

論文の内容の要旨

論文題目 Electrochemical and spectroscopic studies on mechanism of
 photocatalytic overall water splitting
 (電気化学・分光法を利用した水分解光触媒の機能解明)

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This thesis describes mechanistic aspect of photocatalytic overall water splitting about function of noble-metal/Cr₂O₃ core/shell cocatalysts, the change in the Fermi level of the Pt/GaN photocatalyst, the band structure of (Ga_{1-x}Zn_x)(N_{1-x}O_x) photocatalyst, and the preparation of Lanthanoid-layer/Rh cocatalysts by electrochemical and spectroscopic analyses. The thesis consists of 6 chapters and appendix. The abstracts of each chapter in this thesis are summarized below.

Chapter 2 stated the study on mechanism of hydrogen evolution by a core/shell noble-metal/Cr₂O₃ particulate as a highly efficient cocatalyst for overall water splitting under visible light using the photocatalyst (Ga_{1-x}Zn_x)(N_{1-x}O_x) by electrochemical and in-situ spectroscopic measurements of model electrodes. It is stated that the Cr₂O₃ layer does not interfere with hydrogen evolution and that proton reduction takes place at the Cr₂O₃/noble-metal interface, although the reduction of oxygen to water was suppressed only in the Cr₂O₃-coated samples. Thin films with similar function can therefore be considered additional candidates for the modification of noble metals to inhibit the back-reaction in overall water splitting. Organic passivation layers such as ion-exchanged polymers may also provide selective permeation characteristic suitable for the present photocatalytic system, although preparing such materials on the noble-metal core and ensuring durability for photocatalytic reactions remain significant challenges. It is thus believed that there is considerable further scope for refinement of the cocatalyst modifier leading to increases in the activity of this photocatalytic system for overall water splitting. Lanthanoid oxide layers in **Chapter 5** were examined on the basis of the content of **Chapter 2**.

Chapter 3 showed the shift in the Fermi level of Pt cocatalyst on the GaN photocatalyst under irradiation by in-situ ATR-SEIRAS observation with adsorbed CO on Pt cocatalyst as a probe molecule. This study demonstrates the first successful direct probing of the Fermi level of

cocatalyst (Pt) on photocatalyst (GaN) during UV irradiation by in-situ ATR-SEIRAS measurement with monitoring of adsorbed CO vibrational frequency. This probing method can be applied to many other photocatalyst systems to reveal the working state of charge separation during water splitting. The interfacial electron transfer processes between a photocatalyst and a cocatalyst are yet to be investigated to understand the reaction mechanism and improve efficiency. The author believes the in-situ ATR-SEIRAS measurement with monitoring of CO absorption will reveal more detailed carrier dynamics from the view of electrochemistry for the first time.

The subject in the **Chapter 4** was the study on electronic structures of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ solid solution by photoluminescence spectroscopy and plane wave based density functional method. The visible light response of this material was found to be originated from the electron transition from the Zn acceptor level to the conduction band. Clarifying the origin of the visible light absorption in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ solid certainly stimulates worldwide researchers' interests in development of light-induced water splitting materials. The author expects the finding derived from this study will be useful for further new developments of visible-light-driven photocatalyst,

In the **Chapter 5**, lanthanoid-oxide/noble-metal/ $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalysts were found to work for overall water splitting under visible light, although the noble-metal/ $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalyst doesn't work. The characterization and function of the cocatalysts were discussed. The prepared lanthanoid-oxide/noble-metal cocatalysts correspond to the first trial for application of lanthanoid elements to a cocatalyst modifier for overall water splitting. There appears to be considerable scope for refinement of the cocatalyst modifier, which may potentially lead to further increases in photocatalytic activity for overall water splitting.

In the **Chapter 6**, the findings in the **Chapters 2-5** are summarized.

The photocatalytic reaction for overall water splitting is directly associated with various dynamic behaviors of semiconductor physics, surface science, or electrochemistry. Photocatalyst materials absorb photons with greater energy than band-gap of the material, which generates photoexcited electron-hole pairs in the bulk. These carriers migrate from bulk to surface. Hydrogen gases are considered to be evolved when hydrogen evolution sites are negative enough against hydrogen evolution reaction by photogenerated electrons. On the other hand, oxygen gases are likely to be evolved when oxygen evolution sites are positive enough against oxygen evolution reaction by photogenerated holes. However, the mechanistic aspect has not been understood, although the photocatalyst has been paid attention to hugely. In-situ electrochemical and spectroscopic analyses are proved to be one of the most powerful methods

for study on the photocatalytic reaction, as shown in the above. Moreover, X-ray spectroscopy, Raman spectroscopy, Sum-frequency generation (SFG) spectroscopy, and electrochemical scanning tunneling microscope (STM) are also very useful for measurements of photocatalyst samples in solution. These methods will work as powerful techniques to reveal mechanistic aspects of photocatalytic overall water splitting and the findings give useful information for development of high efficient photocatalyst in the future.