藤森宏高
	副　　査：　吉田真明
論文題目	Development of Highly Functional $SrTiO_3$ Photocatalyst for Overall H_2O Splitting (H_2O 分解反応のための高機能性 $SrTiO_3$ 光触媒の開発)

【論文審査の結果及び最終試験の結果】

光触媒による水分解反応は、光エネルギーを利用して水から水素を生成させる持続社会の水素の製造法として注目されている。しかし、これまでに開発された光触媒の活性は低く、実用的に用いるには不十分であり、この反応に実用レベルの高い活性で作用できる光触媒の開発が期待されてきた。本研究は、水分解反応に実用レベルの高い活性を有する光触媒開発を目的として、390 nm の近紫外光域までこの反応に作用できる $SrTiO_3$ 光触媒に着目し、その活性向上に関する検討を行った。本論文の構成は、第一章、「序論」は、本研究の一般的な背景、持続社会の水素製造法としての光触媒による水分解反応の意義および半導体光触媒による水分解反応の原理とその光触媒活性向上への要件を示し、本研究の目的と論文の内容を述べた。第二章、「Na イオンのドープによる H_2O 分解反応に高い活性を示す $SrTiO_3$ 光触媒の検討」は、$SrTiO_3$ 光触媒の水分解反応に対する光触媒活性向上に有効である Na イオンドープ $SrTiO_3$ 光触媒について、その有効な調製法、調製要件を明らかにし、Na イオンのドーピングによる $SrTiO_3$ 光触媒の水分解反応に対する活性向上機構を解明した。第三章、「水分解反応に究極の量子収率を示す金属イオンドープ $SrTiO_3$ 光触媒の調製条件・修飾条件の検討」は、フラックス法により調製した Al イオンドープ $SrTiO_3$ 単結晶微粒子に光析出法により水素生成反応助触媒、Cr_2O_3-Rh と酸素生成反応助触媒、CoOOH を組み合わせた光触媒が水分解反応において、光触媒の光吸収が飽和する波長である 360 nm 以下の単色光の照射時、この反応の見かけの量子収率(AQY)が 95%を超え、光触媒が吸収した光のほぼ 100%を利用して水分解反応を進行させることを見出した。さらに、その光触媒機構について解明した。続いて、フラックス法で調製した Mg イオンドープ $SrTiO_3$ 単結晶微粒子に同様な方法で助触媒の Cr_2O_3-Rh と CoOOH を組み合わせた光触媒が Al ドープ $SrTiO_3$ の場合と同様に光触媒が吸収した光のほぼ 100%を利用して水分解反応を進行させることが出来ることを確認し、究極の効率で水分解できる光触媒が Al 以外のドーパント

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をドープした $SrTiO_3$ でも実現できることを見出した。第四章、「$SrCl_2$ をフラックスとして利用した可視光応答性金属イオンドープ $SrTiO_3$ 光触媒の調製」は、$SrTiO_3$ 光触媒の光応答性を改善させ可視光応答化できる Rh イオンを含む 2 種類以上のイオンをドープした $SrTiO_3$ 単結晶微粒子光触媒の調製にフラックス法を応用し、調製した可視光応答 $SrTiO_3$ の基本的な光触媒特性を検討した。第五章、「総括」は、本論文で得られた成果について総括し、研究の将来的な見通しを述べた。

公聴会は Zoom による遠隔方式で行い、学内外から 24 名が出席した。公聴会・審査会での主な質問は、1) $SrTiO_3$ にドープした金属イオンの状態とその時の $SrTiO_3$ 光触媒自体の状態について、2) 金属イオンをドープした $SrTiO_3$ の状態の光触媒活性向上への寄与について、3) フラックス法で調製した金属イオンドープ $SrTiO_3$ 上への各助触媒の析出機構について、4) 光触媒の寿命について、であり、学術・実用両側面からの多岐にわたる内容で活発な質疑応答がなされ、どの質問に対しても発表者から的確な回答がなされた。

以上より、本論文は独創性、有効性、実用性ともに優れ、博士（工学）の論文に十分値するものと判断した。

論文内容および審査会、公聴会での質問に対する応答などから、最終試験は合格とした。

なお、主要な関連論文の発表状況は下記のとおりである。(関連論文　計３編)

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3) J. Jiang, K. Kato, H. Fujimori, A. Yamakata, Y. Sakata, Investigation on the highly active $SrTiO_3$ photocatalyst toward overall H_2O splitting by doping Na ion, Journal of Catalysis, 390 pp. 81-89. 2020.