学　位　論　文　内　容　の　要　旨

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Plasmon Enhanced Photocurrent Generation and Water Splitting on Photoanode of Gold Nanoparticles Loaded Gallium Oxide
（金ナノ粒子を担持した酸化ガリウム光アノードによるプラズモン増強光電流発生と水分解）

Gallium (III) oxide (Ga_2O_3) is a wide bandgap semiconductor (～4.8 eV) with a very negative conduction band (CB) potential, making it applicable not only for the reduction of water but also for the reduction of CO_2 and other substances requiring negative reduction potentials. However, the large band gap of Ga_2O_3 has made it difficult to use visible light. To resolve this problem, in this thesis, the photocurrent generation and water splitting under the visible irradiation using a plasmonic photoanode based on gold nanoparticles (Au-NPs)/Ga_2O_3 were mainly studied.

To harvest visible light, Au-NPs with different sizes were loaded on each single crystal Ga_2O_3 (SC-Ga_2O_3) substrate by annealing of deposited Au-films on the substrates with different thicknesses. As a result, generation of photocurrent by visible light irradiation was observed in Au-NPs loaded SC-Ga_2O_3 substrate as the photoanode due to hot carrier generation based on localized surface plasmon resonance (LSPR) of Au-NPs. In addition, the 15 nm-sized Au-NPs loaded SC-Ga_2O_3 substrate exhibited the largest incident photon to current conversion efficiency (IPCE) (Chapter 2).

To further enhance the IPCE of Au-NPs/SC-Ga_2O_3 as a photoanode, an attempt was made to deposit a thin TiO_2 layer at the Au-NPs/SC-Ga_2O_3 interface because it is known that TiO_2 is effective in trapping hot holes. First, it was found that depositing a TiO_2 thin layer between the Au-NPs and the Ga_2O_3 substrate suppresses hot electron injection from the Au-NPs to Ga_2O_3, resulting in a decrease in IPCE. On the other hand, when the Au-NPs on the Ga_2O_3 substrate were partially embedded by TiO_2, the hole-trapping ability was enhanced and IPCE was found to increase obviously. Furthermore, the thickness dependence of the TiO_2 layer on IPCE was also revealed that 2 nm TiO_2-modified Au-NPs/SC-Ga_2O_3 exhibited the highest IPCE, 1.5 times higher than that of Au-NPs/SC-Ga_2O_3 (Chapter 3).

To further improve the light harvesting and water oxidation reaction efficiency, a structure of TiO_2/Au-NPs/Ga_2O_3/TiN/Au-film (TAGA) to achieve modal strong coupling between the LSPR of Au-NPs and the Fabry-Pérot nanocavity was employed. In the TAGA, TiN acted as a protection layer for Au-film and Ga_2O_3 film, which exhibited excellent semiconductor properties, was deposited on the TiN/Au-film reflective mirror. The TiN/Au-film exhibited satisfactory electrochemical properties and served as a reflective mirror for the nanocavity. The modal strong coupling was constructed by overlapping the resonance wavelength of the nanocavity with the LSPR wavelength of the Au-NPs partially embedded in the TiO_2 layer. Under the modal strong coupling condition, the optical absorption increased dramatically and the IPCE was enhanced. In this structure, the Au-NPs partially embedded in the TiO_2 layer showed an important role in enhancing the strength of the modal strong coupling and hole-trapping ability. The use of the TAGA with very negative CB potential led to successful water splitting at zero bias potential under visible light irradiation (Chapter 4).

In summary, it was demonstrated that hot carriers generated by the LSPR of Au-NPs were injected into the CB of Ga_2O_3, and hot holes could further induce water oxidation, generating a photocurrent under visible irradiation. In addition, partial embedding of Au-NPs in a TiO_2 layer, which had a higher hole-capturing ability than Ga_2O_3, improved the efficiency of charge separation of hot carriers generated in the Au-NPs, resulting in improved IPCE. Furthermore, it was found that modal strong coupling between the LSPR of Au-NPs and the nanocavity that was expressed in the TAGA photoanodes improved their visible light-harvesting ability and effectively increased IPCE. Finally, visible light-driven water splitting at zero bias potential was also achieved using the TAGA photoanodes.