別紙様式５(Attached Form 5)

学位論文要旨 Abstract of Thesis

所属専攻 Field:　　工学　　　専攻(Field)
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Title of Thesis

Photocatalysts for Water Splitting Using Monolayer Oxide and Nitride Nanosheets
酸化物および窒化物単層ナノシートを用した水分解用光触媒

Abstract（within 1600 words）

Photocatalytic water splitting into hydrogen and oxygen using semiconducting photocatalysts has been intensively researched, with the goal of mitigating issues related to dwindling energy resources and climate change. However, the solar to hydrogen efficiencies are still insufficient for practical applications. The primary reasons for such low photocatalytic efficiencies are charge carrier recombination and backward reactions. Therefore, two major challenges of "recombination" and "backward reaction" in photocatalytic water splitting reaction will be addressed in the present study.

In the case of "electron-hole recombination", the oxynitride materials of tantalum nitride (Ta_3N_5) is a promising photocatalytic for visible light photocatalytic water splitting. However, the photocatalytic performance is quite weak due to the fast electron-hole recombination and low charge separation efficiency. One of the candidate structures to suppress the recombination is two-dimensional structure (nanosheet). Because these sheets are only 1-2 nm thick, the photogenerated electrons and holes can migrate to the surface much more rapidly compared to the bulk photocatalyst, thus suppressing recombination. Until now, development of a highly active photocatalyst based on Ta_3N_5 nanosheets has not been studied yet. In the present study, we report a successful example of preparation of Ta_3N_5 nanosheets from the $[TaO_3]^-$ nanosheet, and demonstrate that Ta_3N_5 nanosheets act as one potential candidate for photocatalytic H_2 evolution under visible light irradiation.

In the case of "backward reaction", it is believed that the roles of the cocatalyst are to introduce reaction sites, to decrease the overpotential, and promote the H_2 generation rate in photocatalatic water splitting. In particular, nanosheets doped with isolated single-atom reaction sites for hydrogen evolution are a potential means of suppressing recombination during photocatalytic water splitting. However, overall water splitting into hydrogen and oxygen from pure water has not yet been achieved on such materials because backward reactions of oxygen reduction reaction (ORR) are also

accelerated at these same reaction sites. In this study, we investigate calcium niobate nanosheets incorporating Rh single-atom reaction sites covered with ultrathin NiO_x atomic layers that prevent oxygen penetration but allow H^+ to access the Rh reaction sites. The results demonstrate that evolved hydrogen and oxygen from water in the expected 2:1 stoichiometric ratio, and achieve photocatalytic activity for H_2 and O_2 evolution from pure water under light irradiation.

This thesis is composed of 4 chapters.

Chapter 1

Introduction

In this chapter, the general background, the principle of photocatalytic water splitting, the properties of nanosheet, the challenge of photocatalysts, and aim of the present study are described as introduction.

Chapter 2

Water Splitting Using a Photocatalyst with Single-Atom Reaction Sites

In this study, we prepared calcium niobate nanosheets incorporating Rh single-atom reaction sites covered with ultrathin NiO_x atomic layers, which was found to evolve hydrogen and oxygen from water in the expected 2:1 stoichiometric ratio. This is the first demonstration of overall water splitting using a photocatalyst with single-atom reaction sites. The NiO_x layers were 0.4-0.5 nm thick with lateral sizes in the range of 5-10 nm. These ultrathin layers covered the Rh single-atom reaction sites to effectively suppress the undesirable O_2 reduction reaction and provide photocatalytic activity during overall water splitting.

Chapter 3

Preparation of Tantalum Nitride Nanosheet by Nitridation of Monolayer Tantalum Oxide Nanosheet

In this study, the ultrathin (1.5 nm) Ta_3N_5 nanosheet was successfully prepared from tantalum oxide (TaO_3) nanosheet. In particular, we found that the fabricated Ta_3N_5 nanosheet had a strong [110] preffered orientation in the in-plane direction after the nitridation process. In addition, this ultrathin Ta_3N_5 nanosheets exhibited higher photocatalytic activity for H_2 generation than the bulk Ta_3N_5 powder under 550 nm visible ligt irradiation.

Chapter 4

Conclusions

In this chapter, the general conclusions of the present thesis are described.