論 文 の 内 容 の 要 旨

論文題目　Study on photoelectrodes prepared from oxynitride particles for water splitting with visible-light

（酸窒化物粒子から調製した可視光水分解用光電極の研究）

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Water splitting by a photoelectrochemical (PEC) cell utilizing solar energy is an attractive means of hydrogen production. In the PEC cell, a semiconductor electrode is the main equipment of the device. An n-type semiconductor and a p-type semiconductor electrode function as a photoanode and a photocathode, respectively. The combination of a photoanode and a photocathode is beneficial way to drive water splitting efficiently under sunlight because of applicability of narrow gap semiconductor materials which can capture the light of wider wavelength region by combining driving force of photocathode and photoanode. From the view point of capturing more sunlight, development of photoelectrodes with visible-light response is indispensable, because almost half of energy in sunlight is composed of visible-light.

Colored metal oxynitrides are hopeful candidates of photoanode material for sunlight driven water splitting, because some oxynitrides have proper band structure for water splitting. The chemical stability is also advantageous point of oxynitrides; some photocatalysts stably generate oxygen gas form an aqueous solution under visible-light, suggesting that the oxynitride materials have durability for PEC water oxidation. In fact, some Ti^{4+}, Ta^{5+}, and Nb^{5+} based oxynitiride electrode functions as photoanode for water oxidation with relatively small applied bias voltage under visible-light.

Herein, $LaTiO_2N$ which is composed of relatively abundant metals (La, Ti) and responsive to up to 600 nm were investigated in detail as photoanode material for water splitting. From the view point of practical and large scale application, low cost and simple preparation of photoelectrodes are preferable. Particularly for oxynitride materials, the powder sample can be synthesized easily. Semiconductor powder based photoelectrodes with less inter-particle boundaries and proper connection between the particle and the conductor are desirable. Therefore, development of the preparation method is important for an efficient photoelectrode consisting of semiconductor particles.

It is known that over potential of water oxidation reaction is relatively large. Thus, decreasing the over potential is indispensable for efficient water splitting. Surface modification with co-catalyst which decreases over potential for oxidation of water significantly affects the PEC properties of a photoanode. Although IrO_2 is an efficient co-catalyst material composed of noble metal, from the view point of practical application, non-noble metal co-catalysts such as cobalt catalyst are promising candidates and the catalytic effects are still debatable.

In addition, characterization of flat band potential which suggests the band structure of the semiconductor material is also important in order to judge possibilities for photocatalyst and/or photoelectorde material for water splitting. The discussion would provide statistics for development in near future photoanodes for water splitting.

Accordingly, following three topics for the $LaTiO_2N$ electrode prepared from the powder sample are focuses in this study; (1) fabrication method and effects of the structure (2) effects of surface modification with co-catalyst, (3) flat band potential of (oxy)nitiride electrodes, and hence these were investigated.

Contents of this thesis were classified as follows;

Chapter 1. General Introduction; The first chapter describes general backgrounds of the research and basic principal of PEC water splitting, characteristic of (oxy)nitride materials, role of structure in photoelectrode, and effects of co-catalyst for water oxidation.

Chapter 2. $TiCl_4$ Treatment Effect on the Photoelectrochemical Properties of $LaTiO_2N$ Electrodes; $LaTiO_2N$ electrodes were prepared by an ink method with the powder sample and a fluorine doped tin oxide (FTO) coated glass substrate, and the PEC properties were investigated. The as-prepared $LaTiO_2N$/FTO electrode generated low photocurrent probably because of poor connection between the particles in the $LaTiO_2N$ film and/or the particles and the FTO conductor substrate. However, $LaTiO_2N$ photoelectrodes with $TiCl_4$ treatment which introduced

TiO_2 like binder into the $LaTiO_2N$ film generated several times higher photocurrent than those without $TiCl_4$ treatment, because the introduction of titanium species facilitated migration of photoexcited electrons in $LaTiO_2N$ toward the FTO substrate.

Chapter 3. Morphological effects on the Photoelectrochemical Properties of $LaTiO_2N$ Electrodes; Effects of morphology in $LaTiO_2N$ particles which were employed for photoelectrodes prepared by an electrophoresis deposition (EPD) method on the PEC properties for water splitting were investigated. Various $LaTiO_2N$ particles synthesized from crystalline $La_2Ti_2O_7$ of various particle sizes with featureless shape and micro-crystals of plate like shape derived from a flux method were used. Untreated $LaTiO_2N$ electrodes consisting of the smaller particles tended to generate higher photocurrent, whereas $TiCl_4$-treated electrodes prepared from $LaTiO_2N$ particles of micro-meter size tended showed higher PEC performance than that consisting of the several ten nano meter sized particles, probably because of the less inter particle boundaries. A photoelectrode consisting of plate like shaped $LaTiO_2N$ micro-crystals which would be advantageous for shorter necessitate diffusion length of photogenerated holes in $LaTiO_2N$ for water oxidation generated larger photocurrent than those formed from the particles of featureless shape. These results provide a strategy for structure of an efficient semiconductor-particles-based photoelectrode which consists of the semiconductor micro-crystals appropriately fixed onto a conductor substrate.

Chapter 4. Photoelectrochemical Properties of $LaTiO_2N$ Electrode Prepared by Particle-Transfer Method; $LaTiO_2N$ photoanodes consisting of 1-3 layers of $LaTiO_2N$ micro-crystals which firmly anchored by continuous metal film were prepared by a novel particle-transfer (PT) method. The PEC properties were dependent on contact layer material which directly connected to $LaTiO_2N$ particles and functions as conductor in the electrode, and contact layer of Ta metal was proper material for the $LaTiO_2N$ photoelectrode. The $LaTiO_2N$/Ta electrode prepared by PT method generated higher photocurrent than that fabricated by EPD method with $TiCl_4$ treatment. The IrO_2 modification was remarkably more effective to improve PEC properties of $LaTiO_2N$ photoelectrode (PT) than that (EPD), indicating that surface modification with co-catalyst is more important for the electrode (PT) than that (EPD). The

$LaTiO_2N$ electrode (PT) in an electrolyte containing a redox regent showed more negative potentials where large photocurrent was obtained than that in a supporting electrolyte, suggesting that less recombination rate in $LaTiO_2N$ leads to more negative potential for large photocurrent.

Chapter 5. Modification Effects of Cobalt-based Co-catalyst on Photoelectrochemical Properties of $LaTiO_2N$ Electrode Prepared by Particle-Transfer Method; Effects of surface modification with cobalt (Co) based co-catalyst for water oxidation on PEC properties of $LaTiO_2N$ electrode prepared by PT method were investigated. Initial photocurrent density and stability of photocurrent generated from the $LaTiO_2N$ photoanode conflicts each other by controlling loading amount of Co co-catalyst. However, addition of optimal amount of Fe species into Co co-catalyst on $LaTiO_2N$ particles leaded to an improvement in stability of the photocurrent without decreasing the initial photocurrent, probably because the addition of Fe species improved dispersibility of the co-catalyst on $LaTiO_2N$ and/or the catalytic properties for water oxidation. The optimized Co-Fe/$LaTiO_2N$ photoanode generated stoichiometric amount of oxygen gas, and showed solar energy conversion efficiency of ca. 0.6 %.

Chapter 6. Flat Band Potentials of Metal (Oxy)nitride Electrodes; Flat band potentials of Ti^{4+}, Ta^{5+}, or Nb^{5+} based (oxy)nitiride electrodes prepared by PT method were estimated by the Mott-Schottky plots, and band structure of the materials were estimated. Band edges of these (oxy)nitride materials straddle the potentials of water reduction and oxidation, indicating a possibility for application of these materials to photocatalyst and photoanode materials for water splitting. The band structures of some narrow gap oxynitride suggest necessity of proper modification with co-catalyst and/or band engineering for oxygen evolution reaction over the material.

Chapter 7. Summary; The results of chapter 2-6 were summarized, and outlooks of this study were discussed.