論 文 の 内 容 の 要 旨

論文題目　　　Development and Kinetic Assessment of Photocatalysts for Water Splitting Reaction
　　　　　　　（水分解反応を目的とした光触媒の開発及び光触媒作用の速度論的検討）

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　　This thesis describes development of a novel oxynitride photocatalyst with visible light activity, improvement of preparation methods of (oxy)nitride photocatalysts, and kinetic investigation on water splitting reaction using heterogeneous photocatalysts. The thesis consists of 7 chapters, all of which are written in English.

　　In Chapter 1, background of the present research, general principles of water splitting reaction on a heterogeneous photocatalyst, kinetic aspects of photocatalytic water splitting reaction, strategies to develop visible-light-driven photocatalysts, current state of photocatalyst development for water splitting, and general experimental procedures for photocatalyst development were described.

　　In Chapter 2, physical properties of zinc titanium nitride oxides ($Zn_xTiO_yN_z$) were discussed as a novel photocatalytic material with visible light response. A series of $Zn_xTiO_yN_z$ having a spinel structure were obtained by nitriding an oxide precursor derived from a polymerized complex method under an NH_3 flow at 1023 K. The $Zn_xTiO_yN_z$ spinel obtained was metastable because the Zn in the nitride oxide volatilized during the nitridation process. Both Zn and Ti cations of the $Zn_xTiO_yN_z$ spinel were essentially located in the same cation sites as the inverse spinel phase of Zn_2TiO_4; Zn species at the octahedral sites were volatilized in preference to those at tetrahedral sites. The bandgap energy of the $Zn_xTiO_yN_z$ spinel decreased as the amount of N species increased, eventually stabilizing at 2.3 eV. $Zn_xTiO_yN_z$ reduces H^+ to H_2 and oxidizes H_2O to O_2 in the presence of a sacrificial electron donor and acceptor under visible light irradiation ($\lambda > 420$ nm). Optimally prepared $Zn_xTiO_yN_z$ showed an apparent quantum efficiency of 1.0% for the O_2 evolution reaction, while an apparent quantum efficiency of less than 0.01% for the H_2 evolution reaction.

　　In Chapter 3, ordered mesoporous Ta_2O_5 and Ta_3N_5 with crystalline thin-wall structures

were obtained from an amorphous mesoporous Ta_2O_5 by calcination at 1118 K under an ambient atmosphere and nitridation at 1073 K under a NH_3 flow of 500 mL min^{-1}, respectively. Silica layer, deposited on the pore wall by chemical vapor deposition of tetramethyl orthosilicate and easily removed by alkaline treatment, was indispensible for maintaining the original mesostructure against phase transition during crystallization and nitridation. Direct phase transition from amorphous Ta_2O_5 to orthorhombic Ta_3N_5 was achieved by the nitridation of silica-coated mesoporous Ta_2O_5 at 1073 K for 3 h under NH_3 flow. Mesoporous Ta_3N_5 has mesoporosity and mesoporous structure similar to that of amorphous Ta_2O_5, together with crystallized pore wall with orthorhombic Ta_3N_5. BET surface area, pore size, and wall thickness of mesoporous Ta_3N_5 were approximately 100 m^2 g^{-1}, 4 nm, and 2 nm, respectively. Mesoporous Ta_3N_5 loaded with Pt nanoparticles was active for photocatalytic H_2 evolution reaction from an aqueous methanol solution under visible light ($\lambda > 420$ nm). The photocatalytic activity of mesoporous Ta_3N_5 was three times higher than that of conventional bulk-type Ta_3N_5 under the same reaction conditions because of the crystallized pore wall (ca. 2 nm in thickness) enabling efficient charge transfer of photoexcited electrons and holes to surface active sites.

In Chapter 4, aspects of water splitting mechanism on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst powder was discussed based on the effects of cocatalyst loading, light intensity, hydrogen/deuterium isotopes, and reaction temperature on photocatalytic activity. When the loading amount of $Rh_{2-y}Cr_yO_3$ as a H_2 evolution cocatalyst was insufficient, the reaction order for light intensity was lower than unity. This is because photoexcited electrons accumulated in the photocatalyst and recombined with photoexcited holes more frequently than they contributed to the water-splitting reaction. When a sufficient amount of cocatalyst was loaded, on the other hand, accumulation of photoexcited electrons was suppressed and the water splitting rate increased monotonically with light intensity. At a light intensity equivalent to solar irradiation, AM 1.5, the water-splitting rate using modified $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ remained under the light-intensity-proportional regime. The weak isotope effect and small apparent activation energy on overall water splitting using $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ arose from the limited number of photoexcited carriers present in the $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$. A kinetic model of photocatalytic water splitting suggests that the reaction probability of photoexcited holes for O_2 evolution versus recombination with intrinsic electrons of the photocatalyst determines the photocatalytic activity of the $Rh_{2-y}Cr_yO_3/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$.

In Chapter 5, Zn-added Ga_2O_3 modified with $Rh_{2-y}Cr_yO_3$, which marked the excellent apparent quantum efficiency for photocatalytic water splitting, was employed for isotopic and kinetic study on water splitting reaction using a heterogeneous photocatalyst. The key finding is that the apparent activation energy and the hydrogen-deuterium isotope effect for photocatalytic water splitting reaction were much smaller than those for typical electrochemical and catalytic

reactions reported. These results were consistent with lack of photoexcited carriers available for surface redox reactions because of inevitable charge recombination. Based on this idea, it is concluded that enhancement of bulk processes, such as inhibition of recombination, rather than that of surface redox reactions should be necessary for improving the overall photocatalytic activity for water splitting.

In Chapter 6, the influence of starting materials on the physical and photocatalytic properties of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ were investigated in an attempt to improve the bulk properties and thus water splitting performance of the photocatalyst. The solid solution was successfully prepared by nitriding a starting mixture of ZnO and Ga_2O_3. The photocatalytic activity of the resultant $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ was found to be sensitive to the surface area of starting Ga_2O_3 although the crystallinity, surface area, composition, and absorption characteristics were invariant. Modification of starting Ga_2O_3 with Zn and addition of excessive ZnO to a precursor improved the photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ because formation of GaN as an impurity phase was suppressed. The results demonstrated the importance of selecting appropriate starting materials and nitridation conditions for maximizing the photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ for overall water splitting under visible light.

In Chapter 7, the results described in Chapter 2–6 were summarized and the future outlook was described.