

論文の内容の要旨

論文題目 Development of a Novel Visible-Light-Responsive Photocatalyst for Overall Water Splitting

(水の完全分解反応を指向した新規可視光応答型光触媒の研究開発)

氏名 前田 和彦

This thesis describes a development of a novel visible-light-responsive photocatalyst, in particular (oxy)nitrides, for overall water splitting, focusing on the refinement of preparation conditions, controlling the reaction condition, and devising a new cocatalyst to maximize the efficiency. The thesis consists of 12 chapters and 3 appendices, all of which are written in English.

In the Chapter 1, the background of this research, basic principle of overall water splitting on a heterogeneous photocatalyst, and the progress in the development of visible-light-responsive photocatalysts that has been made to date are described.

In the Chapter 2, germanium nitride, $-\text{Ge}_3\text{N}_4$, dispersed with RuO_2 nanoparticles is presented as the first example of a non-oxide photocatalyst for the stoichiometric decomposition of H_2O into H_2 and O_2 . Nitridation of GeO_2 at 1153 K for 10 h under a flow of NH_3 results in the production of well-crystallized $-\text{Ge}_3\text{N}_4$ particles with a phenacite structure belonging to the hexagonal crystal system. Although the as-prepared $-\text{Ge}_3\text{N}_4$ displays negligible activity for overall water splitting, the material becomes photocatalytically active under ultraviolet (UV) irradiation ($\lambda > 200$ nm) when loaded with RuO_2 nanoparticles as H_2 evolution sites. The photocatalytic activity of RuO_2 -loaded $-\text{Ge}_3\text{N}_4$ for overall water splitting is strongly dependent on the reaction conditions. The highest activity is obtained when the reaction is carried out in 1 M H_2SO_4 aqueous solution. The rates of both H_2 and O_2 evolution decreases as the reaction progresses, attributable to photoreduction of O_2 , collapse of the catalyst surface by elusion of Ge cations, and loosened interfacial contact between the $-\text{Ge}_3\text{N}_4$ and loaded RuO_2 nanoparticles. Up to 80% of the initial activity can be recovered by calcination of the used catalyst at 673 K in air for 5 h followed by reloading with RuO_2 .

In the Chapter 3, Ge_3N_4 powder prepared by thermal ammonolysis of GeO_2 is examined as a photocatalyst for overall water splitting. Nitridation of GeO_2 under a flow of NH_3 at temperatures higher than 1123 K for 10 h results in the production of either a single phase of $-\text{Ge}_3\text{N}_4$ or a mixture of elemental Ge, α - Ge_3N_4 , and $-\text{Ge}_3\text{N}_4$, depending on the nitridation conditions. $-\text{Ge}_3\text{N}_4$ exhibits activity for the stoichiometric decomposition of pure water into H_2 and O_2 under UV irradiation ($\lambda > 200$ nm) when loaded with nanoparticulate RuO_2 as a cocatalyst. Improving the crystallinity of the $-\text{Ge}_3\text{N}_4$ catalyst results in greater activity for overall water splitting and markedly reduced N_2 release due to self-decomposition by

photogenerated holes.

In the Chapter 4, a novel solid solution of GaN and ZnO with a band gap of 2.58 – 2.76 eV, modified with RuO₂ nanoparticles is presented as a photocatalyst for overall water splitting under visible light. In contrast to the conventional non-oxide photocatalysts, such as CdS, the solid solution is stable during the overall water splitting reaction. This is the first example of achieving overall water splitting by a photocatalyst with a band gap in the visible light region, which opens the possibility of new non-oxide-type photocatalysts for energy conversion.

In the Chapter 5, the physical and photocatalytic properties of a novel solid solution between GaN and ZnO, (Ga_{1-x}Zn_x)(N_{1-x}O_x), are investigated. Nitridation of a mixture of Ga₂O₃ and ZnO at 1123 K for 5 – 30 h under NH₃ flow results in the formation of a (Ga_{1-x}Zn_x)(N_{1-x}O_x) solid solution with $x = 0.05 - 0.22$. With increasing nitridation time, the zinc and oxygen concentrations decrease due to reduction of ZnO and volatilization of zinc, and the crystallinity and band gap energy of the product increase. The highest activity for overall water splitting is obtained for (Ga_{1-x}Zn_x)(N_{1-x}O_x) with $x = 0.12$ after nitridation for 15 h. The crystallinity of the catalyst is also found to increase with increasing the ratio of ZnO to Ga₂O₃ in the starting material, resulting in an increase in activity.

In the Chapter 6, the formation and structural characteristics of Ru species applied as a cocatalyst on (Ga_{1-x}Zn_x)(N_{1-x}O_x) are examined by scanning electron microscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy. RuO₂ is an effective cocatalyst that enhances the activity of (Ga_{1-x}Zn_x)(N_{1-x}O_x) for overall water splitting under visible-light irradiation. The highest photocatalytic activity is obtained for a sample loaded with 5.0 wt% RuO₂ from an Ru₃(CO)₁₂ precursor followed by calcination at 623 K. Calcination is shown to cause the decomposition of initial Ru₃(CO)₁₂ on the (Ga_{1-x}Zn_x)(N_{1-x}O_x) surface (373 K) to form Ru(IV) species (423 K). Amorphous RuO₂ nanoclusters are then formed by agglomeration of finer particles (523 K), and the nanoclusters finally crystallize (623 K) to provide the highest catalytic activity. The enhancement of catalytic activity by Ru loading from Ru₃(CO)₁₂ is thus shown to be dependent on the formation of crystalline RuO₂ nanoparticles with optimal size and coverage.

In the Chapter 7, modification with a two-component cocatalyst consisting of Cr and another transition metal is examined in an attempt to improve the photocatalytic activity of (Ga_{1-x}Zn_x)(N_{1-x}O_x) for overall water splitting. The activity of (Ga_{1-x}Zn_x)(N_{1-x}O_x) modified with various transition metals is enhanced by coloaded Cr, although modification with Cr alone is not effective for promoting activity in this reaction. The activity of the coloaded catalyst is found to be strongly dependent on the amount of loaded Cr, which in turn varies according to the paired transition metal. The improvement in activity is attributed to the formation of suitable reaction sites by intimate interaction between Cr and the paired metal component. Among the various transition metals examined, the largest improvement in activity is obtained when (Ga_{1-x}Zn_x)(N_{1-x}O_x) is loaded with a mixed oxide of Rh and Cr, achieving the apparent quantum efficiency of ca. 2.5% at 420 – 440 nm.

In the Chapter 8, the photocatalytic activity of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ loaded with Rh – Cr mixed-oxide ($\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$) nanoparticles for overall water splitting under visible light irradiation ($\lambda > 400 \text{ nm}$) is investigated with respect to reaction pH and gas pressure. The photocatalytic performance of the catalyst is found to be strongly dependent on the pH of the reactant solution, but largely independent of gas pressure. The present photocatalyst exhibits stable and high photocatalytic activity in an aqueous solution of pH 4.5 for 72 h. The photocatalytic performance is much lower at pH 3.0 and pH 6.2, attributable to corrosion of the cocatalyst and hydrolysis of the catalyst. The dispersion of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ as a cocatalyst on the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ surface promotes hydrogen evolution, which is considered to be the rate-determining step for overall water splitting on this catalyst.

In the Chapter 9, the structure of Rh – Cr mixed-oxide ($\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$) nanoparticles dispersed on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is characterized by electron microscopy and X-ray spectroscopy. $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ nanoparticle is an efficient cocatalyst for photocatalytic overall water splitting on the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ solid solution, and is loaded onto the catalyst by impregnation from an aqueous solution containing $\text{Na}_3\text{RhCl}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ followed by calcination in air. Impregnation of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with 1 wt% Rh and 1.5 wt% Cr followed by calcination at 623 K for 1 h provides the highest photocatalytic activity. Structural analyses reveal that the activity of this photocatalyst is strongly dependent on the generation of trivalent Rh – Cr mixed-oxide nanoparticles with optimal composition and distribution.

In the Chapter 10, noble-metal/ Cr_2O_3 (core/shell) nanoparticles as new type of cocatalysts for H_2 evolution are presented. The core/shell nanoparticles are prepared on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ through an in-situ photodeposition method. The obtained materials function as a photocatalyst for overall water splitting under visible light irradiation ($\lambda > 400 \text{ nm}$). This preparation method can be applicable to other photocatalysts such as SrTiO_3 and NaTaO_3 for overall water splitting, offering a new strategy for the development of a H_2 evolution cocatalyst and a highly efficient heterogeneous photocatalytic system for overall water splitting.

In the Chapter 11, photodeposited Rh/ Cr_2O_3 (core/shell) nanoparticles on a $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalyst are studied as a cocatalyst for overall water splitting. Irradiation of Rh-loaded $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with visible light ($\lambda > 400 \text{ nm}$) in aqueous K_2CrO_4 solution results in the formation of core/shell-structured nanoparticles consisting of an Rh core and Cr_2O_3 shell through the site-selective photoreduction of CrO_4^{2-} anions to Cr_2O_3 on Rh nanoparticles. The shell thickness increases with concentration of K_2CrO_4 in the reactant solution to a maximum of ca. 2 nm, at which a uniform Cr_2O_3 coating is obtained. The Cr_2O_3 shell suppresses water formation from H_2 and O_2 on Rh nanoparticles, allowing stoichiometric decomposition of pure water to be achieved. The core/shell structure also provides enhanced H_2 evolution compared to bare Rh nanoparticles.

In the Chapter 12, the results described in the Chapters 2 – 11 are summarized and future outlook is described.

